

Transformation and retention of nitrogen in a coastal forest ecosystem

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Abstract. Transformations and fluxes of N were examined in three forested sites located along a gradient of soil texture in the coastal forests of the Waquoit Bay watershed on Cape Cod. Total N leaching losses to ground water were 0.5 kg ha⁻¹ yr⁻¹ in the loamy sand site and 1.5 kg ha⁻¹ yr⁻¹ in the fine sand site. Leaching loss to groundwater was not measured in the coarse sand site due to the prohibitive depth of the water table but total N leaching loss to 1m depth in the mineral soil was 3.9 kg ha⁻¹ yr⁻¹. DON accounted for most of the leaching losses below the rooting zone (77–89%) and through the soil profile to ground water (60%–80%). Differences in DON retention capacity of the mineral soil in the sites along the soil texture gradient were most likely related to changes in mineral soil particle surface area and percolation rates associated with soil texture. Forests of the watershed functioned as a sink for inorganic N deposited on the surface of the watershed in wet and dry deposition but a source of dissolved organic N to ground water and adjoining coastal ecosystems.

Introduction

Dramatic increases in atmospheric N deposition over the past few decades have fueled concerns about the degradation of forest health and water quality in many regions throughout the world. Accordingly, research has focused on understanding how forest ecosystems process this N input. Most of this research, which has been conducted in upland forest ecosystems, suggests that retention of atmospherically deposited N is largely dependent upon the successional stage of the forest as well as soil C:N ratios. Young aggrading stands that are actively sequestering N in biomass and soil tend to exhibit small leaching losses of N while more mature stands have N outputs that are approximately equal to inputs (Vitousek & Reiners 1975; Van Miegroet et al. 1992; Emmet et al. 1993).

Less attention has been directed towards understanding the dynamics of atmospherically deposited N in coastal forest ecosystems of the eastern US.

In a recent study, Lajtha et al. (1995) found no relationship between stand age and N leaching losses below the rooting zone, but the calculated losses were larger than expected in an aggrading successional forest based on studies in upland forests. They suggested that edaphic factors related to soil texture were the dominant regulators of N retention in these systems. This hypothesis is consistent with the results of Coûteaux and Sallih (1994) who found leaching losses of ^{15}N applied to cores taken from various forest soils to be positively correlated with particle size.

The ability of coastal forest ecosystems to retain atmospheric N deposition has ramifications for estuarine ecosystems. Coastal marine ecosystems have been widely affected by eutrophication caused by anthropogenic nitrogen loading from adjacent watersheds (Nixon et al. 1986). Along the eastern seaboard of the US, it has been estimated that a large fraction (30–40%) of nitrogen delivered to coastal waters may be derived from atmospheric deposition (Valiela & Costa 1988; Fisher & Oppenheimer 1991). Thus, from a management perspective, it is critical to understand the capacity of these coastal forests to reduce the transport of atmospheric N deposition from coastal watersheds to adjoining estuarine ecosystems.

In this study we examined the transformations and fluxes of N in water moving through the ecosystem to the water table in forest sites positioned along a gradient of soil texture in the Waquoit Bay watershed on Cape Cod. We predicted that stands on more coarsely textured soils would be more susceptible to N losses relative to stands on more finely textured mineral soil. We expected that edaphic factors associated with soil texture would override the generally greater capacity of younger successional stands to retain N relative to more mature stands. Based on preliminary data in these sites, we expected that DON would be an important vector of N loss. Thus, we hypothesized that much of the capacity of a site to retain N would be directly related to its potential to adsorb DON in mineral soil during the percolation of soil water down to ground water.

Methods

Study location

The study area is located in the Waquoit Bay watershed on the southwestern shore of Cape Cod, Massachusetts (41°34' N, 70°32' W). The average annual rainfall for the area is 115 cm with little seasonal variation. Mean annual air temperature is 9.8 °C. Soils of the region were developed from parent material deposited by the Sandwich Moraine outwash during the Wisconsin glaciation. The outwash deposits consist primarily of sand and gravel and

range in depth from approximately 15 to 65 m (LeBlanc 1984). In spite of their similar origin, the soils of the watershed are heterogeneous in texture, ranging from loamy sands to coarse sands. The area is primarily drained by infiltration to ground water as slopes are gentle and there is virtually no surface runoff. Podzolization is the dominant soil forming process.

Vegetation in the watershed represents a mosaic of aggrading secondary forests of various ages that are recovering from widespread agricultural clearing. Forested areas range over the successional sequence from younger pitch pine (*Pinus rigida*)-dominated stands to more mature mixed hardwood stands consisting primarily of various oak (*Quercus*) and maple (*Acer*) species (Lajtha et al. 1995). Vegetation is occasionally limited to pure pitch pine stands by edaphic factors such as water stress and nutrient availability in areas of the watershed developed on extremely coarse substrate.

