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Nitrogen Addition Increases Carbon Storage in Soils, But Not in Trees, in an Eastern U.S. Deciduous Forest

Gary M. Lovett,[1]* Mary A. Arthur,[2] Kathleen C. Weathers,[1] Ross D. Fitzhugh,[3]** and Pamela H. Templer[4]

[1]*Cary Institute of Ecosystem Studies, P.O. Box AB, Millbrook, New York 12545-0129, USA;* [2]*Department of Forestry, University of Kentucky, Lexington, Kentucky 40546-0073, USA;* [3]*Department of Plant Biology, University of Illinois, Urbana, Illinois 61801 USA;* [4]*Department of Biology, Boston University, Boston, Massachusetts 02215, USA*

Abstract

Forest ecosystems in most industrialized and agricultural regions receive elevated rates of atmospheric nitrogen (N) deposition from air pollution. To evaluate the effects of excess N deposition on carbon (C) and N cycling, we experimentally added N (as NH_4NO_3) to naturally-occurring, single-species plots of five different tree species that are common in the Northern Hardwood forests of northeastern North America: sugar maple (*Acer saccharum* Marsh), American beech (*Fagus grandifolia* Ehrh.), yellow birch (*Betula alleghaniensis* Britton), eastern hemlock (*Tsuga canadensis* (L.) Carr), and northern red oak (*Quercus rubra* L.). The experiment was performed in the Catskill Mountains of southeastern New York State, USA, and used a paired-plot design with six replicate plots per species. After 6 years of treatment, most species showed increases in foliar N concentrations in N-treated plots, but only for maple and birch were those increases statistically significant. No significant effects of the N treatment were observed on woody biomass increment or aboveground net primary production (ANPP) for any species. In the oak plots, the N treatment increased acorn production in mast years. In the soils, the N treatment was associated with a significant decline in potential N mineralization and nitrification rates in the mineral horizon but not in the forest floor, and in the mineral horizon the effect of the N treatment varied among species. The N treatment caused a significant increase in C stock, N stock and C:N ratio in the forest floor, with the largest effect in the hemlock plots. Nitrate leaching increased significantly in treated plots compared to controls. Dissolved organic carbon (DOC) in soil solution was unaffected by the N treatment, but the variation in DOC across plots was correlated with the C stock in the forest floor. These results suggest that the ANPP of these forests is not limited by N availability, but that excess N may cause accumulations of C in the forest floor, particularly in hemlock stands, perhaps through inhibition of decomposition rates or by altering phenolic chemistry of the litter. The magnitude, and sometimes the direction of the N treatment responses varied among species, suggesting that predictions of forest responses to elevated N deposition should take into account spatial and temporal variation in tree species composition.

Key words: forest; nitrogen deposition; carbon; nitrogen; fertilization; Catskill mountains.

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Author Contributions: GML, MAA, and KCW conceived and designed the study, and all authors contributed to performing the research, analyzing the data, and writing the paper.

**Ross D. Fitzhugh is currently unaffiliated.

**Corresponding author; e-mail:* lovettg@caryinstitute.org

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Introduction

Human activities have increased the concentrations of reactive nitrogen (N) species and carbon dioxide (CO_2) in the atmosphere globally.

Because N is the nutrient most limiting to productivity in many temperate forest ecosystems (Vitousek and Howarth 1991), increased atmospheric N deposition could stimulate forest productivity, increasing carbon (C) capture from the atmosphere and possibly C sequestration in the woody biomass (Driscoll and others 2003; Thomas and others 2010). Indeed, N fertilization is often used in silvicultural applications to increase forest growth (Johnson 1992). Thus, most ecosystem and earth system models for temperate forests assume that N deposition will stimulate forest productivity and result in increased C storage in wood (Townsend and others 1996; Holland and others 1997; Aber and others 1997; Thornton and others 2009).

In contrast to expectations and models, field studies on the effects of chronic N deposition on C storage in forests present a more variable picture. In a synthesis of eddy covariance measurements in Europe and North America, Magnani and others (2007) reported a large increase in net ecosystem productivity (NEP) associated with increasing N deposition at forested sites, but that study has been criticized as predicting unrealistically high rates of C storage per unit of N added (deVries and others 2008; Sutton and others 2008). Hyvonen and others (2008) calculated that excess N deposition in southern Sweden has increased wood C storage in *Picea abies* stands. In the eastern U.S., studies of forest growth along gradients of N deposition have shown that some tree species show increased growth in response to elevated N deposition, while others do not (Bedison and McNeil 2009; Thomas and others 2010).

Experimental N addition studies in north temperate forests have shown that the effect of N addition on net primary productivity (NPP) ranges from positive (for example, Hyvonen and others 2008; DeVries and others 2009) to negative (McNulty and others 2005; Lovett and Goodale 2011). In some cases, N addition has caused increased tree mortality and a reduction in live tree biomass (Magill and others 2004; McNulty and others 2005; Wallace and others 2007). Most experimental N fertilization studies in temperate forests show that most of the added N is retained in the soil organic matter and only a small fraction is found in the trees. This has been observed both in studies that budget the total N applied (for example, Magill and others 2004; Lovett and Goodale 2011) and in those that use enriched ^{15}N tracers to examine the fate of N (for example, Nadelhoffer and others 1999; Templer and others 2012). Nitrogen that is sequestered in the soil does not contribute to increased C storage in trees, at least in the short-term, however it may lead to increased C storage in the soil organic matter (for example, Nave and others 2009). Several studies have shown that excess N may reduce the production of some decomposition enzymes, particularly those that degrade lignin (Waldrop and others 2004), and this can slow soil respiration, reduce decomposition, and result in increased soil-organic matter accumulation in fertilized soils (Pregitzer and others 2008; Nave and others 2009; Janssens and others 2010). This observed effect is consistent with earlier research showing that litter with higher N concentrations reduces the late-stage litter decomposition rates of tree leaves in studies using litter bags (Berg and others 2001; Berg and Dise 2004). The N-induced reduction in forest litter decomposition appears to be greater for litter with higher lignin concentration (Carreiro and others 2000).

The studies cited above suggest that the net effect of N addition on C storage in forests, both in wood and in soil, is likely to vary among tree species. However, N addition studies on natural ecosystems (that is, not plantations) have been done almost exclusively on mixed-species plots and thus cannot be used to distinguish the effects of individual species on the result. This leaves us unable to determine how much of the variation in forest response to N deposition is due to variation in species composition, or to predict how species compositional shifts will influence responses to N deposition in the future.

Here we report the results of a 6-y N addition experiment on single-species plots of five tree species that are important components of the Northern Hardwood forest type in the northeastern United States. We have previously shown that these tree species differ in their N cycling characteristics (Lovett and others 2004; Templer and others 2005; Christenson and others 2009). Our goals in this study were to determine how the C and N dynamics differed among tree species and how they were affected by N addition. Our experimental design—a replicated, paired-plot N addition study on single-species plots—is unique in the world, to the best of our knowledge. We hypothesized that (1) N addition would increase aboveground NPP and lead to greater C storage in woody biomass, (2) that N addition would increase C storage in the forest floor, and (3) that the magnitude of both of these effects would differ among the species studied.

Methods

Site Description

The research plots were located in the forests of the Catskill Mountains, an area of flat-topped mountains and deeply incised valleys encompassing about 5000 km^2 in southeastern New York State. The bedrock in the higher elevations (>500 m) is relatively homogeneous, consisting primarily of flat-lying sandstones, shales and conglomerates of Devonian age (Stoddard and Murdoch 1991), and is overlain by glacial till of variable depth (Rich 1934). Soils of this region are classified as Lithic Dystrochrepts (Loamy skeletal, mixed, and mesic). They are shallow, moderately to somewhat excessively well drained and are formed on glacial till derived from sandstone, siltstone, and shale (Tornes 1979). Mean soil texture in our research plots was 56% sand, 30% silt, and 14% clay (Table 1) (Lovett and others 2004). The climate of the area is characterized by cool summers and cold winters. The Slide Mountain weather station at 808 m in the central Catskills has a mean annual temperature of 4.3°C (January mean = −8.5°C, July mean = 16.7°C) and a mean annual precipitation of 153 cm, about 20% of which falls as snow. During the period of this study (1997–2005), annual average wet N deposition at the National Atmospheric Deposition Program site in the south-central Catskills was 5.9 kg N ha^{-1} y^{-1} (including NO_3^- and NH_4^+), and annual average dry deposition at the EPA CASTNet dry deposition in the south-central Catskills was 3.1 kg N ha^{-1} y^{-1} (including HNO_3 vapor and particulate NO_3^- and NH_4^+), for a total of 9.0 kg N ha^{-1} y^{-1} (NADP data http://nadp.sws.uiuc.edu/data/ntndata.aspx, site NY 68; CASTNet data http://epa.gov/castnet/, site CAT175). Because the models used to estimate dry deposition are not well suited to such complex terrain, and because atmospheric deposition varies considerably across mountain landscapes (Lovett and Rueth 1999; Weathers and others 2000, 2006), this estimate of N deposition must be considered approximate.

Table 1. Mean Soil Properties by Species and N Treatment, Catskill Mountains, NY

Species	Treatment	pH	% Sand	% Silt	% Clay
Beech	C	3.27 (0.09)	58 (8)	30 (6)	13 (2)
Beech	N	3.23 (0.08)	54 (7)	32 (5)	13 (2)
Hemlock	C	3.20 (0.07)	45 (12)	40 (8)	15 (4)
Hemlock	N	3.07 (0.22)	41 (17)	43 (10)	16 (7)
Maple	C	3.91 (0.30)	56 (7)	26 (4)	17 (4)
Maple	N	3.95 (0.13)	52 (10)	26 (4)	22 (7)
Oak	C	3.87 (0.12)	48 (5)	36 (2)	16 (4)
Oak	N	3.62 (0.08)	49 (5)	35 (4)	15 (1)
Birch	C	3.31 (0.08)	62 (9)	26 (6)	12 (3)
Birch	N	3.42 (0.12)	53 (10)	32 (6)	15 (3)

Soil texture and pH were measured on mineral soil from the plots prior to start of treatment in 1997, using methods described by Lovett and others (2004). Data are means with standard error in parentheses from n = 6 plots per category. C = control, N = N added.

