



Dissolved organic carbon and nitrogen relationships in forest litter as affected by nitrogen deposition

Alison H. Magill*, John D. Aber

Complex Systems Research Center, University of New Hampshire, Morse Hall, Room 481, Durham, NH 03824, USA

Accepted 29 September 1999

Abstract

Dissolved forms of carbon and nitrogen have become recognized for their importance in forest nutrient cycling. The role of dissolved organic carbon (DOC) as an energy source for microbial metabolism is of particular interest. A laboratory decomposition experiment was conducted to examine the relationship between potential increased N inputs (via acid deposition) and DOC production in the forest litter layer and subsequent effects on DOC availability in the forest floor. Air-dried leaf litter (seven species) was treated with nitrogen (nitrate or ammonium) or deionized (DI) water at weekly intervals throughout 15 weeks and leached with DI water at 1 or 2 week intervals. Leachate was analyzed for DOC, inorganic nitrogen (NO_3^- -N and NH_4^+ -N) and dissolved organic nitrogen (DON). Litter was analyzed for percent C, percent N, weight loss and percent cellulose and lignin. Nitrogen treatments did not greatly affect DOC concentrations in litter leachate. Differences in DOC concentrations were primarily due to a wide range of initial litter chemistries, where species with high extractives and low lignin had the highest DOC leachate concentrations. Nitrogen treated samples showed greater weight loss than controls although nitrate and ammonium treatments were not significantly different. Between 6 and 39% of total carbon loss was leached as DOC. These findings suggest that different forest types could vary greatly in the quantity of carbon consumed or released and that nitrogen inputs appear to affect this overall cycle by increasing respiration (as measured by weight loss), rather than increasing DOC release into the soil solution. Further examination of the fate of DOC as it moves down in the soil profile and measurements of CO_2 evolution during laboratory decomposition, are necessary to better understand these processes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Decomposition; Forest floor; N inputs; Litter chemistry

1. Introduction

Increases in atmospheric nitrogen deposition over the last several decades have led to concerns regarding the ability of forest ecosystems to assimilate and retain additional nitrogen (Ågren and Bosatta, 1988; Aber et al., 1989; Durka et al., 1994; Stoddard, 1994; Wright and van Breemen, 1995; Dise and Wright, 1995). Although forests are often N-limited (Mitchell and Chandler, 1939; Aber et al., 1989; Aber, 1992), assimilation

of N by vegetation is small relative to the quantity of N retained by soil organic matter (Aber et al., 1993; Magill et al., 1996; 1997; Nadelhoffer et al., 1995). The processes by which N retention and incorporation occur and the effect on soil nitrogen cycling dynamics are not well understood.

Many important transformations of nitrogen within the soil system are microbially driven (Coleman and Crossley, 1996), including immobilization and mineralization of N during decomposition. A source of labile carbon is necessary to drive immobilization processes, particularly in ecosystems exposed to elevated N deposition. Annual production of foliar litter in temperate forests is a large source of high C-to-N ratio material containing a range of different carbon compounds

* Corresponding author. Tel.: +1-603-862-4098; fax: +1-603-862-0188.

E-mail address: alison.magill@unh.edu (A.H. Magill).

(Swift et al., 1979; Aber and Melillo, 1991; Qualls et al., 1991) and may provide the carbon substrate necessary for incorporation of added N.

Numerous decomposition and mineralization studies have examined carbon and nitrogen availability under ambient environmental conditions (Bocock, 1964; Anderson, 1973; Fogel and Cromack, 1977; Berg and Staaf, 1980; Melillo et al., 1982; McClaugherty et al., 1985; Blair, 1988) or under laboratory conditions (Daubenmire and Prusso, 1963; Taylor et al., 1989). These confirm that carbon quality and nitrogen content of the material control both mass loss and nitrogen dynamics of decomposition (Berg, 1986; Aber et al., 1990). However, little experimental work has been done on micro-scale changes in carbon and nitrogen cycling under elevated nitrogen concentrations.

Labile soil carbon is a relatively small fraction of total soil carbon (Killham, 1994; Lynch, 1982; Vance and David, 1991). Recent work has begun to emphasize the importance of dissolved organic forms of C and N in ecosystem processes and nutrient balances. A number of investigations have shown that in forest ecosystems, solutions passing through the organic soil horizon are enriched with both dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) (e.g. McDowell and Likens, 1988; Qualls and Haines, 1991; Currie et al., 1996). McClaugherty (1983) determined that 33% of the soluble compounds in sugar maple litter were subsequently leached to the DOC pool in the forest floor. In addition, Qualls and Haines (1992) measured the biodegradability of dissolved organic matter (DOM) in different forest solutions and found that degradation of leaf leachate and throughfall (40–70% degraded) was greater than degradation of solutions from lower in the soil profile (30% degraded). These results suggest that leaf litter is an important source of easily metabolized DOC for microbial metabolism. What is unknown is whether increased availability of labile nitrogen from nitrogen deposition will alter the flux of DOC from the decomposing litter layer and change the labile carbon pool.

A laboratory leaf litter decomposition experiment was initiated to investigate DOC and nitrogen dynamics in litter leachate. The following assumptions were made: (i) that the primary source of microbially available carbon in temperate forest soils is in the form of dissolved organic carbon, which is added to the soil as root exudates (Smith, 1969; Killham, 1994), as by-products of litter decomposition and as throughfall and; (ii) that DOC is present in low concentrations which can become limiting to microbial growth. Given these conditions, the experiment was designed to examine the litter layer as the top horizon in the soil profile and to determine: (i) its role as a DOC source or sink; (ii) the effect of nitrogen additions on the release of DOC, DON and inorganic nitrogen to the soil solution

and (iii) the effect of nitrogen additions on weight loss and DOC release from decomposing litter.

2. Materials and methods

2.1. Field collections

Fresh leaf litter was collected in the fall of 1992. Litter collectors were located at the University of New Hampshire's Woodman Experimental Farm, a wooded area containing a mix of natural and introduced species. Litter from nine tree species common to New England forests was collected using nylon screens and plastic baskets. Foliage was gathered in paper bags, air dried at room temperature then separated by species. Species were selected to cover a wide range of chemical characteristics such as carbon-to-nitrogen ratios. The following species of litter were used, listed here by common name, Latin name and abbreviation used in figures of this paper: black oak (*Quercus velutina* L.), BO; black birch (*Betula lenta* L.), BB; red maple (*Acer rubrum* L.), RM; sugar maple (*A. saccharum* Marsh.), SM; white ash (*Fraxinus americana* L.), WA; black cherry (*Prunus serotina* Ehrh.), BC; shagbark hickory (*Carya ovata* Mill.), HI; American beech (*Fagus grandifolia* Ehrh.), AB and; white pine (*Pinus strobus* L.), WP.

