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Dissolved organic nitrogen budgets for upland, forested ecosystems in New England

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Abstract. Relatively high deposition of nitrogen (N) in the northeastern United States has caused concern because sites could become N saturated. In the past, mass-balance studies have been used to monitor the N status of sites and to investigate the impact of increased N deposition. Typically, these efforts have focused on dissolved inorganic forms of N (DIN = NH_4-N + NO_3-N) and have largely ignored dissolved organic nitrogen (DON) due to difficulties in its analysis. Recent advances in the measurement of total dissolved nitrogen (TDN) have facilitated measurement of DON as the residual of TDN − DIN. We calculated DON and DIN budgets using data on precipitation and streamwater chemistry collected from 9 forested watersheds at 4 sites in New England. TDN in precipitation was composed primarily of DIN. Net retention of TDN ranged from 62 to 89% (4.7 to 10 kg ha^{-1} yr^{-1}) of annual inputs. DON made up the majority of TDN in stream exports, suggesting that inclusion of DON is critical to assessing N dynamics even in areas with large anthropogenic inputs of DIN. Despite the dominance of DON in streamwater, precipitation inputs of DON were approximately equal to outputs. DON concentrations in streamwater did not appear significantly influenced by seasonal biological controls, but did increase with discharge on some watersheds. Streamwater NO_3-N was the only fraction of N that exhibited a seasonal pattern, with concentrations increasing during the winter months and peaking during snowmelt runoff. Concentrations of NO_3-N varied considerably among watersheds and are related to DOC:DON ratios in streamwater. Annual DIN exports were negatively correlated with streamwater DOC:DON ratios, indicating that these ratios might be a useful index of N status of upland forests.

Introduction

The importance of dissolved organic nitrogen (DON) in ecosystem nutrient budgets has been largely ignored due to poor analytical methods. However, the recent application of high-temperature combustion techniques has eliminated many difficulties associated with measurement of total dissolved N (TDN), and has led to rapid, quantitative methods that yield high recovery rates (Merriam et al. 1996; Suzuki et al. 1985; Walsh 1989). These advances have made it possible to include DON (obtained as TDN − DIN) in N budgets for small watersheds, and to begin evaluating the relative importance of DON in the N cycle. Although most N capital in forested ecosystems occurs as an organic form in soil organic matter and to a lesser extent forest biomass, knowledge of the processes and controls on DON cycling is limited. Since most N is organically bound, it is not surprising that the few studies available have shown that DON can comprise about 50% or more of the TDN flux in throughfall (Lajtha et al. 1995; Qualls et al. 1991; Sollins & McCorison 1981), soil leachates (Currie et al. 1996; Lajtha et al. 1995; Qualls et al. 1991; Sollins & McCorison 1981; Yavitt & Fahey 1984), and streamwater (Chapman et al. 1998; Hedin et al. 1995; Kortelainen et al. 1997; McDowell & Asbury 1994; Newbold et al. 1995).

In recent years there has been growing concern about the impacts of human-related emissions and deposition of N. Currently, many forested ecosystems throughout New England are N-limited, but continued N deposition may cause available N to exceed biological demands. Such a system is then considered N saturated and no longer has the capacity to assimilate additional N (Aber et al. 1989; Ågren & Bosatta 1988). One characteristic of a site that is approaching N saturation is increased leaching of NO_3-N. In contrast to NO_3-N the capacity of soils to retain DON is often considerable because of the ability of mineral soils to adsorb organic matter (Qualls & Haines 1992). However, N fertilization experiments have shown that this capacity is not limitless. In a study of the effects of chronic N additions on soil leachates, Currie et al. (1996) and McDowell et al. (1998) found that under high N loading (150 kg ha^{-1} yr^{-1} for 7 years), DIN and DON but not DOC increased in leachates. As a result there was a decrease in the organic C:N ratio of soil leachates with increasing N additions. In a study of streams draining forested watersheds in Finland, Kortelainen et al. (1997) concluded that 72% of the variation in NO_3-N flux from streams was explained by a combination of organic C:N ratios and N deposition. Harriman et al. (1998) found similar results in the United Kingdom and suggested that DOC:DON ratios may provide a measure of the capacity of watersheds to immobilize N into the soil N pool. Based on these observations, DOC:DON ratios in streams may be an important indicator of the N status of sites. Areas with low DOC:DON ratios in streams would be expected to have the greatest NO_3-N losses.

To determine the importance of DON in the context of N deposition, we measured the input-output budgets and net flux of TDN, DON, and DIN across a range of forested sites in the northeastern United States where relatively high deposition of N occurs, and where DIN has been monitored for decades. Our objectives were to calculate watershed budgets for N and to quantify the percentage of DON in precipitation and streamflow. On the basis of these values, we wanted to determine whether including DON in N budgets affected the net retention of TDN. We also investigated the possibility of using C:N ratios in streamwater as an indicator of N saturation based on the hypothesis that as N saturation proceeds, there would be a consequent decrease in the flux of streamwater DOC relative to DON.