Forests of the Catskill Mountains are dominated by the Northern Hardwood forest type (McIntosh 1972). We studied five of the most dominant species: sugar maple (*Acer saccharum* Marsh), American beech (*Fagus grandifolia* Ehrh.), yellow birch (*Betula alleghaniensis* Britton), eastern hemlock (*Tsuga canadensis* (L.) Carr), and northern red oak (*Quercus rubra* L.). For brevity, henceforth we refer to these species as maple, beech, birch, hemlock, and oak, respectively. For each species we chose six pairs of monospecific plots located throughout the central Catskills in a region of about 60 × 60 km roughly centered on 42°07′N and 74°15′W (Figure 1). For each species, plots were chosen in three different watersheds to encompass spatial variation across the Catskill region. The single-species plots were chosen within mixed-species stands with the following criteria estimated by observation in the field: (1) greater than 90% dominance of the canopy by mature trees of the target species, (2) pure or nearly pure litter composition from target species, and (3) no evidence of recent disturbance such as logging or fire. Each plot was 12 m in diameter, and measurements of soil and focal trees were made within the inner 6 m diameter circle to avoid edge effects. The inner 6 m circle included two or three canopy dominant trees. The plots were chosen in pairs, with the two plots of each pair located within about 20 m of each other. Nitrogen was added to one plot of each pair and the other plot was left untreated as a control. Thus there were 60 plots in total: five species × two N treatments × six replicates. Nitrogen was added to the forest floor of the full 12 m diameter treatment plot as granular NH_4NO_3 four times per year (June, July, August, and November) starting in November 1997. The total annual dose was equivalent to 50 kg N ha^{-1} y^{-1}. Both N-treated and control plots also received the ambient N deposition of approximately 9 kg N ha^{-1} y^{-1} (see above).

Measurements of ecosystem parameters were made at various times throughout the period 1997–2005, as described below. We generally report the data from the latest measurement for each variable, sometimes with prior measurements provided for context.

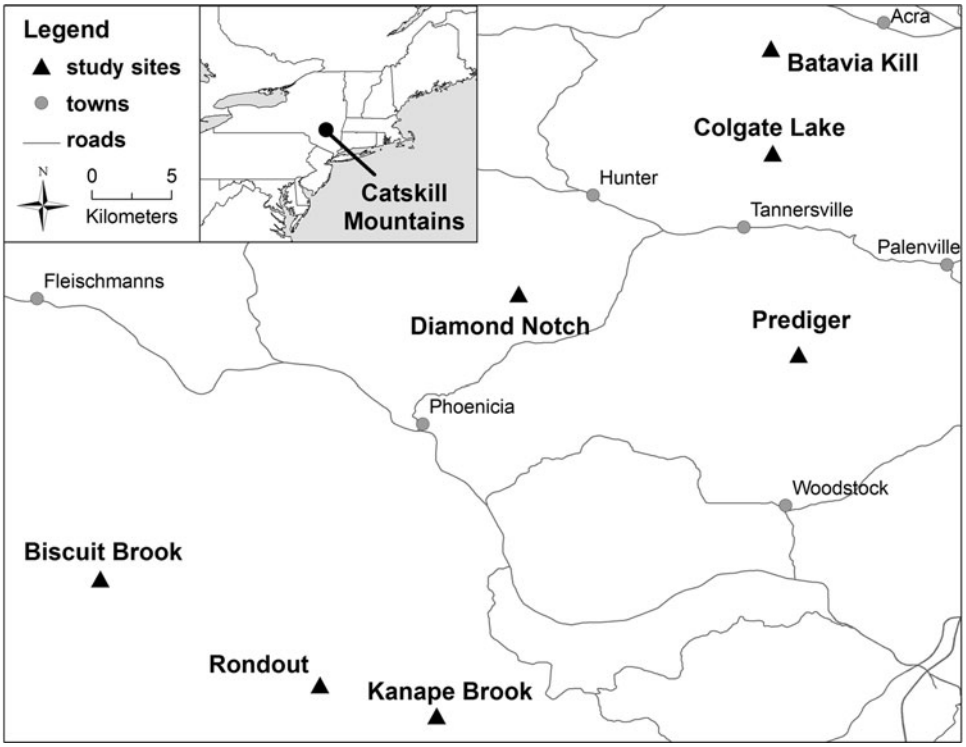

Figure 1. Map of study area in Catskill Mountains of New York State. Major roads and towns are shown with location of study sites. *Inset* map shows location of Catskill region within the northeastern U.S. Single-species plots are distributed among the study plots as follows, with each study site having two pairs of plots for the species noted: sugar maple and American beech—Diamond Notch, Rondout, and Biscuit Brook; yellow birch and hemlock—Prediger, Rondout, and Biscuit Brook; red oak—Colgate, Batavia Kill, and Kanape Brook.

Field and Laboratory Methods

Green foliage was sampled in early August of 1997, 1998, 2000, and 2003 by shooting leaves from the mature canopy trees in each plot with a shotgun using steel shot. Three samples of sunlit leaves near the tops of the trees were collected per plot. Samples were dried in a 60°C oven, ground in a ball mill, and C and N concentration was measured by dry combustion with a Leco CN2000 or a CE Elantech element analyzer.

Litterfall was collected using three plastic baskets (each 0.23 m^2 area) per plot. Each basket contained a fiberglass screen that trapped the litter and kept it above the ground until it could be collected. Litter collections were made biweekly during September–November (except during the heaviest litterfall period of early October, when weekly collections were made) of 1997–2000 and 2003. Collections for each basket were composited across all time periods before being sorted by litter type (leaves of dominant species, leaves of other species, seeds, and other litter), dried in an oven at 60°C, ground, and analyzed for N concentration with the CN analyzer.

Tree diameters at breast height (DBH) were measured in 2001 and 2005 for all trees on the plot. The trees were tagged for identification and a nail was placed in the wood 5 cm below the DBH measurement level; subsequent measurements were made 5 cm above the nail. Aboveground woody biomass (bole + branches) were calculated for each plot based on allometric equations in Jenkins and others (2004). Woody biomass increment was calculated as the difference in estimated woody biomass between 2005 and 2001, and woody biomass C and N increment were calculated from the product of the woody biomass increment and the wood N concentration in each plot (measured on tree cores taken in 2002) and C concentration (estimated as 50% of dry matter).

Litter lignin concentration was measured in 1999, two years after the initiation of the N treatment, as follows. Samples were ground through a 1 mm screen with a Cyclotec (Foss Tecator, Hoeganaes, Sweden) sample mill. Duplicate 0.5 g samples were placed into filter bags (Ankom #F57, Ankom Technology, Fairport, NY) and refluxed for 60 min with acid detergent solution (Van Soest and others 1991) using an Ankom 200 Fiber Analyzer. Samples were washed three times with hot (95°C) distilled water and then once with acetone. Air-dried bags were dried in a forced-air oven (100°C) for a minimum of 4 h before weighing to determine amount of fiber residue present. Bags were then submerged in 72% H_2SO_4 for 3 h, washed with boiling, distilled water until the pH of rinse water was neutral, rinsed once with acetone, and dried in a forced-air oven (100°C) for a minimum of 4 h before weighing to determine the amount of lignin residue. Bags were then ashed in a muffle furnace at 550°C and residual ash weights were obtained.

Lignin concentrations were calculated as the difference between the lignin residue weight and the ash residue weight (including blank bag correction), divided by the weight of the original sample dry matter.

Litter phenolic concentrations were measured on a composite sample of litter collected from each plot in the autumn of 2000, using the following procedures.

Polyphenol Extraction and Purification Five grams of lyophilized leaf powder were washed in 100 ml of ether for 30 min to remove pigments and waxes, and then extracted 3× in 125 ml 70% acetone at 40°C for 1 h under sonication. Ascorbate (10 mM) was added to the acetone to prevent oxidation. Acetone was removed by evaporation under reduced pressure, and distilled water was added to the aqueous extracts to a constant volume of 125 ml. Semipurified polyphenol standards were prepared as described by Hagerman and Klucher (1986). A slurry of 50 g of Sephadex LH_20 (Pharmacia, Piscataway, NJ) and approximately 1 l of 95% reagent grade ethanol was equilibrated overnight, and then mixed thoroughly with 125 ml of crude extract from the procedure described above. Using a large Buchner funnel and vacuum filtration, monomeric polyphenols were eluted from the slurry by washing it with 95% ethanol. Mostly-polymeric polyphenols (=tannins) were subsequently eluted with 70% acetone, which was removed from the filtrate by evaporation under reduced pressure. The extract was freeze-dried and stored under nitrogen at −10°C. Yields of the off-white powder averaged 5% of the dry weight of the leaf. Use of standards comprising the actual polyphenols present in samples provides an accurate dry weight-based quantification (Appel and others 2001).

Polyphenol Assays Purified tannins of each species were assayed for (1) *folin-reactive phenols* using the Folin–Denis assay (Swain and Hillis 1959) which measures the ability of phenolics to reduce a mixture of phosphomolybdic and phosphotungstic acids, (2) *condensed tannins* using the butanol–HCl assay (Batesmith 1977) which quantifies hydrolyzed proanthocyanidin residues, and (3) *hydrolyzable tannins* using the potassium iodate method modified for quantitative use (Schultz and Baldwin 1982; Hartzfield and others 2002) which quantifies galloyl esters. Polyphenol contents are reported as means of triplicate absorbance measurements of single extracts from each sample.

The colorimetric folin-reactive phenols measure assesses the redox potential of a phenolic-containing extract. When used with a standard having the same composition as the samples (prepared as described above), this measure approximates the total concentration of all phenolic molecules, plus any other reducing agents that may be present. This fraction comprises a complex mixture of protein-binding, antioxidant, toxic, and signaling phenolic molecules. The tannin fractions contain protein- and cation-binding phenolic polymers. Condensed tannins are composed of anthocyanin monomers, are only slightly soluble in acidified water, and can be hydrolyzed only with strong acid. Hydrolyzable tannins are polymers of glucose and esterified phenolic acids; they are quite water-soluble and hydrolyze readily in slightly acidic water, producing phenolic acid residues that may be antifeedant or toxic to decomposer organisms (Zimmer 1999). Although their impact on nutrient cycling has not been reported, hydrolyzable tannins may comprise the major portion of the polyphenols in litter from the tree species studied here.

Soil properties were measured on four soil samples per plot collected in July of 2000 and 2003. Fresh litter was brushed away, and a soil core was taken to a depth of 12 cm from the surface unless obstructed by a rock or large root. The core was separated into two samples representing organic (Oe + Oa) and mineral (A and/or B) horizons. The 12-cm core generally included the entire organic horizon and a variable depth of mineral soil. In cases where mineral soil was not encountered at a depth of 12 cm, the core was deepened until a mineral horizon was reached and a sample was taken from approximately the top 5 cm of the mineral soil, and this sample was used for chemical comparisons but not for calculations of soil mass to 12 cm depth. This sampling procedure permits comparison of soil chemistry for the forest floor (Oe and Oa horizons) and upper mineral soil. It also permits comparison of the mass and C and N pool sizes for two depth categories: (1) forest floor, and (2) total mass to 12 cm, including the forest floor and whatever depth of mineral soil was encountered to the 12 cm depth. It does not allow direct comparisons of mineral soil mass or pool sizes because the depth of the sampled mineral soil varied among plots, therefore we do not report mineral soil mass results below.