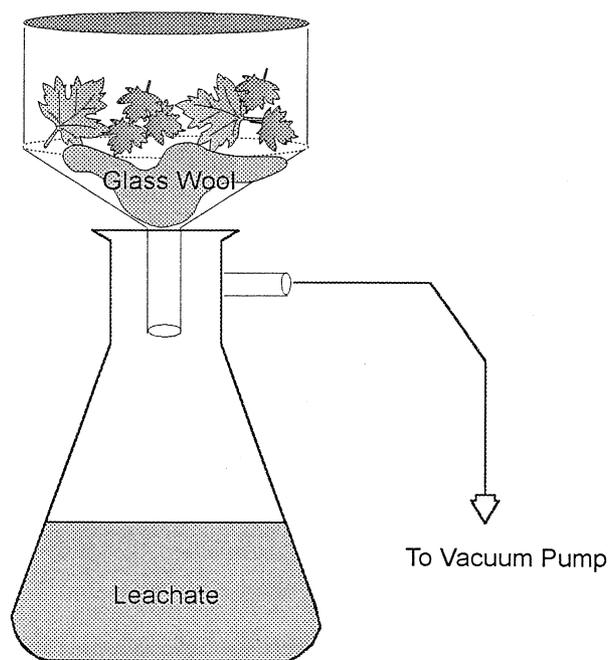


Fig. 1. Schematic of the incubation and filtration apparatus used to incubate and leach decomposing litter samples. Cups were stored on racks between leaching.

2.2. Incubation experiment

Two sets of preliminary experiments were run in order to determine the following variables: (i) leaf sample size; (ii) type of filter to use in the bottom of the incubation cup; (iii) technique for application of the fertilizer or water treatments; (iv) desirable moisture content and; (v) stage of decomposition at which DOC is released. As a result of these tests, the following procedure was used.

Litter was incubated for 15 weeks in 90 mm dia polypropylene cups with flat, perforated bottoms that were attached to a funnel (Fig. 1). Cups were lined with approximately 5 g acid-washed glass wool (soaked in 10% HCl for 24 h then DI rinsed), oven dried at 70°C for 24 h and then weighed. Air-dried litter was cut into pieces 2 × 4 cm in size. Each cup was filled with 3.8 ± 0.2 g of cut litter, covered with plastic wrap and secured with an elastic band. This weight was equivalent to annual litter production for a mixed hardwood stand (3000–4000 kg litter ha⁻¹ yr⁻¹), scaled to the area of the cup. Both plastic cover and cups were labeled with a unique number for each sample, hung on plywood racks and placed in a wooden cabinet. Air temperature inside the cabinet was recorded twice weekly and averaged between 20 and 23°C.

Three fertilizer treatments (Table 1) were used: control (DI water), nitrate (50 kg N ha⁻¹ yr⁻¹ equivalent as NaNO₃) and ammonium (50 kg N ha⁻¹ yr⁻¹ equivalent as (NH₄)₂SO₄). Amendments were added weekly using a graduated cylinder and spray bottle mechanism. The plastic covering was removed, fertilizer sprayed on and the cover replaced for each individual

cup in order to prevent fertilizer contamination. The first nine fertilizer applications were at the rate of 25 ml per cup. After 9 weeks, the samples appeared to be saturated, so treatments were reduced to 15 ml per cup for the remaining applications. Concentration of the fertilizer was increased to maintain the same application rate throughout the experiment.

Sample cups were leached with 200 ± 1 ml of DI water according to the schedule in Table 1. Samples were leached on Monday and fertilizer was added on Thursday of each week. Following the initial leaching, 5 ml of inoculant was added to each cup. Inoculant was made by combining 1 l of throughfall with 150 g of organic soil, mixing for 2 h, allowing it to settle overnight and then filtering the mixture through a G6, 1.5 µm filter.

The combined volume of fertilizer and leaching water (395 mm over 105 d) was equivalent to the expected volume of fall precipitation in the region, relative to the size of the cup. Average precipitation at the Harvard Forest, Oct–Jan 1992 and 1993 was 427.5 mm over 123 d or 364.9 mm calculated as a 105 d rate. Leachate was stored in HDPE bottles and refrigerated for up to 1 week prior to analysis.

2.3. Leachate analysis

Leaf leachate was analyzed for NO₃⁻-N and NH₄⁺-N using a Bran & Luebbe Traacs 800 Autoanalyser. NH₄⁺-N was analyzed using the Berthelot Reaction chemistry (Technicon Method 780-86T; Technicon Industrial Systems, 1978); NO₃⁻-N was determined using hydrazine sulfate reduction (Technicon Method

Table 1
Experimental design

<u>Treatment</u>	<u>Species</u>	<u>Replicates</u>	<u>Fertilizing Schedule</u>	<u>Leaching Schedule</u>	<u>Leachate Analysis</u>	<u>Litter Analysis</u>
•CONTROL: Deionized Water	CONTROL	• four replicates	• weekly applications for 15 weeks	• initial (time 0)	•Dissolved Organic Carbon (DOC)	•Weight Loss
•NITRATE: 50 kg N ha ⁻¹ yr ⁻¹	TREATED:	within each treatment:	initiated 3 days following initial leaching	• weeks 1, 2, 3, 4, 5, 7, 9, 11, 13 and 15	•Dissolved Organic Nitrogen (DON)	•Total Nitrogen
or 0.0318 g N sample ⁻¹ *	•Amer. Beech •Black Birch •Black Oak •Red Maple •Sugar Maple	twelve blank cups (glass wool only)			•Dissolved Inorganic Nitrogen (DIN)	•Carbon Fractionation
•AMMONIUM: 50 kg N ha ⁻¹ yr ⁻¹	•White Ash •White Pine					
or 0.0318 g N sample ⁻¹ *	CONTROL ONLY: •Black Cherry •Hickory sp.					

* Total added over the 15 week incubation.

782-86T; Technicon Industrial Systems, 1977). Detection limits for both NO_3^- -N and NH_4^+ -N are 0.20 mg l^{-1} using these techniques.

Total Dissolved Nitrogen (TDN) was determined using an adaptation of the persulfate-base digestion technique commonly used for analysis of nitrogen in seawater (Solorzano and Sharp, 1980; Kalff and Bentzen, 1984). This method is preferred over the Total Kjeldahl Nitrogen (TKN) method for samples containing high amounts of NO_3^- since NH_4^+ and organic nitrogen are converted to NO_3^- (Smart et al., 1981). Digested samples were then analyzed for NO_3^- -N on the Traacs Autoanalyser. DON was calculated as $\text{TDN}-\text{DIN}$ (Dissolved Inorganic Nitrogen) where $\text{DIN} = \text{NO}_3^-$ -N + NH_4^+ -N.

DOC was measured using a Shimadzu TOC-5000 Total Organic Carbon analyzer. Samples were acidified with 2 N HCl and sparged with ultra zero grade CO_2 free air to remove all inorganic carbon. Sparged samples were combusted at 680°C and CO_2 detected using a nondispersive infrared (NDIR) detector.

