

Forest canopy uptake of atmospheric nitrogen deposition at eastern U.S. conifer sites: Carbon storage implications?

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Abstract. Dry deposition determinations, along with wet deposition and throughfall (TF) measurements, at a spruce fir forest in central Maine were used to estimate the effect of atmospherically deposited nitrogen (N) uptake on forest carbon storage. Using nitric acid and particulate N as well as TF ammonium and nitrate data, the growing season (May–October) net canopy uptake of atmospheric, predominantly anthropogenic, N deposition was found to be 1–5 kg N ha⁻¹. The ratio of growing season net canopy N uptake to that of recycled root N uptake (10–30 kg N ha⁻¹ during the growing season) suggests a substantial modification of the N cycle at this Maine spruce fir forest over the past decade. The growing season 1–5 kg ha⁻¹ canopy N uptake may induce an enhanced annual carbon (C) storage of 250–1350 kg C ha⁻¹ yr⁻¹. This magnitude of N-stimulated C storage may be compared with measured annual C sequestration of ~2000 kg C ha⁻¹ for each of the years 1996–1998 at this Maine site. Consideration of four other eastern U.S. forest sites for which net canopy N uptake data are available suggests that from 285 to 2950 kg C ha⁻¹, annual C sequestration may be occurring at these conifer sites, consistent with the Maine site results.

1. Introduction

Atmospheric wet and dry nitrogen (N) deposition contributes 5–35 kg N ha⁻¹ yr⁻¹ to U.S. forest ecosystems [Johnson and Lindberg, 1992]. This N, which is primarily derived from the combustion of fossil fuels, the manufacture and use of fertilizers, livestock, and the burning of biomass [Schlesinger, 1997], may contribute to enhanced forest growth and carbon (C) storage [Houghton et al., 1995]. The atmospherically deposited N may be retained by the forest canopy (the predominant atmospheric deposition receptor at mature forest sites), pass through the forest ecosystem in streamflow and groundwater flow, or be distributed throughout forest biomass and soil compartments. Enhanced forest growth may result especially from the N deposited to and retained by the canopy, given that photosynthesis increases proportionally with the N content of foliage and that the upper portion of the canopy is the site of most photosynthesis [Field and Mooney, 1986; Evans, 1989]. Additional forest carbon sequestration (simply referred to here as C storage) may be maintained by canopy retained N as long as N remains the limiting growth nutrient. If the canopy foliage C/N ratio should drop significantly due to retained N, detrimental effects on forest growth may eventually be observed. Erisman et al. [1998] indicate such detrimental effects at spruce fir forests may occur once foliar C/N ratios decline below 20–25.

Enhanced forest growth and C storage have contributed to estimates of North American terrestrial C storage over the past decade or two [Birdsey et al., 1996; Bosquet et al., 1999; Fan et al., 1998; Houghton et al., 1999]. The magnitude of this estimate varies greatly from 200–300 kg C ha⁻¹ yr⁻¹, based on forest inventory data [Birdsey et al., 1996], to 1500–2500 kg C ha⁻¹ yr⁻¹, based on tower measurements [Goulden et al., 1996; Hollinger et al., 1999], and more [Fan et al., 1998]. Thus estimation of the magnitude of C storage resulting from canopy retained N is of interest.

It is important to consider canopy retained N rather than N deposition alone. This can be seen by considering Figure 1 which presents an overview of the N cycle in forest ecosystems. New N inputs (i.e., added from outside as opposed to internally recycled N) to a forest ecosystem are mostly provided by wet and dry deposition of several atmospheric N species. In the eastern United States, generally, the N species providing the large majority of available (nutrient) N are dry deposition of the gases nitric acid (HNO₃) and ammonia (NH₃) and wet as well as particulate matter dry deposition of ammonium (NH₄⁺) and nitrate (NO₃⁻) [Johnson and Lindberg, 1992]. Most of this deposited N is derived from anthropogenic sources [Vitousek et al., 1997] and is applied to the canopy of forest ecosystems. This, in comparison with naturally derived available N which is supplied in limited quantities at the forest floor by N₂ fixation, either asymbiotically by soil bacteria or symbiotically by bacteria in conjunction with plant roots [Schlesinger, 1997], atmospherically deposited N is supplied to the forest canopy. The canopy has been shown to be an active collection surface, with leaching of some elements and uptake of others consistently observed [Johnson and Lindberg, 1992].