Experimental sites

Three sites were selected in the watershed to represent a gradient of soil texture (Figure 1). Specific details on soil analysis are available in Seely (1996). The first site, located approximately 7 km inland and referred to as loamy sand (LS), is a 96-year-old predominantly mixed-oak stand with some mature pitch pine. The site contains a sparse understory and an O2 horizon 6.5 cm in depth. The mineral soil is a loamy sand with a relatively high silt content in the upper horizons underlain by a coarse sand at about 1 m (Table 1a). The O2 horizon has a high total N content relative to the other study sites in the watershed (Table 1b). The second site, fine sand (FS), located nearer (<2 km) to Vineyard Sound, is a 48-year-old stand consisting of mixed oak species, pitch pine and eastern white pine (*P. strobus*) with a significant understory consisting primarily of blueberry (*Vaccinium spp.*), inkberry (*Ilex glabra*) and wintergreen (*Gaultheria procumbens*). The mineral soil in this site is a well-sorted fine to coarse sand with a well developed E horizon underlying a 5 cm O2 horizon. The total N content of the mineral soil (0–15 cm) is approximately one third smaller than that of LS while the total N content of the O2 horizon is not different from that of LS. The third site, coarse sand (CS), located adjacent to LS but on the other side of an access road, is a young pitch pine stand (41 yrs.) developed on a soil that appears to have been disturbed by excavation or sand removal in the past. This site has thin forest floor (~2 cm) overlying a coarse sand with a low N content and a high C/N ratio.

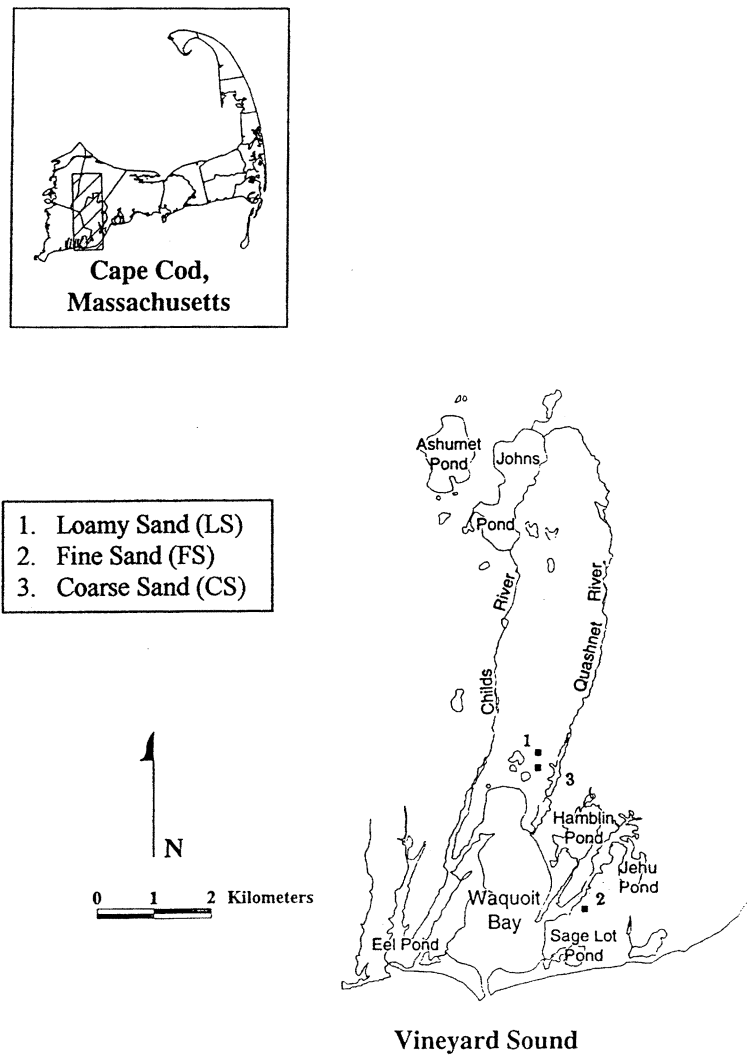


Figure 1. Map of Cape Cod with the Waquoit Bay watershed and experimental sites.

Precipitation, throughfall, lysimeter and ground water collection

A precipitation collector was installed above the canopy in both FS and LS. Data from the LS precipitation collector were used for CS as this site is directly adjacent to LS and should not be appreciably different. Collectors consisted of 15 cm-diameter, high density polyethylene funnels attached to the end of a 4 m length of 2 cm-diameter, PVC pipe. The pipe was fastened to the tallest tree in each site so that the funnel was elevated approximately 1.5

Table 1. A) Soil texture of mineral soil (0–15 cm) and B) mean ($n = 3$) bulk density, total N and C/N for the O2 horizon and mineral soil (0–15 cm) in each site.

A.

Site	Soil texture			
	Silt	Fine sand	Coarse sand	Gravel
	%			
LS	24	22	52	2
FS	5	24	71	0
CS	1	14	76	9

B.

Site	Bulk density ($\text{g}\cdot\text{cm}^{-3}$)		Total N ($\text{g N}\cdot\text{m}^{-2}$) (se)		C/N (se)	
	O2 Horizon	Mineral soil	O2 Horizon	Mineral soil	O2 Horizon	Mineral soil
LS	0.38 (0.03)	1.32 (0.03)	136 (22)	107 (14)	22.7 (2.7)	33.9 (2.7)
FS	0.40 (0.03)	1.51 (0.02)	122 (14)	68 (14)	29.9 (0.9)	35.0 (1.5)
CS	0.52 (0.04)	1.62 (0.05)	48 (1)	21 (2)	49.8 (9.8)	52.2 (6.1)

m above the canopy. The lower end of the pipe was connected with Tygon tubing to a 2 L collection bottle positioned at the base of the tree.