Extractable NH_4^+ and NO_3^-, total C and N, and potential net N mineralization and nitrification were measured on each soil sample. The samples were returned to the laboratory, passed through an 8 mm sieve, weighed, and thoroughly homogenized. A subsample was dried in an oven at 60°C to determine moisture content; a second subsample was used to determine field capacity gravimetrically

after saturating the sample and allowing it to drain overnight. Each sample was then wetted with deionized water to a moisture content of 60% of the field capacity. A subsample of approximately 10 g was extracted by adding 100 ml of 2M KCl to the sample, shaking the sample twice within the first hour, allowing it to stand overnight, and then filtering the extract into clean polyethylene bottles through Whatman 41 filter paper. Another 10 g subsample was incubated for 28 d at 20 $\pm$ 4°C in a plastic specimen cup covered with polyethylene film. After the 28 days incubation, the sample was extracted as above. Potential net N mineralization was calculated from the change in extractable N (NH_4^+ + NO_3^-) from initial to final extractions, and the potential net nitrification was calculated from the change in NO_3^-. Another subsample was dried, ground, and analyzed for C and N concentration by dry combustion on the CN analyzer. On a composite mineral soil sample from each plot we also measured pH (in a 1:1 mixture with water), and soil texture using the Lowy pipette method, with pretreatment to destroy organic matter (Gee and Bauder 1986).

Soil solution chemistry was measured on 40 of the 60 plots, including four pairs of plots per species. Two tension lysimeters (Soil Moisture Corp. Model 1900) were installed at each of the 40 plots during the summer and autumn of 2001 to sample soil solutions draining from the deep mineral soil below the rooting zone where nutrients are likely to be physically separated from plant uptake and most prone to leaching loss. The tension lysimeters consisted of a ceramic cup (maximum pore size 1 micron) attached to a PVC pipe 91 cm long and 4.8 cm in outside diameter. Prior to installation, the ceramic cups of the lysimeters were cleaned in the laboratory by acid-washing in 1N HNO_3 for 24 h and then thoroughly rinsing with deionized water. A 5.1 cm diameter soil auger was used to remove soil at a 45° angle to the soil surface in the upslope direction, an orientation which, in steep mountain slopes of the Catskills, should maximize collection of water from soil unaffected by installation of the lysimeters. Soil was removed until the interface between the B and C horizons was reached (determined visually based on soil color and abundance of gravel), a soil zone where fine roots were largely absent. The vertical depth between the forest floor and the deepest point of the lysimeters varied between 14 and 45 cm, averaging 27 cm. A mixture of silica flour and deionized water was poured into the bottom of the hole and the ceramic cup was inserted until seated firmly at the lowest possible point. As the lysimeter was only slightly smaller in diameter than the soil auger, only small amounts of soil were used to backfill around the PVC pipe. After setting a tension of 15 kPa, a low pressure that should collect relatively mobile water, soil solution was allowed to collect in the PVC pipe until the next sample collection. Soil solutions were collected at approximately monthly intervals from April 2002 (6–8 months after installation) to August 2003. In each collection, all solution was evacuated from the lysimeter pipe and the tension was reset at 15 kPa. Samples were collected on average 31 days after the tension was set. Samples from the duplicate lysimeters at each plot were combined by volume. All samples were kept on ice after collection in the field and during transport to the laboratory.

At half of the plots where tension lysimeters were installed, zero-tension lysimeters were also installed to sample soil solutions freely draining below the forest floor. Zero-tension lysimeters were installed at these ten plot pairs (two plot pairs per species), using methods similar to Fitzhugh and others (2001). A 1 m wide square pit was excavated approximately 0.6 m deep, taking extreme care to minimize disturbance to soil upslope of the pit. Duplicate PVC cups were inserted into the upslope face of the pit immediately below the interface between the forest floor and the mineral soil. The cups drained to separate 2 l reservoirs. Cups were installed on average 12 cm below the surface of the forest floor, ranging from 4 to 20 cm deep. After lysimeter installation, the pits were carefully backfilled. Samples of soil solution from the zero-tension lysimeters were collected on the same dates as the tension lysimeters. Samples from the duplicate zero-tension lysimeters at each plot were combined by volume on each sampling date.

In the laboratory, samples of soil solutions were filtered through pre-ashed glass-fiber filters (Whatman 934-AH) and pH was measured potentiometrically with a glass electrode, typically within 24 h of sample collection. Soil solutions were then kept at 4°C until analysis. Total dissolved nitrogen (TDN), ammonium (NH_4^+), were analyzed using continuous flow injection on a Lachat Quikchem 8000. Measurement of TDN was via in-line, ultraviolet light-enhanced, alkaline, persulfate digestion at 105°C, followed by reduction on a cadmium column, reaction with sulfanilamide, and detection as NO_2^-. Ammonium (NH_4^+) was determined by reaction with alkaline phenol and hypochlorite. Nitrate (NO_3^-) was analyzed by ion chromatography on a Dionex 120. Beginning in November 2002, dissolved organic carbon (DOC) was determined by adding phosphoric acid and sparging with oxygen to remove DIC, followed by platinum-catalyzed

combustion on a Shimadzu TOC-V. Dissolved organic nitrogen (DON) was calculated as the difference between TDN and the sum of NH_4^+ plus NO_3^-.

The fluxes of water leaving the forest floor and the deep mineral soil horizons were estimated using a hydrological model developed for temperate northern hardwood forests, BROOK90 version 3.24 (Federer 1995). Meteorological data from the Slide Mountain weather station located in the central Catskills were used to drive the model (daily values of precipitation and minimum and maximum air temperatures). Slide Mountain is the closest weather station to the lysimeter plots; the mean distance between the plots and Slide Mountain is 16 km and Slide Mountain is on average at 198 m higher elevation than the lysimeter plots. As measurement of the processes contributing to hydrological variability among the lysimeter plots was beyond the scope of the current research program (for example, measurements of soil hydraulic potential, porosity, and throughflow), water fluxes through the soil horizons were assumed to be equal among plots. Catchment parameters for watershed 6 of the Hubbard Brook Experimental Forest were used, except that: (1) latitude was changed to that of the Slide Mountain weather station, and (2) soil layer depths were adjusted to fit the mean depth of the forest floor and the depth of the lysimeters. The BROOK90 model was run with climate data beginning in 1995, allowing 7 years for soil water storage to ''equilibrate.'' Soil water fluxes leaving the mean depths of the forest floor and deep mineral soil lysimeters were computed on a daily basis. To calculate soil water solute fluxes, solute concentrations measured on any given sampling date were assumed to be representative of soil water chemistry from the day following the previous sampling date through the date of the given sampling. Solute fluxes in soil water were calculated from April 2002 through August 2003 by multiplying solute concentrations in the tension lysimeters by the simulated soil water flux for the time of the sampling period.

Statistical Analysis

Statistical analysis was performed using the SAS system (SAS Institute 1989). Tree species and N treatment differences were tested by mixed-model analysis of variance (SAS MIXED procedure) using fertilization and tree species as fixed effects and site as a random effect. We used a nested model with site nested within tree species. When multiple samples were taken within a plot, the ANOVA was performed on plot means with $n = 60$ (5 species $\times$ 6 plots $\times$ 2 N treatments per species), $n = 40$ for B-horizon lysimeters, or $n = 20$ for forest floor lysimeters. Differences among individual means were tested using the SAS ''pdiff'' statement on the least squares means. Correlation was tested with the Pearson correlation coefficient using the CORR procedure in SAS.

Results

Vegetation

Foliage, Litter, and Seeds

Mean N concentration in green foliage varied significantly among species, with hemlock having the

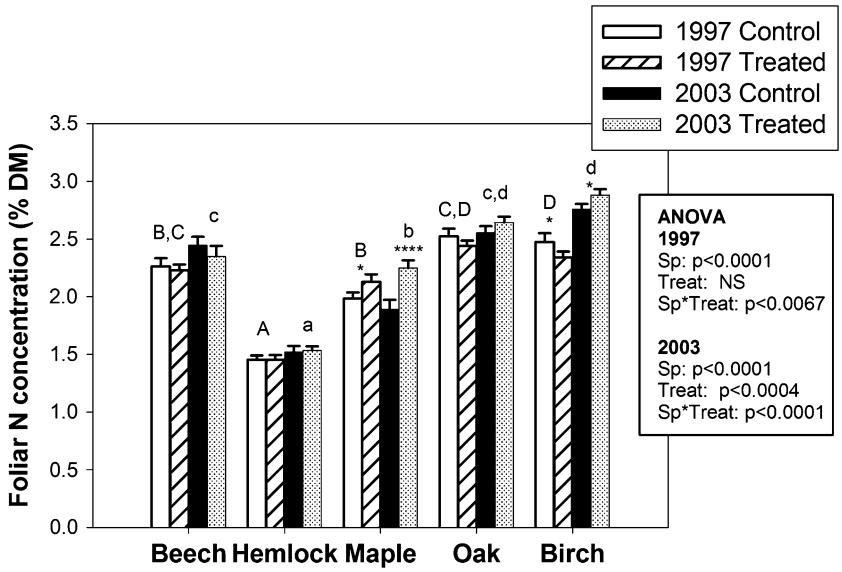

Figure 2. Mean (+1 SE) foliar N concentrations (%DM) pre-treatment (1997) and in 2003. Within a year, significance of N treatment effect is given as $*P < 0.05$, $**P < 0.01$, $***P < 0.001$, $****P < 0.0001$. Differences among species are noted by *upper-case letters* for 1997 and *lower-case letters* for 2003. Species sharing the *same letter* (within a year) are not significantly different from one another.

lowest concentrations and yellow birch and red oak the highest (Figure 2). In 2003, there was overall a significant N treatment effect and N treatment × species interaction, but only in maple and birch plots did the N concentration in the treated plots significantly exceed the control plots. There was no overall statistically significant difference in foliar N concentration between control and treated plots in 1997, prior to the initiation of the treatment (Figure 2). The difference in mean foliar N in treated compared to control plots in 2003 was −4% for beech, +1% for hemlock, +4% for oak and birch, and +19% for maple.

Nitrogen concentration in foliar litter showed a stronger response to the N treatment than did green foliage. Overall, there were significant effects of species, N treatment and N treatment × species interaction on N concentrations in foliar litter (Figure 3A). Hemlock, maple, and oak had significantly higher N concentrations in foliar litter in N-treated compared to control plots. The target leaf litterfall was significantly lower in treated plots compared to controls in beech and birch plots (Figure 3B). The target leaf litter N deposition (that is, N flux in leaf litterfall) was significantly reduced by the N treatment in beech and birch plots, and significantly increased by the treatment in hemlock plots (Figure 3C). There were no significant differences in litter N concentration between treated and control plots prior to the initiation of the treatment in 1997, nor in the first year of the treatment (1998), but in 2000 significant effects of the N addition were observed for litter N concentration in hemlock ($P < 0.0001$). Significant effects of N addition on N concentration in maple and oak litter were not observed until 2003 (Figure 3A).