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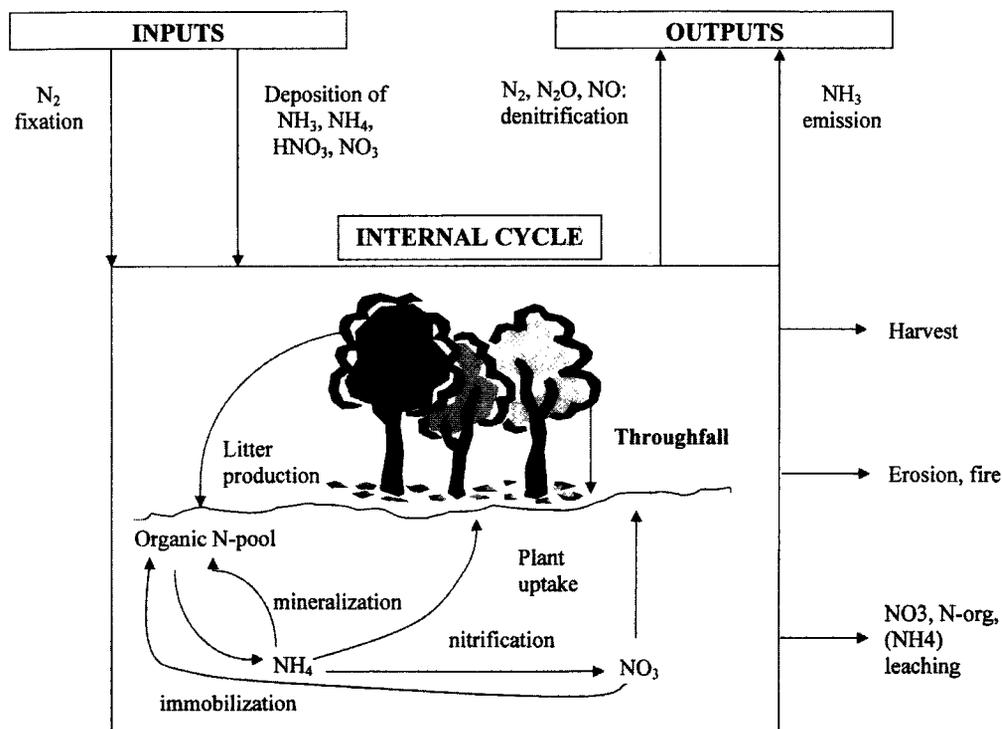


Figure 1. Simplified illustration of the nitrogen cycle in forests.

Measurement of the throughfall (in Figure 1) precipitation flux and TF comparison with wet and dry deposition has confirmed this for most elements. There are a few elements (e.g., Na and often S) which appear to be neither leached nor taken up by the canopy [Johnson and Lindberg, 1992].

The largest single flux of N in forest ecosystems occurs within the soil as organic N in litterfall is transformed into inorganic N, a multistep process often referred to as mineralization [Schlesinger, 1997] even though several distinct steps (e.g., ammonification, immobilization, mineralization, and nitrification) are active. Figure 1 portrays this multistep process. Mineralized, inorganic N is made available to trees by way of root uptake of NH_4^+ or NO_3^- for use in photosynthesis or other N-consuming processes within trees. Overall, this recycled N flux may be referred to as the litterfall-mineralization-root uptake pathway.

Loss of N from the forest ecosystem may occur due to NH_3 emission, soil denitrification, and leaching into ground and stream waters, among others (see Figure 1). Generally, in forest ecosystems, the cycling of N is quite efficient, with small fixation inputs compensating for small denitrification and leaching outputs. Thus if dry and wet deposition of anthropogenically derived N is significant in magnitude, a substantial perturbation of the N cycle in forest ecosystems may occur.

Nadelhoffer *et al.* [1999] suggested that "N deposition makes a minor contribution to carbon sequestration in temperate forests" using NITREX program data in a recent article with that title. However, the NITREX program applied ^{15}N -labeled nitrogen to forest floors at a number of European and North American sites, not to the forest canopy. As a result, the NITREX program effort did not simulate atmospheric N deposition. Jenkinson *et al.* [1999] and Sievering [1999] both made note of this error. As stated earlier, it is at the canopy of most forests that N deposition may be efficiently utilized. Estimation of forest canopy retained N may be obtained by measuring (1) wet deposition (WD) of

ammonium and nitrate in precipitation, (2) dry deposition (DD) of dominant N species, and (3) N species content in throughfall precipitation, i.e., TF [Lovett and Lindberg, 1984]. The retained N, designated as net canopy exchange (NCE), is then given by $\text{TF} - \text{WD} - \text{DD}$. For calcium, magnesium, and other nutrients, NCE is generally found to be positive due to leaching of their ions from forest canopies. However, for ammonium and nitrate, NCE is invariably found to be negative [e.g., Johnson and Lindberg, 1992] owing to canopy retention of these ions. The absolute magnitude of NCE for N, or net canopy N uptake, is indicative of the portion of atmospherically deposited N that may be utilized for growth by the forest canopy.

