



# Mineralization and nitrification patterns at eight northeastern USA forested research sites

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## Abstract

Nitrogen transformation rates in eight northeastern US research sites were measured in soil samples taken in the early season of 2000 and the late season of 2001. Net mineralization and nitrification rates were determined on Oa or A horizon samples by two different sampling methods—intact cores and repeated measurements on composite samples taken from around the cores. Net rates in the composite samples ( $n = 30$ ) showed three different temporal patterns: high net nitrification with minimal  $\text{NH}_4^+$  accumulation, high net nitrification and high  $\text{NH}_4^+$  accumulation, and minimal net nitrification and moderate  $\text{NH}_4^+$  accumulation. The 4-week net rates in intact cores were about half that of the rates from the composite samples but were well related ( $R^2 > 0.70$ ). Composite samples from sites that exhibited high net nitrification were incubated with acetylene and net nitrification was completely stopped, suggesting an autotrophic pathway. Gross mineralization and nitrification (2000 only) rates were estimated using the isotope dilution technique. Gross rates of nitrification and consumption in intact cores were relatively low. Gross rates of mineralization and net rates of nitrification were both related to the soil C/N ratio, with higher rates generally occurring in sites containing *Acer saccharum* as a dominant or co-dominant species. The comparison of methods suggests that all provide a similar hierarchy of potential rates but that the degree of net nitrification is strongly influenced by the degree of sample disturbance. Differences between sites appear to be related to an interaction of soil (C/N) and vegetation (*A. saccharum* contribution) characteristics.

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## 1. Introduction

Accurate measurements of forest soil N transformation rates are needed for nutrient cycling studies and ecosystem studies on the effects of elevated nitrogen deposition. Recent isotopic evidence has shown that the nitrate in deposition is cycled through the microbial pool before export (Murdoch et al., 1998; Burns

and Kendall, 2002; Mayer et al., 2002). Thus, the relationship between nitrogen deposition and watershed nitrogen loss can only be understood if we gain a better understanding of soil nitrification processes. Additionally, accurate nutrient cycling measurements are needed to be able to assess potential effects of ecosystem management, climate change and other perturbations.

Mineralization and nitrification rates have been related to numerous watershed characteristics. In addition to soil properties such as the C/N ratio, these include topography (Zak et al., 1991; Fisk et al., 1998;

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Ohrui et al., 1999), elevation (Kneopp and Swank, 1998; Bohlen et al., 2001), moisture and temperature variation (Gilliam et al., 2001), tree species (Finzi et al., 1998; Kneopp and Swank, 1998; Boerner and Koslowsky, 1989; Lovett et al., 2000, 2002, in press; Christ et al., 2002; Mitchell et al., 2003) and land-use or disturbance history (Zak et al., 1991; Goodale and Aber, 2001; Andersson et al., 2002). These relationships vary between watersheds and are not always consistent. For example, Verchot et al. (2001) and Bohlen et al. (2001) did not find a relationship between forest type and N transformation rates, and Walley et al. (1996) did not find a topographical effect on mineralization and nitrification rates. Also, the factors that affect differences in rates can be interrelated—landscape position has been found to determine species composition (Peterjohn et al., 1999) and elevation (besides the obvious effect on temperature) has been shown to affect the thickness of the forest floor and soil N pools (Lawrence et al., 2000; Bohlen et al., 2001).

Rates have been measured using many different sampling techniques and incubation conditions and time (see Binkley and Hart (1989) for a comprehensive review of methodology). Many researchers have used 4-week in situ incubations of either intact cores or bulked samples (e.g. Kneopp and Swank, 1998; Peterjohn et al., 1999; Gilliam et al., 2001); others have used shorter (e.g. Verchot et al., 2001) or longer field incubations (e.g. Ohrui et al., 1999), while others have used laboratory incubations, often at relatively warm temperatures (e.g. McNulty et al., 1991; Fernandez et al., 2000). Differences between intact cores and more disturbed, bulked samples have often been found to be minor. In a study of forested sites in Sweden and Denmark, Persson et al. (2000) found little difference in net N mineralization between intact cores and sieved soils. However, Ross and Bartlett (1990), Van Miegroet (1995) and Ross and Hales (2003) showed that soil  $\text{NO}_3^-$  concentrations could change dramatically within hours of obtaining bulked samples. In “sensitive” soils, short-term (3-day) net nitrification rates were over four times higher in bulked samples than intact cores (Ross and Hales, 2003). Not only is the incubation technique critical but the rapidity of the increase in net nitrification, in response to disturbance, also dictates that the initial measurements of  $\text{NH}_4^+$  and

$\text{NO}_3^-$  be taken as soon as possible after sampling. Comparisons between studies are obviously confounded by the different methodology.

