



Nitrogen biogeochemistry of three hardwood ecosystems in the Adirondack Region of New York

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Key words: atmospheric deposition, decomposition, dissolved organic nitrogen, experimental additions, forests, mass balances, ¹⁵N isotopes, nitrate, nitrogen, soils

Abstract. The biogeochemistry of nitrogen (N) was evaluated for three forest ecosystems [Woods Lake (WL), Pancake-Hall Creek (PHC) and Huntington Forest (HF)] in the Adirondack region of New York, U.S.A. to evaluate the response of a range of N atmospheric inputs and experimental N additions. Bulk N deposition was higher at sites in the west than those in the central and eastern Adirondacks. These higher atmospheric N inputs were reflected in higher bulk throughfall fluxes of N (WL and PHC, 10.1 and 12.0 kg N ha⁻¹ yr⁻¹, respectively) in the western Adirondacks than at HF (4.6 kg N ha⁻¹ yr⁻¹) in the central Adirondacks. Nitrogen was added to plots as (NH₄)₂SO₄ at 14 and 28 kg N ha⁻¹ yr⁻¹ or as HNO₃ at 14 kg N ha⁻¹ yr⁻¹. Litter decomposition rates of *Fagus grandifolia* and *Acer rubrum* were substantially higher at WL and PHC compared to HF but were not affected by experimental N additions. Results using mineral soil bags showed no effects of N addition on N and C concentrations in soil organic matter, but C and N concentration increases were less at WL and PHC compared to HF. Soil solution nitrate (NO₃⁻) concentrations at 15-cm depth in the reference plots were higher at PHC than at WL and HF while at 50-cm concentrations were higher at PHC and WL than at HF. The reference plots at the two sites (WL and PHC) with the highest atmospheric inputs of N exhibited lower N retention (53 and 33%, respectively) than HF (68%) in reference plots. The greatest increase in NO₃⁻ loss in response to the experimental treatments occurred at HF where the HNO₃ additions resulted in the highest NO₃⁻ concentrations and lowest N retentions. In contrast, at WL and PHC increases in soil water NO₃⁻ were not evident in response to experimental N additions. The results suggest that the two sites (WL and PHC) in the western Adirondacks did not respond to additional N inputs although they have experienced elevated atmospheric N inputs and higher N drainage losses in reference plots than the HF site in the central Adirondacks. Some of these differences in site response may have also been a function of stand age of WL and PHC that were younger (24 and 33 years, respectively) than the HF (age ~ 70). Highest NO₃⁻ fluxes in the reference

plots across the sites corresponded to higher $\delta^{15}\text{N}$ values in soil and plants. An experimental addition experiment at PHC found that the forest floor and the mineral soil were the largest sinks for experimentally added N.

Introduction

Understanding relationships between atmospheric nitrogen (N) deposition and forest ecosystem biogeochemistry is critical in assessing the effects of elevated N inputs. Elevated levels of N in ecosystems due to anthropogenic activities alter biotic diversity and N cycling (Vitousek et al. 1997). Recently attention has focused on evaluating the 'N saturation' status of forest ecosystems (Aber et al. 1989, 1997, 1998; Fenn et al. 1998) and resultant increases in nitrate (NO_3^-) in surface waters that can contribute to freshwater acidification (Stoddard 1994) and coastal eutrophication (Howarth et al. 1996; Paerl 1997).

Studies in the U.S. (Adams et al. 1997; Christ et al. 1995; Fernandez et al. 1999; Kahl et al. 1999; Magill et al. 1997; McNulty et al. 1996; Rustad et al. 1993; Steudler et al. 1989) and Europe (Feger et al. 1991; Hultberg & Greenfelt 1986; Wright et al. 1986; Wright & van Breemen 1995) have used chemical additions to experimentally evaluate the response of forest ecosystems to changing inputs of atmospheric deposition. Results from N additions at the Harvard Forest have shown N cycling and retention can vary markedly among different forests with a *Pinus resinosa* Ait. stand exhibiting conditions closer to N saturation than a mixed-*Quercus* stand (Magill et al. 1997). McNulty et al. (1996) working with experimental N additions in high elevation spruce-fir stands in New England (U.S.A.) found with N addition caused foliar nutrient imbalances and changes in species composition and structure. In the NITREX project in Europe, researchers found that, although some of the dissolved inorganic nitrogen (DIN) losses from forests were a function of DIN atmospheric inputs, there was substantial variation in losses across sites over a large range of inputs (<1 to ~ 70 kg N ha⁻¹ yr⁻¹; Dise et al. 1998). The response of the NITREX sites to experimental N additions also showed substantial variation in NO_3^- leaching, ranging from low losses at sites with 'low N status' to substantially higher losses at sites with 'high N status' (Gundersen et al. 1998b). Nitrogen additions to plots (David et al. 1990; Mitchell et al. 1994a; Rustad et al. 1996) and to an entire watershed (Kahl et al. 1999) at Bear Brook Watershed in Maine showed that both soil water and stream water NO_3^- responded rapidly to experimental treatments. A study of NO_3^- addition at the Experimental Lakes Area of Ontario, Canada found that N retention varied with seasons with relatively high retention

during the growing season and low retention during snowmelt (Lamontagne & Schiff 1999).

The present study was part of the Adirondack Manipulation and Modeling Project (AMMP) in which chemical manipulations were conducted at four sites (Woods Lake, WL; Pancake-Hall Creek, PHC; Huntington Forest, HF; and Pack Forest, PF) from 1991 through 1993 (Mitchell et al. 1994b; Mitchell et al. 1998). The current study focused on the three sites (WL, PHC and HF) with similar vegetation (all northern hardwoods) and soils (Haplorthods) and thus excluded PF which was a *P. resinosa* plantation underlain by a Typic Udipsamment soil (Mitchell et al. 1994b). The PF site was only used for monitoring deposition in the current study. The AMMP is the only study to date to evaluate the effects of S and N additions on the biogeochemistry of forest ecosystems in the Adirondack region of New York State. The Adirondacks have been severely impacted by elevated inputs of atmospheric sulfur (S) and N (Driscoll et al. 1991). Surface waters in the region have shown less recovery in response to sulfur dioxide emission than other regions (NAPAP 1998; Stoddard et al. 1999). In the Adirondack region elevated NO_3^- concentrations have been found in surface waters and this may have contributed to the limited recovery (Driscoll et al. 1991; Driscoll et al. 1998; Kretser et al. 1989; Mitchell et al. 1996, 2001). The drainage losses of NO_3^- in conjunction with other mobile anions especially sulfate (SO_4^{2-}) also may influence the losses and concentrations of nutrient base cations [calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+)] and potentially toxic hydrogen (H^+) and aluminum (Al^{n+}) ions (Reuss & Johnson 1986).

The overall objective of our study was to evaluate the N biogeochemistry of three forest ecosystems including their response to chemical manipulations. We hypothesized that N inputs would generally decrease from west to east in the Adirondacks (Driscoll et al. 1991; Ito et al. 2001). We predicted that those sites with greatest atmospheric inputs of N would also be most responsive to additional N inputs since it would be expected that ambient N inputs at these sites would meet the biotic demand for this element (Aber et al. 1998). We also hypothesized that N loss rates would be more sensitive to NO_3^- additions as compared to ammonium (NH_4^+) additions due to the greater mobility of the former ion. We predicted that patterns in ^{15}N natural abundance could be related to N concentrations in vegetation and soil and/or N solute fluxes (Emmett et al. 1998; Nadelhoffer & Fry 1994). Lastly, we hypothesized that most of the added $^{15}\text{NH}_4^+$ used as a tracer would be found in the forest floor and mineral soil (Nadelhoffer et al. 1999a,b).

Nitrogen was added to small plots in two chemical forms as $(\text{NH}_4)_2\text{SO}_4$ at 14 and 28 kg N ha^{-1} yr^{-1} , respectively or as HNO_3 at 14 kg N ha^{-1}

yr⁻¹. We expected that these N treatments would increase the N loading to more than twice previously estimated ambient atmospheric inputs over the entire region (~11 kg N ha⁻¹ yr⁻¹; Driscoll et al. 1991). Other chemical treatments included H₂SO₄ and (Ca&Mg)SO₄ at 32.1 kg S ha⁻¹ yr⁻¹. The different types of treatments were used to evaluate the effects of the associated various cations (Ca²⁺, Mg²⁺, NH₄⁺ and H⁺) and anions (NO₃⁻ and SO₄²⁻) on N biogeochemistry. These chemical treatments were done as part of a larger effort to evaluate changes in elemental loadings on the elemental dynamics of these sites (Hurd et al. 1998; Mitchell et al. 1994b, 1998). We used ¹⁵N as a tracer at PHC to evaluate the fate of added NH₄⁺. Litter loss, buried mineral soil bags and natural ¹⁵N abundances were also used to evaluate the differences in N cycling among sites and ascertain the effects of chemical additions on specific biogeochemical processes including decomposition rates and changes in organic matter in the mineral soil. Information on N concentrations and fluxes were used to interpret differences among sites in N cycling and retention.

Site descriptions

The three sites (WL, PHC and HF) were chosen to encompass the geographical range of the Adirondack region and a gradient of N inputs and acidic deposition (Driscoll et al. 1991; Ito et al. 2001; Mitchell et al. 1998) (Figure 1; Table 1). Each of the three sites has a history of biogeochemical studies (Cronan 1985; Cronan et al. 1990; Geary & Driscoll 1996; Mitchell et al. 1994b, 1998). The three sites have similar soils (Haplorthods) and vegetation (northern hardwoods). *Fagus grandifolia* (American beech), *Betula alleghaniensis* (yellow birch), *Acer saccharum* (sugar maple), and *Acer rubrum* (red maple) were the dominant trees at all three sites. In comparing the three sites, trees at WL were of intermediate age and biomass, but greatest tree density. The PHC site had the most heterogenous structure, perhaps due to past occasional selective tree harvesting. The site at PHC had the youngest average tree age, lowest densities and greatest biomass but some of the oldest individual trees among all three sites. The HF had greatest average tree age and intermediate tree density and lowest biomass compared to WL and PHC. Two additional sites [Number Four (N4) and Pack Forest (PF)] were used to expand the coverage for monitoring atmospheric N deposition (Figure 1).



Figure 1. Location of sites used in the Adirondack Manipulation and Modeling Project (AMMP). The three hardwood sites (Woods Lake, Pancake-Hall Creek and Huntington Forest) were the focus of the current study with Number Four and Pack Forest sites used only for monitoring atmospheric deposition.