Three trough throughfall collectors, 15 cm \times 35 cm \times 10 cm deep, were randomly positioned on the forest floor under the canopy in each of the three sites. Each polypropylene collector was covered with a 0.5 mm mesh screen to keep out debris. Stemflow was not collected as it represents less than 5% of water flux in these stands (Lajtha et al. 1995).

During the fall of 1992, two replicate 0.75 m \times 2 m \times 1.5 m deep soil pits were excavated in CS and FS, and four in LS, for installation of zero-tension lysimeters. Zero-tension lysimeters were constructed from 50 cm lengths of 10 cm-diameter, PVC pipe cut in half longitudinally and fitted with end pieces. A piece of fiberglass screen was placed in each lysimeter, and all were filled to the rim with acid-washed sand. Lysimeters were installed adjacent to the pits by excavating tunnels in the pit face, underlying undisturbed forest floor and soil horizons, at depths of 15 cm, 50 cm, and 100 cm below the surface of the mineral soil. Lysimeters positioned at 50 cm depth were below the effective rooting zone in all sites. Lysimeters were inserted into the tunnels and wedged up against the top of the tunnel to further improve collection efficiency (Radulovich & Sollins 1987). Each lysimeter was connected to a 2 L collection bottle stored at the bottom of the soil pit. A total of 9 lysimeters were installed at both FS and CS, 3 at each depth; 18 were installed at LS, six at each depth. Each was carefully positioned so that the shallow lysimeters

would not overlap or interfere with deeper ones. Lysimeters were left to drain freely for six months prior to any sample collection to avoid measuring installation artifacts (Shepard et al. 1990).

Four 5 cm-diameter, PVC wells were installed in LS and FS during the fall of 1992 using a manual soil auger. The wells were screened just below the surface of the ground water table (~2 m below soil surface) to ensure that the water from which samples were taken was representative of the most recently percolated soil water. Due to the prohibitive depth of the water table in CS (>10 m), ground water samples could not be taken at this site, thus total leaching losses from this site were based on losses captured in lysimeters at 1m depth. All wells were purged several times following installation and left for 6 months prior to sample collection to avoid measuring installation artifacts. Ground water was sampled monthly throughout the duration of the study period; wells were purged two times prior to sample collection during each sampling event.

Sample collection began in June 1993 and continued through May 1995. Two replicate samples were collected in 20 mL acid-washed polypropylene vials after each rainfall event, from each precipitation and throughfall collector and from each lysimeter collection bottle. Samples could not be collected between mid December and the beginning of March each year due to freezing conditions. During each sampling event total volume was measured and collection bottles were rinsed and emptied. Following collection, all samples were transported to the laboratory where they were filtered through 0.45 μm Millipore filters. One of the two replicate 20 mL samples was acidified to ~pH 2.0 using 5 M HCl (1 μL 5 M HCl: 1 mL sample), and both replicates were subsequently stored at 4 °C until analysis.

NO_3^- , NH_4^+ and PO_4^{3-} were determined colorimetrically in the acidified samples using a Lachat autoanalyzer. Total persulfate N (TPN) was measured in the non-acidified replicates as NO_3^- following persulfate oxidation (Ameel et al. 1993). Bromide (Br^-), considered to be a conservative ion in soil water (Bowman 1984; Silvertooth et al. 1992), was used as a reference ion to compare changes in dissolved N and P content in soil water as it percolated through soil horizons. Br^- was determined in the non-acidified replicates using a Corning bromide probe in conjunction with a Corning double junction reference electrode connected to an Orion 710A pH/selective ion meter with a resolution of 0.1 mv.

Modelling soil water flux

To determine total soil water flux through the soil profile to ground water we applied an unsaturated-zone water flux model. The WaVES (Water Vegetation Energy Solute) model developed by Dawes and Hatton (1993) was selected

for its suitability and sensitivity to soil texture and associated edaphic factors. WaVES is a one-dimensional process model with a daily time step designed to simulate the interaction of plants, water, and energy balance in soil profiles. The model was applied in each experimental site to simulate water flux through unsaturated soil horizons using local climate data in conjunction with site specific vegetation and soil parameters. For a complete description of the application of the model in these sites, see Seely (1996).

Statistical analysis

One-way analyses of variance of volume-weighted concentrations were performed for throughfall, each lysimeter collection depth and ground water using the General Linear Model procedure in SAS with site as the main effect. Analyses were conducted for dormant season (October 16 to April 14) and growing season (April 15 to October 15) data. Similar analyses of total annual flux of dissolved constituents were also performed for throughfall, soil water at each soil depth and ground water. The Least Squares Means procedure in SAS was used to determine differences among sites at the 0.05 significance level (SAS 1985).

Results

Changes in concentrations of N species and PO_4^{3-} through the ecosystem

Concentrations of NO_3^- , DON and PO_4^{3-} increased significantly in all sites following passage through the canopy (Table 2). NH_4^+ concentrations did not change during either season for any of the sites. There were no significant differences in throughfall concentrations of all dissolved N species and PO_4^{3-} among sites.