2.4. Litter analysis

A subsample of each species was oven dried for 48 h at 70°C to determine the initial moisture content of the litter and an air dry–oven dry conversion factor was calculated. Initial samples were ground using a Wiley Mill with a 1 mm mesh screen and analyzed for total nitrogen and carbon content on a Perkin Elmer 2400 CHN elemental analyzer. Initial carbon chemistry was measured with a sequential extraction digestion technique (McClaugherty et al., 1985; Newman et al., 1994); percent polar and nonpolar compounds, cellulose and lignin were determined for all sub-samples (Table 2). Incubated litter samples were weighed to 10 mg both initially and at the end of the 15 weeks and total weight loss was determined. Final decomposed samples were analyzed for total carbon and nitrogen in the same manner as initials and for percent nitrogen, lignin and cellulose using near-infrared spectrometry (Bolster et al., 1996).

2.5. Statistics and calculations

Oneway analysis of variance (ANOVA) was used to test for significant differences ($P = 0.05$) between treatments and within species. All leachate concentrations were reported as mg of measured compound g^{-1} initial litter weight. These values were calculated for each individual cup and averaged for the four replicates per species. Cumulative concentrations were calculated by summing the concentrations from each leaching event on an individual cup basis, then averaging the summed values to obtain a mean cumulative value.

2.6. Budget calculation

A carbon budget was calculated for each treatment and species combination by measuring initial litter carbon concentration, subtracting DOC losses and measuring final carbon content. Total carbon losses were assumed to be the sum of DOC loss and respiration loss, the latter calculated as the difference between total C loss and DOC loss.

2.7. Terminology

Nitrate and ammonium were added to leaf litter as fertilizer treatments and were also measured in leachate. For clarity, fertilizer treatments are written out as nitrate and ammonium and measured leachate concentrations are referred to as NO_3^- -N and NH_4^+ -N.

3. Results and discussion

The original experiment was designed to examine the effects of N additions on DOC release from decomposing litter. Measurement of litter characteristics allowed for examination of nitrogen treatments on litter chemistry and weight loss as well.

Table 2

Carbon fractions as percent of total carbon compounds and carbon-to-nitrogen ratio of initial litter samples

Species	Nonpolar	Polar	Lignin	Cellulose	C-to-N ratio	Lignin-to-N ratio
Am. beech	2.58	17.60	27.14	52.68	56.5	61.79
Black birch	7.56	26.45	22.37	43.62	49.3	43.29
Black oak	3.48	33.62	24.34	38.56	65.7	50.40
Red maple	4.50	52.98	15.72	26.80	90.7	47.86
Sugar maple	3.32	44.61	15.68	36.39	99.3	77.01
White ash	3.21	26.40	17.99	52.40	56.6	63.14
White pine	12.28	22.96	25.62	39.14	165.3	118.60
Black cherry	3.92	30.26	18.62	47.20	62.5	61.91
Hickory sp.	3.00	20.63	26.63	49.74	42.7	44.81

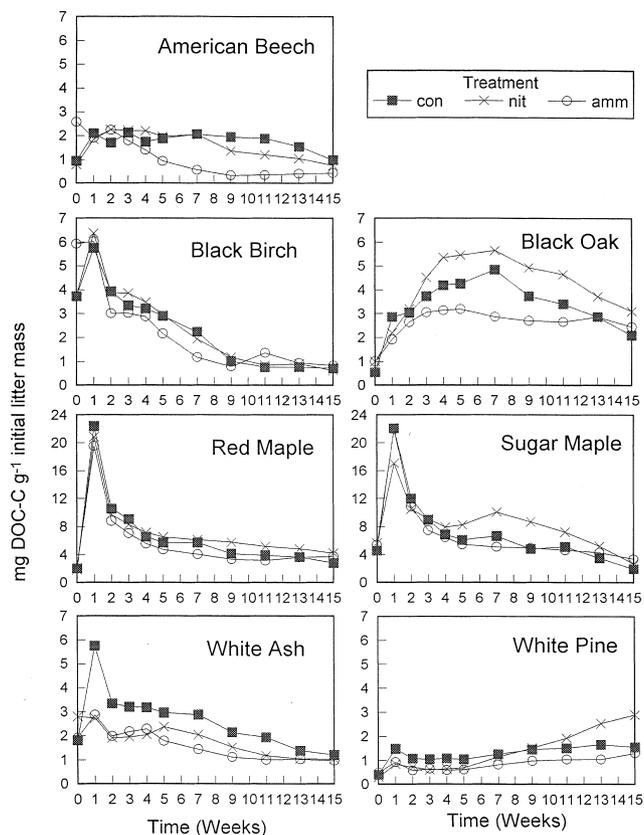


Fig. 2. Time series graphs of weekly DOC-C leached from decomposing litter over the 15 weeks as mg C g⁻¹ initial litter. Each point represents the mean of four replicate cups within each species and treatment. Note the scale differences for red and sugar maple litter. Statistical data presented in Table 3.

3.1. Leachate DOC

Leachate chemistry was compared for each of the seven species receiving fertilizer applications. Overall, differences in concentration of DOC leached due to

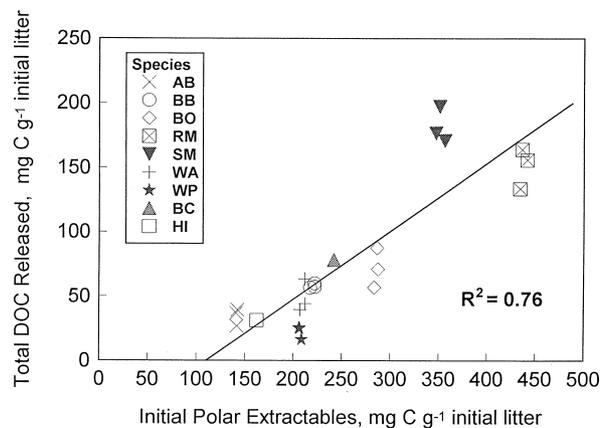


Fig. 3. Relationship between initial polar extractive content in litter and total DOC released during the 15 week incubation. *n* = 4 replicates for each treatment and for initial litter analysis.

nitrogen treatment during the incubation period were few (Fig. 2, Table 3). Significant differences between treatments were found for some species on a weekly basis (Table 3). Where these occurred, ammonium-treated litter generally released less DOC than control or nitrate treatments, suggesting slightly increased metabolism of DOC in the presence of the most easily assimilated form of mineral nitrogen. Soil solution samples collected below the forest floor in six ammonium nitrate treated plots at the Harvard Forest, Petersham MA (Aber et al., 1993; Magill et al., 1997) also showed little or no change in DOC even at amendment N rates of 150 kg N ha⁻¹ yr⁻¹ (McDowell et al., 1998). The same lack of response was seen in lysimeters placed below the rooting zone (Magill et al., unpublished data).