In addition to the difference in techniques, most studies that attempt to relate N transformation rates to watershed characteristics have been performed in only one watershed. This also confounds comparisons between studies and we undertook the present investigation to compare consistent methodologies across a number of research sites in the northeastern US. We examined both net and gross N transformations in intact cores and also examined patterns of net  $\text{NH}_4^+$  and  $\text{NO}_3^-$  accumulation in bulked samples incubated for a 4-week period. The focus was on the Oa or A horizon because these usually have the highest transformation rates.

## 2. Methods and materials

### 2.1. Site descriptions

Eight research sites across the northeast were chosen to provide a range in geography and soil conditions (Table 1, Fig. 1). In the late season of 2000 (end of July–October), 16 samples were taken from these 8 research sites (Table 2). All but two were revisited in the early season (May–June) of 2001 and another sample taken within 10 m of the previous location. Brush Brook (Ross et al., 1994; Ross and Hales, 2003), Buck Creek (Lawrence, 2002), Cone Pond (Bailey et al., 1995; Hornbeck et al., 1997), Hubbard Brook Experimental Forest (HBEF) (Likens and Bormann, 1995), and Sleepers River (Shanley et al., 2002a,b) all have ongoing watershed research described in the associated citations. The sites sampled at HBEF study were adjacent to plots established outside of control watershed W6. We sampled outside of the nearest “low” plot and “high” plot described in Bohlen et al. (2001). The samples from Lye Brook and Mt. Mansfield were taken adjacent to recently established soil monitoring plots, part of a study designed by the Vermont Monitoring Cooperative to detect chemical changes over the next 200 years. Campbell et al. (2000, 2002) have investigated the stream chemistry in the Lye Brook Wilderness Area. The samples from the Neversink River basin, in the Catskill

Table 1

Characteristics of the sampling sites (the dominant tree species are those within a 5 m radius of the sampling site)

Site	Location	Elevation (m)	Dominant tree species
Brush Brook, D watershed	44°18.22'N, 72°53.48'W	710	<i>Betula alleghaniensis</i> , <i>A. saccharum</i>
Brush Brook, G watershed	44°18.16'N, 72°53.53'W	720	<i>B. alleghaniensis</i> , <i>A. saccharum</i>
Buck Creek, south watershed	43°44.32'N, 74°42.60'W	660	<i>F. grandifolia</i> , <i>B. alleghaniensis</i>
Buck Creek, north watershed	43°44.67'N, 74°42.56'W	620	<i>Picea rubens</i> , <i>F. grandifolia</i> , <i>B. alleghaniensis</i>
Cone Pond, in watershed	43°54.37'N, 71°36.47'W	515	<i>P. rubens</i> , <i>B. alleghaniensis</i>
Cone Pond, above pond	43°54.33'N, 71°36.39'W	500	<i>P. rubens</i> , <i>Tsuga canadensis</i>
HBEF, lower hardwood WS6	43°56.94'N, 71°44.08'W	525	<i>F. grandifolia</i> , <i>B. alleghaniensis</i>
HBEF, spruce–fir WS6	43°57.43'N, 71°44.39'W	775	<i>P. rubens</i> , <i>Betula papyrifera</i> , <i>B. alleghaniensis</i>
Lye Brook Trail Site	43°05.35'N, 73°02.44'W	810	<i>B. papyrifera</i> , <i>P. rubens</i> , <i>Abies balsamea</i>
Lye Brook Roadsite	43°03.42'N, 73°02.39'W	740	<i>F. grandifolia</i> , <i>A. saccharum</i>
Mt. Mansfield, Ranch Brook	44°29.75'N, 72°47.85'W	600	<i>A. saccharum</i> , <i>B. alleghaniensis</i>
Mt. Mansfield, Forehead	44°31.25'N, 72°48.94'W	1110	<i>P. rubens</i> , <i>A. balsamea</i>
Sleepers River, W9-C	44°29.54'N, 72°09.49'W	560	<i>F. grandifolia</i> , <i>B. alleghaniensis</i> , <i>P. rubens</i>
Neversink, ridgetop Maple A	41°58.09'N, 74°30.33'W	840	<i>F. grandifolia</i> , <i>A. saccharum</i>
Neversink, midslope Maple C	41°57.94'N, 74°30.86'W	730	<i>F. grandifolia</i> , <i>A. saccharum</i>