It is not surprising that atmospherically deposited N is taken up by forest canopies since growth in forest ecosystems is commonly limited by the availability of N [Schlesinger, 1997]. Forest ecosystems can partially compensate for the limited available N in their environments through mechanisms such as efficiently recycling N through the soil or reabsorbing N from foliar elements prior to abscission. Elevated atmospheric N deposition from anthropogenic sources may substantially modify the N cycle in forest ecosystems [e.g., Johnson and Lindberg, 1992].

An extensive N wet deposition and throughfall database from the Howland, Maine, coniferous forest research site offers an opportunity to study canopy N processes. Ambient air concentration data for several N species are available to estimate N dry deposition and NCE at this site. Uncertainty in the NCE estimates can oftentimes be large, especially because of uncertainty in dry deposition. A comparison of the NCE estimate, and its uncertainty, with estimates of N recycled annually by N mineralization of organic N in the soil is also available. To extrapolate these results to eastern forest sites more generally, additional data from the Integrated Forest Study (a multisite, several-year study) is also considered. The objectives of this study are (1) to determine the range in magnitude of NCE for N due to uncertainties in data and estimation

procedures at the Maine coniferous forest site, (2) estimate the range in C storage resulting from this canopy N uptake for comparison with recent CO₂ sequestration data obtained at this site [Hollinger *et al.*, 1999], and (3) estimate potential C storage at forest sites in the eastern United States more generally.

2. Site Description

The Howland Forest spruce fir study site, located in central Maine (45°12' N, 68°44' W), has been a focal point for atmospheric deposition and throughfall measurements since 1988. The site includes a 27-m tower extending above the canopy from which N species air concentration and CO₂ flux data are obtained along with meteorological data. The site is flat, has a growing season of ~140 days during May–October, and has annual precipitation of 106 cm. Soils are moderately well drained to poorly drained.

Vegetation is predominantly red spruce and balsam fir, although the balsam fir component now is ~5% of the total forest basal area due to spruce budworm infestation in the 1970s. White cedar, eastern hemlock, white pine, red maple, and yellow birch complete the forest makeup. Stand age ranges from 40 to 140 years with only sparse understory vegetation. A portion of the growth of live trees and, also, the accumulation of dead biomass may be a continuing response to logging which took place in the late 19th century [Hollinger *et al.*, 1999]. There may also be a small annual increment in soil organic matter at this site.

3. Methods

WD is sampled with a wet-only Aerochem Metric collector and bulk collectors located in a forest clearing ~2 km from the study site. WD has been collected weekly since January 1988 using National Atmospheric Deposition Program protocols. TF data were obtained across the 1988–1995 period using several protocols [McLaughlin *et al.*, 1996] for the months April through November. Wet-only TF data from two Aerochem Metric collectors are used here. Air concentrations for gaseous sulfur dioxide (SO₂) and nitric acid (HNO₃) as well as total- and fine-particle nitrate (NO₃⁻) and ammonium (NH₄⁺) have been measured continuously throughout the late 1980s and the 1990s. Gaseous ammonia (NH₃) has been measured since the spring of 1998.

WD and TF were determined as the product of volume weighted concentrations and hydrologic flux on a weekly time base. DD fluxes were estimated using the inferential, parameterized deposition velocity (V_d) approach as the product of air concentrations (C) and V_d ; thus $C(V_d)$. Deposition velocities for HNO₃ were estimated using the big-leaf model of Hicks *et al.* [1987]. Deposition velocities for fine-particle NH₄⁺ (assumed mass median dry diameter (MMDD) of 0.2 μm) and coarse-particle NO₃⁻ (assumed MMDD of 2 μm) were estimated using the procedure of Peters and

Eiden [1992]. Ammonia (NH₃) may be deposited or emitted at the forest-atmosphere interface. Under low NH₃ concentration conditions (of order 10 nmol NH₃-N m⁻³) expected at the Howland Forest site, emission should dominate [Duyzer *et al.*, 1994; Wyers and Erisman, 1998]. Ammonia flux estimation also utilizes the $C(V_d)$ approach; here V_d may be positive (deposition) or negative (emission). Air concentrations of NH₃ were obtained using two acid impregnated filters within a filter pack arranged to first remove particles and HNO₃ vapor by the use of Teflon and nylon filters placed ahead of the impregnated filters within the filter pack [Sievering *et al.*, 1996]. Using citric acid impregnated Whatman 41 filters, the NH₃ collection efficiency was found to be ~85%; use of two such filters in series results in better than 95% NH₃ collection efficiency [Calanni *et al.*, 1999].