For all species, N-treated plots had lower lignin concentrations in foliar litter than control plots, and both the fertilization and species effects were statistically significant (Figure 3D). In general, beech and oak and birch had the highest lignin levels whereas maple and hemlock had lower

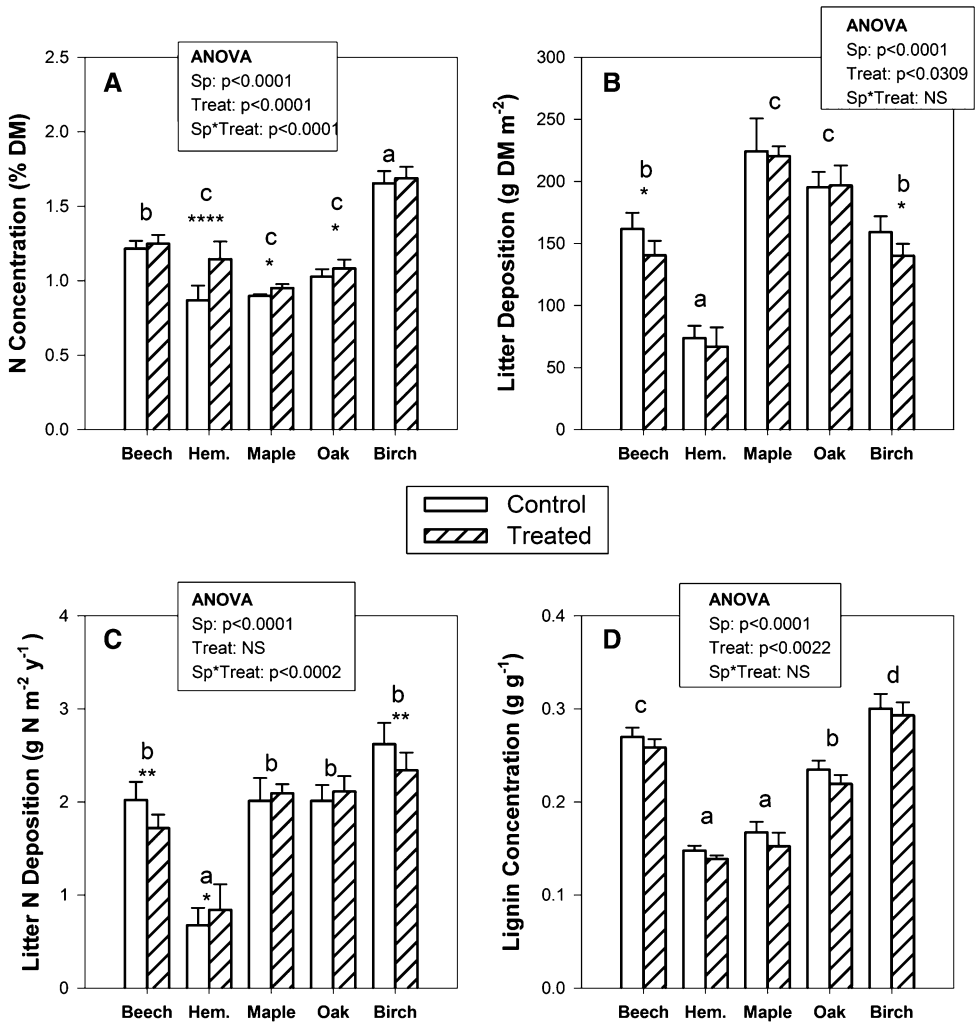

Figure 3. Mean (+1 SE) N concentration (**A**), dry mass deposition (**B**), N deposition (**C**), and lignin concentration (**D**) for leaf litter of target species in 2003. Within a species, significance of N treatment effect is given as $*P < 0.05$, $**P < 0.01$, $***P < 0.001$, $****P < 0.0001$. Differences among species are noted by *lower-case letters*; species sharing the *same letter* are not significantly different from one another.

levels. There were significant differences among species and N treatments and significant species × treatment interactions for Folin-reactive phenols and condensed tannins, whereas for hydrolyzable tannins the species and interaction effects were significant but the N treatment effect was not (Figure 4). The strongest N treatment effects were an increase in Folin-reactive and condensed tannins in the hemlock plots and an increase in hydrolyzable tannins in the birch plots.

N treatment resulted in highly significant increases in seed production in oak plots in the mast years 1998 and 2000 (Figure 5). Treated plots also had higher seed flux prior to the start of fertilization (1997), suggesting that there may have been some pre-existing differences in seed production in the plots, but the differences between treated and controls plots were much stronger in 1998 and 2000 compared to 1997. There were no treatment effects on seed production for the other four species, except that in 2003 beech treated plots had somewhat lower seed production than controls ($P < 0.05$) and maple-treated plots had higher seed production than controls ($P < 0.05$).

Woody Biomass and ANPP

There were no significant effects of N fertilization on aboveground woody biomass (trees >10 cm DBH) C or N increment in the period 2001–2005 for any of the species we studied (Figure 6A, B).

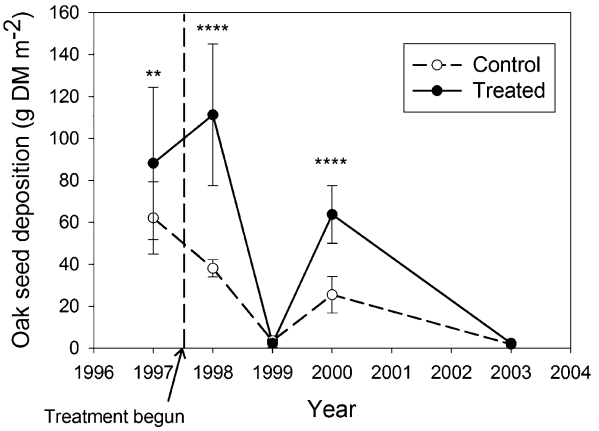

Figure 5. Mean (±1 SE) seed deposition in the N-treated and untreated oak plots. Significance of N treatment effect is given as $^{**}P < 0.01$, $^{****}P < 0.0001$.

Woody biomass C and N increment were significantly greater in oak plots than in the plots of the other species, with the exception that the N increment in oak was not significantly different from that of beech.

The woody biomass C and N increments in Figure 6 are adjusted for average basal area. Because our study plots were small and chosen to be centered around several large canopy trees, they are not representative of the average woody biomass or basal area of the Catskill forest. For example, basal area of our plots averages 39–59 $m^2\ ha^{-1}$,

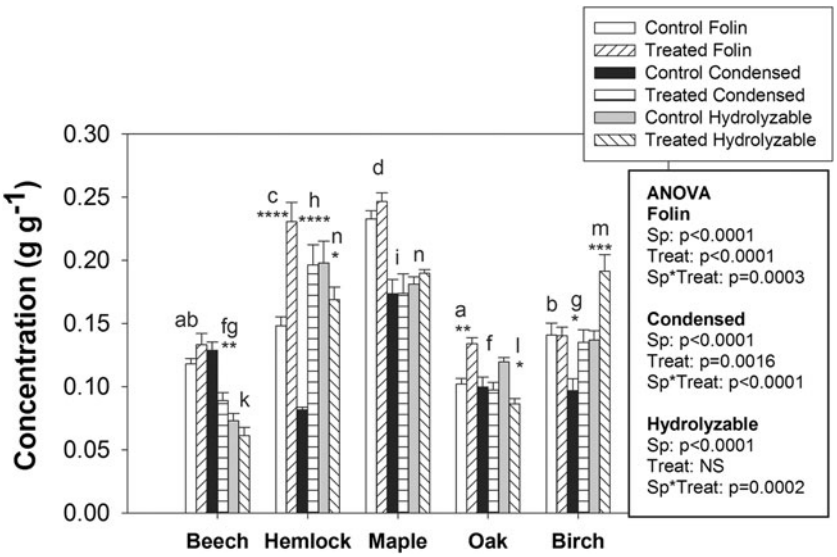

Figure 4. Mean (±1 SE) concentration of Folin-reactive phenols, condensed tannins, and hydrolyzable tannins in the foliar litter from the plots. Within a species and tannin type, significance of N treatment effect is given as $^{*}P < 0.05$, $^{**}P < 0.01$, $^{***}P < 0.001$, $^{****}P < 0.0001$. Differences among species within a tannin type are noted by letters *a–e* for Folin-reactive phenols, *f–j* for condensed tannins, and *k–n* for hydrolyzable tannins. Species sharing the *same letter* (within a tannin type) are not significantly different from one another.

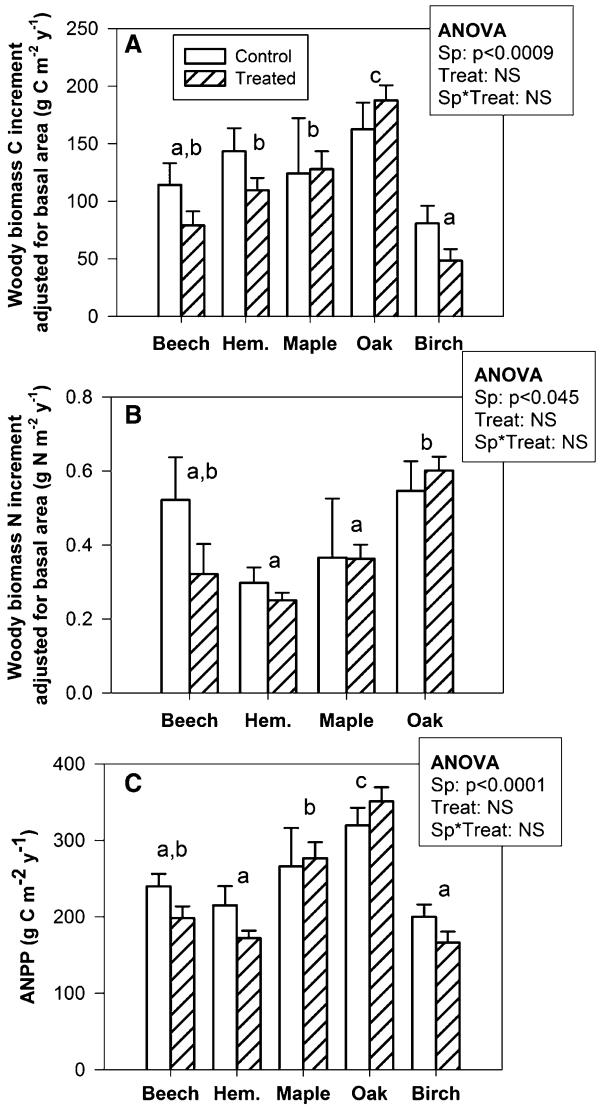

Figure 6. Mean (+1 SE) C increment (**A**) and N increment (**B**) in aboveground woody biomass for the period 2001–2005, adjusted for basal area. The basal area adjustment is described in the text and Table 2. No wood N data are available for birch plots. **C** Aboveground net primary production (ANPP), calculated as the sum of the adjusted woody biomass C increment and leaf and fruit deposition in litterfall. Within a species, significance of N treatment effect is given as $*P < 0.05$, $**P < 0.01$, $***P < 0.001$, $****P < 0.0001$. Differences among species are noted by *letters*; species sharing the *same letter* are not significantly different from one another.

depending on the species, whereas the mean basal area of randomly sampled stands in the Catskill forest averages 25–31 m^2 ha^{-1} for the same species, based on our broad-scale vegetation sampling (Lovett and others 2002; Driese and others 2004). To compare these C and N increment data to other studies and have a more accurate estimate of C and N fluxes on an areal basis, we adjusted the data to be more representative of the Catskill forest. We calculated adjustment factors for our species as the average basal area of stands dominated by that species in the Catskill-wide vegetation survey, divided by the average basal area of that species in our study plots (calculations shown in Table 2). We defined ''dominance'' by a species as stands in which the target species had the highest basal area of any species on the site, and its basal area comprised greater than 33% of the total stand basal area. Using these factors we adjusted the woody biomass and woody biomass increment for C and N to be more representative of a typical stand.