Methods

Treatments

Within sites, three blocks were established and plots (either 5×5 m or 10×10 m) within a block were assigned chemical treatments or designated as reference plots (Table 2). Additions of $(\text{NH}_4)_2\text{SO}_4$ as a dry salt were applied once each year during the spring (late May or early July) of 1991, 1992 and 1993 at all three sites. At WL and HF additional plots were treated biweekly during the growing season (June–September) by backpack sprayer with solutions of H_2SO_4 , $(\text{Ca}\&\text{Mg})\text{SO}_4$ or HNO_3 . Further details on the sites and treatments are available in Mitchell et al. (1994b, 1998).

Table 1. Site characteristics of the three hardwood Adirondack Manipulation and Modelling Project (AMMP) sites. Vegetation information from Hurd et al. (1999)

Site (Abbreviation)	Latitude Longitude	Elevation (m)	Dominant overstory vegetation	Tree density (individuals ha ⁻¹)	Average tree DBH diameter breast height (cm)	Tree age (average)	Soil type
Woods Lake (WL)	43°53' N 74°57' W	678	<i>Betula alleghaniensis</i> <i>Acer rubrum</i>	1117	15	33	Lithic Haplorthod Lyman Series
Pancake-Hall Creek (PHC)	43°50' N 74°51' W	635	<i>A. saccharum</i> <i>Picea rubens</i> <i>Fagus grandifolia</i>	750	16	24	Typic Haplorthod Adams series
Huntington Forest (HF)	43°59' N 74°14' W	530	<i>A. rubrum</i> <i>B. alleghaniensis</i> <i>A. saccharum</i>	894	20	70	Typic Haplorthod Becket-Mundal Association

Table 2. Chemical treatments used in the Adirondack Manipulation and Modeling Project (AMMP)

Treatment (Plot size)	kg N ha ⁻¹ yr ⁻¹	Sites ⁷
Reference	ambient	WL, PHC, HF
H ₂ SO ₄ (5 × 5 m)	ambient	WL, HF
(Ca&Mg)SO ₄ (5 × 5 m)	ambient	WL, HF
HNO ₃ (5 × 5 m)	14 + ambient	WL, HF
Low (NH ₄) ₂ SO ₄ (10 × 10 m) except at PHC (5 × 5 m)	14 + ambient	WL, PHC, HF
High (NH ₄) ₂ SO ₄ (10 × 10 m) except at PHC (5 × 5 m)	28 + ambient	WL, PHC, HF

WL = Woods Lake; PHC = Pancake-Hall Creek; HF = Huntington Forest.

Sampling and analyses

Atmospheric deposition

Information was obtained to evaluate spatial and temporal changes of atmospheric N deposition. Deposition sampling in the AMMP was performed at five sites from west to east: N4, WL, PHC, HF and PF (Mitchell et al. 1994b). The N4 and the PF sites were used only for deposition monitoring in the current study. Collectors for measuring deposition varied among the sites depending on the availability of towers and associated instrumentation needed for dry deposition estimates [N4 (1993) and HF (1992–1993)] and the presence of open spaces for measuring bulk (two collectors per site) and wet only (AeroChemMetrics; ACM) precipitation [N4, HF and PF (1993)]. Bulk throughfall (TF) (9 collectors in reference plots) was measured (1991–1993) at the three hardwood sites (WL, PHC and HF) that were used for other measurements of N biogeochemistry. Ideally it would be useful to have measurements of dry and wet deposition and TF at all sites to quantify the relative importance of all forms of N input and the effects of canopy processes on N inputs to the forest floor (Johnson & Lindberg 1992; Lindberg et al. 1986). However, it was not feasible to have all these measurements at the three hardwood sites due to the availability of towers and electricity. Collector designs and protocols for calculating fluxes followed those used previously in the IFS (Integrated Forest Study) and the HF (Hicks et al. 1987; Lindberg et al. 1989; Johnson & Lindberg 1992; Shepard et al. 1989).

Soil solution

In each plot, three to four pairs of ceramic porous cup tension lysimeters (4-cm diameter with PVC pipe) were installed in 1990 at 15 and 50-cm. Lysimeters were evacuated to 276 kPa. Solutions were collected at approximately biweekly intervals during snowmelt from late March through early May. Between June and December samples were collected monthly. During the winter, samples were collected as permitted by weather conditions. Initially, chemical analyses were done separately for each lysimeter. Beginning in December 1991, when we were certain that all lysimeters were functioning and producing consistent results, lysimeter samples were bulked by plot and depth to save on time and costs of chemical analyses. Slightly elevated NO_3^- concentrations were found early in the study that were likely due to disturbance associated with lysimeter installation (Shepard et al. 1990). Such effects were less evident in subsequent years, and thus the results from the 1990 collection were excluded from the data analyses.

Litter inputs and litter bags

Litter fluxes were quantified using litter traps (0.25 m²). Two traps were placed in reference plots and those receiving $(\text{NH}_4)_2\text{SO}_4$ additions. Litter for mass and chemical analyses was collected biweekly in August, September, and October and monthly during the other snow-free months. Nylon-mesh litter bags were installed during late autumn 1991 with air dried *F. grandifolia* and *A. rubrum* litter. An equivalent of ~15 g of oven dry (60 °C) leaf litter was placed in each bag and the initial mass recorded. Three litter bags were removed from each plot in the spring of 1992 and autumns of 1992 and 1993. The mass of the litter bags was determined by oven drying at 60 °C and the litter was then pulverized for subsequent chemical analyses.

Buried mineral soil-bags

To evaluate the effects of chemical treatments on B-horizon soil chemistry, soil-bags were used. The soil-bag approach allows the evaluation of changes in the chemistry of forest soil over time by minimizing spatial variability. We have previously reported the results on the S constituents of soil-bags and soil solution for the AMMP (Mitchell et al. 1998). Bulk soil was collected from the Bh horizon within each site. The soil was passed through a 6-mm sieve, thoroughly homogenized, placed in 15 × 15 × 2.5 cm (250 μm nylon mesh) bags and installed beneath the Oa horizon during the late summer and early fall of 1990. For the reference plots at WL and PHC, soil-bags using soil from HF were also installed to evaluate the effects of initial soil characteristics. Further details on the bag construction, deployment and sampling are given in Mitchell et al. (1998). After collection, the soil was freeze-dried and stored for subsequent chemical analyses.

¹⁵N Sampling

Natural abundance – Various compartments of the forest ecosystem were sampled to determine $\delta^{15}\text{N}$ values in reference plots. During August of 1990, 1991, 1992 and 1993, fronds of *Dryopteris intermedia* were sampled using a quadrat harvest approach (Hurd et al. 1998). Understory (1–5 cm d.b.h.) *F. grandifolia* was sampled from the upper third of the crown. At HF and WL, overstory (> 5 cm d.b.h.) *F. grandifolia* was sampled from the middle third of the crown of the trees using pole pruners or by shooting down a branch.

Five mature (> 70 years old) individuals of *A. saccharum* were identified, marked, and aged at PHC and HF. If present, trees were selected from reference plots, but in some cases trees were outside of reference plots. All these trees were always > 25 m from the nearest chemical treatment plot, thus insuring that no effects of the chemical treatments. Due to an early leaf fall, only litter, soil, and roots were sampled in 1992. In 1993, the live strata (foliage and twigs) were sampled before leaf fall. Foliage and twigs were sampled from the upper third of the crown using pole pruners. *A. saccharum* leaf litter was collected from under each tree during leaf fall. Forest floor (Oe horizon) and roots were obtained by removing the overlying material and excavating a block from the soil surface. Mineral soil and roots (B horizon) were obtained by excavating a block of upper mineral soil. Fine roots (< 3 mm diameter) were separated from the bulk material by rinsing in deionized water and hand sorting.

In 1992 and 1993 organic horizons were sampled by cutting around a template and removing a 5.5 cm (diam) disk of each layer. Mineral horizons were sampled using a 2-cm diameter soil corer and horizon thickness was recorded. Subsamples of each horizon were dried at 60 °C and pulverized.

Experimental Additions of ¹⁵N – The fate of added ¹⁵N was monitored only at PHC. Ammonium sulfate was reconstituted using 10% (¹⁵NH₄)₂SO₄ mixed with unlabelled (NH₄)₂SO₄ fertilizer ($\delta^{15}\text{N} = -0.6\text{‰}$) resulting in (¹⁵NH₄)₂SO₄ with a $\delta^{15}\text{N}$ value of 379‰ used for experimental additions. This (¹⁵NH₄)₂SO₄ was added in 1991, 1992 and 1993 using the same protocol as described previously for chemical additions. The sampling of the ecosystem compartments was the same as that described for the sampling for ¹⁵N natural abundance except that sampling was within the chemical treatment plots.

Chemical analyses

Following collection, soil solutions were stored at 1 °C until further analysis. Samples were analyzed for NO₃⁻ (ion chromatography) and NH₄⁺ (Wescan) using methods described by Shepard et al. (1989). Total dissolved N (TDN)

was determined using persulfate oxidation (Ameel et al. 1993). Dissolved organic nitrogen (DON) was calculated as the TDN - ($\text{NO}_3^- + \text{NH}_4^+$). Foliage, leaf litter, forest floor, roots and soil were analyzed for C, H and N using a Perkin-Elmer 2400[®] CHN Analyzer. Total dissolved carbon (DOC) was determined by persulfate oxidation with quantification of CO_2 by IR spectrophotometry (Driscoll & van Drearon 1993).

Isotopic analyses

Pulverized samples with relatively high organic matter content (foliage and organic soils) were placed in tin vials and loaded into a Heraeus[®] elemental analyzer coupled to a Finnigan CT-CN cryogenic trapping box, which was interfaced with a Finnigan Delta-S isotope ratio mass spectrometer (Boston University Stable Isotope Laboratory) for automated analysis. Samples containing lower amounts of organic matter (mineral soils) were loaded into stainless steel vials containing ~1 g CuO and pulverized a second time using a Wig-L-Bug[®]. The samples were then poured into pre-combusted quartz tubes and ~0.5 g of pre-cleaned Cu wire added. These tubes were evacuated, heat sealed and combusted at 900 °C (1 hr), 650 °C (2 hr), 600 °C (1 hr), and cooled overnight to room temperature. Combustion products were separated cryogenically and N_2 was collected on silica gel (6–16 mesh) for manual dual inlet analysis. All stable isotope data are presented using conventional per mil (‰) notation. Stable isotope replicate analytical precision was usually within 0.2(‰).

Quality assurance/quality control(QA/QC)

An extensive QA/QC protocol was utilized in the analyses including the use of certified standards (National Institute of Standards and Technology) and participation in the Long Range Transport of Air Pollution (LRTAP) program for solution chemistry. For the solute analyses, known standards were used at the beginning of each day of analyses. Blanks were analyzed and matrix spikes performed on at least 5% of the samples analyzed. For leaf litter standards included internal laboratory standards for *A. rubrum* and *F. grandifolia* as well as certified NIST standards (apple leaves #1515, peach leaves #1547, citrus #1572). For the mineral soil-bags, the chemical analyses were compared to laboratory reference standards prepared from the original bulk mineral soil from each site. For these analyses, accuracy was within 5% of the standards and precision among samples was within 5% of the relative standard deviation.