Given that WD, DD, and TF are estimated as above, monthly NCE of NO₃⁻ and NH₄⁺ were determined as follows:

$$\text{NCE}(\text{NO}_3^-) = \text{TF}(\text{NO}_3^-) - \text{WD}(\text{NO}_3^-) - \text{DD}(\text{HNO}_3) - \text{DD}(\text{FNO}_3) - \text{DD}(\text{CNO}_3) \quad (1a)$$

$$\text{NCE}(\text{NH}_4^+) = \text{TF}(\text{NH}_4^+) - \text{WD}(\text{NH}_4^+) - \text{DD}(\text{NH}_3) - \text{DD}(\text{FNH}_4) - \text{DD}(\text{CNH}_4). \quad (1b)$$

F and C are the fine- and coarse-particle fractions of NO₃⁻ and NH₄⁺ in particulate matter.

Net N mineralization (defined as net ammonification plus net nitrification) was determined in the O horizon (forest floor) and top 10 cm of the B horizon (mineral soil) at the Howland Forest from 1993 to 1995 using the in situ buried soil bag technique [Eno, 1960]. In this method, 20 pairs of samples were collected from each horizon at 6-week intervals throughout the growing season. One of each pair was taken back to the laboratory and extracted for NH₄⁺ and NO₃⁻ (1 N KCl, 36 hours). The other sample of each pair was placed in a thin, polyethylene bag and returned to the soil to incubate until the next collection period, after which it was retrieved and analyzed for NH₄⁺ and NO₃⁻ as described above. The difference in NH₄⁺ between initial and incubated soils was considered net N ammonification; the difference in NO₃⁻ content between initial and incubated soils was considered net N nitrification. The sum of these two is net N mineralization. Although an additional set of bags was allowed to winter over for annual net N mineralization determination, we report here on growing season values (140 days during May–October).

4. Results and Discussion

4.1. NCE Estimation for NO₃⁻ and NH₄⁺

The NCE (NO₃) results are presented in Table 1, including uncertainty in results stated as 90% confidence interval values (in parentheses). WD and DD contribute about equally to the total atmospheric NO₃ input to the forest canopy. The average uncer-

Table 1. Nitrate (NO₃) Dry Deposition (Sum of HNO₃ and Particulate NO₃ Deposition), Wet Deposition, Throughfall, and Net Canopy Exchange (see equation (1a)) for All Months for Which Throughfall Data Were Available^a

	DD(NO ₃), Kg N ha ⁻¹	WD(NO ₃), Kg N ha ⁻¹	TF(NO ₃), Kg N ha ⁻¹	NCE(NO ₃), Kg N ha ⁻¹
April	0.160	0.204	0.114	-0.251 (0.188)
May	0.183	0.261	0.051	-0.394 (0.184)
June	0.238	0.255	0.043	-0.450 (0.151)
July	0.284	0.239	0.049	-0.474 (0.221)
August	0.260	0.260	0.083	-0.437 (0.160)
September	0.157	0.181	0.033	-0.305 (0.088)
October	0.226	0.352	0.063	-0.515 (0.248)
November	0.200	0.254	0.124	-0.329 (0.164)

^aNumbers in parentheses are 90% confidence interval values.

tainty for the growing season, May–October, NCE is $\pm 40\%$ with a total NCE (NO_3^-) across this period of $-2.6 \text{ kg N ha}^{-1}$. The ratio of NCE (NO_3^-) to WD plus DD of NO_3^- and HNO_3 during the growing season is quite high, 0.89, with a month-to-month variation of only ± 0.03 . This ratio is higher than that for either April (0.69) or November (0.73), indicating that only $\sim 10\%$ of dry plus wet deposited nitrate passes through the canopy to the forest floor during the growing season.