Different species varied considerably in the pattern of DOC released regardless of treatment. Red maple and sugar maple exhibited a large DOC pulse in the

Table 3

Effect of treatment on DOC production as shown in Fig. 2. Letters that differ within species and week indicate significant differences between treatment at the *P* = 0.05 level. Differences determined using ANOVA and the Bonferroni mean separation test. Letter in the first position = control, second position = nitrate, third position = ammonium e.g. for black oak, week 3, nitrate was significantly different from control and ammonium, control and ammonium were not different from each other

Time (week)	Am. beech	Black birch	Black oak	Red maple	Sugar maple	White ash	White pine
0	a,a,b	a,a,b	a,a,a	a,a,a	a,a,a	a,a,a	a,a,a
1	a,a,a	a,a,a	a,b,b	a,a,a	a,a,a	a,b,b	a,b,b
2	a,b,b	a,a,a	a,a,a	a,a,a	a,a,a	a,b,b	a,b,b
3	a,a,b	a,a,a	a,b,a	a,a,a	a,a,b	a,b,b	a,b,b
4	a,b,a	a,a,a	ab,a,b	a,a,a	a,a,a	a,a,a	a,b,b
5	a,a,b	a,a,b	a,b,a	ab,a,b	ab,a,b	a,ab,b	a,b,b
7	a,a,b	a,a,a	a,a,b	a,a,a	a,b,a	a,ab,b	a,a,a
9	a,a,b	a,a,a	a,b,c	a,b,a	a,b,a	a,ab,b	a,a,b
11	a,ab,b	a,a,a	a,b,c	a,b,a	ab,a,b	a,b,b	a,a,b
13	a,ab,a	a,a,a	a,b,a	a,a,a	a,b,ab	a,a,a	a,b,c
15	a,a,a	a,a,a	a,b,ab	a,a,a	a,ab,b	a,a,a	a,b,a

first week (20 mg DOC g⁻¹ litter), dropping to half that amount by week 2 (Fig. 2). The same pattern was seen for white ash and black birch, although initial DOC pulse concentrations were less than half that of the maples. In contrast, white pine DOC concentrations were low initially and increased gradually over time. DOC concentration in leachate from beech litter remained relatively constant over the 15-week incubation. These species differences can be explained in part by initial carbon chemistry (Table 2); high DOC concentrations are correlated with high percent polar extractable compounds in initial litter (Fig. 3.). Although differences in litter quality are recognized as having an effect on decomposition rates (Berg, 1986; Aber et al., 1990), these data demonstrate the potential for litter quality of different forest or community types to influence soil solution DOC concentrations as well.

3.2. Leachate nitrogen

Inorganic nitrogen concentrations in leachate increased directly as a result of treatments (Fig. 4). NO₃⁻-N was released from nitrate-treated samples and NH₄⁺-N from ammonium-treated samples. Small amounts of the non-treatment compound were detected in some samples (i.e. NO₃⁻-N in ammonium treated leachate), but never comprised more than 3% of total dissolved inorganic nitrogen (DIN).

DON in leachate varied depending upon species, but overall, concentrations were much lower than DIN. There was no clear, overall effect of nitrogen treatment on cumulative DON released (Fig. 4), although DON in leachate from nitrate-treated cups was consistently higher than from controls. This suggests that a portion

of the added nitrate may be converted to DON. DON in leachate from ammonium-treated cups varied greatly, from the highest of the three treatments for black birch, to zero or negative values in some species. Negative values resulted because of the manner in which DON is calculated [(TDN-(NO₃⁻-N+NH₄⁺-N)] and could indicate that the persulfate digestion technique was not completely converting NH₄⁺-N to NO₃⁻-N. This would result in post-digest TDN values which were lower than pre-digest measurements of inorganic nitrogen (NO₃⁻-N+NH₄⁺-N). The combination of high inorganic N concentrations due to fertilizer additions and the inherent error in the TDN method due to repeated dilutions, could account for the inability to accurately detect DON at such low concentrations.

DON accounted for 93 to 100% of TDN released from litter in control cups, although cumulative concentrations of TDN were never greater than 2 mg N g⁻¹ initial litter. Red and sugar maple were the only species to release DIN from untreated cups and both species had substantially higher DOC concentrations in leachate than any other litter type. This suggests that highly leachable species have the potential to lose nitrogen during the initial stages of decomposition. Although few decomposition studies to date have quantified this amount, Aerts and de Caluwe (1997) measured potential N leaching from litter of four *Carex* species (96 h lab incubation in distilled water) and found that between 4–20% of initial N was removed into solution. These data support the ideas of Berg and Staff (1980), who theorized that prior to immobilization, some nitrogen may be lost via leaching.

Hedin et al. (1995) found that DON comprised up to 95% of total nitrogen in streams draining a high-elevation, coniferous forest in Chile. Organic N comprised from 17–30% of total N in the leachate from

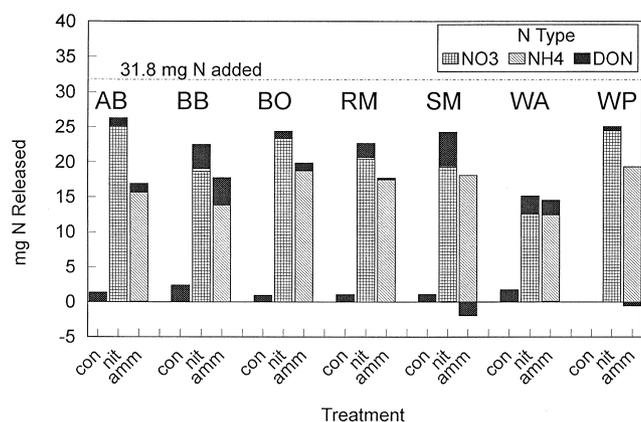


Fig. 4. Total dissolved nitrogen released from litter over 15 weeks, by treatment for the seven treated species of litter. NO₃⁻-N or NH₄⁺-N were released primarily from cups to which that type of fertilizer was added and DON is the major N type leaching from unfertilized litter. WP litter in control cups released no detectable nitrogen. Values are sums of the three N compounds measured in litter leachate.

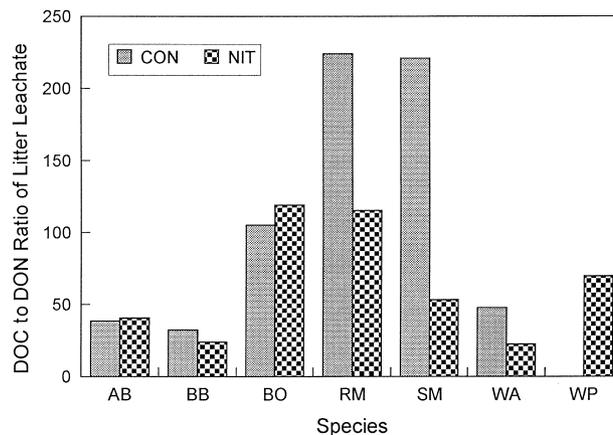


Fig. 5. Leachate DOC:DON ratios for control and nitrate treated samples only. Ratios derived from 15-week cumulative values, $n = 4$. Nitrogen was not detected in WP control litter therefore ratio could not be calculated.

laboratory incubated mineral soils (Robertson et al., 1988). Sollins and McCorison (1981) measured inorganic and organic nitrogen in a Douglas fir watershed in Oregon. Their data revealed that DON comprised 72 and 70% of total dissolved nitrogen in throughfall and litter leachate, respectively and they emphasized the necessity to include DON measurements in any watershed study that is attempting to accurately measure nitrogen fluxes.