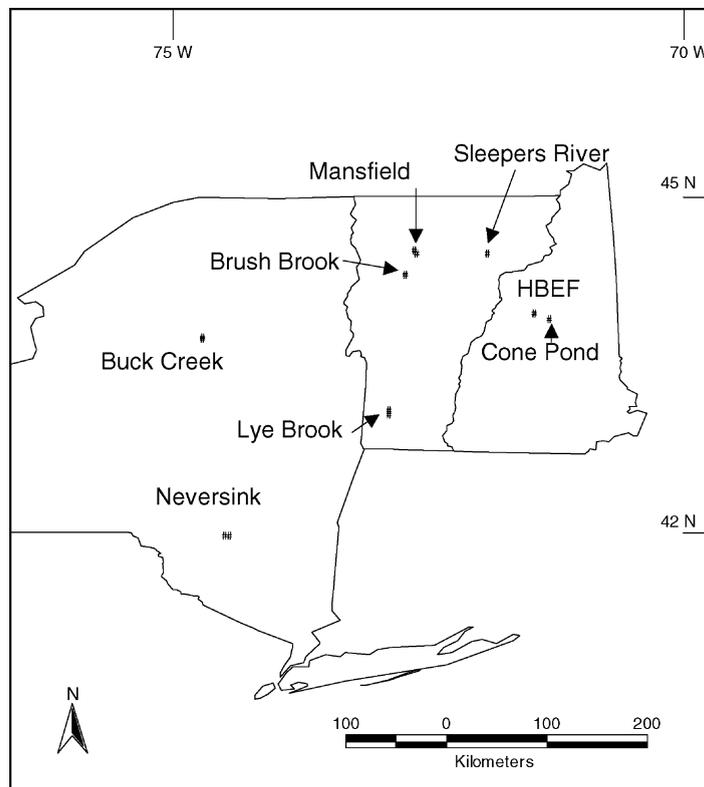


Fig. 1. Map showing location of research sites.

Table 2  
Sampling date and characteristics of the horizons sampled

Site	Sampling date	Horizon depth (cm)	C (%)	N (%)	C:N	CEC <sub>c</sub> (cmol <sub>c</sub> kg <sup>-1</sup> )	Ca/CEC	pH (1 mM CaCl <sub>2</sub> )	H <sub>2</sub> O (kg kg <sup>-1</sup> )
Brush Brook, D watershed	9 August 2000	5.2*	26.2	1.58	16.5	15.3	0.10	3.6	1.97
	8 May 2001	5.4	18.4	1.13	16.3	11.9	0.11	3.4	1.33
Brush Brook, G watershed (sampled four times)	25 July 2000	3.5	16.5	1.02	16.3	19.4	0.41	4.0	1.19
	2 October 2000	5.8	12.4	1.02	12.2	11.6	0.12	3.1	1.39
	25 May 2001	4.8	29.8	1.48	20.2	9.7	0.26	3.3	1.45
	19 June 2001	4.6	15.5	1.09	14.2	11.7	0.17	3.5	1.09
Buck Creek, south watershed	13 September 2000	4.2+	39.1	2.31	16.9	17.4	0.05	3.6	2.18
	23 May 2001	7.1	21.3	0.93	22.8	13.7	0.10	4.1	1.05
Buck Creek, north watershed	13 September 2000	5.1+	51.3	2.36	21.7	27.8	0.40	4.0	2.82
	23 May 2001	4.0+	50.2	2.50	20.1	27.8	0.29	3.0	2.94
Cone Pond, in watershed	31 August 2000	4.3+	50.1	2.20	22.8	28.7	0.06	3.2	1.68
	31 May 2001	4.5+	50.2	1.80	27.9	23.2	0.20	3.3	2.22
Cone Pond, above pond	31 August 2000	4.3+	43.5	2.05	21.2	22.1	0.05	3.2	1.83
	31 May 2001	4.1	46.9	1.38	34.1	25.7	0.28	3.4	2.05
Hubbard Brook, lower hardwood WS6	27 September 2000	5.0	36.3	1.80	20.2	14.3	0.43	3.4	1.53
	26 June 2001	4.8	44.9	2.01	22.3	13.0	0.40	4.3	2.21
Hubbard Brook, spruce–fir WS6	27 September 2000	6.3+	48.9	2.24	21.8	23.1	0.34	3.5	2.29
	26 June 2001	4.7+	50.7	2.10	24.1	23.6	0.38	4.0	2.33
Lye Brook Trailsite	2 August 2000	6.1+	45.2	2.26	20.0	20.6	0.47	3.6	2.58
Lye Brook Roadsite	2 August 2000	3.5	18.9	0.97	19.6	8.2	0.27	3.6	1.22
	12 June 2001	3.5	16.1	0.92	17.5	10.2	0.12	3.1	1.31
	31 July 2000	3.9	13.0	0.94	13.9	15.7	0.68	3.1	0.74
Mt. Mansfield, Ranch Brook	31 July 2000	4.0	36.6	2.52	14.5	22.2	0.04	3.0	3.51
	21 June 2001	3.6	40.1	2.18	18.4	19.1	0.10	3.3	3.11
Sleepers River, W9-C	25 October 2000	4.5+	8.9	0.49	18.1	7.4	0.45	3.3	0.36
	17 May 2001	2.7	42.0	2.10	20.0	30.1	0.64	3.4	1.55
Neversink, ridgetop Maple A	20 September 2000	3.2	37.4	2.21	17.0	21.3	0.09	3.5	2.11
	6 June 2001	2.8	32.8	1.85	17.7	18.8	0.09	3.4	1.73
Neversink, midslope Maple C	20 September 2000	3.7	15.9	0.94	16.9	10.2	0.13	3.2	0.76
	6 June 2001	1.9	8.1	0.46	17.5	8.7	0.12	3.2	0.57