Methods

Study sites

Data were collected on 5 small watersheds in New Hampshire, 3 north facing and 1 south facing on the Hubbard Brook Experimental Forest (HB) and the Cone Pond Watershed (CP), and on 4 watersheds in Vermont, the Sleepers River Watershed (SR) and 3 watersheds in the Lye Brook Wilderness Area (LB) (Table 1, Figure 1). Forests at these sites consist of deciduous tree species, such as American beech (*Fagus grandifolia*), yellow birch (*Betula alleghaniensis*), and maple (*Acer*) species at lower elevations, and red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and paper birch (*Betula papyrifera*) at higher elevations. The vegetation at each of the 4 research locations has been altered to varying degrees by both anthropogenic and natural disturbances. At HB, SR, and LB, the watersheds were harvested during the early 1900's (Likens & Bormann 1995; Thorne et al. 1988). Little of CP has been harvested but approximately 85% of that watershed was heavily burned by fire around 1820 (Buso et al. 1984; Hornbeck & Lawrence 1997). The forests at every site were damaged to some degree by the 1938 hurricane.

Soils at the study sites are typically Spodosols; the exception is SR, where much of the watershed soil consists of Inceptisols with higher concentrations of exchangeable Ca^{2+} and Mg^{2+} than at the other sites (Thorne et al. 1988). Base-rich till at this site is derived from calcareous bedrock that underlies the watershed. The geological substrate of the other sites consists of bedrock and till that is more base poor, resistant to weathering, and characteristically acidic. Characteristics of the study sites are listed in Table 1.

Table 1. Summary of study site characteristics.

Watershed	Weir location	Streamflow measurment	Area (ha)	Elevation (m)	Aspect	Forest type and age	Soil type
HB6	43°57′ N, 71°44′ W	V-notch weir, flume	13	550–790	S	Northern hardwoods; evenaged 80–90 years	Coarse, loamy, mixed, frigid, Typic Haplorthod
HB7	43°55′ N, 71°46′ W	V-notch weir, flume	76	620–900	N	Mixed northern hardwoods and conifers; evenaged 80–90 years	Coarse, loamy, mixed, frigid, Typic Haplorthod
HB8	43°55′ N, 71°45′ W	V-notch weir, flume	59	610–900	N	Mixed northern hardwoods and conifers; evenaged 80–90 years	Coarse, loamy, mixed, frigid, Typic Haplorthod
HB9	43°55′ N, 71°45′ W	V-notch weir	68	680–900	N	Mixed northern hardwoods and conifers; evenaged 80–90 years	Coarse, loamy, mixed, frigid, Typic Haplorthod
CP	43°54′ N, 71°36′ W	V-notch weir	33	485–650	S	Mixed northern hardwoods and conifers; all ages to 260 years	Coarse, loamy, mixed, frigid, Typic and Lithic Haplorthod
SR	44°28′ N, 72°05′ W	V-notch weir	41	519–679	S	Northern hardwoods; evenaged 60–70 years	Coarse, loamy, mixed, mesic, Typic Dystrochrept
LB4	43°07′ N, 73°03′ W	Modeled	163	305–830	N	Mixed northern hardwoods and conifers; evenaged 80–90 years	Coarse, loamy, mixed, frigid, Typic and Lithic Haplorthod
LB6	43°07′ N, 73°02′ W	Modeled	106	570–850	W	Mixed northern hardwoods and conifers; evenaged 80–90 years	Coarse, loamy, mixed, frigid, Typic and Aquic Haplorthod
LB8	43°07′ N, 73°02′ W	Modeled	130	725–850	W	Mixed northern hardwoods and conifers; evenaged 80–90 years	Coarse, loamy, mixed, frigid, Typic Humaquept, Epiaquad, and Haplorthod

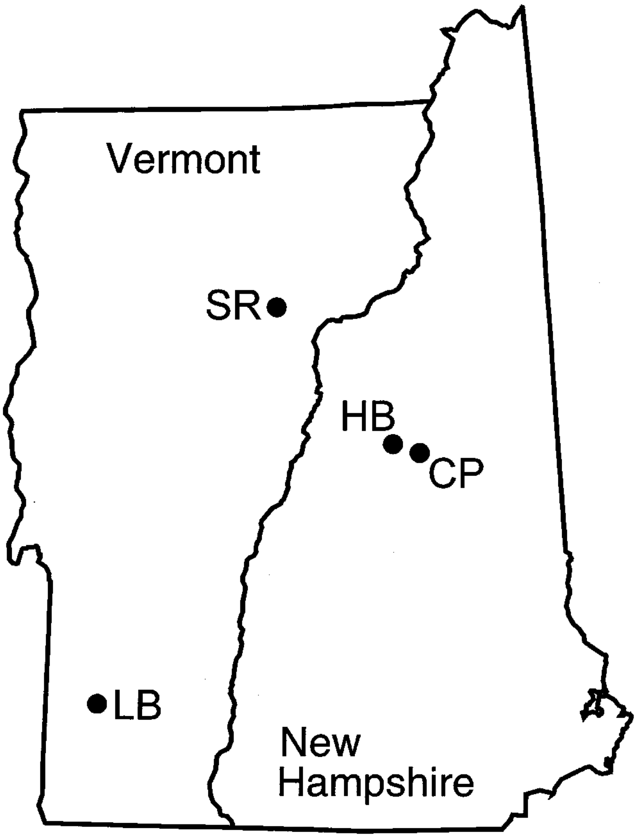

Figure 1. The Hubbard Brook (HB), Cone Pond (CP), Sleepers River (SR), and Lye Brook (LB) study sites.