Aboveground net primary production (ANPP) was calculated as the sum of the basal area-adjusted woody C increment and the litterfall fluxes of leaf and fruit C for each plot. Branch litterfall was not measured. The ANPP varied between 166 and 351 g C m^{-2} y^{-1} (Figure 6C). There was a significant species effect, with oak plots having the highest ANPP and birch stands the lowest, but there was no significant effect of the N treatment, nor was there a species × N treatment interaction.

Soils

Nitrogen Mineralization and Nitrification

Potential net N mineralization rate varied significantly among species in both the organic (Figure 7A) and mineral (Figure 7B) horizon. In the mineral horizon, maple had the highest N mineralization rate whereas in the organic horizon yellow birch was the highest. There were no significant effects of the N treatment on N mineralization rate in the organic horizon, but in the mineral horizon N addition significantly reduced N mineralization rate in the maple and oak plots (Figure 7B).

Potential net nitrification rate also varied among species, with oak and hemlock soils having the lowest rates and maple the highest rates in both horizons (Figure 7A, B). In the mineral horizon, the N treatment significantly reduced the nitrification rate in maple and oak stands, paralleling the N mineralization effect (Figure 7B). In maple, nitrification rates have declined over time in the N-treated plots, but not in the control plots, such that the treated-plot nitrification rates were greater than the control plots in 1998, similar in 2000, and less in 2003 (only 2003 data shown, Figure 7). This parallels the trend in N mineralization in maple plots over this period. For the oak plots, the significant treatment effect was present in 1998 and continued throughout the study. This pattern is

Table 2. Basal Area Adjustment Factors, Woody Biomass C and N, and Adjusted Woody Biomass C and N, Catskill Mts., NY

Species	Mean BA of study plots (m^2 ha^{-1})	Mean BA of this stand type[1] (m^2 ha^{-1})	Adjustment factor	N treatment	Mean woody biomass C 2001 (g C m^{-2})	Mean woody biomass C 2005 (g C m^{-2})	Mean woody biomass N 2001 (g N m^{-2})	Mean woody biomass N 2005 (g N m^{-2})	Adjusted woody biomass C 2001 (g C m^{-2})	Adjusted woody biomass C 2005 (g C m^{-2})	Adjusted woody biomass N 2001 (g N m^{-2})	Adjusted woody biomass N 2005 (g N m^{-2})
Beech	39.4	25.1	0.637	Control	14,097	14,814	63.6	66.9	8,980	9,437	40.5	42.6
				N Treated	12,329	12,824	47.7	49.7	7,853	8,169	30.4	31.6
Hemlock	58.9	31.8	0.540	Control	18,427	19,489	38.4	40.7	9,951	10,524	20.8	22.0
				N treated	14,603	15,414	34.5	36.3	7,885	8,323	18.6	19.6
Maple	52.0	28.4	0.546	Control	16,606	17,515	47.5	50.2	9,067	9,563	25.9	27.4
				N treated	18,839	19,775	54.2	56.9	10,286	10,797	29.6	31.1
Oak	59.4	28.5	0.480	Control	19,579	20,936	67.2	71.8	9,379	10,028	32.2	34.4
				N treated	24,549	26,114	79.5	84.6	11,759	12,509	38.1	40.5
Birch	42.2	24.6	0.583	Control	12,955	13,510	ND	ND	7,540	7,863	ND	ND
				N treated	12,600	12,932	ND	ND	7,333	7,526	ND	ND

[1] *From broad-scale vegetation sampling in Catskill Mountains, see text.*

largely attributable to one of the six control plots which has had a relatively high nitrification rate for unknown reasons, across the years and in both mineral and organic horizons (in the other 11 oak plots, control and fertilized, potential net nitrification rates are consistently near 0) (Figure 8). In the organic horizons, the N treatment increased nitrification in maple and birch plots, despite lack of significant change in the N mineralization rates (Figure 7A). The N treatment effect was first observed in maple plots in 2003, but in the birch plots the treatment effect was also significant in the 1998 and 2000 data.

Across all plots and horizons (n = 120), nitrification rate is linearly related to N mineralization rate, but N mineralization explains only about 58% of the variation in nitrification rate. The relationship between mineralization and nitrification is much stronger, and the slope is higher, in the mineral horizon compared to the organic horizon (Mineral: Nitrif = 0.8094*Nmin − 0.4238, R^2 = 0.7658; Organic: Nitrif = 0.5748*Nmin − 3.1387, R^2 = 0.5044). The nitrification fraction (nitrification/mineralization) in the organic horizons is inversely related to the soil C:N ratio (Figure 8). This relationship is stronger across species than within a species, and is driven largely by maple plots having low C:N ratios and high nitrification fractions whereas the hemlock plots have high C:N and low nitrification fraction. Beech and birch are intermediate, and oak has nitrification fractions near zero for almost all plots despite a range of C:N ratios (Figure 8).

Soil Mass and C and N Stocks

Organic horizon mass, C and N stocks, and C:N ratios all varied significantly among species in the 2003 sampling; hemlock plots had the highest values for all four variables across all species and treatments (Figure 9). For organic horizon mass, there was a significant interaction effect between species and N treatment, such that hemlock forest floors had significantly higher mass in the treated plots and yellow birch had lower mass (Figure 9A). With all species taken together, the N addition caused a significant increase in organic horizon C stock and N stock. The comparison of individual species means showed that the pattern of increased C and N stock in N-treated plots occurred for all species except birch, but was statistically significant only in hemlock plots (Figure 9B, C). This N treatment on organic horizon mass and C and N stocks was not significant in the soil sampling done in 2000, indicating that the effect developed over

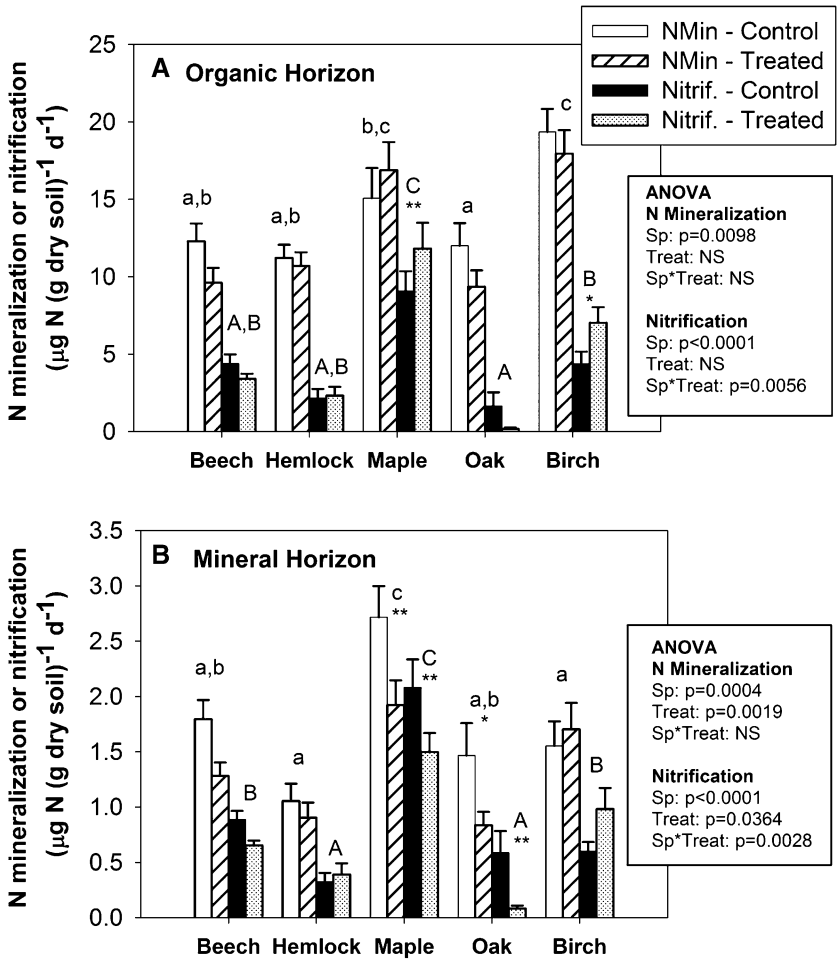

Figure 7. Potential net N mineralization and nitrification rates in the (**A**) organic and (**B**) mineral horizons. Mean rates are shown with *error bars* of 1 SE. Within a species, significance of N treatment effect is given as $*P < 0.05$, $**P < 0.01$. Differences among species are noted by *lower-case letters* for N mineralization and *upper-case letters* for nitrification. Within either the mineralization or nitrification data, species sharing the *same letter* are not significantly different from one another.

time during the treatment. (C and N stock data were not available for the full set of plots in 1998.)

Organic horizon C:N ratio increased significantly in response to the N treatment (Figure 9D). The individual species analysis showed that the increases were statistically significant in beech, hemlock and oak plots (Figure 9D). The N treatment effect on organic horizon C:N ratios was significant in 2000 ($P = 0.002$) and it became highly significant by 2003 ($P < 0.0001$), illustrating that the effect developed over time during the treatment.

The C and N stocks in the total soil to 12 cm (which includes the organic horizons and whatever depth of mineral horizon occurs between the bottom of the organic horizon and 12 cm) showed similar patterns as the organic horizon (data not shown). (The organic horizon mass ranges from roughly 10–30% of the total soil mass to 12 cm.) Hemlock typically had the highest C and N stocks to 12 cm among the different species. The N treatment effect was significant for C stocks ($P = 0.009$) and C:N ratio ($P = 0.024$) with N-treated plots having higher mean values than control plots in both cases. The N treatment effect on N stocks to 12 cm was not statistically significant.