3.3. DOC-to-DON ratios

DOC-to-DON ratios are used to estimate the C-to-N ratio of organic materials in the soil solution (Melillo et al., 1989; Qualls et al., 1991; Currie et al., 1996). Control and nitrate-treated cup DOC-to-DON ratios were calculated (Fig. 5) using 15-week cumulative DOC and DON. DOC-to-DON ratios from ammonium-treated cups were not calculated due to the uncertainty in measuring TDN for those samples. Cumulative values were used because of the low weekly concentrations of DON in litter leachate. Red maple and sugar maple DOC-to-DON ratios were 224 and 221, respectively, with DI water additions and 115 and 53, respectively, with nitrate additions. The large decrease in DOC-to-DON with nitrate additions is due to small absolute increases in DON concentration, although relative amounts are 2 to 3 times that of the controls. DOC-to-DON ratios for the other species were substantially lower than the maples and differences between control and nitrate treatments were small. High maple DOC-to-DON ratios were due to high DOC leaching from those species during the first week of incubation, which resulted in elevated cumulative DOC, as compared to other species.

Average, autumn DOC-to-DON ratios of Oa lea-

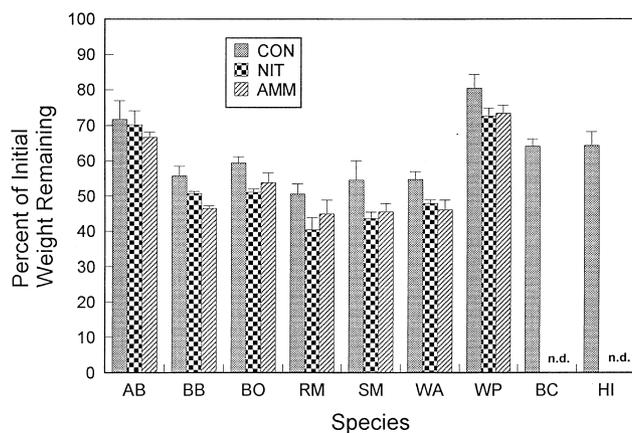


Fig. 6. Percent of initial litter weight remaining after 15 weeks of decomposition. Error bars are one S.D., $n = 4$. BC and HI samples were not included in the fertilizer portion of the experiment. n.d. = no data.

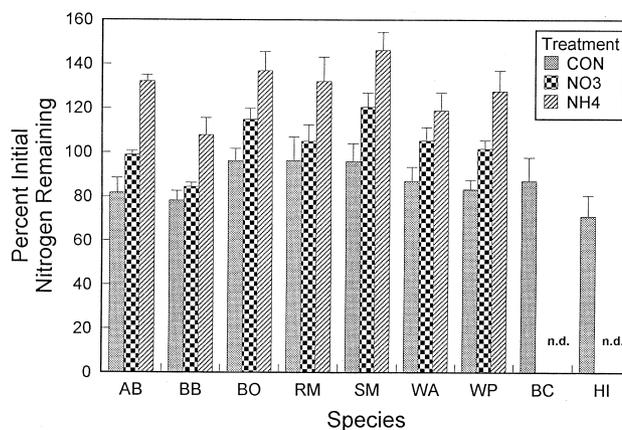


Fig. 7. Percent of initial nitrogen remaining after 15 weeks of decomposition. Error bars are one S.D., $n = 4$. BC and HI samples were not included in the fertilizer portion of the experiment. n.d. = no data.

chate (i.e. soil water draining from below the organic horizon) were 40 in a red pine stand and 35 in a mixed hardwood stand at the Harvard Forest (Currie et al., 1996). Qualls and Haines (1991) measured similar ratios (46 in August and 50 in December) in Oa leachate from a mixed hardwood forest in North Carolina. These field measurements of Oa leachate DOC-to-DON ratios were low compared with litter leachate DOC-to-DON ratios from this study (Fig. 5). Since small changes in DON resulted in large changes in the DOC-to-DON ratio of litter leachate, it is likely that additional DON sources in the organic horizon could cause the decrease in Oa leachate DOC-to-DON ratios observed by Currie et al. (1996) and Qualls and Haines (1991). Although it is difficult to make direct comparisons between laboratory and field values, results from this study do provide an estimate of litter leachate inputs to the forest floor.

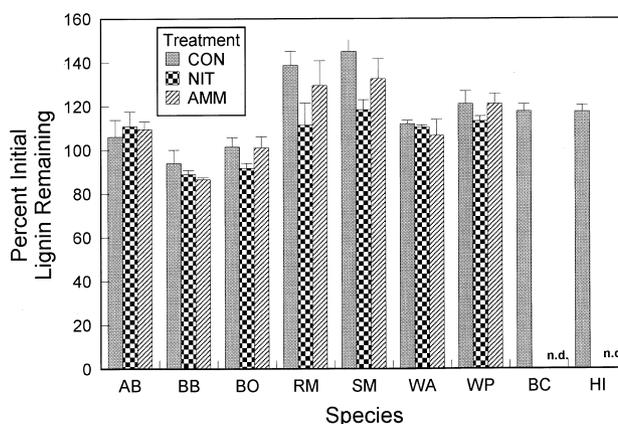


Fig. 8. Percent of initial lignin remaining after 15 weeks of decomposition. Error bars are one S.D., $n = 4$. BC and HI samples were not included in the fertilizer portion of the experiment. n.d. = no data.

3.4. Litter mass loss and chemistry

Mass loss was accelerated by nitrogen additions for most species, but the form of N added was rarely significant (Fig. 6). As nitrogen treatments did not affect total DOC losses from litter (Fig. 2), this suggests that differences in weight loss were a function of carbon losses via respiration of nonsoluble carbon compounds.

Litter chemistry of decomposed samples was reported as percent of original nitrogen, lignin or cellulose remaining over time (Figs. 7–9). Increases in net nitrogen immobilization in response to N additions were large relative to increases in mass loss, suggesting increased N incorporation g^{-1} of carbon respired. Incorporation of NH_4 generally exceeded that for NO_3 , although mass losses were similar. There was no net N immobilization in the control cups as no external source of N was available.