The estimation of NCE (NH_4^+) not only entailed the application of deposition velocities (V_d) for NH_4^+ fine- and coarse-particulate matter using the model of *Peters and Eiden* [1992] but must also apply appropriate values of V_d for NH_3 . Ammonia concentration measurements during the growing seasons of 1998 and 1999 were nearly always $< 20 \text{ nmol NH}_3\text{-N m}^{-3}$, with mean concentrations of $7.8 \text{ nmol NH}_3\text{-N m}^{-3}$ for 1998 and $12.1 \text{ nmol NH}_3\text{-N m}^{-3}$ for 1999. This is 1/3 to 1/2 of the summertime mean of a large data set obtained at the Harvard Forest in central Massachusetts [Lefer, 1997]. Such very low concentrations can only prevail if a strong atmospheric sink for NH_3 exists. Particulate matter in the eastern United States contains large amounts of sulfate which may become acidic unless NH_3 is available to neutralize it. As opposed to acidic H_2SO_4 formation in particulate matter, the availability of NH_3 will preferentially result in NH_4HSO_4 or $(\text{NH}_4)_2\text{SO}_4$ formation. This can provide a strong atmospheric sink for NH_3 ; the longer the transport time from pollutant source areas, the larger this sink. This, very likely, explains why NH_3 concentrations at Howland Forest are only 1/3 to 1/2 that found at Harvard Forest. In turn, low NH_3 air concentrations may lead to its release from the canopy if these concentrations are below the NH_3 concentration in substomatal cavities of the forest canopy foliage [Farquhar et al., 1980; Sutton et al., 1995]. At a Danish spruce forest, *Andersen et al.* [1999] observed NH_3 emission across a range of NH_3 concentrations up to 200 nmol m^{-3} . *Sievering et al.* [1994], at a more polluted spruce forest site in Germany, indicated that NH_3 emission may have been a response to large dry-plus-wet deposition of HNO_3 and particulate NO_3^- . In both cases, emission velocities $< 2 \text{ cm s}^{-1}$ were observed by measuring NH_3 gradients above these spruce forest sites, consistent with NH_3 exchange velocities observed at other conifer sites under low-concentration conditions [Wyers and Erisman, 1998].

Given that the average NH_3 concentration observed above the Howland Forest was only $7.8 \text{ nmol NH}_3\text{-N m}^{-3}$ (1998) and $12.1 \text{ nmol NH}_3\text{-N m}^{-3}$ (1999), emission of NH_3 must have prevailed. Canopy loss of N as NH_3 may be estimated by applying a $1\text{--}2 \text{ cm s}^{-1}$ emission velocity to NH_3 concentrations observed during the growing season, May–October. Across the entire growing season the resultant canopy loss due to NH_3 is at most $0.1\text{--}0.2 \text{ kg N ha}^{-1}$, a quite small value due to the very low observed NH_3 concentrations. Dry deposition of NH_3 may have occurred occasionally

along with the general trend of NH_3 emission [Sutton et al., 1998; Wyers and Erisman, 1998]. In light of these additional considerations, the growing season canopy NH_3 emission was substantially $< 0.2 \text{ kg N ha}^{-1}$. It was likely to be of similar magnitude but opposite in direction to the very low NO/NO_2 plus HONO deposition at this site; they may be assumed to cancel each other in the determination of NCE for total N.

The NCE (NH_4^+) results are presented in Table 2. Uncertainty is again stated as 90% confidence interval values (in parentheses). The total growing season NCE (NH_4^+) is $-1.0 \text{ kg N ha}^{-1}$ with a large uncertainty of $\pm 85\%$. A substantial fraction of this uncertainty is due to the large uncertainty in our knowledge of V_d for fine particles [Peters and Eiden, 1992; Sievering, 1984]. Since 94% of NH_4^+ at Howland Forest was found to be associated with fine particles, this large uncertainty propagates through the NCE (NH_4^+) calculation. In contrast, over 70% of NO_3^- was found to be associated with coarse particles for which uncertainty in V_d is substantially less than that for fine particles [Peters and Eiden, 1992].

4.2. Growing Season Net Canopy N Uptake

The mean NCE for NO_3^- plus NH_4^+ for the Howland Forest was $-3.6 \pm 1.8 \text{ kg N ha}^{-1}$ per growing season across the 1988–1995 period for which TF data are available. Thus growing season net canopy N uptake may be stated to be in the range of $1.8\text{--}5.4 \text{ kg N ha}^{-1}$. A complication is introduced by the fact that TF sampling at other eastern U.S. sites [Johnson and Lindberg, 1992] generally shows the presence of organic N in TF. This organic N may arise from the efflux of N-containing compounds from internal pools. Washoff of foliage and branch surfaces also contributes to the organic N observed in TF [Schaefer and Olson, 1984]. From the viewpoint of the N utilized for C storage, much of the organic N found in TF contributes to C storage before being released in TF. Organic N has also been observed in wet deposition samples in the eastern United States. At a Virginia forest site, organic N was 8–11% of the total N in WD (W. Keene, personal communication, 2000). Consideration of any wet deposition organic N that may be present at Howland Forest (no data are available) would increase the annual net canopy N uptake. Given an assumption that organic N is $\sim 10\%$ of total N in WD and considering the small TF organic N database available at Howland Forest, effective (C sequestering) net canopy uptake of organic plus inorganic N may have been reduced by $0.4\text{--}0.8 \text{ kg N ha}^{-1}$. Thus net canopy N uptake may be stated as slightly less than the $1.8\text{--}5.4 \text{ kg N ha}^{-1}$, the range now being $1\text{--}5 \text{ kg N ha}^{-1}$.