Soil Solution Chemistry and Flux

Treated plots had significantly higher concentrations of NO_3^- in the O-horizon and the B-horizon soil solution than did the control plots (Figure 10A). Among the control plots, maple plots had the highest NO_3^- concentrations in soil solution, but among the fertilized plots, and across all plots taken together, beech had the highest NO_3^- concentrations. There was a strong interaction effect, indicating that in some species the N treatment only slightly increased the NO_3^- concentration in soil

solution (for example, oak) whereas in other species the treatment caused large increases (for example, beech, hemlock, birch).

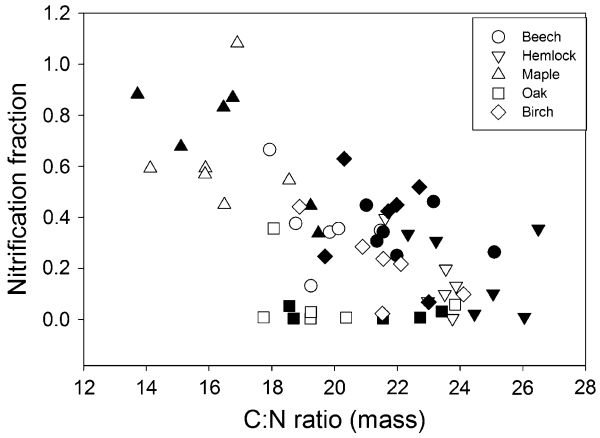

Figure 8. Plot means of soil C:N ratio versus nitrification fraction (nitrification/mineralization) for organic horizons. *Symbol* shapes represent species as shown in the legend; *open symbols* are control plots, *filled symbols* are treated plots.

Fluxes of NO_3^- in soil solution (as calculated from measured concentrations and modeled water flow as predicted by the BROOK90 model) varied from 0.17 to 0.49 g N m^{-2} y^{-1} in the control plots (with maple plots highest and hemlock plots lowest), and from 0.46 to 8.6 g N m^{-2} y^{-1} in the fertilized plots (with beech plots highest and oaks lowest) (Figure 10B). We did not perform the ANOVA on the flux data because the water flow measurements are modeled values and are assumed to be the same for all species and treatments.

Dissolved organic carbon (DOC) concentrations in B-horizon soil solution varied significantly among species, largely because hemlock plots had higher DOC than most of the hardwood plots (the exception being one birch plot which had DOC concentrations in the same range as hemlock) (Figure 10C). DOC concentrations in the forest floor soil solution were in general higher than those of the B horizon, and there were no significant effects of species or treatment (Figure 10C). Note that the methodology was somewhat different for the two horizons—in the forest floor we used

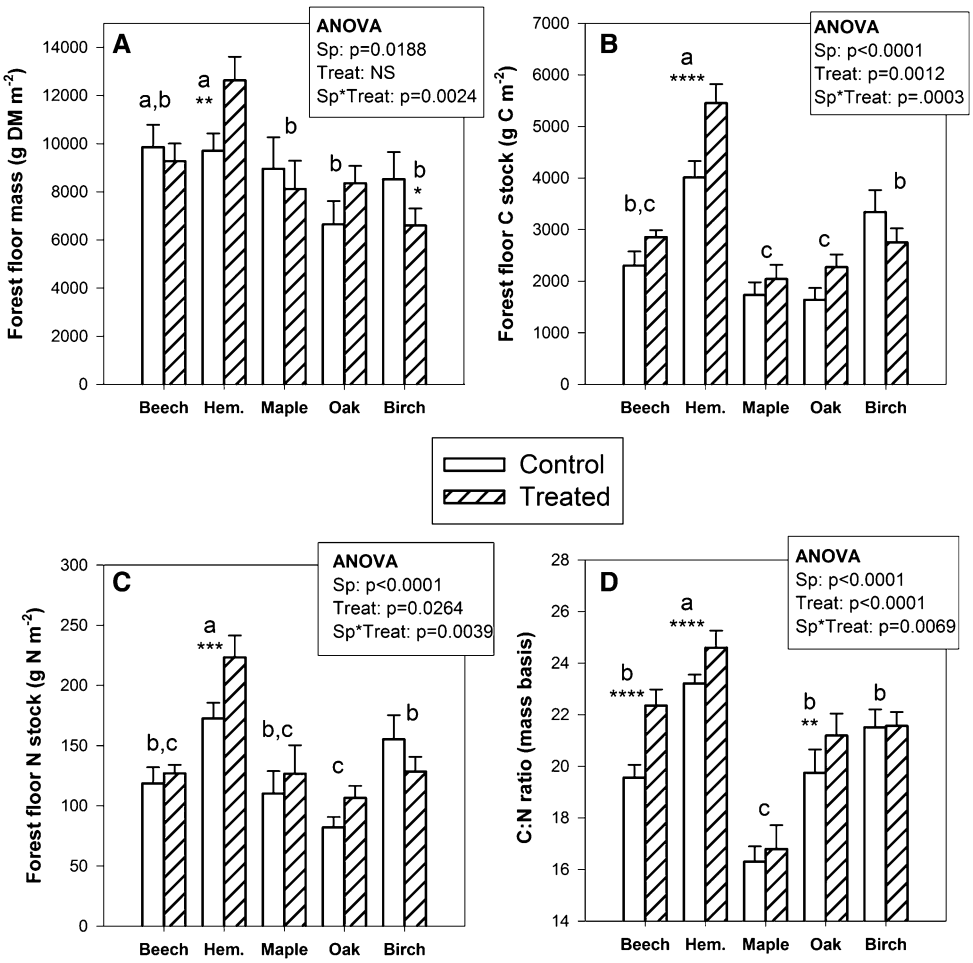

Figure 9. Mean (+1 SE) mass (**A**), C stock (**B**), N stock (**C**), and C:N ratio (**D**) in the Oe and Oa horizons of the forest floor in 2003. Within a species, significance of N treatment effect is given as $*P < 0.05$, $**P < 0.01$, $***P < 0.001$, $****P < 0.0001$. Differences among species are noted by *letters*; species sharing the *same letter* are not significantly different from one another.

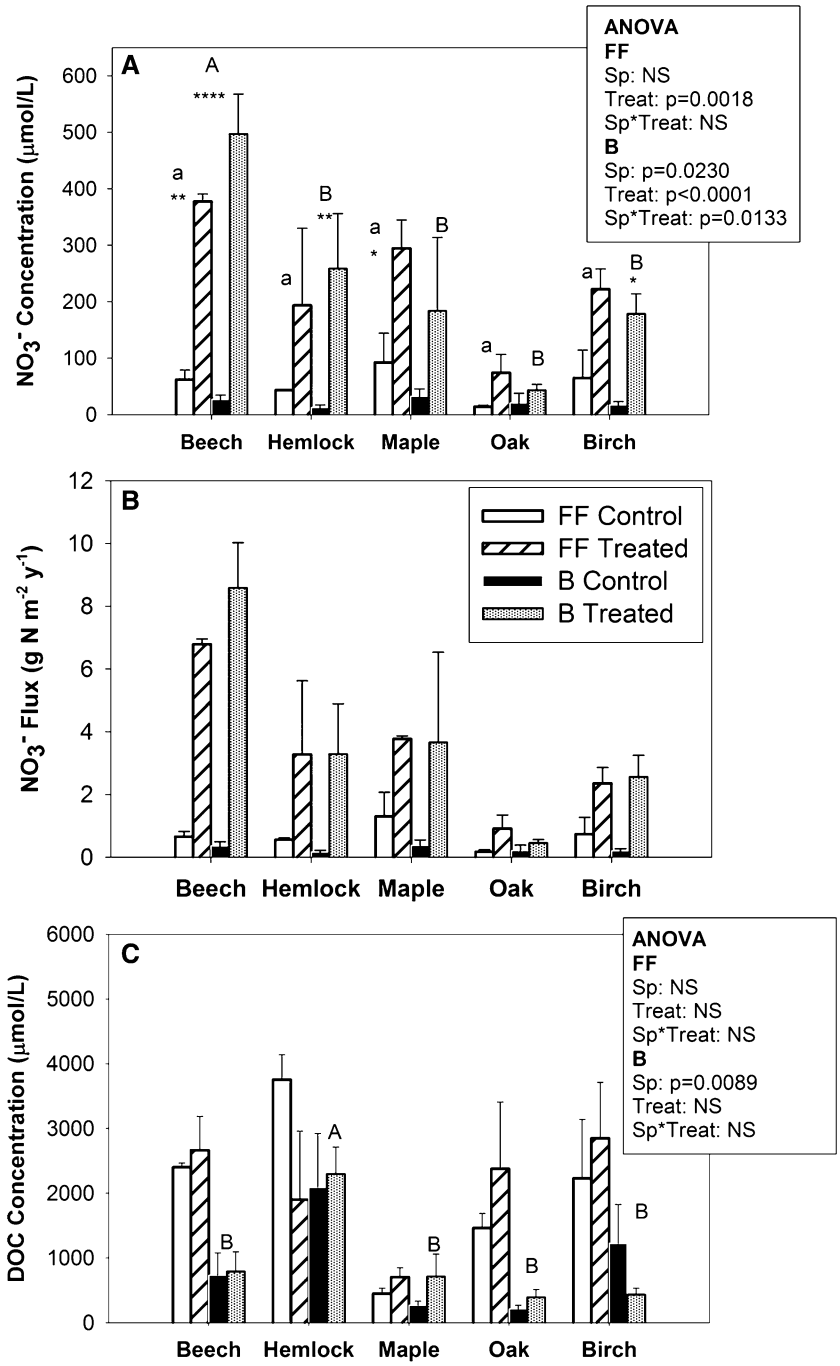

Figure 10. Concentration (**A**) and flux (**B**) of NO_3^-, and concentration of DOC (**C**) in soil solution lysimeters below the forest floor (FF) and in the lower B horizon. Means are shown with *error bars* of 1 SE; $n = 4$ plots per species for B horizon and 2 plots per species for FF lysimeters. Within a species, significance of N treatment effect is given as $^*P < 0.05$, $^{**}P < 0.01$, $^{***}P < 0.001$, $^{****}P < 0.0001$. Differences among species are noted by *lower-case letters* for FF lysimeters and *upper-case letters* for B horizon lysimeters. Within either the FF or the B horizon data, species sharing the *same letter* are not significantly different from one another. No statistical analysis is reported for the NO_3^- fluxes for reasons explained in the text.

zero-tension lysimeters and had only two plots per species, whereas in the B horizon we used tension lysimeters and had four plots per species. The DOC concentrations in the B horizon were correlated with forest floor depth, and the correlation was driven largely by deep forest floors and high DOC in some (but not all) of the hemlock plots (Figure 11). DOC concentrations in FF soil solution showed a similar pattern as the B horizon data but with fewer samplers (data not shown).