Hydrological fluxes

Although comparisons of N solute chemistry concentrations can provide insight on some aspects of N cycling in forest ecosystems, measurements

of N solute flux rates are needed to quantify N losses through soil leaching. It is difficult to obtain direct measures of N solute flux and commonly investigators rely on models of water flux combined with measurements of soil water concentration to estimate leaching losses (Currie et al. 1999; Holmes & Zak 1999; Mitchell et al. 1992a). We used a hydrological model to predict water flux at 15 and 50-cm soil depth at WL, PHC and HF.

Of the three study sites, HF had the most detailed meteorological and hydrological data that included precipitation, temperature and stream discharge. The HF has a meteorological and a NADP/NTN station located ~1 km from the study plots. Shepard et al. (1989) summarized meteorology and chemical atmospheric deposition of HF. The major inlet of Arbutus Lake at HF drains 130 ha and has been monitored since 1994 using a H-flume equipped with automated logging of discharge. We used discharge data from 1995 and 1996 calendar years to calibrate the BROOK90 (Version 3.24) hydrological simulation model (Federer 1995).

BROOK 90 simulates water budgets on a daily basis after initial snow water and initial ground water storage are defined. The model requires daily values of maximum air temperature, minimum air temperature, precipitation, average wind speed, solar radiation and vapor pressure, of which the latter three may be calculated within the model. For our calibration, we had direct measurements on all input parameters with the exception of vapor pressure which was thus calculated using the model. The soil physical and chemical properties were based upon measurements made at HF and the canopy characteristics were kept the same as those used in the parameter file provided for the Hubbard Brook Experimental Forest (HBEF) has similar soils and vegetation as HF (David et al. 1987). To obtain the best fit of model calculations, some minor adjustments were made that resulted in standard deviation on a daily basis, daily relative root mean squared error and overall mean bias error being 2.47, 2.88 and -0.073 , respectively. These values compare favorably with results for the HBEF (Federer 1995). The daily simulated and measured drainage values for HF are shown in Figure 2.

For obtaining soil water flux, the soil was divided into seven layers. Depths 3 and 7 corresponded to 16 and 52 cm, respectively, and the predicted water fluxes from these layers were used to estimate solute transport flux by multiplying mean monthly solute concentration (15 and 50-cm lysimeters, respectively) by monthly water flux for each depth. To apply the model to the WL and PHC sites we assumed that the soils, which also were Haplorthods (Table 1), had the same hydrological characteristics of HF, but precipitation and temperature were site specific. Differences in precipitation were estimated by comparing TF amount for WL and PHC with that at HF. The TF values at WL and HF were 30 and 35% respectively greater than at HF,

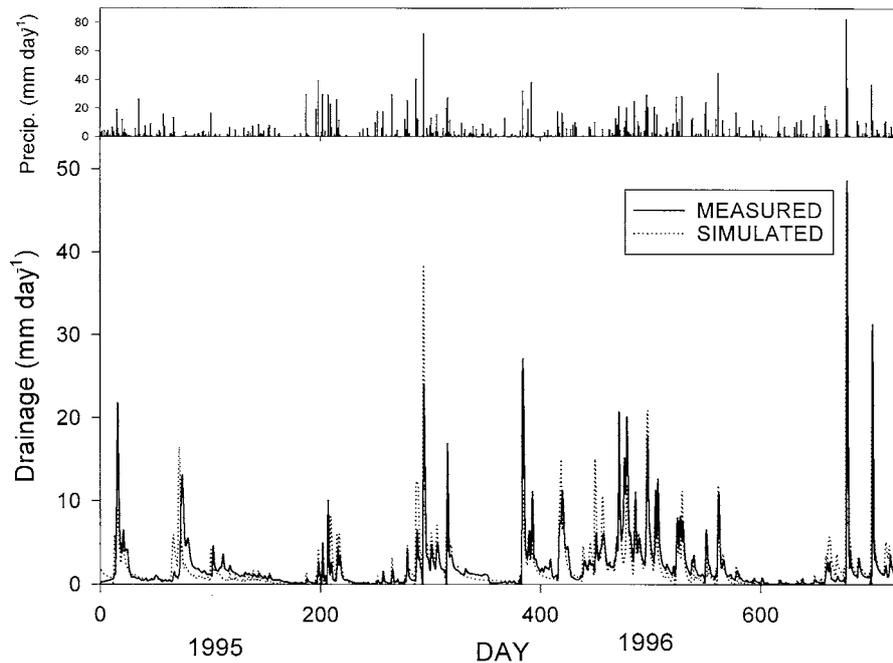


Figure 2. Daily precipitation inputs and discharge rates (measured and simulated by BROOK90) at the inlet of Arbutus Lake at Huntington Fores (HF) in Adirondack Mountains of New York.

consistent with previously observed spatial patterns of precipitation across the region (Driscoll et al. 1991; Ito et al. 2001). Daily temperatures at WL and PHC were modified to account for the elevational differences among the sites (Table 1) by decreasing the daily temperature recorded at HF by $0.6^{\circ}\text{C}/100\text{ m}$ elevation (Ricklefs 1979).

Statistical analyses

Mean values for solute chemistry were calculated using all samples of a specific type (i.e. site, treatment and depth) for each calendar year. Means were not weighted by sample volumes since there was no direct relationship between volume of solution collected and hydrological fluxes. Analysis of variance (ANOVA) was used to examine treatment effects on solution chemistry, litter inputs, litter chemistry and the soil-bag chemistry within each year for each site separately. Differences in litter mass, chemistry and mass loss were compared among sites and also among plant species for reference plots. Repeated measure analysis was used for analyzing the results for the entire three year study period for each site (Littell et al. 1991). A randomized complete-block design was used. Mean separation at the 5% level using

Duncan's multiple range test as was done in a previous study focusing on S (Mitchell et al. 1998). First order decomposition rates of litter were calculated using linear regression with differences in decomposition rates evaluated using Student's t-test for evaluating differences among means. The Statistical Analyses System for personal computers was used for all data analyses (SAS Institute 1988).

Results and discussion

Deposition

Dry deposition

Air concentrations of HNO_3 vapor concentrations were the same at N4 and at HF while concentrations of NO_3^- and NH_4^+ aerosols were lower at N4 than at HF (Table 3). The HNO_3 vapor concentrations were identical, but NO_3^- and NH_4^+ aerosol concentrations were lower than measured previously (1986–1988) at the HF (Shepard et al. 1989). Measurements at Big Moose from 1988–1989 (EPA-OEN 1991) found lower HNO_3 vapor concentrations, but higher concentrations of NO_3^- and NH_4^+ aerosols than found at N4 or HF for the present study. In the IFS, EPA-OEN and the present study, air samples were collected during only a fraction of the non-raining hours at each site thus providing one possible explanation for differences in average air concentrations between studies. Deposition velocities at HF during the present study were similar to those reported during IFS (Shepard et al. 1989). For the N4 site, deposition velocities (DV) were smaller than at HF for HNO_3 vapor, but somewhat greater for NO_3^- and NH_4^+ aerosols.

Total dry N deposition was similar at the HF during the present study as reported previously during the IFS (Table 3). All forms of dry deposition were lower at N4 than HF (lower DV's outweighing higher air concentrations). During the IFS (but not AMMP), coarse particle sedimentation fluxes were measured. For NO_3^- and NH_4^+ ions respectively, sedimentation contributed an additional 19 and 26% to the other forms of dry deposition (vapor deposition and aerosol impaction) in that study. Therefore, dry deposition of N inferred in AMMP from DV's and air concentrations should be viewed as lower limits.

Wet deposition and throughfall fluxes

Nitrate and NH_4^+ inputs in wet deposition were higher at N4 than at HF and PF (Table 3). These data are generally consistent with higher wet deposition in the southwestern Adirondacks (N4) than more eastern Adirondack areas (HF and PF) (See also Ito et al. 2001). These result support our hypothesis that N inputs generally decrease from west to east in the Adirondacks. In

Table 3. Deposition of N in the Adirondack region for AMMP sites [N4, Huntington Forest (HF), Pack Forest (PF)] and Big Moose

Measurement	Chemical Species	Site (period of measurement)					
		N4 (1993) ⁸	HF (1992– 1993) ⁸	HF (1986– 1988) ⁹	Big Moose (1988– 1989) ¹⁰	PF (1992– 1993) ⁸	PF (1986– 1987) ¹¹
Air Concentration ($\mu\text{g m}^{-3}$)	HNO ₃ (vapor)	1.80	1.80	1.80	0.80	NA ¹²	NA
	NO ₃ ⁻ (aerosols)	0.11	0.19	1.10	0.16	NA	NA
	NH ₄ ⁺ (aerosols)	0.57	1.00	1.30	0.85	NA	NA
Dep. Velocity (cm s^{-1})	HNO ₃ (vapor)	1.20	2.00	2.10	NA	NA	NA
	NO ₃ ⁻ (aerosols)	0.12	0.02	0.02	NA	NA	NA
	NH ₄ ⁺ (aerosols)	28.50	16.70	21.70	NA	NA	NA
Dry Deposition ($\text{kg N ha}^{-1} \text{ yr}^{-1}$)	HNO ₃ (vapor)	1.50	2.50	2.40	NA	NA	NA
	NO ₃ ⁻ (aerosols)	< 0.01	< 0.01	< 0.01	NA	NA	NA
	NH ₄ ⁺ (aerosols)	0.02	0.06	0.06	NA	NA	NA
	Total	1.52	2.56	2.46	NA	NA	NA
Wet Deposition (bulk) ($\text{kg N ha}^{-1} \text{ yr}^{-1}$)	NO ₃ ⁻	4.20	2.70	3.65	NA	2.5	4.5
	NH ₄ ⁺	2.20	1.30	2.52	NA	1.1	1.1
Wet Deposition (wet only) ($\text{kg N ha}^{-1} \text{ yr}^{-1}$)	NO ₃ ⁻	2.50	2.50	2.80	4.70	2.6	NA
	NH ₄ ⁺	1.60	1.30	2.00	2.90	1.2	NA

⁸This study.

⁹IFS (Shepard et al. 1989).

¹⁰EPA-OEN (1991).

¹¹Shepard et al. (1991).

¹²Not available.