The Integrated Forest Study [Johnson and Lindberg, 1992], a comprehensive three-year study, considered organic N in TF and WD, allowing for a more direct estimation of net canopy N (organic+inorganic) uptake. For the six eastern U.S. sites, four coniferous and two mixed hardwoods sites, at which organic N data were obtained, net canopy N uptake was found to lie in a

Table 2. Ammonium (NH_4^+) Dry Deposition, Wet Deposition, Throughfall, and Net Canopy Exchange (see equation (1b)) for All Months for Which Throughfall Data Were Available^a

	DD(NH_4^+), Kg N ha^{-1}	WD(NH_4^+), Kg N ha^{-1}	TF(NH_4^+), Kg N ha^{-1}	NCE(NH_4^+), Kg N ha^{-1}
April	0.026	0.160	0.043	-0.143 (0.195)
May	0.060	0.119	0.031	-0.148 (0.134)
June	0.057	0.180	0.043	-0.194 (0.156)
July	0.059	0.148	0.031	-0.176 (0.122)
August	0.058	0.162	0.095	-0.125 (0.109)
September	0.057	0.144	0.029	-0.142 (0.121)
October	0.030	0.192	0.027	-0.195 (0.190)
November	0.028	0.092	0.042	-0.077 (0.151)

^aSee text for contribution of NH_3 exchange to the DD (NH_4^+) and NCE (NH_4^+) results. Numbers in parentheses are 90% confidence interval values.

wide range from 0 to 5.9 kg N ha⁻¹ yr⁻¹. For the four coniferous sites the range was 1.1–5.9 kg N ha⁻¹, encompassing the 1–5 kg N ha⁻¹ growing season range of possible values for Howland Forest. The annual net canopy N uptake at Howland Forest may thus be indicative of processes operative over a large area of the eastern United States. However, this magnitude of net canopy N uptake must be considered in the context of the N annually cycled through the Howland Forest as a whole to assess its impact or importance.

4.3. Comparison of Net Canopy N Uptake With Forest Recycled N

The litterfall-mineralization-root uptake pathway provides a major recycling mechanism for the N needed in photosynthesis. Litterfall was measured at the Howland Forest site from 1986 through 1988, and mineralization was measured from 1993 through 1995. Mean litterfall N is 12.2 kg N ha⁻¹, and mean growing season mineralization is 19.1 kg N ha⁻¹ in the soil O horizon and 1.4 kg N ha⁻¹ for the upper 10 cm of the B horizon. Although root uptake is notoriously difficult to measure, we can assume that the minimum growing season root uptake is approximately equal to the litterfall flux (~12 kg N ha⁻¹). The maximum root uptake is approximately equal to N mineralized during the growing season in the O-horizon plus that in the upper B-horizon, the region of nearly all-rooting density. Year-to-year variability in mineralization was found to be quite substantial, 20.5±11.3 kg N ha⁻¹, or a range from 10 to 30 kg N ha⁻¹ per growing season. The upper bound of 30 kg N ha⁻¹ assumes that inorganic N in TF passes through the mineralization pathway and that all mineralized N is available to tree roots for uptake. This latter assumption is unlikely to be true; yet, we have no data to indicate the fraction of N mineralization which is actually taken up by the roots. Thus growing season root N uptake is estimated to be from 10 to 30 kg N ha⁻¹. Net canopy N uptake of 1–5 kg N ha⁻¹ thus supplies, during any one growing season, between 3 and 50% additional N to forest foliage, when compared to estimated growing season root N uptake. Over several years time, this percentage is likely to be 10–20%.

The range of 10–20 kg N ha⁻¹ per growing season provides an estimate of the N that can be supplied by the natural N cycle to trees at the Howland Forest for annual uptake. The N available for growth is often the limiting factor for C storage in conifer trees [Cole and Rapp, 1981; Schlesinger, 1997]. The ratio of net canopy N uptake to root N uptake, 0.03–0.5, may serve as an index for the extent to which the natural N cycle at the Howland Forest has been altered by DD and WD of N. Well over half of the sum of HNO₃, NO₃⁻ plus NH₄⁺ in WD and DD in the eastern United States is known to be anthropogenically derived [e.g., Lefter, 1997]. Considering this fact, it appears that between 2% and as much as 30–40% additional N is being supplied, each growing season, by anthropogenic sources to forest foliage at the Howland Forest. This finding is significant in its own right since it suggests that canopy N uptake, if fairly constant over time, will add as much new N in several years time to this spruce fir forest as is recycled during the growing season.