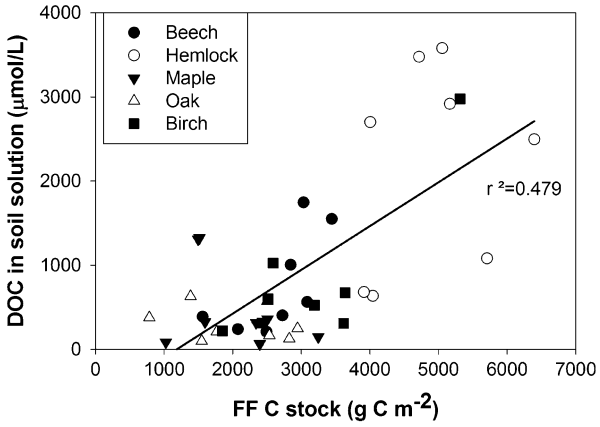

Figure 11. Concentration of DOC in B-horizon soil solution versus the C stock in the forest floor (Oe and Oa horizons) for the plots. *Line* is a linear regression through all the data.

Dissolved organic N (DON) and DOC concentrations were highly correlated in soil solution, especially in the control plots (r^2 = 0.92 in control plots, r^2 = 0.40 in treated plots), and the mean DOC:DON ratio in B horizon soil solution was 32.9. There was no significant species, treatment, or species*treatment interaction effect on DON concentration (data not shown).

Discussion

Synopsis

Overall, the observed tree responses to the N addition were muted, despite the fact that N was added to the treated stands at a rate over five times the ambient deposition rate. Some tree species increased in foliar N concentration, and some increased in litter N concentration. No tree species had a significant increase in growth or wood C increment in response to the N treatment. However, forest floor C pools and C:N ratios were higher in treated plots than in control plots, indicating that N addition increased C sequestration in the organic horizons of the soil, most significantly in hemlock plots. Nitrate leaching increased markedly in response to the N addition in all species, indicating that the addition rate of N (5 g N m^{-2} y^{-1}) exceeded the N retention capacity of vegetation and soils in these plots.

Tree Responses and N Limitation

There is little evidence of N limitation of tree production in these stands. Six years of N addition to these plots increased foliar N concentration significantly in only two of the species, maple and birch, and in those species N concentration increased by only 4–19%. Leaf litter N concentration increased slightly in hemlock, maple and oak stands, and none of the species had a significant increase in litter mass in response to the N addition. Likewise, no species had significant increases in woody biomass increment or ANPP in the treated plots. Taken together, these data do not indicate that N limits tree growth in this region, despite the fact that temperate forests are often considered to be N limited (Vitousek and Howarth 1991). The relative insensitivity of these trees to N addition is consistent, however, both with the results of a ^{15}N tracer addition study in these plots, which showed that less than 2% of the applied ^{15}N tracer was recovered in the trees after one year (Templer and others 2005), and other experimental addition studies from forested regions in the northeastern US (McNulty and others 2005; Wallace and others 2007). Two caveats are worth noting. First, we did not measure belowground NPP. It is possible that belowground NPP increased in response to the N treatment, but this seems unlikely because Templer and others (2005) reported lower fine root biomass in N treated compared to control plots in a subset of these plots. Second, we applied N to the soil, whereas most ambient N deposition first interacts with the canopy, where it may be taken up directly by foliage, bark and epiphytes, potentially stimulating NPP. However, several studies have shown that although some deposited N is often retained in the canopy, it is generally a small fraction of total plant N uptake (Lovett and Lindberg 1993) and that the mechanism of retention may be largely physicochemical exchange or adsorption, leading to little increase in C assimilation (Dail and others 2009).

The lack of N limitation may be the result of years of accumulated N deposition from chronic air pollution in this region, or it may be the result of another more limiting resource, or both. Studies of an N deposition gradient across the Northeastern U.S. have shown that two indicators of N availability, soil N:C ratio and foliar N concentration, increase in general with increasing N deposition, although the patterns are noisy and subject to much site-to-site variation (Lovett and Rueth 1999; Crowley and others 2012). Because the Catskill Mountains are at the high end of that deposition gradient, they may be relatively enriched in N and thus less N-limited. We have not done a phosphorus (P) addition experiment, but other work in these plots has not shown strong evidence of P limitation (Weand and others 2010b). Base cation (Ca, K, and Mg) availability is low in these plots (for example, mean exchangeable Ca concentrations

in mineral soil average 0.53, 0.97, 3.56, 1.7, and 0.86 cmol+/kg for untreated beech, hemlock, maple oak and birch plots, respectively) and the scarcity may be exacerbated by the high levels of NO_3^- leaching in the N-treated plots, which can further strip base cations from soil exchange sites. The resulting soil acidification may cause cation deficiencies and increased inorganic Al mobility that prevent the trees from responding to extra N addition with increased growth.

On the other hand, in the oak plots it is evident that N addition increased fruit production by approximately threefold in mast years. This result suggests that although N may not increase ANPP or wood growth, it may stimulate reproductive effort in red oaks. Similarly, Callahan and others (2008) reported that acorn production was increased by N fertilization in a mixed oak-maple stand in western Massachusetts, and the increase was greater in a mast year than in a non-mast year. We did not measure N concentration in acorns in this study, but other measurements of red oak acorns in this region indicate acorn N concentrations of about 0.9% (Lovett unpublished data), which together with the data in Figures 3C and 4 indicates that acorn N flux could approach half of the leaf litter N flux in mast years. In oak forests, acorns are a key source of food for many animals, especially small mammals, and small mammal population cycles are frequently driven by acorn dynamics (Ostfeld and others 1996). Small mammals are important predators of insects and some songbirds, and are important prey for raptors, foxes and many other predators, suggesting that increased N availability may have ramifications throughout the forest food web (Jones and others 1998; Ostfeld and Keesing 2000).

Soil Responses

In general, measurement of forest floor and soil C and N stocks is subject to considerable uncertainty because of the high spatial variability in soil characteristics within and among plots, especially in rocky soils like those of Catskill region forests. We used extensive replication, with 8 cores per plot and 12 plots per species (6 treated + 6 control), and the results showed that N-treated plots had significantly higher forest floor C pools, N pools, and C:N ratios than control plots. All species showed this pattern except yellow birch. Hemlock plots, with the largest forest floors, showed the largest N treatment effect. Because leaf litterfall did not increase for any species (Figure 3B) it is likely that the increase in forest floor C pools was the result of N inhibition of decomposition, as discussed further below. The C:N ratio is easier to measure because it depends only on soil chemistry rather than pool size, and the N treatment produced a highly significant increase in C:N ratio in the organic horizons, indicating C was accumulating in these plots faster than N (which is also reflected in the pool size measurements).

It should be noted that we have more statistical power to detect changes in soil pools than in aboveground biomass increment because the biomass values are plot inventories (thus there is one value per plot, $n = 60$) whereas for the soil data we have within-plot replication ($n = 240$, four samples per plot in a nested ANOVA). Nonetheless, the woody biomass increment and ANPP data (Figure 6) show that in beech, hemlock, and birch plots, the treated plots had lower mean biomass increment and ANPP than the controls, whereas in maple the means of treated and control plots were nearly equal. Only in oak might greater replication have revealed a significant positive response of woody biomass increment or ANPP to the N treatment. Thus our conclusion that the N treatment increased C storage in soils but not in the aboveground woody biomass is likely not affected by the different statistical power of the two data sets, with the possible exception of ANPP in the oak plots.

These results of increased C accumulation, N accumulation and C:N ratio in N-treated plots are consistent with several other studies in the literature. For instance, in a recent review of N effects on C storage in north temperate forests, Nave and others (2009) found that elevated N input (either from N fixing plants, fertilization, or simulated chronic N deposition) increased C pools in soils, although the significant effect was limited to mineral soil pools. However, Nave and others (2009) also reported that N additions decreased soil C:N ratio, contrary to our results. Liu and Greaver (2010) reviewed studies from several kinds of terrestrial ecosystems and found that N addition increased C storage in the organic horizons but not the mineral horizons. The mechanism for the increased C storage has been suggested to be N inhibition of microbial enzymes that degrade lignin (for example, Carreiro and others 2000; DeForest and others 2004), thus producing a buildup of humic material in the forest floor. In our sites, Weand and others (2010a) showed that the N treatment significantly reduced the activity of phenol oxidase (a lignin-degrading enzyme) in hemlock and yellow birch plots, but not in the other species. Although reduction in phenol oxidase activity is one possible cause of the buildup of

the forest floor, our data suggest another possibility—that N treatment changed the chemistry and decomposability of the litter. We observed that N treatment reduced litter lignin concentrations (Figure 3D), and this may be responsible for the reduced phenol oxidase activity observed by Weand and others (2010a). Moreover, the N treatment increased condensed tannins and folin-reactive phenols in hemlock litter, and these compounds may be capable of reducing litter decomposition (Kraus and others 2003). Our hemlock responses contrast with other studies that have shown reduced phenolic concentrations in response to increased N availability (for example, King and others 2001; Huttunen and others 2009).

Although the N treatment may have reduced the decomposition of organic matter, it was not reflected in the DOC concentration in soil solution. DOC concentration was not significantly affected by N addition in this study, but we note that there is a trend for higher DOC in N-treated plots that is manifested in all species except hemlock for the forest floor lysimeters and all species except birch for the B horizon lysimeters. With only four plot pairs per species for the B horizon lysimeters and two plot pairs per species for the forest floor lysimeters, we have limited power to detect significant differences. The lack of a significant N effect on DOC is consistent with the results of a similar N treatment experiment at Harvard Forest in Massachusetts (McDowell and others 2004). However in the Harvard Forest study, DON concentrations were increased by N addition, whereas we did not observe a significant effect on DON. In our study, the main factor controlling among-plot differences in DOC concentration was the C stock in the organic horizon in the plots. Evans and others (2008) reported that N additions do not produce a consistent change in DOC leaching from forested plots, and that the direction of the response (increase, decrease, or no change) is more closely tied to the N effects on soil acidification than to the rate of N addition itself. In our study, the N treatment appears to be increasing organic horizon mass and C content, and organic horizon C content is positively correlated with DOC leaching, so if N addition were to continue we would expect eventually to see differences in DOC leaching between control and N-treated plots.

Several reviews of the literature have shown that soil respiration also generally declines as a result of N additions (Janssens and others 2010; Liu and Greaver 2010). It is not clear whether the inhibitory effect on decomposition is an artifact of the intermittent high doses of N used in experimental manipulations, or whether the same effect could be expected from elevated levels of ambient N deposition. However, two lines of evidence suggest that this response is more than an experimental artifact. First, Janssens and others (2010) reported a decrease in soil respiration per unit NPP in response to higher levels of ambient N deposition. Second, a similar inhibitory phenomenon has been noted in leaf litter decomposition studies, in which high N in leaf litter is associated with an increase in the recalcitrant fraction of the litter, potentially leading to a buildup of decomposition-resistant material in the forest floor (for example, Berg and Dise 2004).