Table 4. Bulk throughfall inputs to Woods Lake (WL), Pancake-Hall Creek (PHC) and Huntington Forest (HF)

Site	Year	Water	NH ₄ ⁺	NO ₃ ⁻
		mm	kg N ha ⁻¹ (conc. μmol L ⁻¹)	
WL	1991 ¹³	582	1.5 (16)	3.2 (37)
	1992	1321	3.6 (19)	6.5 (39)
	1993	1234	1.8 (12)	8.4 (45)
	flux mean (1992–1993)	1278	2.7 (16)	7.4 (40)
	conc. (1991–1993)			
PHC	1991	604	1.5 (17)	2.9 (34)
	1992	1372	4.2 (19)	8.3 (44)
	1993	1282	2.2 (13)	8.7 (47)
	mean (1992–1993)	1327	3.2 (16)	8.8 (42)
	conc. (1991–1993)			
HF	1991	446	1.0 (13)	2.3 (27)
	1992	1014	1.9 (11)	3.6 (34)
	1993	818	0.8 (7)	3.0 (33)
	mean (1992–1993)	916	1.3 (11)	3.3(31)
	conc. (1991–1993)			

¹³Only August–December for 1991.

all cases, NH₄⁺ deposition was about one-third of total wet deposition. Other data are available to examine temporal changes in N deposition fluxes in the Adirondacks (Table 3). There is some suggestion that N deposition amounts were higher in previous studies. These results agree with analyses at the NADP site at the HF that have found a decrease over time in wet only NO₃⁻ deposition from 1978–1994 (Driscoll et al. 1995).

Mean NO₃⁻ concentrations (volume weighted means for all three years) of TF were higher ($p < 0.01$) at WL and PHC than at HF. Similarly, mean NH₄⁺ concentrations were higher ($p < 0.01$) at WL and PHC than at HF. The greater amounts of TF water flux at WL and PHC compared to HF, combined with higher concentrations of NO₃⁻ and NH₄⁺, resulted in more than twice the TF fluxes of DIN at WL and PHC compared to HF (Table 4). During the IFS (1985–1998) higher concentrations of NO₃⁻ (55 μmol L⁻¹) and NH₄⁺ (26 μmol L⁻¹) were found in TF at HF in a northern hardwood forest in close proximity to the present study location (Mitchell et al. 1992a). The TF fluxes at WL and PHC were also higher than for any site studied in the IFS except for a high elevation spruce site in the Smokies Mountains (Johnson & Lindberg 1992).

Table 5a. Litter inputs for the Adirondack Manipulation and Modeling Project (AMMP) sites [Woods Lake (WL), Pancake-Hall Creek (PHC) and Huntington Forest (HF)] with results from reference and treated plots combined (n = 9)

Site	Dry mass	N	C	C:N
	kg ha ⁻¹ yr ⁻¹ ± S.D.			
WL	2672 + 468	38 ± 9	1366 ± 243	36
PHC	3120 + 133	36 ± 1	1568 ± 76	44
HF	3109 + 275	36 ± 4	1552 ± 143	43

These TF results are consistent with the measurements of wet deposition and suggest that the western Adirondacks experience higher rates of N deposition than the eastern Adirondacks. The absence of an east to west gradient in dry deposition is not surprising because previous studies have indicated different spatial patterns of wet and dry deposition. Wet deposition persists further from source areas than dry deposition (Hicks 1989; Schaefer 1992; Summers & Fricke 1989). During the current study, dry deposition of N accounted for 39% of total N deposition which is similar to the 44% contribution during the IFS (Shepard et al. 1989).

Litter

Inputs

There were greater ($p < 0.05$) litter mass and C inputs in the reference plots, at PHC and HF than at WL. This same pattern was also evident if results from all treatment and reference plots were used in an intersite comparison (Table 5a). Litter N inputs were similar at all three sites. Treatments did not affect litter fluxes relative to reference plots. However, at HF mass of litter inputs and C inputs were, however, greater ($p < 0.05$) in the low (NH₄)₂SO₄ treatment (3290 kg ha⁻¹ yr⁻¹ and 1640 kg C ha⁻¹ yr⁻¹) than in the high (NH₄)₂SO₄ treatment (2950 kg ha⁻¹ yr⁻¹ and 1470 kg C ha⁻¹ yr⁻¹) plots. The leaf litterfall flux at HF was similar to the value (3130 kg ha⁻¹ yr⁻¹) reported previously for the IFS (Johnson & Lindberg 1992). In another upland hardwood site within the Arbutus Watershed at HF, litterfall inputs in 1995 and 1996 for September–November (the period that dominates the litter inputs) were 2730 kg ha⁻¹ (Ohruj et al. 1999).

Litter decomposition and elemental composition

There were no significant differences in N concentrations or C:N ratios of litter between *A. rubrum* and *F. grandifolia* or between sites (Table 5b).

Table 5b. Elemental concentrations in litter in reference plots

Leaf tree species	Parameter	Site		
		WL	PHC	HF
		mean \pm S.E. (N)		
	g N kg ⁻¹ litter			
<i>Acer rubrum</i>		14.5 \pm 2.0 (4)	16.9 \pm 1.0 (18)	15.7 \pm 1.00 (18)
<i>Fagus grandifolia</i>		16.5 \pm 1.9 (5)	16.1 \pm 1.4 (8)	16.5 \pm 0.97 (16)
	C:N			
<i>Acer rubrum</i>		35.7 \pm 2.0 (4)	29.9 \pm 1.9 (18)	33.9 \pm 3.2 (18)
<i>Fagus grandifolia</i>		31.5 \pm 3.5 (5)	31.6 \pm 2.8 (8)	31.5 \pm 2.5 (16)

Table 5c. Litter decomposition rates with reference and treated plots combined

Leaf tree species	Site			
	WL	PHC	HF	
		k (yr ⁻¹) mean \pm S.E. (N)		
<i>Acer rubrum</i>	0.45 \pm 0.09 (11)	0.40 \pm 0.01 (51)	0.29 \pm 0.07 (56)	
<i>Fagus grandifolia</i>	0.51 \pm 0.04 (14)	0.42 \pm 0.001 (32)	0.25 \pm 0.02 (53)	

There were no significant effects of chemical treatment on loss of litter mass at any of the sites. Litter decomposition rates were not significantly different between WL and PHC, but both were significantly higher than at HF (Table 5c). At HF, *A. rubrum* litter had a greater ($p \leq 0.05$) mass loss than *F. grandifolia*. Previous work has found the *F. grandifolia* litter decomposes more slowly than *A. saccharum* due to its higher lignin content (Melillo et al. 1982). In a comparison of N cycling between Turkey Lakes, Ontario and HF, the higher amounts of NO₃⁻ leaching in the former site may have been due high decomposition rates and the absence of *F. grandifolia* (Mitchell et al. 1992b). Lovett and Rueth (1999) reported that in the northeastern U.S. that *A. saccharum* stands showed a strong correlation between N deposition and N mineralization and nitrification while no such correlations were found for *F. grandifolia* stands.

There were a few significant treatment effects on leaf litter chemical composition. *Fagus grandifolia* litter at HF had higher N concentrations (17.8 g N kg⁻¹ litter), higher N contents (0.25 g N) and lower C:N ratios (29.2) in the high (NH₄)₂SO₄ treatment compared to the reference plots. Similar

patterns were also found for the other sites for both *F. grandifolia* and *A. rubrum* litter, but these were not statistically significant.

Mineral soil-bags

All the buried bags showed an increase in N and C concentrations and a narrowing of C:N ratios compared to the bulk soil initially placed in the bags (Table 6). There was no significant treatment effect on C or N concentrations in the mineral soil bags and thus only means across all treatments are reported. These results are similar to those reported at Bear Brook Watershed in Maine where buried mineral soil bags also showed an increase in C and N concentrations during the first four years after being placed back in the soil, likely due to illuviation (Mitchell et al. 1994a; Rustad et al. 1996). For HF soil that was placed in the reference plots at WL and PHC, the C and N concentrations were lower than HF buried-bags returned to the same HF site (Table 6). These lower concentrations of HF soil at WL and PHC site are consistent with more rapid organic matter leaching in the sites of the western Adirondacks with their greater water fluxes (Table 4).

Soil solution concentrations

Nitrate

In the reference plots, NO_3^- was the dominant solute in all three sites except the 15-cm depth at the HF with relatively high DON concentrations (Figure 3). The mean soil solution NO_3^- concentrations in the reference plots were higher at PHC than at WL and HF at 15-cm over the entire study period. At 50-cm the concentrations were higher at PHC and WL than at HF. Generally NO_3^- concentrations decreased during the three years of the study (Figures 4 and 5), suggesting that the higher concentrations at the early period of the study may have been partly attributed to disturbance associated with lysimeter installation (Shepard et al. 1990). The greatest NO_3^- response to the chemical manipulations was at HF where the HNO_3 additions resulted in the highest concentrations (Figures 4 and 5). This result supports our hypothesis that N loss rates are more sensitive to NO_3^- additions as compared to NH_4^+ additions. The low $(\text{NH}_4)_2\text{SO}_4$ treatment also resulted in NO_3^- concentration that was greater than that in the reference plots at 15-cm. Treatment with $(\text{Ca}\&\text{Mg})\text{SO}_4$ increased NO_3^- only in 1991 and 1993 at 15-cm. This effect of HNO_3 addition was still evident at 50-cm where NO_3^- concentrations were greater than the reference plots. At PHC no significant response of NO_3^- concentrations resulted from the chemical manipulations although the treated plots tended to have higher NO_3^- concentrations. At WL, only the high $(\text{NH}_4)_2\text{SO}_4$ treatment resulted in NO_3^- concentrations being greater than

Table 6. Mineral soil bags using soil from Bh horizon from Woods Lake (WL), Pancake-Hall Creek (PHC) and Huntington Forest (HF) (mean \pm S.E.)