Precipitation measurements and sampling

Sampling periods spanned the 1994–1995 water year (June 1–May 30) at LB watersheds and the 1995–1996 and 1996–1997 water years at HB, CP, and SR. Daily precipitation for HB, CP, and SR was measured with conventional rain gages and chart recorders. Precipitation volume for LB watersheds was obtained from the National Weather Service cooperative observation station at Dorset, VT, located about 10 km northwest of the sampling sites at 284 m. The elevation of this station is somewhat lower than the LB watersheds (Table 1).

The HB, CP, and SR watersheds each had 1 precipitation collector used to obtain samples for chemical analyses. Samples were collected weekly from a collector that consisted of a polyethylene funnel and sample bottle in summer and polyethylene bucket in winter. Scudlark et al. (1998) show that some DON may be lost from precipitation collectors during weekly sampling intervals. This loss of DON is highly variable and the mechanisms are not known, although DON does not appear to be converted to inorganic forms because NO_3-N and NH_4-N concentrations remain stable. Precipitation chemistry data were not collected at LB during the study period, so HB precipitation chemistry was used as surrogate data. Since samples at HB were not analyzed for TDN during the 1994–1995 water year, LB values were estimated from N data collected during the 1995–1996 water year. Use of this surrogate data assumes that chemical concentrations in precipitation exhibit little spatial variability between the 2 locations, and that the annual variability in the chemical concentrations is minimal. These assumptions were based on the homogeneity of N in precipitation collected over the 2-year sample period at HB, CP, and SR (discussed later).

Streamwater measurements and sampling

Streamflow at HB, CP, and SR was measured continuously at gaging stations. Streamflow at the LB watersheds was not measured directly because the construction of structures, e.g., weirs, is prohibited within the boundary of the wilderness. Consequently, at the four LB watersheds, streamflow was estimated using the BROOK90 hydrologic model (Federer 1997). This model is largely based on 2 earlier versions, BROOK and BROOK2, which have been used extensively to simulate water cycles for small, forested watersheds (Federer & Lash 1978; Hornbeck et al. 1986). The BROOK90 model requires daily precipitation and maximum and minimum temperature data, which were obtained from the Dorset weather station. Other site-specific parameters related to catchment, canopy, and soil were determined from available literature. The model was used to estimate daily values for streamflow in mm per unit area. Stream grab samples were collected for chemical analyses in polyethylene bottles at each of the 10 watersheds studied. Streamwater and precipitation samples were stored frozen prior to analysis and in keeping with standard practices at Hubbard Brook and other studies (Scudlark et al. 1998), were not filtered. Because the autosampler of the organic carbon analyzer precludes entry of most particulates and samples were never visibly turbid, we refer to our analysis as dissolved. Some particulate C and N may be included in our analysis; however at Hubbard Brook DOC comprises 84% of TOC (Likens et al. 1983). Samples from HB, CP, and SR were collected at weekly intervals from June 1995 through May 1997. Samples from LB were collected biweekly from June 1994 through May 1995.

Chemical analyses

DOC was measured using a Shimadzu 5000 Total Organic Carbon (TOC) Analyzer and TDN was measured using the combustion furnace and auto-sampler of the TOC analyzer combined with an Antek chemiluminescent N detector (Merriam et al. 1996). Measurements of NH_4-N for all samples were obtained with a continuous flow colorimeter. NO_3-N + NO_2-N (hereafter referred to as NO_3-N) for SR and CP was measured using a continuous flow colorimeter. NO_3-N for HB and LB was measured using ion chromatography. DON was calculated by subtracting NH_4-N and NO_3-N from TDN. In this paper, all references to C:N ratios for streamwater refer to the dissolved organic fractions of C and N and were calculated by dividing DOC by DON. Chemical analyses were performed at the Northeastern Research Station in Durham, NH, except for inorganic N values for the HB watersheds, which were measured at the Institute of Ecosystem Studies, Millbrook, NY, and the LB chemistry, which was measured at the University of New Hampshire.

Budget calculations

Annual input-output budgets were determined for TDN, NH_4-N, NO_3-N, DON, and DOC for water years beginning June 1 and ending May 31. Inputs in precipitation and outputs in streamwater were obtained by multiplying the weekly (biweekly in the case of LB) concentrations (mg L^{-1}) by the measured daily water fluxes (L ha^{-1} day^{-1}) surrounding each chemical sample. Daily mass inputs and outputs were summed over the water year and are reported as kg ha^{-1} yr^{-1}. In keeping with past convention (Likens & Bormann 1995), inputs in precipitation minus streamwater outputs are used to express net gains or losses from the watersheds. Volume-weighted, mean monthly concentrations for ions in precipitation and streamwater were obtained by dividing the monthly mass flux by the monthly water flux.

Results

Hydrologic budgets

The volume of precipitation and streamflow have significant roles in determining nutrient budgets. Data from extremely wet or dry years or years with unusual or uneven distribution of precipitation can be misleading relative to average or long-term considerations. For the years of our study, annual precipitation ranged from 1,040 mm at LB to 1,860 mm at HB9 (Table 2). The LB value is about 10% below a 30-year mean of 1,150 mm calculated for the Dorset station. Long-term HB records (Federer et al. 1990) indicate that precipitation measured during the 1995–1996 and 1996–1997 water years was, respectively, 21 and 12% greater than a 30 year average. Shorter records for Sleepers River and Cone Pond suggest that both of these watersheds also had wetter than average water years during 1995–1996 and 1996–1997. Thus precipitation for the years of study ranges from below average at LB to above average for the other locations, but the input budgets for N and C should still be reasonably representative.