4.4. Impacts of Net Canopy N Uptake on C Storage

The timescale over which net canopy N uptake may contribute to C storage must be addressed. Callani et al. [1999] found that the amino acid content of spruce needles responds to changes in atmospherically deposited N in several hours. It is known that still less time is required for amino acids to convert into photosynthetic enzymes and that the photosynthetic capacity of plants is determined by their photosynthetic enzyme content [e.g., Wong, 1979]. Canopy N uptake at conifer forest sites may thus contribute to C storage on a rapid, diurnal timescale. Longer-term trends in C

storage, such as the 15,000 kg C ha⁻¹ increase inferred from tower-based CO₂ net ecosystem exchange measurements at the Harvard mixed hardwood forest site over the 1992–1998 period (S. Wofsy, personal communication, 1999), may be due partly to chronic anthropogenic N deposition.

The additional C storage that may be due to canopy N uptake can only be imperfectly estimated at the present time. (Poor knowledge regarding the magnitude of organic N in TF as well as poor knowledge regarding how much of this organic N may be leached from the canopy before contributing to C storage is an argument for this imperfection.) Data on the C/N ratio and biomass of the bole, branch, and foliar components at the Howland Forest [Johnson and Lindberg, 1992] provides an aboveground C/N ratio of 250–270. Taking the 1–5 kg N ha⁻¹ from above as the annual growing season canopy N uptake, an added C storage from as little as 250 to as much as 1350 kg C ha⁻¹ yr⁻¹ (270 × 5) is estimated.

We may broaden this Howland Forest C storage to the eastern United States more generally by considering the 1.1–5.9 kg N ha⁻¹ for canopy N uptake found by the Integrated Forest Study at four eastern U.S. conifer forests. The C/N ratio for these forests (biomass weighted-average of foliar/branch/bole/root C/N ratios) varies from 260 to over 500 [Johnson and Lindberg, 1992]. Together, the canopy N uptake values and forest C/N ratios provides a range from 285 to 2950 kg C ha⁻¹ yr⁻¹ for C storage estimation at eastern U.S. conifer forest sites due to canopy N uptake.

Forest inventory data in various parts of Europe [e.g., Eriksson and Johansson, 1993; Kauppi et al., 1995] document increased wood production in areas with increased N deposition. However, spruce forest fertilizer experiments show that N additions alone do not always influence growth [Dralle and Larsen, 1995]. Further, at high atmospheric N inputs, e.g., >40 kg N ha⁻¹ yr⁻¹, prolonged N inputs may cause growth decline [Mohren, 1986]. This may be due to a decrease in both root length and the root-shoot ratio of forests [De Visser, 1998] which can endanger the uptake of soil nutrients and water. European N deposition, with the exception of the Netherlands, is generally not above 40 kg N ha⁻¹ yr⁻¹. Atmospheric N inputs in the eastern United States are well below this magnitude, except, perhaps, in high-elevation areas [Johnson and Lindberg, 1992] where cloud and fog interception may contribute strongly to atmospheric N deposition. Another approach to delineating whether N deposition leads to C storage or to detrimental effects upon conifer forests has been developed in the Netherlands [Erisman et al., 1998]. If the N content of needles is <1.4% of needle dry weight, then N is considered to be in short supply. For the range 1.4–2.3% of dry weight, N content is considered to be sufficient or optimal, and >2.3% of dry weight indicates that needle N content is detrimental to growth. The needle N content of spruce needles at the Howland Forest was observed to be 1.1–1.2% of dry weight [Fernandez et al., 1990], clearly in the range for N in short supply. All of the Integrated Forest Study sites had foliar N content significantly <2% of dry weight [Johnson and Lindberg, 1992]. Thus increased C storage resulting from increased N deposition in the eastern United States may be expected.

Hollinger et al. [1999] present results of CO₂ exchange measurements at the Howland Forest indicating C storage of 2100±500 kg C ha⁻¹ in 1996 with a C storage of ~6000 kg C ha⁻¹ for the 1996–1998 period (D. Hollinger, personal communication, 1999). Growing season averaged net midday, summer CO₂ uptake at Howland Forest was higher than at several Boreal Ecosystem-Atmosphere Study program coniferous forests [Hollinger et al., 1999]. It is possible that the higher atmospheric nitrogen concentrations at the Howland Forest contributed to this difference. In that light, our estimation that canopy N uptake led to enhanced C storage of 250–1350 kg C ha⁻¹ in the 1996–1998 period at the Howland Forest site (10–70% of total C storage) seems quite reasonable.