Parameter	Unit	Initial chemical characteristics						Chemical characteristics (1991, 1992, 1993)					
		Native soil			Site			Native soil			HF soil		
		WL	PHC	HF	WL	PHC	HF	WL	PHC	HF	WL	PHC	HF
n		9	9	9	197	107	197	107	197	26	15		
pH		4.2 \pm 0.0	4.3 \pm 0.0	4.3 \pm 0.0	4.2 \pm 0.1	4.3 \pm 0.1	4.3 \pm 0.1	4.3 \pm 0.1	4.3 \pm 0.1	4.3 \pm 0.1	4.3 \pm 0.1	4.3 \pm 0.1	
C	g kg ⁻¹	45.8 \pm 5.5	25.1 \pm 2.2	47.7 \pm 5.0	50.1 \pm 9.9	30.6 \pm 5.6	56.5 \pm 13.8	50.4 \pm 9.3	52.2 \pm 14.1				
H	g kg ⁻¹	2.7 \pm 1.8	0.6 \pm 0.5	4.2 \pm 2.5	4.5 \pm 2.8	2.7 \pm 1.6	6.4 \pm 4.1	5.1 \pm 3.4	4.4 \pm 1.6				
N	g kg ⁻¹	1.6 \pm 0.3	0.9 \pm 0.3	1.7 \pm 0.5	2.5 \pm 0.7	1.6 \pm 0.4	2.7 \pm 0.7	2.4 \pm 0.6	2.4 \pm 0.7				
C:N		28.6	27.9	28.0	20.0	19.1	20.9	21.0	22.8				

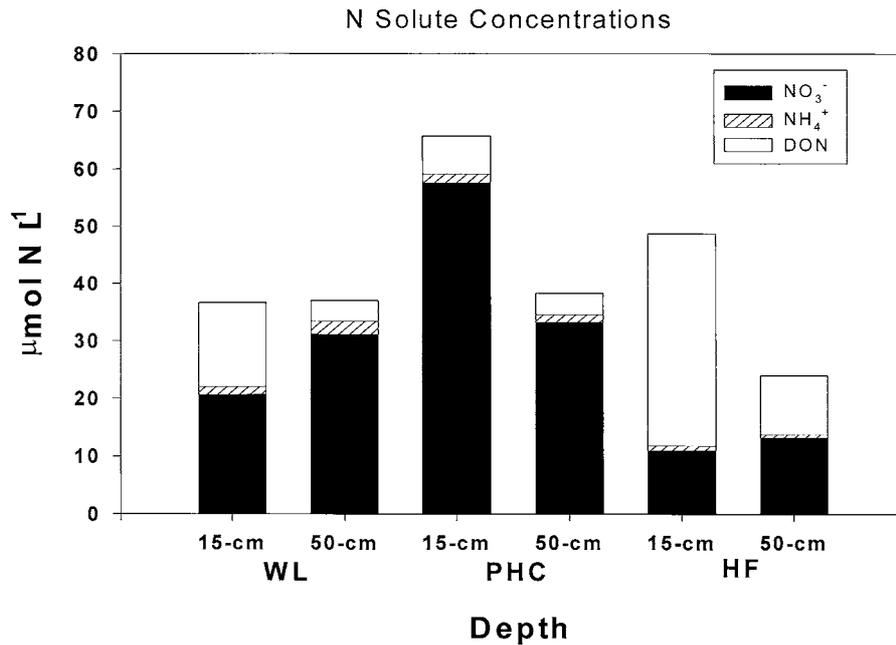


Figure 3. Mean N solute concentrations at 15 and 50-cm depths in reference plots Woods Lake (WL), Pancake-Hall Creek (PHC) and Huntington Forest (HF).

that of the reference plots. There was no effect of the H₂SO₄ treatment on soil water NO₃⁻ concentrations at either WL or HF.

Ammonium

The NH₄⁺ concentrations in the reference plots at all three sites were generally low ($3 \leq \mu\text{mol L}^{-1}$) at both 15-cm and 50-cm and constituted < 7% of total N solute concentrations (Figure 3). There was a significant treatment effect on NH₄⁺ concentrations at WL, where the high (NH₄)₂SO₄ treatment increased the concentration at 15-cm (Figure 6). There was also a significant treatment effect at 50-cm at WL resulting in lower NH₄⁺ concentrations at 50-cm that was due to a relatively high NH₄⁺ concentration in the reference plots at 50-cm in 1993 at WL (Figure 7).

DON

Concentrations of DON in the reference plots at WL and HF at 15-cm contributed substantially to TDN (40 and 76% respectively) while at PHC, DON contributed only 10% (Figure 3). At 50-cm depth DON was less than 10% of TDN at WL and PHC, but comprised 43% at HF. There was no effect due to chemical additions of N on DON or DOC concentrations. McDowell et al.

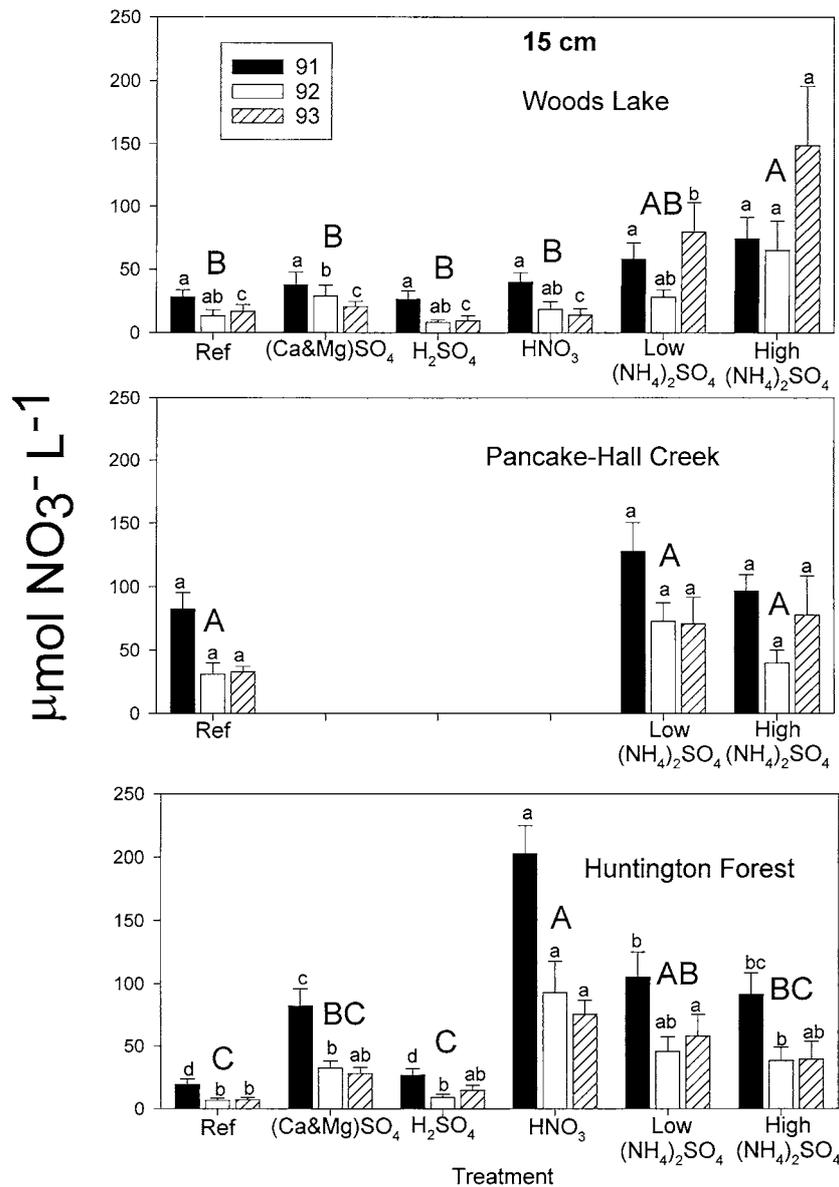


Figure 4. Concentration of NO_3^- in soil solution at 15 cm depth at Woods Lake (WL), Pancake-Hall Creek (PHC) and Huntington Forest (HF) study sites in reference and treated plots. Different lowercase letters indicate statistically significant differences ($p < 0.05$) among treatments within a year. Different uppercase letters indicate statistically significant differences ($p < 0.05$) among treatments for all years combined.

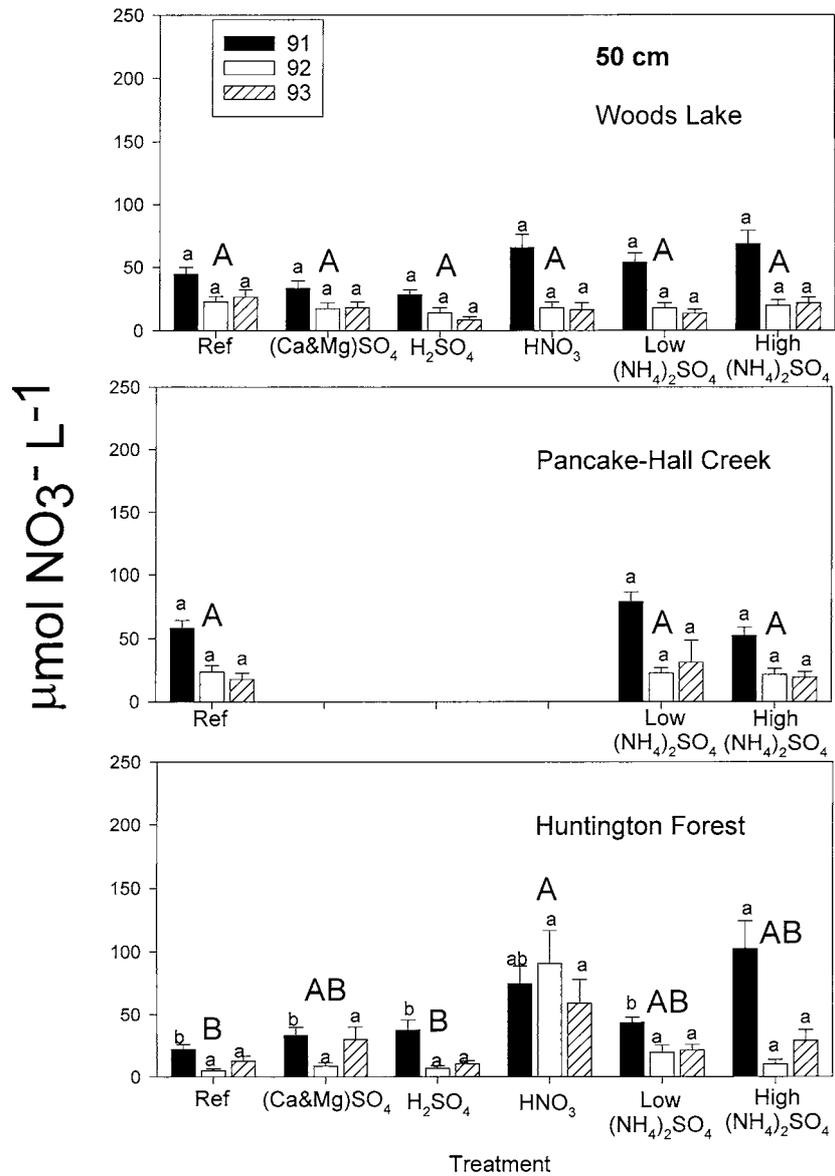


Figure 5. Concentration of NO_3^- in soil solution at 50 cm depth at Woods Lake (WL), Pancake-Hall Creek (PHC) and Huntington Forest (HF) study sites in reference and treated plots. Different lowercase letters indicate statistically significant differences ($p < 0.05$) among treatments within a year. Different uppercase letters indicate statistically significant differences ($p < 0.05$) among treatments for all years combined.