Streamflow ranged from 430 mm or 42% of precipitation at LB8 to 1,400 mm or 77% of precipitation at HB6 (Table 2). Evapotranspiration determined as precipitation minus streamflow ranged from 410 mm at HB6 to 640 mm at CP. The annual streamflow and evapotranspiration values were within the ranges of long-term annual values (Federer et al. 1990).

Nitrogen concentrations

Concentrations of NO_3-N, NH_4-N and DON in precipitation varied from month to month but did not exceed 0.8 mg L^{-1} among the 4 sites (Figure 2). NO_3-N was the dominant form of N in precipitation, averaging about 0.32 mg L^{-1} (54%), followed by NH_4-N at 0.17 mg L^{-1} (28%), and DON at 0.11 mg L^{-1} (18%). There were no obvious seasonal trends in the concentrations for precipitation, and marginally greater concentrations occurred in the second year than the first (Figure 2).

DON was the dominant form of N in streamwater at HB, CP and LB8 watersheds and mean annual concentrations of streamwater DON were highest at LB8 (0.38 mg L^{-1}) and lowest at SR (0.10 mg L^{-1}) (Figure 3). NO_3-N was below detection levels at CP during much of the year and highest in streamwater at LB6 (mean annual concentration = 0.41 mg L^{-1}). For all forms of N sampled, NO_3-N in streamflow showed the only seasonal pattern, with concentrations lowest during the growing season and higher during the dormant season and snowmelt runoff (Figure 3). There was a significant positive correlation ($r^2 = 0.09$ to 0.49, $P < 0.05$) between streamwater TDN and discharge for HB and LB watersheds, but not CP and SR. Streamwater DON and NO_3-N were significantly correlated ($P < 0.05$) with discharge at 5 of the 9 watersheds. Concentrations of NH_4-N showed no significant correlation with discharge at any watershed. Concentrations of DON generally were lower in precipitation (average = 0.11 mg L^{-1} for all watersheds) than in streamflow (average = 0.14 mg L^{-1}) (Figures 2–3).

Table 2. Annual hydrologic budgets (mm ha^{-1} yr^{-1}). Evapotranspiration (ET) obtained as precipitation minus streamflow. Streamflow and ET also expressed as percentage of total precipitation.

	HB6		HB7		HB8		HB9		CP		SR		LB4	LB6	LB8
Item	95–96	96–97	95–96	96–97	95–96	96–97	95–96	96–97	95–96	96–97	95–96	96–97	94–95	94–95	94–95
Precipitation	1810	1610	1830	1660	1830	1640	1860	1650	1530	1460	1640	1390	1040	1040	1040
Streamflow	1400	1190	1330	1160	1330	1110	1300	1120	890	820	1040	820	450	440	430
(%)	77	74	73	70	73	68	70	68	58	56	63	59	43	42	41
ET	410	420	500	500	500	530	560	530	640	640	600	570	590	600	610
(%)	23	26	27	30	27	32	30	32	42	44	37	41	57	58	59