There was a sharp decline from relatively high throughfall NO_3^- concentrations to much lower values in lysimeters at 15 cm depth (Table 2). This decline was observed in all sites during both seasons. NO_3^- concentrations in the 15 cm deep lysimeters did not differ among sites. In contrast, DON concentrations in lysimeters at 15 cm depth increased relative to throughfall inputs during both seasons in both LS and FS, but not in CS. Accordingly, 15 cm lysimeter DON concentrations were significantly higher in both LS and FS relative to CS for both the growing and dormant season. NH_4^+ and PO_4^{3-} concentrations in lysimeters at 15 cm depth were not different among sites for either season.

Mean NH_4^+ and DON concentrations in ground water were lower than those in lysimeters at 50 cm depth for all dissolved N species in both LS and

Table 2. Volume-weighted mean solution concentrations ($\mu\text{mol L}^{-1}$) ($x \pm \text{se}$) from bulk precipitation collected above the canopy, throughfall, lysimeters at 15 cm, 50 cm, and ground water in each of the three sites from June 1993 through May 1995. Concentrations are listed separately for samples collected during the growing season (April 15–October 15) and the dormant season (October 16–April 14).

Measurement	Site	Growing season				Dormant season			
		NH_4^+	NO_3^-	DON	PO_4^{3-}	NH_4^+	NO_3^-	DON	PO_4^{3-}
Bulk precipitation	LS ^a	8.4	16.4	17.7	0.1	5.0	7.5	11.4	0.1
	FS	11.5	25.4	18.2	0.2	1.7	11.0	7.7	0.2
	CS ^a	8.4	16.4	17.7	0.1	5.0	7.5	11.4	0.1
Throughfall	LS	13.0 ± 1.7	36.6 ± 3.4	34.0 ± 4.2	0.5 ± 0.11	4.8 ± 0.8	27.9 ± 3.4	24.3 ± 0.8	0.5 ± 0.09
	FS	11.2 ± 0.7	37.0 ± 2.7	25.4 ± 3.0	0.5 ± 0.10	6.8 ± 1.7	25.2 ± 4.0	35.3 ± 7.0	0.6 ± 0.05
	CS	15.0	35.2	36.3	0.3	6.3	17.8	37.5	0.5
15 cm lysimeter	LS	10.2 ± 1.3	5.3 ± 1.8	51.8 ± 7.5	0.2 ± 0.03	3.8 ± 0.6	4.5 ± 1.7	51.3 ± 7.6	0.5 ± 0.14
	FS	7.8 ± 1.0	1.8 ± 0.4	99.4 ± 15.8	0.7 ± 0.30	5.1 ± 0.3	3.3 ± 0.7	73.5 ± 11.7	0.9 ± 0.20
	CS	6.2 ± 0.7	2.4 ± 0.6	27.6 ± 7.1	0.1 ± 0.03	4.2 ± 0.6	2.7 ± 0.4	28.5 ± 3.0	0.2 ± 0.04
50 cm lysimeter	LS	7.1 ± 0.6	1.6 ± 1.0	47.0 ± 20.9	0.2	5.2 ± 1.1	3.4 ± 1.5	31.2 ± 7.1	0.2 ± 0.05
	FS	8.9 ± 3.3	4.2 ± 3.3	75.5 ± 26.4	0.1	4.5 ± 0.2	1.2 ± 0.3	46.0 ± 2.5	0.2 ± 0.09
	CS	8.0 ± 4.0	3.4 ± 1.4	51.4 ± 22.3	0.1 ± 0.01	3.6 ± 0.5	1.7 ± 0.3	30.3 ± 3.4	0.2 ± 0.10
100 cm lysimeter	LS	na	na	na	na	na	na	na	na
	FS	na	na	na	na	na	na	na	na
	CS	2.7 ± 1.1	1.6 ± 0.4	31 ± 5.4	na	3.0 ± 1.4	1.3 ± 1.2	29.4 ± 2.7	na
Groundwater	LS	3.3 ± 0.6	0.9 ± 0.3	4.7 ± 0.8	0.1 ± 0.04	2.2 ± 0.4	0.7 ± 0.3	7.0 ± 2.4	0.2 ± 0.02
	FS	2.5 ± 0.3	1.1 ± 0.2	17.0 ± 3.6	0.1 ± 0.03	2.1 ± 0.4	0.9 ± 0.2	8.7 ± 2.1	0.2 ± 0.04
	CS	na	na	na	na	na	na	na	na

^a Data from the same precipitation collector.

FS; no such decrease was observed for PO_4^{3-} . CS was the only site in which leachate was captured in lysimeters at 1 meter depth in the mineral soil during the sampling period. Ground water DON concentrations were higher in FS than in LS.

Changes in dissolved N species and PO_4^{3-} relative to Br^-

As expected, there was little change in Br^- concentration during transport from throughfall to lysimeters. Any increase in concentration was assumed to be the result of the evaporation of soil water. In order to compare the behavior of dissolved N species and PO_4^{3-} to bromide, the volume-weighted mean concentration of NH_4^+ , NO_3^- , DON, PO_4^{3-} , and Br^- captured in each lysimeter was divided by the volume-weighted mean throughfall concentration of that particular dissolved constituent for the corresponding site and season. Volume weighting was based on the volume of leachate captured in a lysimeter for a specific event.