Goulden *et al.* [1996] presented results of CO₂ exchange measurements at the mixed hardwood Harvard Forest site in the northeastern United States. A long record of CO₂ exchange data exists at this site, and N deposition is typical of low elevation sites in the eastern United States. Carbon storage of 1400–2800 kg C ha⁻¹ yr⁻¹ has been observed [Goulden *et al.*, 1996] with the 1992–1998 total now being ~15,000 kg C ha⁻¹ (S. Wofsy, personal communication, 1999). These magnitudes may be roughly compared with the 285–2950 kg C ha⁻¹ yr⁻¹ storage estimation at four Integrated Forest sites (note, however, this estimation is for eastern U.S. conifer forest sites only).

To test the likelihood that significant C storage at the Howland Forest may have resulted from canopy N uptake, a modeling exercise using C4.1, the CENTURY model modified to consider N canopy exchange [Sievering, 1996], was considered. However, despite the rich C and N database available at Howland Forest, this database was not found to be sufficiently detailed to constrain model outcomes to any significant degree.

4.5. Forest N Cycle Field Sampling and Data Needs

Given that data-constrained modeling was not able to simulate C and N relations at conifer forests at the level of detail needed, the further development of field measurements are essential for explaining C storage as it may relate to canopy N uptake. Both the analysis presented here for the Howland Forest and also that underlying the Integrated Forest Study canopy N uptake results have large uncertainties associated with the estimation of canopy N uptake. Much of this uncertainty is due to our limited capability in estimating N dry deposition, which, in turn, is exacerbated by the number of N species that may contribute to N deposition at any one site. Sites that are removed from N sources may have a lesser number of N species to consider since atmospheric conversion has taken place. Estimation of canopy N uptake, using (1a) and (1b), holds promise as long as dry deposition can be accurately determined. This implies a need to directly measure dry deposition fluxes for the contributing N species, not by the inferential, parameterized V_d approach. Longer-term measurements of N in throughfall and wet deposition, on an event basis, may allow for the application of the regression model approach of Lovett and Lindberg [1984] to estimate dry deposition. This approach has proven useful for estimating the mean dry deposition of total N at forest sites situated in areas with convective storms and extended dry periods but not in areas with frequent or low-intensity rainfall and short dry periods [Draaijers *et al.*, 1996]. Nonetheless, closure regarding the magnitude of dry deposition may be obtained by joining the net canopy exchange formulation of (1a) and (1b) (using direct dry deposition flux measurements) with the regression model approach.

5. Conclusions

Canopy N uptake at the coniferous Howland Forest (Maine) was in the range of 1–5 kg N ha⁻¹ per growing season across the 1988–1995 period for which throughfall data are available. This includes a large contribution from anthropogenic N sources and is a significant input at this forest since root N uptake, the main source of available, recycled N at this coniferous forest, is in the range 10–30 kg N ha⁻¹ per growing season. Given that N availability limits photosynthetic capacity, enhanced C storage is to be expected in response to canopy N uptake. The Integrated Forest Study found canopy N uptake (including the consideration of organic N in TF) at several eastern U.S. coniferous forests to be 1.1–5.9 kg N ha⁻¹ yr⁻¹. Thus enhanced C storage may also be expected at many other eastern U.S. conifer forest sites.

The 1–5 kg N ha⁻¹ per growing season of canopy N uptake at the Howland Forest implies that 250–1350 kg C ha⁻¹ yr⁻¹ of C storage occurs; most of this is due to anthropogenically derived

canopy N uptake. This may be compared with a measured C storage of ~2000 kg C ha⁻¹ yr⁻¹ at the Howland Forest over the 1996–1998 period [Hollinger *et al.*, 1999]. The 1.1–5.9 kg N ha⁻¹ yr⁻¹ of canopy N uptake at several Integrated Forest Study sites suggests that from 285 to 2950 kg C ha⁻¹ yr⁻¹ was stored annually at these four eastern U.S. conifer forests as a result of canopy N uptake. Thus the C storage to be expected, at coniferous forested landscapes in the eastern United States, may be roughly identified as ~1000 kg C ha⁻¹ yr⁻¹. This magnitude of added C storage contributes to but may not fully explain the C storage occurring in the eastern United States inferred from measurements at local forest flux towers [e.g., Goulden *et al.*, 1996].

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