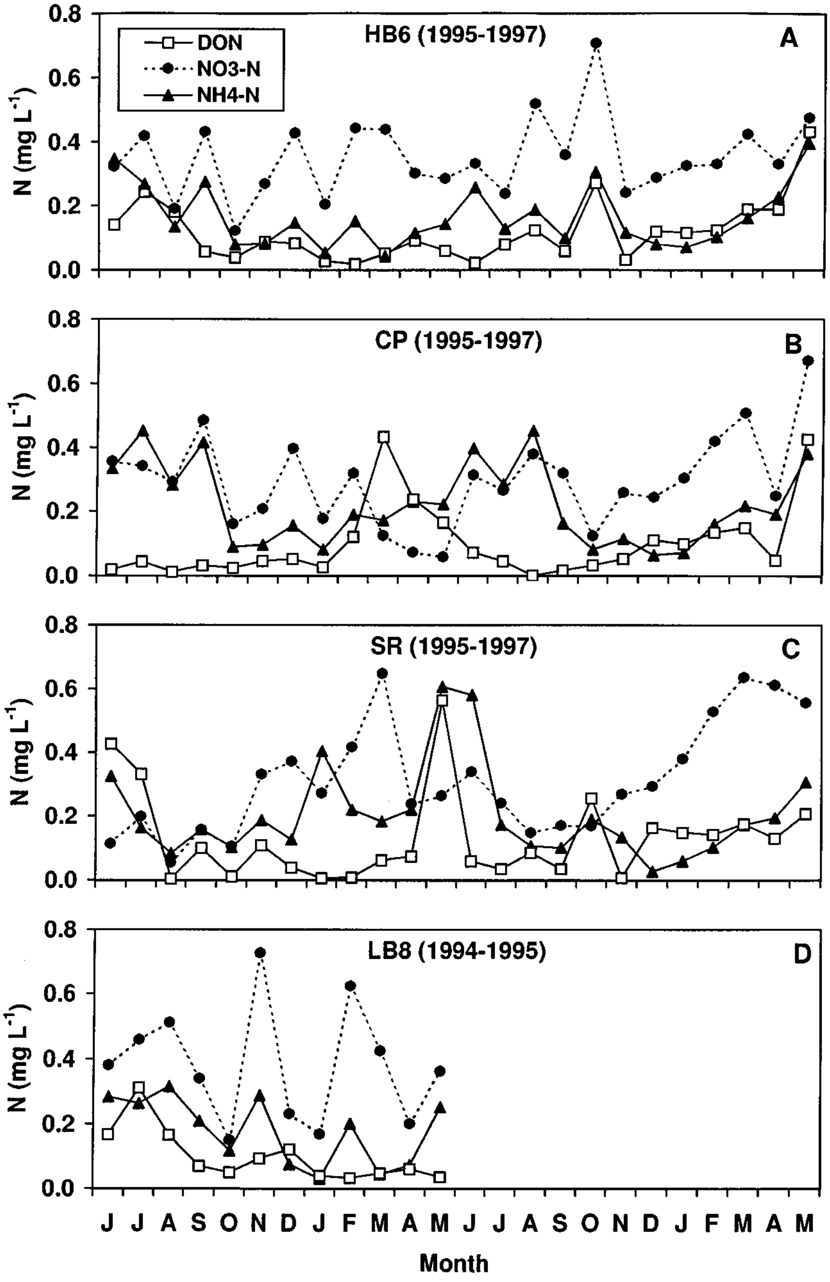

Figure 2. Mean monthly DON, NO_3-N, and NH_4-N concentrations in precipitation (mg L^{-1}) at HB6, CP, SR, and LB8.

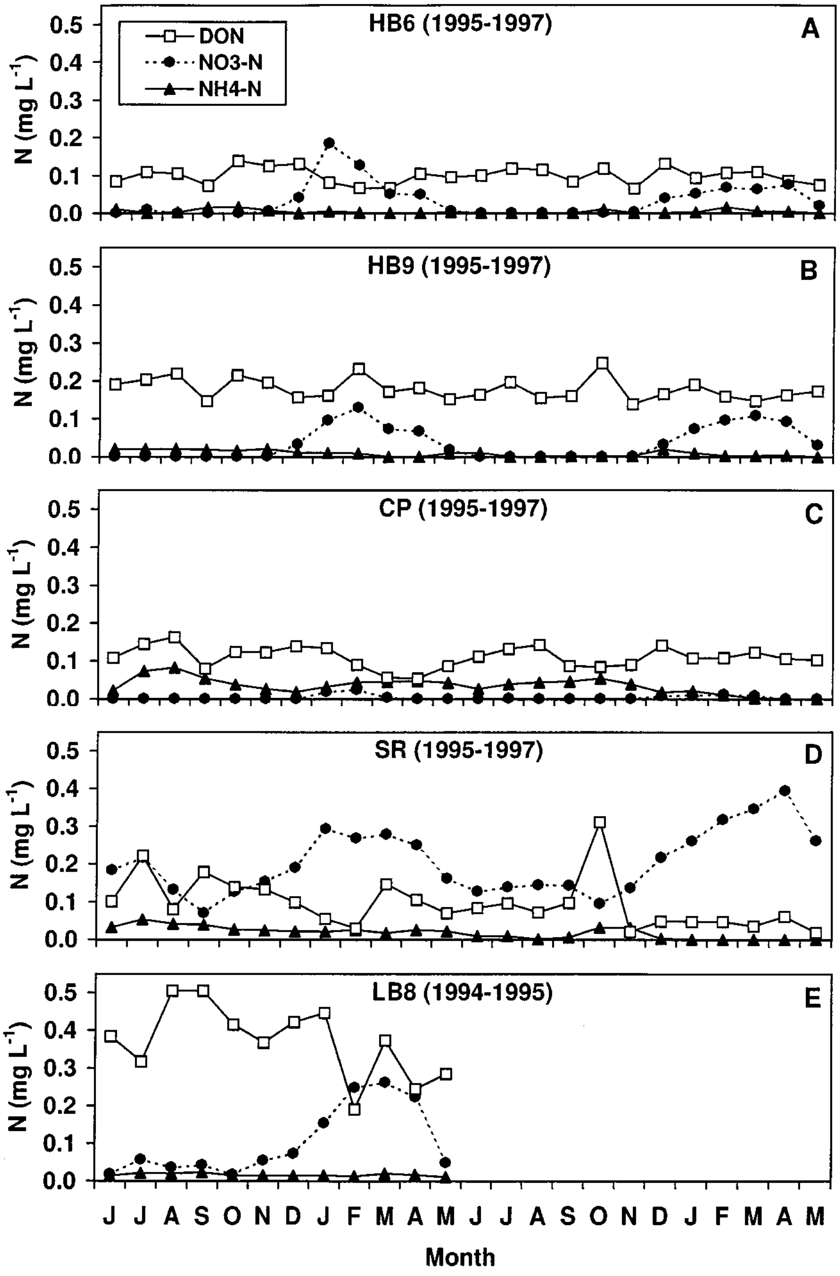

Figure 3. Mean monthly DON, NO_3-N, and NH_4-N concentrations in streamwater (mg L^{-1}) at HB6, HB9, CP, SR, and LB8.