Lignin content of treated samples did not change significantly from controls (Fig. 8). Given the short duration of the laboratory incubation, lignin would not be expected to decompose; most field studies show an increase in lignin concentration for the first 1–2 yr of decomposition followed by a gradual decrease over time (McClaugherty and Berg, 1987; Aber et al., 1990; Magill and Aber, 1998). Cellulose content decreased significantly from initial concentrations and treated litter was significantly lower than control litter in all but AB nitrate-treated samples (Fig. 9). These data indicate that cellulose may be a more important microbial carbon source than soluble forms of carbon, which may be less bioavailable (Yano et al., 1998). One of our assumptions was that small, soluble, low molecular weight compounds are by virtue of their size, labile. However, many of these small compounds, such as

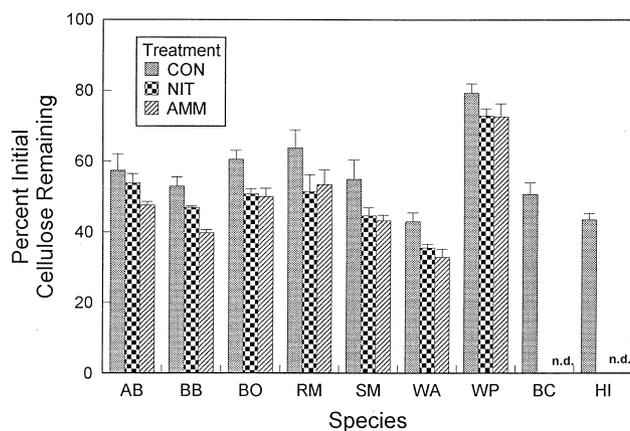


Fig. 9. Percent of initial cellulose remaining after 15 weeks of decomposition. Error bars are one S.D., $n = 4$. BC and HI samples were not included in the fertilizer portion of the experiment. n.d. = no data.

Table 4
Carbon budget for each species by treatment. All values are in units of mg C unless otherwise noted

Treatment	American beech		Black birch		Black oak		Red maple		Sugar maple		White ash		White pine		Black cherry		Hickory		
	Con	Nit	Amm	Nit	Con	Nit	Amm	Nit	Con	Nit	Amm	Nit	Con	Nit	Amm	Con	Nit	Con	
Initial litter C (S.E.)	1354 (14.95)	1368 (7.43)	1361 (11.51)	1363 (5.14)	1375 (22.37)	1378 (17.81)	1392 (14.98)	1391 (5.12)	1308 (13.70)	1294 (25.22)	1273 (13.37)	1315 (22.00)	1550 (16.80)	1553 (14.94)	1533 (2.53)	1344 (4.95)	1350 (13.60)	1350 (13.60)	1350 (13.60)
Final litter C (S.E.)	989.2 (46.87)	975.0 (26.15)	926.9 (9.43)	713.2 (23.13)	827.5 (23.56)	712.3 (12.21)	761.8 (22.59)	573.7 (26.11)	718.1 (36.98)	556.7 (43.32)	580.7 (17.04)	774.7 (23.95)	1220 (36.35)	1091 (10.57)	1110 (7.27)	885.5 (29.06)	874.2 (20.57)	874.2 (20.57)	874.2 (20.57)
Total C loss (by difference)	364.8	393.0	434.1	650.8	547.5	665.7	630.2	817.3	589.9	737.3	692.3	540.3	320.0	462.0	423.0	458.5	475.8	475.8	475.8
Percent total C loss	27.0	28.7	31.9	47.7	39.8	48.3	45.3	58.8	45.1	57.0	54.4	41.1	20.6	29.8	27.6	34.1	35.2	35.2	35.2
DOC-C loss (measured)	53.08	50.26	36.55	78.04	97.75	120.6	79.22	228.1	231.0	255.1	217.5	83.57	38.75	39.53	25.48	105.1	42.09	42.09	42.09
DOC-C loss (as % of total C loss)	14.5	12.8	8.42	13.4	17.9	18.1	12.6	32.3	39.20	34.6	31.4	15.5	8.00	8.54	6.03	22.9	8.86	8.86	8.86
Final litter C-to-N (S.E.)	42.18 (0.74)	33.94 (0.64)	24.30 (0.46)	31.83 (0.19)	41.17 (0.70)	29.61 (0.73)	26.31 (0.37)	40.69 (3.19)	48.64 (0.51)	30.41 (0.42)	26.52 (0.47)	33.59 (0.57)	89.48 (1.93)	64.82 (2.02)	53.37 (2.04)	36.01 (2.97)	29.72 (2.80)	29.72 (2.80)	29.72 (2.80)

tannins or phenols are in fact the among the most resistant to decay. Cellulose, although it is a large polymer, is composed primarily of glucose molecules that can be decomposed by a wide range of microorganisms (Paul and Clark, 1996) and therefore may be more easily accessed and consumed.

Total DOC leached correlates well with initial polar extractable carbon (Fig. 3) but not with initial cellulose, a further indication that many soluble compounds are leaving the litter layer without being degraded and that decomposition of larger polymers is not the primary source of DOC. However, numerous rapidly-occurring biological and physical–chemical processes affect DOC concentrations in the litter layer such that initial labile DOC may be consumed and other dissolved carbon compounds produced or released from litter, resulting in no net change in DOC leaching. Examination of chemical transformations of litter through measurement of specific groups of compounds (i.e. sugars, amino acids etc.) as well as measurements of CO₂ respiration, are necessary to determine specific processes involved in litter weight loss.

3.5. Carbon budget

Total carbon loss was calculated as the difference between initial and final litter carbon and the portion of C loss due to DOC leaching was determined (Table 4). Carbon loss not accounted for as DOC leaching was assumed to have been respired as CO₂. The proportion of total carbon lost via leaching varied widely with species but was not greatly affected by nitrogen treatments. Litterfall mass loss has generally been assumed to be equivalent to respiration (Olson, 1963; Bock, 1964; Blair, 1988; Aber and Melillo,

1991). However, given that 10–30% of carbon loss from decomposing litter can be accounted for by DOC leaching (Fig. 10), models of forest carbon balance which equate litter mass loss with respiration could overestimate soil carbon cycling and CO₂ fluxes to the atmosphere.

The high rate of transfer of carbon from litter to soil in dissolved form emphasizes the importance of understanding the fate of this carbon. Once DOC leaches from the litter layer, it may be respired at a lower point in the soil profile, therefore increasing CO₂ losses to the atmosphere. In contrast, the potential for chelation and sorption of DOC in the mineral horizon is high (McDowell and Wood, 1984; Jardine et al., 1989). Once DOC is retained in lower soil horizons, conversion to CO₂ could be forestalled for decades to centuries resulting in an accumulation of soil organic matter. In addition, transformations of carbon from labile compounds to complex or recalcitrant forms (McClagherty, 1983) would decrease DOC availability as a substrate for microbial respiration. Little is known of the relationship between these various carbon pathways, but the balance between them is a key determinant of carbon dynamics in forest soils.

4. Conclusions

Forest litter is an important source of DOC to the forest floor and lower soil horizons. The flux of DOC from litter to soils can vary widely depending on the species present. Nitrogen availability does not appear to alter the flux of DOC from litter, however, increased N availability does increase the DON flux thereby decreasing leachate DOC-to-DON ratio.

Leaching processes are also important for determining changes in the carbon and nitrogen chemistry of litter. Up to 30% of carbon loss from litter occurs as DOC leaching. N additions increase mass loss from litter without altering DOC leaching rates, indicating that DOC may not be the primary carbon source for microbial respiration. Instead, cellulose appears to be the most degraded carbon fraction.