Ratios of mean 15 cm lysimeter N and PO_4^{3-} concentrations to mean throughfall values were plotted against those for bromide (Figure 2). Points falling below the 1:1 line indicate uptake or retention of that particular constituent relative to Br^- , while points falling above the line indicate a relative release or gain during passage through the forest floor and upper mineral soil (0–15 cm). NH_4^+ was generally retained in the forest floor and upper mineral soil relative to bromide during both seasons. NO_3^- was strongly retained relative to Br^- in all sites during both seasons except for growing season values in FS which fell on the 1:1 line. Conversely, DON strongly increased, or was released, in lysimeters at 15 cm depth relative to bromide in both FS and LS. No relative gain, or release was observed for DON in CS. PO_4^{3-} was generally retained relative to Br^- during the growing season with exception of FS which tended to fall on the 1:1 line. Only CS demonstrated a relative retention of PO_4^{3-} during the dormant season.

Similar patterns of weaker retention for NH_4^+ and stronger retention for NO_3^- were observed in leachate collected in the lysimeters at 50 cm depth (Figure 3). DON in 50 cm lysimeters showed no consistent pattern of gain or retention relative to throughfall concentrations. PO_4^{3-} in lysimeters at 50 cm depth was relatively retained in all sites during both seasons.

Modelled soil water flux to lysimeters

Modelled water flux through the soil column to groundwater over the study period was highest in the coarsely textured soil of CS, followed by FS and LS (Figure 4). Predicted flux in LS was approximately half of that in CS for all soil depths. Based on these predicted flux data, collection efficiencies

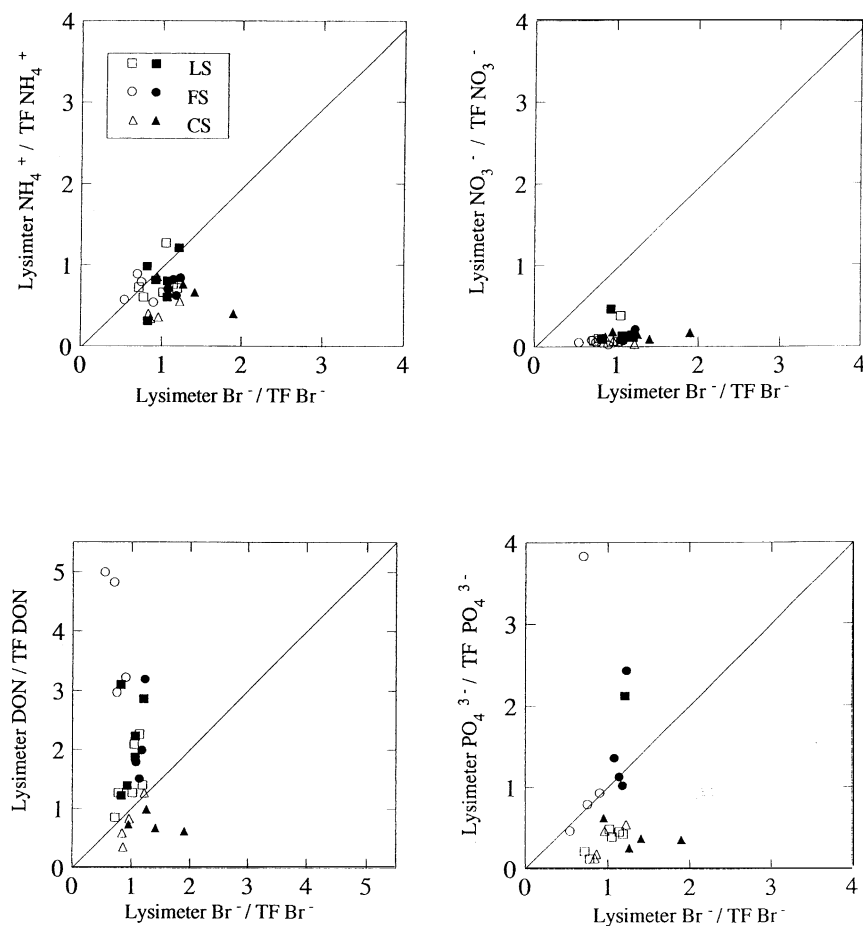


Figure 2. Ratios of mean concentrations of NH_4^+ , NO_3^- , DON and PO_4^{3-} in lysimeters at 15 cm depth to paired mean throughfall concentrations vs. those for Br^- . Filled symbols represent the dormant season and unfilled represent the growing season. Points falling below the 1:1 line indicate uptake or retention of that particular constituent relative to Br^- , while points falling above the line indicate a relative release or gain.

were calculated for each lysimeter. Mean collection efficiency for lysimeters at 15 cm depth was approximately 75% in LS, 50% in CS and 35% in FS. Collection efficiency decreased to 15–25% for all sites in the lysimeters at 50 cm depth. No leachate was collected in lysimeters at 100 cm depth in either FS or LS.