In cases in which N limits plant production, increased soil C could also result from increased litter inputs in N-treated plots. In the present study, however, foliar litter C input was not affected by the N treatment. We did not measure woody C input directly, but wood growth was not affected by N treatment. Root production and its response to the N treatment is not known for these plots, but Templer and others (2005) reported that fine root biomass was significantly decreased by the N addition.

N Leaching and N Budgets

The single-species control plots used in this study showed a highly variable amount of N leaching—the maple plots had the highest concentrations and fluxes of NO_3^- and the oak and hemlock plots the lowest. This is consistent with other studies showing high nitrification and NO_3^- leaching in stands dominated by sugar maple (for example, Finzi and others 1998; Lovett and others 2002, 2004; Lovett and Mitchell 2004; but also see Ross and others 2009). The organic and mineral horizons under sugar maple stands tend to have low C:N ratios, which are associated with high nitrification and high NO_3^- leaching (Dise and Wright 1995; Lovett and others 2002; Ollinger and others 2002). Oak plots had the lowest levels of N leaching, and also had the highest levels of N increment in woody biomass, suggesting that vegetation uptake and sequestration of N may limit N leaching in these plots. Low NO_3^- leaching from oak plots is consistent with watershed-scale results from the Catskill region (Lovett and others 2002) and elsewhere (Lewis and Likens 2000). However, hemlock control plots also had low leaching, but they had relatively low woody biomass N increment, indicating that factors other than vegetation uptake come into play in the regulation of N leaching. In hemlock forest floors, high C pools and C:N ratios probably lead to an efficient microbial N sink that immobilizes N and reduces N leaching.

The N-treated plots had significantly higher NO_3^- leaching than the control plots in all species, and in the N-treated plots beech had the greatest amount of leaching and oak the lowest. The hemlock, maple and birch plots averaged 3–4 g N m^{-2} y^{-1} of leaching, which is over 50% of the N input rate of 5.9 g N m^{-2} y^{-1} (5 from fertilizer + 0.9 from atmospheric deposition). The beech plot NO_3^- leaching rate was 8.6 g N m^{-2} y^{-1}, which is greater than the N input rate. Although the control beech plots appear to be able to retain some of the N deposited on them via ambient deposition, clearly these stands do not have much capacity for retention of extra added N, as the additional N added through the fertilizer was largely leached out. The lack of efficient N uptake probably reflects the impact of beech bark disease on these stands (Hancock and others 2008; Lovett and others 2010). For the output to exceed the input an internal N pool in the system must be declining, but our data show a measurable increase in both forest floor and wood N stocks. The source of the extra N may be a decline in the N stock in mineral soil SOM, or this imbalance may simply reflect the limits of measurement accuracy.

The mass balance of N in the ecosystem requires that inputs of N to the system are balanced by outputs and internal sinks. There are four principal fates of N added to forests—vegetation sinks, soil sinks, gaseous losses, and leaching losses (Lovett and Goodale 2011). We estimated the terms of the N budgets of the five species and two treatments based on the data from this study (Table 3). (Vegetation N increments for birch plots could not be estimated because of a lack of woody N concentration data for this species.) In our N budgets, the residual or difference term (=inputs − vegetation increment − leaching losses) represents the combined soil sink and gaseous loss terms. In these well-drained upland soils we expect gaseous losses to be low, and some preliminary measurements confirm low fluxes of both NO and N_2O (Rodney Venterea and others pers. comm.), but we have not made extensive gas flux measurements to confirm this.

Assuming negligible gaseous losses, the budgets indicate that in the control plots of maple, hemlock and oak, vegetation N increments are greater than deposition rates, yielding a negative soil N retention (that is, an internal source of N from the soil) in the range −0.26 to −0.85 g N m^{-2} y^{-1} (Table 3). This represents net extraction of N from the forest floor or mineral soil to support the growth of the trees, sometimes referred to as ''soil mining'' (for example, Johnson 1992). In contrast, N inputs in the treated plots are more than sufficient to supply the vegetation increment, and the net soil N retention is positive with an estimated sink strength of 0.31–3.8 g N m^{-2} y^{-1}. Based on the budgets, soil sink strengths are greatest in the oak soils for both the control and N-treated plots. Beech, in contrast to the other species, shows net soil N loss for both control and N-treated plots. As discussed above, this is probably due to the deterioration of the beech plots from the beech bark disease. Because we did not observe a reduction in the forest floor N pool, this leaching may represent the loss of mineral soil N. It is interesting to note that although these N budgets indicate that oak had the greatest soil N sink strength among the N-treated plots (Table 3), the greatest forest floor N accumulation based on direct measurement was in the hemlock plots (Figure 9B). In the N-treated hemlock plots, the residual term in the budget suggests a soil N accumulation (forest floor + mineral soil above the B-horizon lysimeter) of about 1 g N m^{-2} y^{-1}, whereas the comparison of control and treated hemlock plots suggests an mean N accumulation rate of about 8 g N m^{-2} y^{-1} (∼50 g N m^{-2} difference between control and treated plots, divided by 6 years). We suggest two possible explanations for this apparent inconsistency: (1) Differences in forest floor N pools between control and fertilized plots do not represent actual accumulation rates over the period of N treatment, and (2) the forest floor may be accumulating N while the mineral soil is losing N to leaching and plant uptake. Our data do not allow us to distinguish between these two explanations, which are not mutually exclusive.

Nitrogen Saturation

Are these plots N saturated? Definitions of N saturation in the literature are vague and variable, but Lovett and Goodale (2011) suggest distinguishing *capacity* N saturation, in which the vegetation and soil N sinks in the system are zero, from *kinetic* N saturation, in which the sinks are positive but their sum is less than the input amount. By these definitions, the control plots do not manifest either form of N saturation, even though some leaching is observed, because on an annual basis the vegetation N sinks are greater than the N input rates. Nitrogen leaching from the plots probably represents a spatial or temporal decoupling of inputs and sinks in the system. For example, N that is deposited or mineralized in the dormant season may leach from the system because of a lack of plant uptake, even though the plants may be mining the soil for extra N in the growing season. In our data, the estimated NO_3^- leaching flux from the control

Table 3. Estimated Mean N Budgets for Species and Treatments

Species	Beech		Hemlock		Maple		Oak		Birch	
Treatment	Control	Treated	Control	Treated	Control	Treated	Control	Treated	Control	Treated
Inputs										
Fertilizer	0	5	0	5	0	5	0	5	0	5
Deposition	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Total	0.9	5.9	0.9	5.9	0.9	5.9	0.9	5.9	0.9	5.9
Wood Increment (2001–2005)	0.84 (0.28)	0.60 (0.17)	0.56 (0.12)	0.46 (0.05)	0.88 (0.41)	0.73 (0.04)	1.37 (0.12)	1.35 (0.06)	ND	ND
Leaching losses (TDN, 2002–2003)	0.68 (0.19)	10.10 (1.78)	0.60 (0.11)	4.37 (1.86)	0.59 (0.17)	4.86 (3.74)	0.38 (0.20)	0.70 (0.13)	0.57 (0.17)	2.67 (0.58)
Residual (=inputs − wood increment − leaching loss) (This is soil storage and/or gaseous loss)	−0.62 (0.29)	−4.80 (1.85)	−0.26 (0.17)	1.06 (1.90)	−0.56 (0.57)	0.31 (3.71)	−0.85 (0.17)	3.84 (0.10)	ND	ND
% Retained (=100 * (input − TDN leaching)/input)	24 (22)	−71 (30)	34 (12)	26 (31)	35 (19)	18 (63)	58 (23)	88 (2)	37 (19)	55 (10)

Values are g N m^{-2} y^{-1}, except % retained which is in percent. Inputs are estimates of atmospheric N deposition from Catskill monitoring sites (see text) and N added as fertilizer. Other values are means of six plots per species/treatment combination, with SE in parentheses.

plots is, on average, more than 2.5-fold greater in the dormant season than the growing season.

The N-treated plots appear to show kinetic N saturation, because the vegetation and soil N sinks are still active, but the input rates exceed the sink strengths, leading to levels of N leaching that are high, though variable by species. Thus, the N treatment pushed non-saturated plots into a state of kinetic N saturation by overwhelming the sink strengths in the system. The budgets in Table 3 suggest that the levels of N addition that would induce kinetic N saturation vary among the species. We estimate the total N sink strength as the sum of the woody N increment and the negative of the residual N term (assuming that to be the soil N sink) in the N-treated plots. The total N sink strength (in g N m^{-2} y^{-1}) ranges from about 1.0 in maple to 5.2 in oak plots. Compared to the other species, the oak plots should be able to absorb more N deposition without inducing kinetic N saturation because of high sink strengths in both the vegetation and the soil.

Implications

These results have several implications for the ecological and environmental sciences. First, the lack of aboveground plant growth response to N treatment shows that, even in areas in which forest production is generally considered to be N limited, N limitation is not a universal phenomenon. This conclusion contradicts the predictions of most ecosystem models, which show a stimulation of forest production in response to N addition (for example, Townsend and others 1996; Aber and others 1997). The assumption that N deposition drives forest production (for example, Magnani and others 2007) is not true at these sites. More research should be focused on what makes forests respond differentially to N addition. Certainly, more mature stands such as those examined in this study may be less responsive to N than younger, faster-growing forests. Also, some species may respond more strongly to N addition than others (Thomas and others 2010), and our results indicate that some species may respond by increasing reproduction, an effect which is likely to ramify throughout the food web of the forest. In addition, secondary effects of excess N, such as soil acidification, may counteract the positive effects of N fertilization.

However, considering our results and other studies reported in the literature, enhanced C sequestration in the organic horizons of the soil may be a more common response than increased

forest growth. This response is not included in most ecosystem models at present, probably because the mechanisms of and constraints on the response are unclear. Also unclear is the extent to which the responses of soil C sequestration are an artifact of experimental N addition as opposed to lower chronic doses of N, as discussed above.

The variation among species in C and N sequestration rates in vegetation and soils, and in the N-leaching responses, indicates that changes in forest species composition will have strong effects on C and N cycling in the future. In addition to successional changes resulting from forest maturation, species composition in northeastern U.S. forests is changing rapidly because of invasions of exotic insects and pathogens (for example, Lovett and others 2006), suppression of fire (Nowacki and Abrams 2008), overabundance of herbivores such as moose and deer (Long and others 2007), and is expected to change further because of climate change (Iverson and others 2008). Four of the species studied here (American beech, eastern hemlock, red oak, and sugar maple) are threatened by introduced insects and diseases which are already causing decline or may lead to decline in the coming decades. Our results indicate that these species changes will alter the forest ecosystem's ability to retain atmospheric N deposition and prevent N leaching into surface waters, and to sequester C in biomass and soils. Models that predict changes in C and N cycling in the future, for instance in response to changes in climate or N loading, should account for likely changes in forest species composition.

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