Understanding the fate of DOC leached from litter to soils is critical for accurate predictions of carbon balances of forest soils. The processes controlling the adsorption, transformation and leaching of DOC are numerous, as are the number of compounds that comprise soil solution DOC. Measurements of total DOC, although applicable on a large scale, are inadequate for determining microbial carbon use dynamics. Fractionation of DOC by chemical class (Leenheer, 1981; David et al., 1989; Qualls and Haines, 1991) and by bioavailability (Yano et al., 1998) is essential for determining sources of labile carbon and understanding fine-scale carbon cycling dynamics.

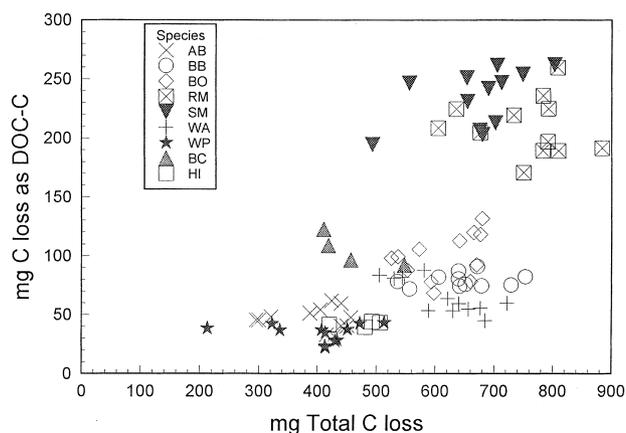


Fig. 10. DOC-C loss versus total C loss in mg C. Y-axis values are mean leached DOC concentration for the 15 weeks ($n = 11$ leachings) for each sample cup. X-axis values are total C loss from litter. Points represent individual cups; all treatments included.

Acknowledgements

Thanks go to Margaret Lefer, Jim Muckenhoupt, Steve Newman, Gloria Quigley and Amy Simoneau for laboratory assistance, to Bill Peterjohn for CHN analysis and to Margaret Lefer, Bill McDowell, Nancy Kinner and Steve Wondzell for valuable insight and contributions to this study.

References

- Aber, J.D., 1992. Nitrogen cycling and nitrogen saturation in temperate forest ecosystems. *Trends in Ecology and Evolution* 7 (7), 220–223.
- Aber, J.D., Melillo, J.M., 1991. *Terrestrial Ecosystems*. Saunders College Publishing, Philadelphia.
- Aber, J.D., Nadelhoffer, K.J., Steudler, P., Melillo, J.M., 1989. Nitrogen saturation in northern forest ecosystems. *Bioscience* 39 (6), 378–386.
- Aber, J.D., Melillo, J.M., McLaugherty, C.A., 1990. Predicting long-term patterns of mass loss, nitrogen dynamics and soil organic matter formation from initial fine litter chemistry in temperate forest ecosystems. *Canadian Journal of Botany* 68, 2201–2208.
- Aber, J.D., Magill, A.H., Boone, R., Melillo, J.M., Steudler, P., Bowden, R., 1993. Plant and soil responses to chronic nitrogen additions at the Harvard Forest, Massachusetts. *Ecological Applications* 3 (1), 156–166.
- Aerts, R., de Caluwe, H., 1997. Nutritional and plant-mediated controls on leaf litter decomposition of *Carex* species. *Ecology* 78 (1), 244–260.
- Ågren, G.I., Bosatta, E., 1988. Nitrogen saturation of terrestrial ecosystems. *Environmental Pollution* 54, 185–197.
- Anderson, J.M., 1973. The breakdown and decomposition of sweet chestnut (*Castanea sativa* Mill.) and beech (*Fagus sylvatica* L.) leaf litter in two deciduous woodland soils. II Changes in the carbon, hydrogen, nitrogen and polyphenol content. *Oecologia* 12, 275–288.
- Berg, B., 1986. Nutrient release from litter and humus in coniferous forest soils — a mini review. *Scandinavian Journal of Forest Research* 1, 359–369.
- Berg, B., Staaf, H., 1980. Leaching, accumulation and release of nitrogen in decomposing forest litter. In: Clark, F.E., Rosswall, T. (Eds.), *Terrestrial Nitrogen Cycles, Processes, Ecosystem Strategies and Management Impacts*, Vol. 33. *Ecological Bulletins-NFR*, Stockholm, pp. 163–178.
- Blair, J.M., 1988. Nitrogen, sulfur and phosphorus dynamics in decomposing deciduous leaf litter in the Southern Appalachians. *Soil Biology & Biochemistry* 20 (5), 693–701.
- Bocock, K.L., 1964. Changes in the amount of dry matter, nitrogen, carbon and energy in decomposing woodland leaf litter in relation to the activities of soil fauna. *Journal of Ecology* 52, 273–284.
- Bolster, K.L., Martin, M.E., Aber, J.D., 1996. Interactions between precision and generality in the development of calibrations for the determination of carbon fraction and nitrogen concentration in foliage by near infrared reflectance. *Canadian Journal of Forest Research* 26, 590–600.
- Coleman, D.C., Crossley, D.A., 1996. *Fundamentals of Soil Ecology*. Academic Press, San Diego.
- Currie, W.S., Aber, J.D., McDowell, W.H., Boone, R.D., Magill, A.H., 1996. Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests. *Biogeochemistry* 35, 471–505.
- Daubenmire, R., Prusso, D.C., 1963. Studies of the decomposition rates of tree litter. *Ecology* 44 (3), 589–592.
- David, M.B., Vance, G.F., Rissing, J.M., Stevenson, F.J., 1989. Organic carbon fractions in extracts of O and B Horizons from a New England spodosol: effects of acid treatment. *Journal of Environmental Quality* 18, 212–217.
- Dise, N.B., Wright, R.F., 1995. Nitrogen leaching from European forests in relation to nitrogen deposition. *Forest Ecology and Management* 71, 153–161.
- Durka, W., Schulze, E.D., Gebauer, G., Voerkelius, S., 1994. Effects of forest decline on uptake and leaching of deposited nitrate determined from ¹⁵N and ¹⁸O measurements. *Nature* 372 (22), 765–767.
- Fogel, R., Cromack Jr, K., 1977. Effect of habitat and substrate quality on Douglas fir litter decomposition in western Oregon. *Canadian Journal of Botany* 55, 1632–1640.
- Hedin, L.O., Armesto, J.J., Johnson, A.H., 1995. Patterns of nutrient loss from unpolluted, old-growth temperate forests: evaluation of biogeochemical theory. *Ecology* 76 (2), 493–509.
- Jardine, P.M., Weber, N.L., McCarthy, J.F., 1989. Mechanisms of dissolved organic carbon adsorption on soil. *Soil Science Society of America Journal* 53, 1378–1385.
- Kalff, J., Bentzen, E., 1984. A method for the analysis of total nitrogen in natural waters. *Canadian Journal of Fisheries and Aquatic Science* 41, 815–819.
- Killham, K., 1994. *Soil Ecology*. Cambridge University Press, Cambridge, England.
- Leenheer, J.A., 1981. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environmental Science and Technology* 15, 578–587.
- Lynch, J.M., 1982. Limits to microbial growth in soils. *Journal of General Microbiology* 128, 405–410.
- Magill, A.H., Downs, M.R., Nadelhoffer, K.J., Hallett, R.A., Aber, J.D., 1996. Forest ecosystem response to four years of chronic nitrate and sulfate additions at Bear Brooks Watershed, Maine, USA. *Forest Ecology and Management* 84, 29–37.
- Magill, A.H., Aber, J.D., Hendricks, J.J., Bowden, R.D., Steudler, P.A., Melillo, J.M., 1997. Biogeochemical response of forest ecosystems to simulated chronic nitrogen deposition. *Ecological Applications* 7 (2), 402–415.
- Magill, A.H., Aber, J.D., 1998. Long-term effects of experimental nitrogen additions on foliar litter decay and humus formation. *Plant and Soil* 203, 301–311.
- Magill, A.H., Aber, J.D., Berntson, G.M., McDowell, W.H., Nadelhoffer, K.J., Melillo, J.M., Steudler, P.A., submitted. Long-term nitrogen additions and nitrogen saturation in two temperate forests. *Ecosystems*.
- McLaugherty, C.A., 1983. Soluble polyphenols and carbohydrates in throughfall and leaf litter decomposition. *Acta Oecologica/Oecologia Generalis* 4 (4), 375–385.
- McLaugherty, C.A., Pastor, J., Aber, J.D., 1985. Forest litter decomposition in relation to soil nitrogen dynamics and litter quality. *Ecology* 66 (1), 266–275.
- McLaugherty, C., Berg, B., 1987. Cellulose, lignin and nitrogen concentrations as rate regulating factors in late stages of forest litter decomposition. *Pedobiologia* 30, 101–112.
- McDowell, W.H., Wood, T., 1984. Podzolization: soil processes control dissolved organic carbon concentrations in stream water. *Soil Science* 137 (1), 23–32.
- McDowell, W.H., Likens, G.E., 1988. Origin, composition and flux of dissolved organic carbon in the Hubbard Brook valley. *Ecological Monographs* 58 (3), 177–195.
- McDowell, W.H., Currie, W.S., Aber, J.D., Yano, Y., 1998. Effects of chronic nitrogen amendments on production of dissolved or-