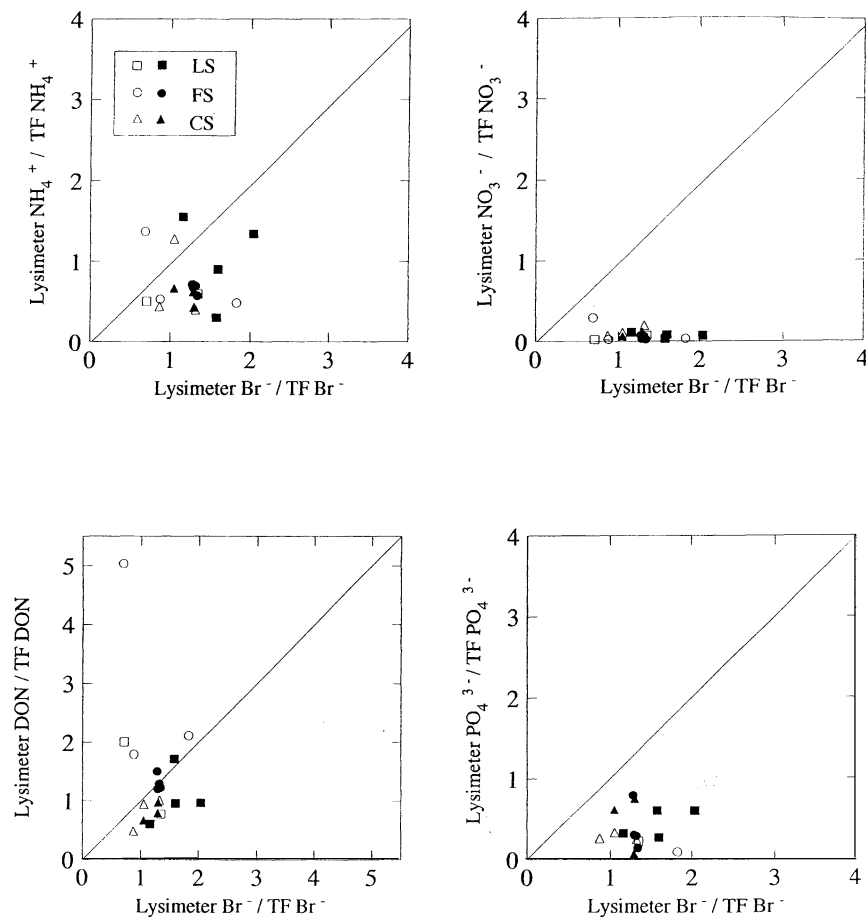


Figure 3. Ratios of mean concentrations of NH_4^+ , NO_3^- , DON and PO_4^{3-} in lysimeters at 50 cm depth to paired mean throughfall concentrations vs. those for Br^- . Filled symbols represent the dormant season and unfilled represent the growing season. Points falling below the 1:1 line indicate uptake or retention of that particular constituent relative to Br^- , while points falling above the line indicate a relative release or gain.

Fluxes of N and PO_4^{3-} through the ecosystem

Mean annual fluxes of dissolved N species and PO_4^{3-} through the soil column to ground water were calculated for each site and soil depth using volume-weighted concentrations and modeled soil water flux (Table 3). Volumes used for weighting were from measured values in lysimeters. There were significant increases in total annual flux of NO_3^- , DON and PO_4^{3-} in bulk precipitation following passage through the canopy. Annual NH_4^+ flux did not increase

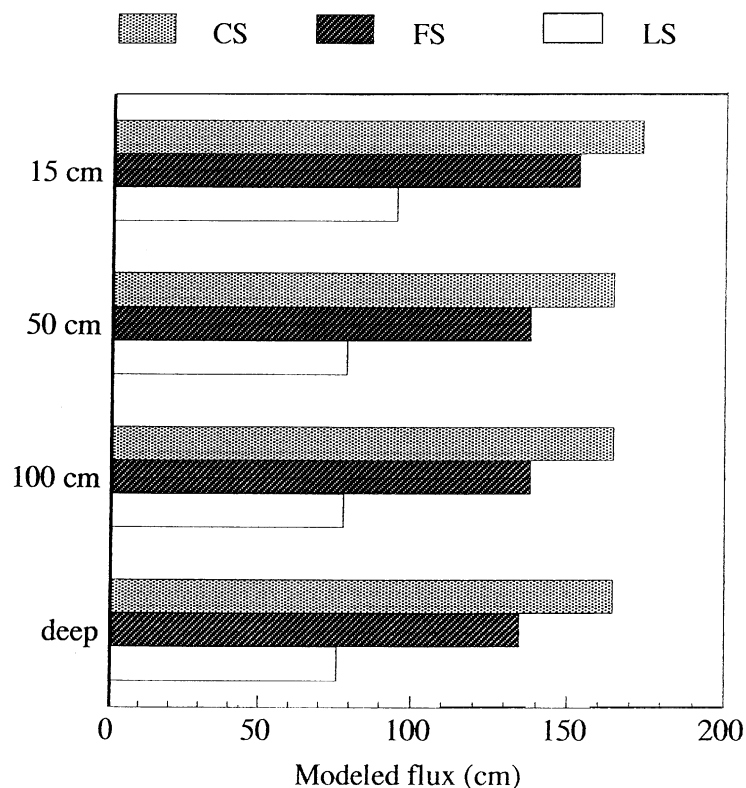


Figure 4. Modeled water flux to various depths in the soil profile during the study period (June 1993 through May 1995).

following passage through the canopy. DON accounted for 89–77% of the N flux to lysimeters at 15 cm depth in all sites. Annual DON flux to lysimeters at 15 cm depth in FS was more than twice that in both LS and CS. Flux of NH_4^+ to lysimeters at 15 cm depth was significantly higher in both CS and FS relative to LS; however, there were no observed differences in NO_3^- flux between sites. Lysimeters at 50 cm depth showed similar patterns to those at 15 cm depth with high DON flux relative to NH_4^+ and NO_3^- . DON flux to lysimeters at 50 cm depth in LS was significantly lower than that in both FS and CS. Losses of DON to ground water were higher in FS than in LS.