Nitrogen budgets

The mean TDN input in precipitation for all watersheds was composed of 28% NH_4-N, 53% NO_3-N, and 19% DON. The average TDN output was composed of 5% NH_4-N, 36% NO_3-N, and 59% DON. At all watersheds except SR, the majority of N entering in precipitation was in an inorganic form and the majority of N leaving in streamflow was in an organic form (Table 3). SR was an exception as most of the N in streamwater at this watershed was in the NO_3-N form (72%) and a smaller fraction was in an organic form (24%).

Inputs of NO_3-N ranged from 3.2 to 6.2 kg ha^{-1} yr^{-1}, NH_4-N ranged from 2.1 to 3.6 kg ha^{-1} yr^{-1}, and DON ranged ranged from 1.3 to 2.4 kg ha^{-1} yr^{-1} (Table 3). The N outputs in streamflow were lowest for NH_4-N ($<$0.3 kg ha^{-1} yr^{-1}), and higher and more variable for NO_3-N (range = $<$0.1 to 2.1 kg ha^{-1} yr^{-1}) and DON (0.5 to 2.4 kg ha^{-1} yr^{-1}). Subtracting outputs from inputs showed that there always were net gains in TDN (4.7 to 10 kg ha^{-1} yr^{-1}), NO_3-N (1.7 to 5.7 kg ha^{-1} yr^{-1}) and NH_4-N (2.0 to 3.3 kg ha^{-1} yr^{-1}). DON was the only form of N not showing a net retention in all watersheds. Net DON values were minimal ($-$0.8 to 1.5 kg ha^{-1} yr^{-1}) but gains were greater and more common than losses (Table 3).

CP was unique among the study sites in that it had a greater percentage of inorganic N leaving the system as NH_4-N (17%) than as NO_3-N (4%). At other watersheds, stream DIN outputs were dominated by NO_3-N, and NH_4-N outputs were less than 10% of TDN. The DON outputs were highest at HB9 (2.4 kg ha^{-1} yr^{-1}, 1995–1996). Also at this watershed, DON made up the greatest portion of TDN (80%) in stream exports during the sampling period. The annual retention of TDN was greatest at HB7 (10.0 kg ha^{-1} yr^{-1} during 1996–97) and smallest at LB6 (4.7 kg ha^{-1} yr^{-1}).

DOC/DON relationships

There were significant correlations between concentrations of DOC and DON in precipitation at all watersheds and in streamwater at all watersheds except LB4. The streamwater relationship was stronger for watersheds with higher concentrations of DOC, such as LB8 ($r^2 = 0.65$, $P < 0.01$) than for watersheds with lower DOC, such as SR ($r^2 = 0.05$, $P = 0.02$). There was a weak but statistically significant relationship between DOC concentrations and stream discharge at all watersheds (r^2 = 0.04 to 0.52). The input-output budgets for DOC differed from those for DON in that annual outputs of DOC in streamwater exceeded inputs in precipitation at all watersheds except for SR during 1996–1997. The resulting net difference of DOC ranged from $-$91.2 kg ha^{-1} yr^{-1} at HB9 during 1995–1996 to 5.7 kg ha^{-1} at SR during 1996–

Table 3. Annual nitrogen budgets (kg ha^{-1} yr^{-1}). Values in parentheses indicate respective percentage of NH_4-N, NO_3-N, and DON in TDN. Net equals difference between inputs and outputs.

	HB6		HB7		HB8		HB9		CP		SR		LB4	LB6	LB8
Item	95–96	96–97	95–96	96–97	95–96	96–97	95–96	96–97	95–96	96–97	95–96	96–97	94–95	94–95	94–95
Input															
NH_4-N	2.4	2.7	2.4	2.9	2.4	2.8	2.4	2.8	3.0	3.0	3.6	2.5	2.1	2.1	2.1
(%)	(26)	(25)	(26)	(25)	(26)	(25)	(26)	(25)	(40)	(34)	(39)	(28)	(28)	(28)	(28)
NO_3-N	5.2	5.8	5.2	6.2	5.1	6.1	5.2	6.1	3.2	4.5	3.8	4.7	4.2	4.2	4.2
(%)	(57)	(54)	(57)	(54)	(56)	(54)	(57)	(54)	(42)	(50)	(41)	(53)	(55)	(55)	(55)
DON	1.6	2.2	1.6	2.4	1.6	2.3	1.6	2.3	1.4	1.4	1.9	1.7	1.3	1.3	1.3
(%)	(17)	(21)	(17)	(21)	(18)	(21)	(17)	(21)	(18)	(16)	(20)	(19)	(17)	(17)	(17)
TDN	9.2	10.7	9.2	11.5	9.1	11.2	9.2	11.2	7.6	8.9	9.3	8.9	7.6	7.6	7.6
Output															
NH_4-N	0.1	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.3	0.1	0.3	0.0	0.0	0.0	0.1
(%)	(4)	(0)	(4)	(0)	(3)	(5)	(3)	(4)	(23)	(10)	(9)	(0)	(0)	(0)	(4)
NO_3-N	0.8	0.4	1.3	0.6	1.2	0.7	0.5	0.4	0.1	0.0	2.1	2.1	1.0	1.8	0.6
(%)	(35)	(25)	(48)	(40)	(39)	(33)	(17)	(16)	(8)	(0)	(62)	(81)	(56)	(62)	(26)
DON	1.4	1.2	1.3	0.9	1.8	1.3	2.4	2.0	0.9	0.9	1.0	0.5	0.8	1.1	1.6
(%)	(61)	(75)	(48)	(60)	(58)	(62)	(80)	(80)	(69)	(90)	(29)	(19)	(44)	(38)	(70)
TDN	2.3	1.6	2.7	1.5	3.1	2.1	3.0	2.5	1.3	1.0	3.4	2.6	1.8	2.9	2.3
Net															
NH_4-N	2.3	2.7	2.3	2.9	2.3	2.7	2.3	2.7	2.7	2.9	3.3	2.5	2.1	2.1	2.0
NO_3-N	4.4	5.4	3.9	5.6	3.9	5.4	4.7	5.7	3.1	4.5	1.7	2.6	3.2	2.4	3.6
DON	0.2	1.0	0.3	1.5	−0.2	1.0	−0.8	0.3	0.5	0.5	0.9	1.2	0.5	0.2	−0.3
TDN	6.9	9.1	6.5	10.0	6.0	9.1	6.2	8.7	6.3	7.9	5.9	6.3	5.8	4.7	5.3