- ganic carbon and nitrogen in forest soils. *Water, Air and Soil Pollution* 105, 175–182.
- Melillo, J.M., Aber, J.D., Muratore, J.F., 1982. Nitrogen and lignin control of hardwood leaf litter decomposition dynamics. *Ecology* 63 (3), 621–626.
- Melillo, J.M., Aber, J.D., Linkens, A.E., Ricca, A., Fry, B., Nadelhoffer, K.J., 1989. Carbon and nitrogen dynamics along the decay continuum: plant litter to soil organic matter. *Plant and Soil* 115, 189–198.
- Mitchell H.L., Chandler R.F., 1939. The nitrogen nutrition and growth of certain deciduous trees of northeastern United States. *The Black Rock Forest Bulletin No. 11*, Cornwall-On-The-Hudson, New York.
- Nadelhoffer, K.J., Downs, M.R., Fry, B., Aber, J.D., Magill, A.H., Melillo, J.M., 1995. The fate of ^{15}N labelled nitrate additions to a northern hardwood forest in eastern Maine. *Oecologia* 103, 292–301.
- Newman, S.D., Soulia, M.E., Aber, J.D., Dewey, B., Ricca, A., 1994. Analyses of forest foliage I: laboratory procedures for proximate carbon fractionation and nitrogen determination. *Journal of Near Infrared Spectroscopy* 2, 5–14.
- Olson, J.S., 1963. Energy storage and the balance of producers and decomposers in ecological systems. *Ecology* 44 (2), 322–331.
- Paul, E.A., Clark, F.E., 1996. *Soil Biology and Biochemistry*, second ed. Academic Press, San Diego.
- Qualls, R.G., Haines, B.L., 1991. Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. *Soil Science Society of America Journal* 55 (4), 1112–1123.
- Qualls, R.G., Haines, B.L., 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution and stream water. *Soil Science Society of America Journal* 56, 578–586.
- Qualls, R.G., Haines, B.L., Swank, W.T., 1991. Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. *Ecology* 72 (1), 254–266.
- Robertson, K., Schnürer, J., Clarholm, M., Bonde, T., Rosswall, T., 1988. Microbial biomass in relation to C and N mineralization during laboratory incubations. *Soil Biology and Biochemistry* 20 (3), 281–286.
- Smart, M.M., Reid, F.A., Jones, J.R., 1981. A comparison of persulfate digestion and the Kjeldahl procedure for determination of total nitrogen in freshwater samples. *Water Research* 15, 919–921.
- Smith, W.H., 1969. Release of organic materials from the roots of tree seedlings. *Forest Science* 15, 138–143.
- Sollins, P., McCorison, F.M., 1981. Nitrogen and carbon solution chemistry of an old growth coniferous forest watershed before and after cutting. *Water Resource Research* 17 (5), 1409–1418.
- Solorzano, L., Sharp, J.H., 1980. Determination of total dissolved nitrogen in natural waters. *Limnology and Oceanography* 25 (4), 751–754.
- Stoddard, J.L. 1994. Long-term changes in watershed retention of nitrogen: its causes and consequences. In: Baker, L.A. (Ed.), *Environmental chemistry of lakes and reservoirs*. American Chemical Society, Washington, DC, pp. 223–228.
- Swift, M.J., Heal, O.W., Anderson, J.M., 1979. *Decomposition in Terrestrial Ecosystems*. University of California Press, Berkeley, CA.
- Taylor, B.R., Parkinson, D., Parsons, W.F.J., 1989. Nitrogen and lignin content as predictors of litter decay rates: a microcosm test. *Ecology* 70 (1), 97–104.
- Technicon Industrial Systems, 1977. *Nitrate and Nitrite in Water and Seawater, Industrial Method 158-74W/A*. Technicon Industrial Systems, Tarrytown, NY.
- Technicon Industrial Systems, 1978. *Ammonium in Water and Seawater, Industrial Method 154-71W/B*. Technicon Industrial Systems, Tarrytown, NY.
- Vance, G.F., David, M.B., 1991. Chemical characteristics and acidity of soluble organic substances from a northern hardwood forest, central Maine, USA. *Geochimica et Cosmochimica Acta* 55, 3611–3625.
- Wright, R.F., van Breemen, N., 1995. The NITREX project: an introduction. *Forest Ecology and Management* 71, 1–5.
- Yano, Y., McDowell, W.H., Kinner, N.E., 1998. Quantification of biodegradable dissolved organic carbon in soil solution with flow-through bioreactors. *Soil Science Society of America Journal* 62 (6), 1556–1564.