Table 3. Total annual fluxes ($\text{kg ha}^{-1} \text{ yr}^{-1}$) in bulk precipitation above the canopy, throughfall, lysimeters at 15 cm, 50 cm and ground water in each of the three sites based on data from June 1993 through May 1995.

Site	Total annual flux				
	N-NH ₄ ⁺	N-NO ₃ ⁻	N-DON	TN	P-PO ₄ ³⁻
Bulk precipitation					
LS*	1.0 a	1.8 a	2.3 a	5.1 a	0.04 a
FS	0.9 a	2.7 a	1.9 a	5.4 a	0.07 a
CS*	1.0 a	1.8 a	2.3 a	5.1 a	0.04 a
Throughfall					
LS	1.1 a	4.4 a	4.0 a	9.5 a	0.16 a
FS	1.2 a	4.2 a	4.5 a	9.9 a	0.18 a
CS	1.3 a	3.4 a	4.3 a	9.0 a	0.14 a
15 cm lysimeter					
LS	0.3 b	0.3 a	3.8 b	4.4 b	0.08 b
FS	0.6 a	0.3 a	8.6 a	9.5 a	0.16 a
CS	0.6 a	0.3 a	3.4 b	4.3 b	0.05 b
50 cm lysimeter					
LS	0.3 a	0.2 a	1.7 b	2.2 b	0.02 a
FS	0.5 a	0.2 a	4.7 a	5.3 a	0.04 a
CS	0.5 a	0.2 a	3.6 a	4.3 a	0.04 a
100 cm lysimeter					
LS	na	na	na	na	na
FS	na	na	na	na	na
CS	0.3	0.2	3.4	3.9	na
Groundwater					
LS	0.2 a	0.0 a	0.3 b	0.5 b	na
FS	0.2 a	0.1 a	1.2 a	1.5 a	na
CS	na	na	na	na	na

Note: Means followed by a common letter do not differ ($p < 0.05$) using the least squares means procedure in SAS (1985).

* Data from the same precipitation collector.

Discussion

Total N losses

The difference in nitrogen leaching loss over the soil texture gradient appears to be related to the retention capacity of DON in the mineral soil. DON

concentrations decreased substantially during percolation through the forest floor to ground water in LS and to a lesser extent in FS. No such decrease was observed in CS. Although not directly tested here, the greater surface area presented by the finer mineral soil particles of LS likely facilitated the adsorption of a larger fraction of soil solution DON relative to the more coarsely textured sites during the percolation of soil water through the soil profile. Additionally, the higher infiltration rates measured in CS and FS may limit the contact time of DON in soil solution with particle surfaces. The larger loss of DON observed below the rooting zone in FS may be due to the presence of a much more developed forest floor in FS relative to CS. Thus, in FS there is a larger pool of organic N in the forest floor from which larger quantities of DON may be leached. Additionally, there was a significantly larger microbial biomass present in the O2 horizon of FS relative to CS which may also account for the larger loss of DON in that site by conversion of DIN to DON through microbial processing (Seely & Lajtha 1977).

Dissolved organic carbon can be immobilized through complex interactions with mineral surfaces (Sibanda & Young 1986; Jardine et al. 1989; Moore et al. 1992). Oxides and hydroxides of Fe and Al as well as the presence of clay minerals appear to account for much of the adsorption capacity in soils, while large amounts of indigenous soil organic matter have been shown to impede DOC adsorption (McDowell & Wood 1984; Jardine et al. 1989). Fe and Al content were not measured in this study but the orange-brown hue of the B horizons, particularly in LS and FS, indicate the presence of iron oxides. The organic matter content of mineral soil (0–50 cm) in these soils is relatively low, ranging from <1% in CS to 2–3% in LS, and therefore is probably not a dominant factor in the control of DON adsorption in these sites.

Fluxes and transformations of N through ecosystem

Relative to bulk precipitation, the canopy acted as a net source of NO_3^- in throughfall. There was no substantial difference between throughfall and bulk precipitation fluxes of NH_4^+ for any site. The substantial increase in NO_3^- during passage through the canopy was most likely due to the wash off of nitrate aerosols and particulates which had been previously deposited on vegetation surfaces via dry deposition. NO_3^- dominates the dry deposition N flux to canopies of forests in the northeastern United States (Lovett & Lindberg 1993).

DON also showed a substantial increase during passage through the canopy in all sites, possibly due to the leaching of organic N from leaf and stem tissues. In addition, some of this DON may have originated as atmospherically deposited inorganic N which was subsequently converted to DON by

microbial activity on canopy surfaces (Friedland et al. 1991; Lovett & Lindberg 1993). Although they have clearly been shown to be present on canopy surfaces (Preece & Dickinson 1971), little is known about the importance of microbes on transformations of N during passage through the canopy.

The forest floor and upper mineral soil (0–15 cm) acted as strong sink for DIN delivered to the forest floor in throughfall. NO_3^- was retained more efficiently than NH_4^+ in all sites. More than 93% of throughfall NO_3^- delivered to the forest floor in these sites was retained in the O2 horizon and upper mineral soil. In comparison, a mean net retention of only 50 to 73% was observed for NH_4^+ . Schimel et al. (1989) theorized that microbial immobilization of NO_3^- in the presence of NH_4^+ could be explained by the occurrence of microsites with an abundance of available C and NO_3^- and low concentrations of NH_4^+ . Additionally, uptake of NH_4^+ may be somewhat inhibited by ion competition due to the presence of marine Na^+ inputs in these coastal sites.