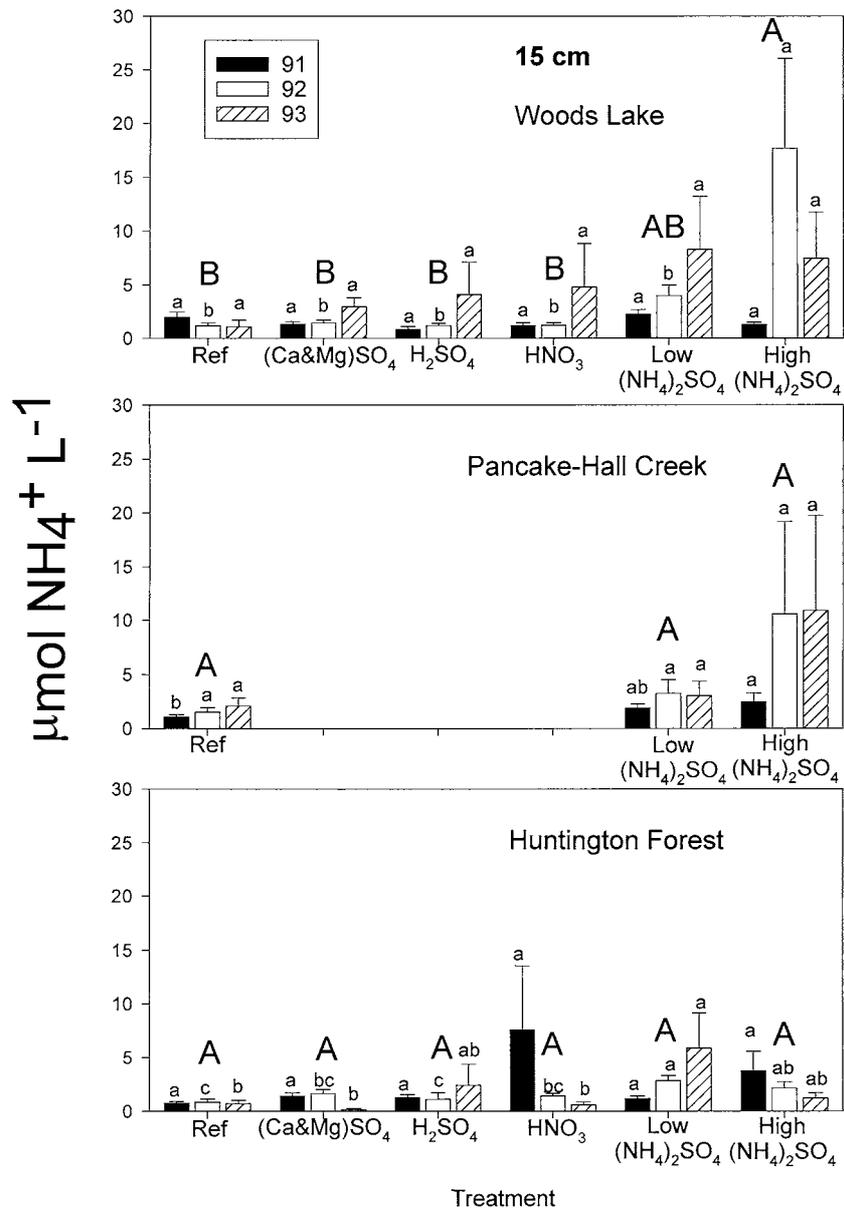


Figure 6. Concentration of NH_4^+ in soil solution at 15 cm depth at Woods Lake (WL), Pancake-Hall Creek (PHC) and Huntington Forest (HF) study sites in reference and treated plots. Different lowercase letters indicate statistically significant differences ($p < 0.05$) among treatments within a year. Different uppercase letters indicate statistically significant differences ($p < 0.05$) among treatments for all years combined.

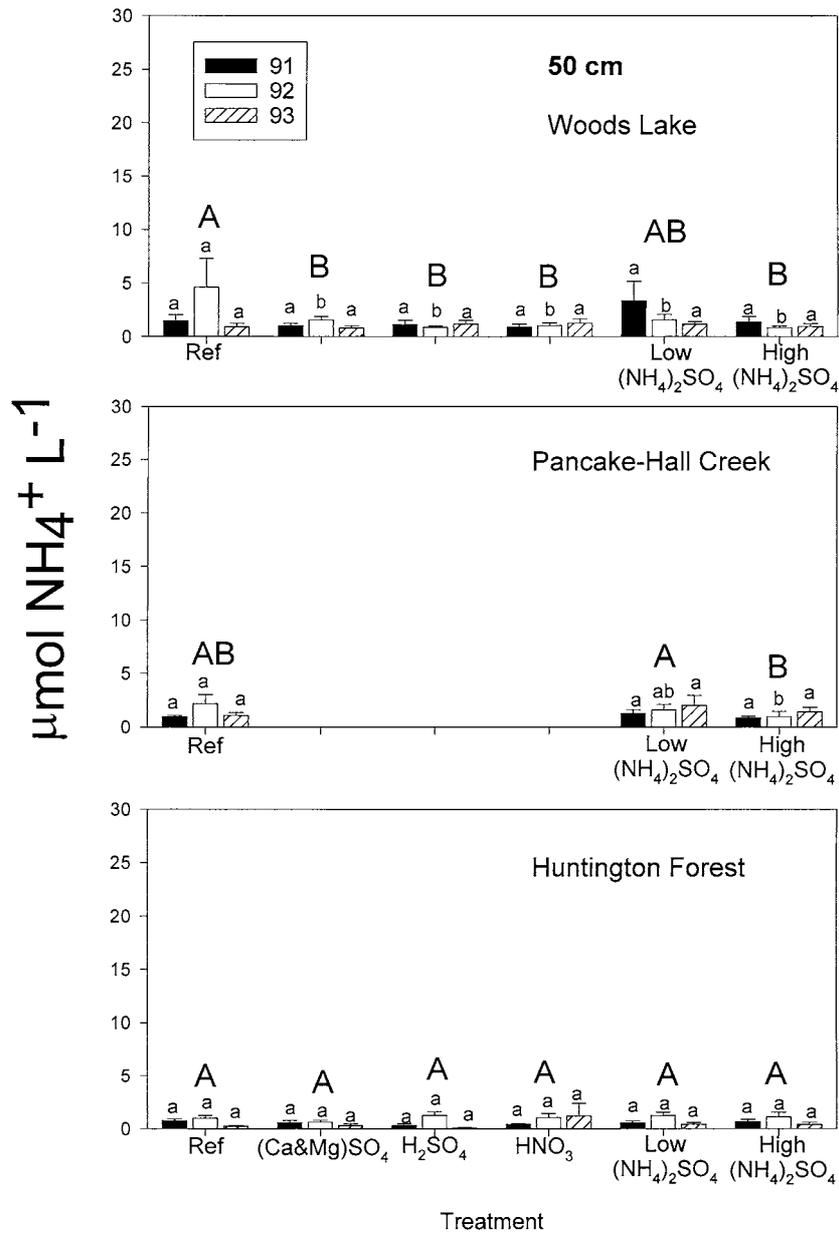


Figure 7. Concentration of NH_4^+ in soil solution at 50 cm depth at Woods Lake (WL), Pancake-Hall Creek (PHC) and Huntington Forest (HF) study sites in reference and treated plots. Different lowercase letters indicate statistically significant differences ($p < 0.05$) among treatments within a year. Different uppercase letters indicate statistically significant differences ($p < 0.05$) among treatments for all years combined.

(1998) and Currie et al. (1996) found at the Harvard Forest that at the highest N additions ($150 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) that there were increases in DON. These N additions were substantially greater than those used in the current study. Similar to the results of McDowell et al. (1998), we observed a significant positive relationship between DOC and DON ($\text{DON } (\mu\text{mol L}^{-1}) = 0.027 \times \text{DOC } (\mu\text{mol L}^{-1}) - 2.54$; $R^2 = 0.76$).

Other studies have also shown that DON may comprise more than 55% of TDN in soil solutions, even under conditions of elevated N deposition (Currie 1999; Currie et al. 1996; Lajtha et al. 1995). At the watershed scale, DON can contribute significantly to N solute flux (Campbell et al. 2000). Similar contributions of DON to N solutes as those found in the present study were reported at the Arbutus Watershed at the HF. At the major inlet to Arbutus Lake, DON comprised 36% of solute flux with NO_3^- and NH_4^+ contributing 61% and 3%, respectively, while at the lake outlet DON was 61% of N solute flux with NO_3^- and NH_4^+ contributing 33% and 6%, respectively (McHale et al. 2000).

Comparisons with previous studies at the AMMP sites

The results from the reference plots of current study agree with results from previous studies at these sites that have shown that NO_3^- is a larger component of DIN than NH_4^+ . Although there were differences in the actual plot locations, sampling depths and sampling devices (tension and zero tension lysimeters) used for obtaining soil waters, earlier studies agree with the current investigation with respect to relative differences in soil solution NO_3^- concentrations among the three sites (Table 7). All studies have found higher NO_3^- concentrations at WL and PHC than HF indicating that these two sites in the western Adirondacks have experienced higher NO_3^- concentrations for an extended period.

Soil solution fluxes and N mass balances

The reference plots at WL and PHC were characterized by higher NO_3^- and NH_4^+ fluxes at 15 and 50-cm than at the HF, while DON fluxes were greater for this latter site. At WL, NO_3^- fluxes at the 15-cm depth were higher in the $(\text{NH}_4)_2\text{SO}_4$ treatments compared to the reference plots and the other treatments (Table 8). At 15 or 50-cm, soil water flux at WL showed no discernable pattern in NO_3^- flux due to treatments. Soil solutions of PHC at 15-cm tended to have greater NO_3^- fluxes in the $(\text{NH}_4)_2\text{SO}_4$ plots than in the reference plot; there was no pattern at 50-cm. At HF, the HNO_3 treatment resulted in substantially higher NO_3^- fluxes at both 15-cm and 50-cm than in the reference plots. The H_2SO_4 treatment had similar NO_3^- fluxes at 15 and 50-cm to those of the reference plots at WL and HF. The $(\text{NH}_4)_2\text{SO}_4$ treatments at HF resulted in

Table 7. Comparisons of N solute concentrations of Adirondack hardwood ecosystems [Woods Lake (WL), Pancake-Hall Creek (PHC), Huntington Forest (HF)]

Site	Soil depth (cm) or horizon	Date(s)	N solute concentration			Reference
			NO ₃ ⁻	NH ₄ ⁺	DON	
$\mu\text{mol L}^{-1}$						
WL	20	1980–1981 Summer	90	2		Cronan (1985)
	20	1980–1981 Winter	116	8		
	50	1980–1981 Summer	28	2		
	50	1980–1981 Winter	76	2		
	Oa	1989–1992	112	7		Geary and Driscoll(1996)
	Bs		91	2		
	15	1991–1993	19	1	10	Current Study Reference Plots
50		32	3	3		
PHC	Oa	1985	80			Cronan et al. (1990)
	Bs		67			
	15	1991–1993	53	2	8	Current Study
	50		31	1	4	
HF	E	1985–1988	39	4		Mitchell et al. (1992a)
	B		18	2		
	15	1992–1993	11	2		McHale and Mitchell (1996)
	15	1991–1993	14	1	38	
	50		14	1	10	Current Study

greater NO₃⁻ fluxes at 15-cm and 50-cm. At all sites and for all treatments NH₄⁺ fluxes were small compared to NO₃⁻ fluxes (Table 8).