1997 (Table 4). The ratio of organic C:N in inputs and outputs (Table 4) reflects these differences with higher ratios in streamwater (range = 17 to 51) than in precipitation (range = 7 to 10).

Discussion

Importance of DON

DON is a measurable component of N in both precipitation and streamwater in the northeastern United States. During the study period, inputs of DON ranged from 1.3 to 2.4 kg ha^{-1} yr^{-1} and outputs ranged from 0.5 to 2.4 kg ha^{-1} yr^{-1}. A substantial amount of TDN in precipitation was composed of DON (16 to 21%), and in some watersheds DON was the dominant form of N (up to 90% at CP) in streamwater (Table 3). Despite the high percentage of DON in TDN, the flux of DON in inputs and outputs was small compared to soil N pools. N capitals at HB, for example, are 1,300 kg N ha^{-1} in the forest floor and 5,900 kg N ha^{-1} in the mineral soil, compared to DON inputs of 2.0 kg ha^{-1} yr^{-1} (Huntington et al. 1988).

Although all of the study watersheds showed a net accretion of N, little of this net accretion was due to net DON retention. The retention of N in study watersheds can be attributed to net retention of both NO_3-N and NH_4-N but not DON resulting in streamwater TDN losses dominated by DON. This dominance of DON in streamwater exports is common in watersheds from various biomes, including remote temperate watersheds in Chile (Hedin et al. 1995), neotropical watersheds in general (Lewis et al. 1999), and boreal watersheds in Finland (Kortelainen et al. 1997). We suspect that only in regions with large anthropogenic inputs of inorganic N will N losses from forested catchments be predominantly inorganic. Although the immediate impacts of DON on aquatic ecosystems are not as significant as those of inorganic N, DON is potentially bioavailable (Seitzinger & Sanders 1997) and must be considered in any budgetary analysis of N flux.

There were no discernable seasonal trends in DON during the study period (Figures 2–3). There was variation in the concentration of DON from month to month, but a comparison of the 2 years showed no indication of a consistent pattern. In other studies in the northeastern United States, DON in forest floor leachates exhibited seasonal increases during the late summer and early fall (Currie et al. 1996). This finding has been attributed to enhanced decomposition of organic matter in the summer and new litter inputs following senescence. We did not see this trend in streamwater (Figure 3) probably because any seasonal response in streamwater is dampened by interactions between DON and mineral soils (Qualls & Haines 1992) or that DON concen-

Table 4. Annual DOC and DON budgets (kg ha^{-1} yr^{-1}) and C:N ratios.

	HB6		HB7		HB8		HB9		CP		SR		LB4	LB6	LB8
Item	95–96	96–97	95–96	96–97	95–96	96–97	95–96	96–97	95–96	96–97	95–96	96–97	94–95	94–95	94–95
Input															
DOC	14.2	16.1	14.3	17.2	14.2	16.8	14.5	16.8	14.1	14.0	17.1	17.2	11.6	11.6	11.6
DON	1.6	2.2	1.6	2.4	1.6	2.3	1.6	2.3	1.4	1.4	1.9	1.7	1.3	1.3	1.3
C:N	9	7	9	7	9	7	9	7	10	10	9	10	9	9	9
Output															
DOC	31.4	26.3	26.5	23.3	44.9	44.3	105.7	97.7	46.3	38.6	17.2	11.5	25.0	29.1	65.4
DON	1.4	1.2	1.3	0.9	1.8	1.3	2.4	2.0	0.9	0.9	1.0	0.5	0.8	1.1	1.6
C:N	22	23	20	26	25	34	44	50	51	42	17	23	31	26	41
Net															
DOC	−17.2	−10.2	−12.2	−6.1	−30.7	−27.5	−91.2	−80.9	−32.2	−24.6	−0.1	5.7	−13.4	−17.5	−53.8
DON	0.2	1.0	0.3	1.5	−0.2	1.0	−0.8	0.3	0.5	0.5	0.9	1.2	0.5	0.2	−0.3

trations are affected by riparian zone (Hedin et al. 1998) or within-stream processes (Sun et al. 1997).