Plant uptake is also likely to be an important processes in the removal of NO_3^- from the forest floor and mineral soil. Seely and Lajtha (1997) estimated that plant uptake accounted for 22–57% of $^{15}\text{NO}_3^-$ applied to the forest floor in these sites. Furthermore, Lajtha et al. (1995) calculated that accretion in vegetation of the Waquoit Bay watershed accounted for approximately 34% of total annual throughfall N inputs. Trenching experiments in northern forest ecosystems have also demonstrated the importance of NO_3^- uptake by roots (Vitousek 1983).

While the forest floor served as an important sink for DIN in all sites it was also a large source of DON in LS and FS. DON concentrations increased significantly in both LS and FS during both seasons following the passage of throughfall through the forest floor; however, no such increase occurred in CS. It appears that the canopy is the only important source of DON in CS, perhaps due to its thin forest floor. Similar increases in DON following the passage of leachate through the forest floor have been observed in other studies (Sollins et al. 1980; Fahey et al. 1985; Friedland et al. 1991; Qualls et al. 1991). With the exception of CS, DON decreased during passage through the lower rooting zone and further decreased during transport to ground water possibly due to adsorption. Once sorbed onto soil surfaces, DON may persist for long periods of time, resulting in the accretion of organic N in the ecosystem. Qualls and Haines (1992) found DON retained in the mineral soil to be highly refractory and suggested that mineralization would only occur slowly over time.

Use of Br^- as a reference ion

In lieu of the use of a water flux model, naturally occurring bromide in throughfall may be used as a relatively conservative reference ion (Bowman

1984) to analyze changes in nutrient concentrations during the passage of water through the forest floor and soil profile, as it provides a means of accounting for changes in nutrient concentrations due to evaporation of soil water. Vitousek (1977) used chloride concentrations in a similar manner to predict NO_3^- losses to mountain streams draining mature stands. Comparisons of lysimeter: throughfall concentration ratios of Br^- to those of the various N species and PO_4^{3-} illustrated the transformations of these nutrients due to biological and soil processes by controlling for changes in concentration resulting from the evaporation of soil water. Relative to Br^- , NO_3^- was strongly retained in the forest floor and upper mineral soil (0–15 cm) in all sites. In the absence of biological assimilation one would expect no difference in the flux of these two highly mobile anions. Thus, these data indicate the presence of a large biological demand for NO_3^- in all sites during both seasons. Assimilation by microbes probably accounts for most of the retention of NO_3^- during the dormant season. A weaker retention in the forest floor and upper mineral soil (0–15 cm) with no clear seasonal pattern was observed across all sites for NH_4^+ relative to Br^- , although relative retention of NH_4^+ increased slightly in the lower mineral soil (15–50 cm). The somewhat reduced capacity for NH_4^+ retention in these sites may be partially explained by a small cation exchange capacity in these sandy soils and by competition for exchange sites with Na^+ from sea spray (Duckworth & Cresser 1991; Blood et al. 1992; Valiela et al. 1996).

As expected, lysimeter: throughfall ratios of DON increased substantially during passage through the forest floor and upper mineral soil (0–15 cm) relative to those of Br^- in all sites except CS which actually showed a net DON retention. These data further support the role of the forest floor as a source of DON in leachate. Below the rooting zone, lysimeter: throughfall ratios of DON showed a net retention of DON relative to Br^- with the exception of FS, in which DON ratios tended to be higher or equal to those for Br^- . The higher ratios of DON observed in FS indicate that DON may be retained less efficiently in this site relative to LS, providing additional evidence that increases in grain size may limit the capacity of a soil to adsorb DON.

With the exception of FS, PO_4^{3-} was generally retained during passage through the forest floor and upper mineral soil (0–15 cm) relative to Br^- . All sites demonstrated a relative retention of PO_4^{3-} in the lower mineral soil (15–50 cm). It is unclear why PO_4^{3-} was not efficiently retained in upper horizons in FS, although it may be due to the slightly but not significantly higher throughfall inputs observed in this site.

DON vs. NO₃⁻ as a vector of N loss

Past research in forest ecosystems generally has found NO₃⁻ leaching to be the dominant vector of N loss to streams and ground water (Likens et al. 1977; Vitousek 1977), and much attention has been focused on the role of NO₃⁻ leaching as an indicator of N saturation in forest ecosystems (Eggen & Bosatta 1988; Aber et al. 1989; Gundersen 1991). Accordingly, there are relatively few measurements of DON leaching from forest ecosystems. In our sites, DON accounted for most of the leaching losses below the rooting zone (77–89%) and through the soil profile to ground water (63–87%). Similarly, in a study at the Coweeta Hydrologic Laboratory in North Carolina, Qualls (1989) found that DON accounted for more than 80% of total N leached through the soil profile to streams. Fahey et al. (1985), also reported that DON was the major form of N leached from both the O₂ horizon and mineral soil in a lodge pole pine forest in southeastern Wyoming. In spite of its high potential for sorption in mineral soil, it is evident that DON may be an important vector of N loss in temperate forest ecosystems and it should be considered in the construction of N budgets.

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