Nitrogen mass balances were calculated as the difference between TF plus any treatment inputs minus N drainage losses at either 15 or 50 cm (Table 8). In the reference plots at WL, PHC and HF, the percent N retentions were lower at WL and PHC than HF. Thus, the two sites (WL and PHC) with the highest atmospheric inputs of N had relatively low N retention in the absence

Table 8. Mass balances for nitrogen for three sites in the Adirondack region [Woods Lake (WL), Pancake-Hall Creek (PHC) and Huntington Forest (HF)] (fluxes in $\text{kg N ha}^{-1} \text{ yr}^{-1}$)

Site	Inputs			15-cm depth				50-cm depth						
	Treatment	TF	Treatment	Total	NO_3^-	NH_4^+	DIN	Reten.	% Reten.	NO_3^-	NH_4^+	DIN	Reten.	% Reten.
WL														
Reference		10.1	0	10.1	4.6	0.16	4.8	5.4	53	5.5	0.36	5.9	4.3	42
(Ca&Mg)SO ₄		10.1	0	10.1	7.6	0.23	7.8	2.4	23	6.9	0.11	7.0	3.1	31
H ₂ SO ₄		10.1	0	10.1	3.5	0.15	3.7	6.5	64	3.7	0.09	3.8	6.4	63
HNO ₃		10.1	14	24.1	5.8	0.13	5.9	18.2	75	6.2	0.11	6.3	17.8	74
Low(NH ₄) ₂ SO ₄		10.1	14	24.1	9.5	0.29	9.8	14.3	59	4.9	0.13	5.0	19.1	79
High(NH ₄) ₂ SO ₄		10.1	28	38.2	9.3	0.45	9.7	28.4	74	4.5	0.08	4.6	33.5	88
PHC														
Reference		11.7	0	11.7	7.7	0.22	7.9	3.8	33	6.8	0.17	7.0	4.7	40
Low(NH ₄) ₂ SO ₄		11.7	14	25.7	12.6	0.37	12.9	12.8	50	6.9	0.22	7.1	18.6	72
High(NH ₄) ₂ SO ₄		11.7	28	25.7	9.5	0.99	10.5	29.2	74	5.9	0.11	6.0	33.7	85
HF														
Reference		4.6	0	4.6	1.4	0.07	1.5	3.1	68	1.0	0.04	1.0	3.6	78
(Ca&Mg)SO ₄		4.6	0	4.6	4.8	0.10	4.9	-0.3	-7	1.8	0.03	1.8	2.7	59
H ₂ SO ₄		4.6	0	4.6	1.8	0.18	2.0	2.7	58	1.9	0.04	1.9	2.7	59
HNO ₃		4.6	14	18.6	10.6	0.84	11.4	7.2	39	6.3	0.05	6.4	12.3	66
Low(NH ₄) ₂ SO ₄		4.6	14	18.6	5.8	0.16	6.0	12.7	68	2.7	0.04	2.7	15.9	85
High(NH ₄) ₂ SO ₄		4.6	28	32.6	4.8	0.16	4.9	27.6	85	4.6	0.04	4.6	28.0	86

of experimental N additions. These two western sites (WL and PHC) also had higher N concentrations in herbaceous species (excluding ferns) than HF and N concentrations in understory vegetation generally reflected the spatial and temporal patterns (yearly) in soil solution N (Hurd et al. 1998). In the N treated plots at WL, PHC and HF, net N retention ranged from 59 to 75%, 74 to 88% and 39 to 85% of N at 15 cm and from 74 to 88, 73 to 85%, and 66 to 86% at 50 cm. The HNO₃ treatments at HF resulted in the lowest N retentions (39% at 15 cm and 67% at 50 cm) of any of the N treated plots in the three study sites supporting our hypothesis that N loss rates would be more sensitive to NO₃⁻ additions compared to NH₄⁺ additions. The (Ca&Mg)SO₄ treatments, conducted only at WL and HF, resulted in low N retention or N losses (23% and 31% at 15 and 50 cm, respectively at WL; -7% and 60% at 15 and 50 cm, respectively at HF). One possible explanation for this pattern is that the addition of Ca and Mg stimulated nitrification and hence generated additional NO₃⁻ (Binkley & Hart 1989; Persson et al. 1991). A study of the effect of landscape position and N mineralization and nitrification in the Arbutus Watershed at the HF suggested that the abundance of base rich minerals may have contributed to the relatively high mineralization and nitrification rates compared to other similar sites (Ohrui et al. 1999). Although the two sites (WL and PHC) with the highest N atmospheric inputs had the greatest fluxes of DIN in soil water, there was no indication that these sites retained less experimentally added N than HF site with lower ambient N inputs. This result does not support our hypothesis that sites with the greatest atmospheric inputs of N would be most responsive to additional N inputs. Analyses of vegetation showed increases in N concentrations due to both NO₃⁻ and NH₄⁺ additions at all three sites with the greatest relative increase at HF (Hurd et al. 1998). The HF site also had the greatest soil solution response to the N additions (Figures 4–7).

Isotopic analyses

Natural abundance measurements

The δ¹⁵N values of the bulk B mineral soil (initial buried bag material) for the three sites were significantly different ($p < 0.001$) from each other with PHC having the highest value (7.3‰), WL being intermediate (6.8‰) and HF being the lowest (6.5‰). Nitrogen concentrations and δ¹⁵N values of overstory and understory *F. grandifolia* foliage at WL foliage were higher than at HF (Table 9a). The δ¹⁵N values for foliage, twigs, litter, roots, and soils of *A. saccharum* at PHC and HF were similar between the two years sampled and thus the results were combined (Table 9b). At both PHC and HF, B horizon roots had lower δ¹⁵N values than B horizon soil, suggesting that inorganic N available for root uptake was depleted in ¹⁵N relative to the total

Table 9a. Means of $\delta^{15}\text{N}$ (‰) and N concentration (g N kg^{-1} dry mass) N) of *F. grandifolia* constituents at Woods Lake (WL) and Huntington Forest (HF) (mean \pm SE(N); p value based upon t-test between sites

Constituent	Measurement	Site		p value
	$\delta^{15}\text{N}$ (‰) or N (g N kg^{-1} dry mass)	WL	HF	
Overstory	$\delta^{15}\text{N}$	0.70 ± 0.07 (2)	0.20 ± 0.52 (6)	< 0.001
	N	27.0 ± 0.28 (2)	23.0 ± 2.6 (6)	< 0.001
Understory	$\delta^{15}\text{N}$	0.40 ± 0.28 (5)	-0.20 ± 0.25 (3)	< 0.001
	N	26.0 ± 1.9 (5)	25 ± 2.5 (3)	< 0.001

soil N pool (Nadelhoffer & Fry 1994). The mean $\delta^{15}\text{N}$ values for most strata were greater at PHC than at HF. There was no consistent relationship between N concentration and $\delta^{15}\text{N}$ values for the same ecosystem components across the three sites. However, there was generally a positive relationship between $\delta^{15}\text{N}$ values and NO_3^- concentrations and fluxes among these sites (Tables 8 and 9) supporting our hypothesis that ^{15}N natural abundances are related to N concentrations and fluxes. The higher $\delta^{15}\text{N}$ values in *F. grandifolia* foliage at WL and PHC as well as the higher $\delta^{15}\text{N}$ values in forest floor and roots at PHC compared to the same constituents at HF corresponded to higher DIN TF and drainage losses at the latter two sites. These results are consistent with other studies which have found higher ^{15}N values or greater enrichment in those sites with greater N fluxes and N cycling rates (Emmett et al. 1998; Garten 1993).

Tracer experiment

The experimental additions using $^{15}\text{N-NH}_4$ as a tracer at PHC showed that the largest N sinks were the forest floor and the mineral soil (Table 10). After three years of N additions most of the N was found in the mineral soil of the low and high $(\text{NH}_4)_2\text{SO}_4$ treatments. The next largest N sink was the forest floor. These results support our hypothesis that most of added $^{15}\text{NH}_4^+$ would be found in the forest floor and mineral soil. Retention of N did not markedly differ with the two N addition rates (36 and 38% of the total added N in the low and high treatment plots, respectively). Because the root systems of the overstory trees within the plots certainly extended beyond the plot boundaries, it was likely that appreciable amounts of unlabelled N by these trees diluted the isotopic tracer. For more details, Owen (1995) can be consulted. These results agree with findings from several forest sites in Europe and North America where most of the added ^{15}N was sequestered in the forest floor and

Table 9b. Means of $\delta^{15}\text{N}$ (‰) and N concentration (g N kg^{-1} dry mass) N) of *A. saccharum* constituents at Pancake-Hall Creek (PHC) and Huntington Forest (HF) (mean \pm SE; N = 5); p value based upon t-test between sites

Constituent	Measurement	Site		p value
	$\delta^{15}\text{N}$ (‰) or N (g N kg^{-1} dry mass)	PHC	HF	
Foliage	$\delta^{15}\text{N}$	-1.1 ± 0.20	-1.7 ± 0.17	0.037
	N	21.7 ± 1.07	18.4 ± 0.8	0.039
Twigs	$\delta^{15}\text{N}$	-0.8 ± 0.22	-1.0 ± 0.30	0.471
	N	10.0 ± 0.43	9.1 ± 0.2	0.395
Litter	$\delta^{15}\text{N}$	-1.2 ± 0.20	-1.8 ± 0.24	0.104
	N	8.4 ± 0.19	10.2 ± 0.36	0.003
Oe horizon	$\delta^{15}\text{N}$	1.1 ± 0.18	0.5 ± 0.22	0.057
	N	18.6 ± 1.91	23.5 ± 1.22	0.063
Oe horizon roots	$\delta^{15}\text{N}$	1.1 ± 0.17	0.5 ± 0.33	0.119
	N	20.1 ± 0.63	18.6 ± 0.28	0.050
B horizon	$\delta^{15}\text{N}$	6.4 ± 0.38	6.7 ± 0.07	0.445
	N	2.3 ± 0.33	3.1 ± 0.34	0.078
B horizon roots	$\delta^{15}\text{N}$	2.6 ± 0.31	1.4 ± 0.28	0.021
	N	9.7 ± 0.58	11.2 ± 0.41	0.078

the mineral soil with relatively small amounts taken up by the vegetation or lost via leaching (Magill et al. 1996, 1997; Nadelhoffer et al. 1999ab; Seely & Lajtha 1997). Moreover, the similar fraction of $^{15}\text{N-NH}_4$ recovered in both treatments in the current study indicates that the increased N addition was sequestered in the forest floor and mineral soil. In contrast Nadelhoffer et al. (1995) found, using $^{15}\text{N-NO}_3$ additions, that N estimated retention in the forest floor did not increase with an increase in added NO_3 . The difference between these two studies may be related to the greater mobility of NO_3^- compared to NH_4^+ .