The 2 years of data collected at HB, CP, and SR show that differences in input-output budgets of N are driven by annual variation in precipitation and streamflow rather than by differences in DON concentrations. Streamwater DON concentrations appear relatively unaffected by hydrological events such as rain storms and snowmelt runoff (see correlations presented earlier). In contrast, increases in DOC with discharge are consistent with results from similar studies and have been attributed to increased leaching of throughfall and changes in flow paths from mineral horizons to organic soils during rainstorms and snowmelt runoff (McDowell & Likens 1988; McDowell & Wood 1984; Newbold et al. 1995). The significant correlation between DOC and DON at most watersheds suggests that both forms of organic matter behave similarly, but DON appears less affected by discharge than DOC.

The importance of DON in the N cycle is difficult to assess because of uncertainties regarding its composition, sinks, sources, and bioavailability. Some of the DON input is presumably of natural origin, as it is found in precipitation from relatively remote areas (Eklund et al. 1997). Human perturbations such as biomass burning and industrial combustion also contribute DON to precipitation (Russell et al. 1998). Sources of streamwater DON include throughfall, leaching, and decomposition of litter and soil organic matter, plant exudates, fine-root and mycorrhizal turnover, and the waste products of macro and microorganisms. Sinks for DON in soils include adsorption in both organic and mineral horizons, and to a far less extent direct removal of DON by roots and mycorrhizae (Finlay et al. 1992; Northup et al. 1995; Qualls & Haines 1992).

DOC:DON (C:N) ratios

Several studies indicate that in the forest floor, mineralization, nitrification, and subsequent losses of DIN in leachates are negatively correlated with soil C:N ratios (Gundersen et al. 1998b; McNulty et al. 1991). We found a similar negative correlation between annual DIN losses (particularly NO_3-N) and streamwater organic C:N ratios (Figure 4). We cannot be certain of the cause of this correlation, but suspect that streamwater C:N ratios reflect soil C:N ratios and hence the availability of inorganic N in each watershed. In areas where the supply of N exceeds the biological demand for N, foliage typically has a higher N content (Aber et al. 1995), which would cause a reduction in the forest floor C:N ratio and an increase in NO_3-N leaching. At the watershed level, this interaction between C and N could result in high DIN losses.

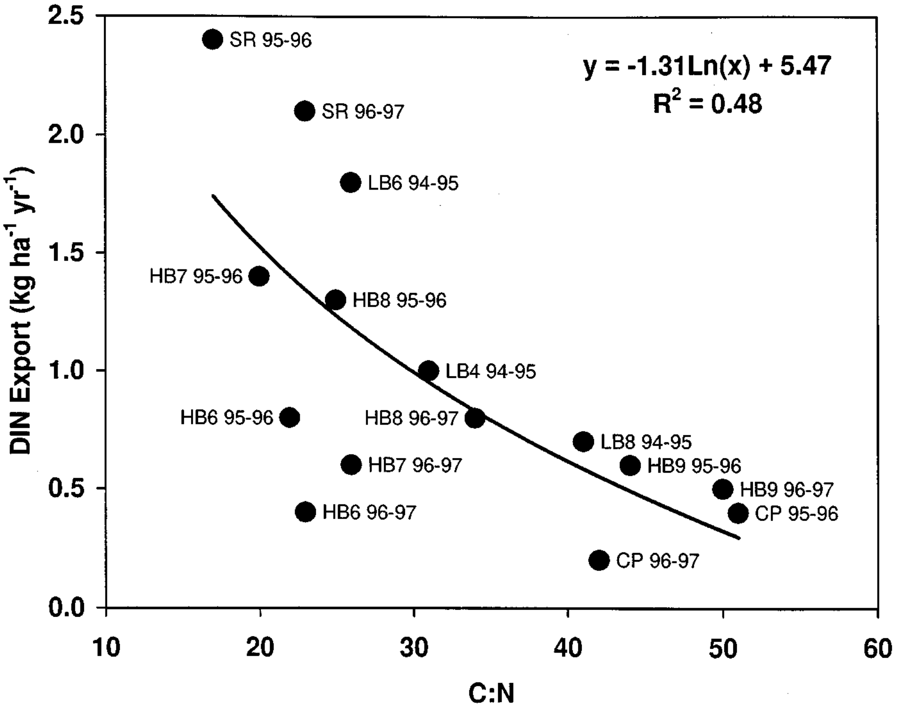

Figure 4. Regression of streamwater DIN exports (kg ha^{-1} yr^{-1}) on streamwater C:N ratio. Points represent the mean annual value for each site.

Streamwater C:N ratios may be an effective indicator of susceptibility to N saturation and could be used to monitor the N status of sites. Gundersen et al. (1998a) suggested this possibility using forest-floor C:N ratios. Measurements of streamwater DOC and DON may offer some advantages over soil C:N ratios because streamwater values are relatively easy to obtain and are not subject to the seasonal fluctuations associated with DIN. Additionally, streamwater C:N ratios provide an integrated signal for the entire watershed and reduce the problem of spatial variability associated with soil sampling. Although concentrations of DOC and DON were variable over time at some of the watersheds we studied, both forms of organic matter behave similarly with respect to hydrologic changes, resulting in relatively constant ratios. Streamwater C:N ratios thus may prove to be a useful tool in characterizing nitrogen dynamics at the watershed scale.

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