Factors affecting nitrogen loss and/or retention

Effect of N addition rates

High retention of experimental additions of inorganic N to forests has been reported in other investigations including those that have used higher N addition rates than those used in the current study. For example, after six years

Table 10. Mass balance estimates of ^{15}N retention at Pancake-Hall Creek after N additions over three years

N pool	N (%)	N pool size (kg N ha ⁻¹)	$\delta^{15}\text{N}_i$	N addition rate							
				$\delta^{15}\text{N}_f$	$\Delta\delta^{15}\text{N}$	$\text{N}_{\text{retention}}$ (kg N ha ⁻¹ yr ⁻¹)	$\text{N}_{\text{retention}}$ (kg N ha ⁻¹)				
						14 kg N ha ⁻¹ yr ⁻¹	28 kg N ha ⁻¹ yr ⁻¹				
						$\delta^{15}\text{N}_f$	$\Delta\delta^{15}\text{N}$	$\delta^{15}\text{N}_f$	$\Delta\delta^{15}\text{N}$	$\text{N}_{\text{retention}}$ (kg N ha ⁻¹)	$\text{N}_{\text{retention}}$ (kg N ha ⁻¹)
Foliage											
overstory	2.32	72.4	-0.4	2.3	2.7	0.5	6.3	6.7	1.3		
woody understory	2.43	14.0	0.1	21.9	21.8	0.8	50.3	50.2	1.9		
herbaceous understory	2.45	4.6	-0.2	44.0	44.2	0.5	53.0	53.2	0.6		
Forest Floor											
decomposing litter											
<i>F. grandifolia</i>	1.12	12.4	0.7	11.3	10.6	0.3	24.0	23.3	0.8		
<i>A. saccharum</i>	0.76	15.3	0.5	11.2	10.7	0.4	18.1	17.6	0.8		
Oe	2.07	86.9	1.2	6.1	4.9	1.1	15.3	14.1	3.4		
Oa	1.15	790.1	4.1	5.5	1.4	3.0	7.0	2.9	6.2		
Mineral soil											
0–10 cm	0.09	1932.0	7.3	8.9	1.6	8.4	10.5	3.2	16.8		
Total added N accounted for.						15.0			31.8		

of N-additions (NH_4NO_3 at 50 and 150 $\text{kg N ha}^{-1} \text{ yr}^{-1}$) at the Harvard Forest, Magill et al. (1997) observed that 85 to 99% of the added N was retained with 50 to 88% of the retained N being associated with a recalcitrant soil pool. Similarly, at Bear Brook Watershed in Maine, 93 to 97% of N [$(\text{NH}_4)_2\text{SO}_4$ at 24 $\text{kg N ha}^{-1} \text{ yr}^{-1}$] inputs were retained in the watershed, and in N-treated plots from 70 to 92% of the N inputs (HNO_3 from 18 to 62 $\text{kg N ha}^{-1} \text{ yr}^{-1}$) remained in the soil (Magill et al. 1996). The NITREX experiments [NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ additions from 8 to 89 $\text{kg N ha}^{-1} \text{ yr}^{-1}$] have demonstrated a hysteresis between N inputs compared N losses via drainage waters (Gundersen et al. 1998b), suggesting substantial N retention. Nadelhoffer et al. (1999b) summarized the results of ^{15}N addition experiments for six sites in Europe and three in North America and found that most of the ^{15}N was retained within the forest ecosystem with the major portion being stored in the litter, forest floor and mineral soil especially at those sites with lower ambient N inputs. The results from the NITREX experiments in Europe (Emmett et al. 1998) and synoptic surveys (Malanchuk & Nilsson 1989; Dise & Wright 1995) have suggested that little N leaching loss occurs if atmospheric N inputs are less than 10 $\text{kg N ha}^{-1} \text{ yr}^{-1}$. For the three sites in the current study, bulk N in TF (Table 4) was considerably less than this threshold and maximum experimental N inputs of 28 $\text{kg ha}^{-1} \text{ yr}^{-1}$ (Table 2) were likely not of sufficient quantity or duration to greatly exceed the capacity of these ecosystems to sequester the added N, especially when added as NH_4^+ . In our study the experimental additions of N during periods of uptake by vegetation would have also enhanced N retention.

Role of denitrification on N mass balances

If there were significant gaseous losses of N due to denitrification, then these mass balance calculations would represent overestimates of N retention. At HF, Richey (1995) measured N_2O losses in upland soils that were small (0.065 $\text{kg N ha}^{-1} \text{ yr}^{-1}$) compared with drainage losses, but similar to values from other forest sites (Robertson et al. 1988; Van Miegroet & Johnson 1993; Lamontagne & Schiff 1999). Denitrification rates are, however, highly variable (Folonoruso & Rolston 1984; Parkin 1987) and can reach 40 $\text{kg N ha}^{-1} \text{ yr}^{-1}$ in poorly drained upland soils (Groffman & Tiedje 1989).

Isotopic evaluations

The two sites in the western Adirondacks (WL and PHC), which exhibited higher atmospheric N inputs and higher losses of NO_3^- (Table 8) in the reference plots, were also characterized by higher $\delta^{15}\text{N}$ values in the soil and vegetation than HF (Table 9). These patterns agree with previous investiga-

tions suggesting that soil and foliar ^{15}N natural abundance increases with increasing N availability and/or decreasing N retention due to preferential losses of the lighter ^{14}N isotope (Gebauer 1991; Gebauer & Schulze 1991; Högberg et al. 1992; Johannisson & Högberg 1994; Garten 1993; Garten & Van Miegroet 1994; Emmett et al. 1998). More rapid rates of litter decomposition rates at WL and PHC would also contribute to more rapid cycling of N compared to HF (Table 5c). Thus, as a possible indicator of forest N status, measurements of ^{15}N natural abundance measurements show promise. Interpretation of foliar $\delta^{15}\text{N}$ values can be complicated and is not completely understood (Handley & Scrimgeour 1997). Other factors determining plant $\delta^{15}\text{N}$ values, in addition to N cycling rates, include types of mycorrhizal associations (Handley et al. 1999a; Hobbie et al. 1999) and moisture regimes (Handley et al. 1999b). These factors may have also influenced the results of our study.

C:N ratios

It has been suggested that mature forests with high N deposition, high soil N pools and low forest floor C:N ratios may be more prone to NO_3^- leaching (Aber et al. 1989, 1998; Fenn et al. 1998; Gundersen et al. 1998a). In the current study, the Bh soils had C:N ratios ~ 28 suggesting a potential for N retention that was confirmed in the mass balance and isotopic results. The IFS showed that forest sites which had mineral soil C:N ratios > 20 generally retained N (Van Miegroet et al. 1992).

Factors affecting N cycling in the Adirondacks

Although WL and PHC had higher inputs and losses of DIN, HF exhibited the greatest soil solution responses to experimental additions of N. These responses may be explained by differences in vegetation responses and patterns of N drainage losses among the sites. The two western sites, WL and PHC, have greater precipitation and greater drainage rates. These rates would result in greater transfer of N solutes through the soil profile. These transfers may be especially important during the dormant season when demand for N by the vegetation is lower. The importance of N solute losses during the dormant season has been demonstrated for forest ecosystems not only in the Adirondacks, but throughout those regions of the U.S. and Canada where snowmelt periods are the most important times for solute transfer (Brooks and Williams 1999; Campbell et al. 2000; Creed & Band 1998; Lamontagne & Schiff 1999; McHale et al. 2000; Mitchell et al. 2001; Stottlemeyer & Toczydlowski 1999). During the growing season, the added N would be more

tightly retained contributing to the lower response of the N additions to WL and PHC sites that also have younger vegetation than that at the HF.

Our results suggest that the response of Adirondack forests to atmospheric inputs of N is a function of a suite of interactions that include hydrological, soil and biotic processes. The long-term history of N deposition to WL and PHC may have altered the N status of these sites. The relatively high NO_3^- concentrations in the reference plots at these two western sites correspond to high concentrations of NO_3^- found in surface waters of the western Adirondacks by synoptic surveys (Driscoll et al. 1991). The N inputs associated with the experimental treatments were small, however, compared with the cumulative inputs of N associated with atmospheric deposition. These results indicate that for sites like WL and PHC changes in deposition of N may have to occur over extended periods to further alter the N status of these forest ecosystems. Understanding the length of time for this alteration to occur is important for evaluating N biogeochemistry of this region and developing policies on that regulate N emissions and subsequently N deposition (EPA 1996).

Other studies have also suggested that temporal patterns of precipitation, including atmospheric N inputs, and hydrological pathways influence both the amount and temporal patterns of NO_3^- losses in drainage waters (Cirino & McDonnell 1997; Burns 1998; Creed & Band 1998; Ohrui & Mitchell 1998; Inamdar et al. 2000). The Adirondack region includes a wide variety of landscape types including forests with different proportions of hardwood and conifer species as well as a complex topography of uplands, wetlands and surface waters (Bischoff et al. 2001). This complex topography underlies a gradient of precipitation and N inputs with higher amounts found within the western Adirondacks (Driscoll et al. 1991). The current study shows that for three hardwood forests with similar vegetation and soils that the N biogeochemistry may be substantially different. Our results indicate that the precipitation patterns and hence soil water fluxes may be a major factor in affecting NO_3^- leaching losses, especially during the dormant season. To understand how these relationships affect the temporal and spatial dynamics of N biogeochemistry in this region, more attention needs to be placed on evaluating hydrological factors and how they interact with biotic processes.

Acknowledgements

This research was funded by the New York State Energy Research and Development Authority (NYSERDA), Empire State Electric Energy Research Corporation (ESEERCO), the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) and the National Science Found-

ation. This research was also supported by the USDA-Cooperative State Research Education and Extension Service. We also thank Todd Anthony, Linda M. Galloway, Todd Hurd, Andre Tanguay and Scott Stoller for assistance in this research. The staff at the Adirondack Ecological Center also contributed by providing facilities for some of this research. We appreciate the help of C. Anthony Federer in the application of the BROOK90 model. The comments of the reviewers were very helpful in improving this manuscript.

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