\* Average depth from all intact cores. A “+” indicates that the horizon was deeper than the bottom of the core.

Mountains of New York, were collected on the ridge top and a midslope position, adjacent to the Dry Creek watershed (described in Burns and Kendall (2002)).

All but two sites (Lye Brook Trail and Mt. Mansfield Ranch Brook) consisted of mature, mixed-age stands with no cutting in at least the last 20 years (at least 80 years at some sites). The Lye Brook Trail and Mt. Mansfield Ranch Brook sites were both pole size stands, also uncut for at least 20 years. The Mt. Mansfield Forehead site was somewhat different from the other sites; it is a typical high-elevation stand dominated by balsam fir, with a canopy height of 10 m, and natural disturbance openings creating a mixed open-closed canopy. At each sampling point,

the dominant tree species within a 5 m radius were noted by both stem density and diameter. The species are listed in Table 1 in the approximate order of their basal area. This listing does not thoroughly describe the site diversity and, because it is only a field description of trees within a 5 m radius, it does not necessarily reflect the watershed as a whole.

## 2.2. Net rate measurements in bulked, homogenized samples

At each sampling location (Table 2), a bulked, homogenized near-surface horizon sample was collected. We sampled the first horizon below the Oe that was at least 2 cm thick. In 22 cases, this was an Oa

(those in Table 2 with >18% C) but there were 6 A horizons and 2 B horizons (Sleepers River, 25 October 2000 and Neversink midslope, 6 June 2001). Approximately 2 l of soil were sampled and mixed by hand (not sieved), removing coarse debris and larger roots. Extraction of 10 ml subsamples with 25 ml of 2 M KCl (in triplicate) was done as soon as possible after initiating sampling (20–30 min). The samples were shaken intermittently by hand for 15 min and put into an ice chest. The bulked horizon sample was kept in a polyethylene bag in a cooler containing “blue” ice until return to the lab and then incubated in the dark at 12 °C. Additional subsamples were extracted 3–5 times over the next 10 h and again after 1 day; 2, 3, and/or 4 days; and 1, 2, 3 (2001 only), and 4 weeks. Samples from the first 10 h were kept on ice until centrifuging, either the same day or the next morning. Preliminary work with samples from Brush Brook showed that delaying centrifugation for as much as 4 days did not affect nitrate concentrations. Increases in ammonium were found but only after 2 days (data not shown). Nitrate and ammonium were determined on a flow-injection autoanalyzer (Lachat QuickChem AE, Lachat Instruments, Milwaukee, WI) using the Cd-reduction method for nitrate and the salicylate-nitroprusside method for ammonium. Duplicate 10 ml samples were weighed and dried at 80 °C to determine both soil moisture content and the solution:soil ratio of the extraction. We use “mineralization” to describe the production of ammonium and “nitrification” to describe the production of nitrate from ammonium.

### 2.3. Net rate measurements in intact cores

At each sampling location (Table 2), intact cores were collected from the same area as the bulk sampling (and prior to) by pressing metal cans (11 cm tall × 8.5 cm diameter) into the soil while cutting around the leading edge with a sharp knife. The cores were twisted and removed, put into polyethylene bags and stored in a cooler until return to the lab. Three cores were taken in 2000 and five in 2001. In the lab, the cores were incubated in the dark at 12 °C with the bags open at the top. After 4 weeks, the cores were dismantled and the horizon sampled for the bulked measurements (usually Oa, see above) was separated. To minimize disturbance from edges, approximately

1 cm was cut and discarded from the outside circumference and, if the sampled horizon was exposed on the bottom of the core, 1 cm was removed from the bottom. The remaining sample was homogenized by hand and triplicate 10 ml samples were extracted with 2 M KCl. After 15 min of reciprocal shaking, the samples were centrifuged and filtered. Inorganic N concentration, soil water content and the dry weight of 10 ml were determined as described above.

### 2.4. Gross rate measurements

Gross rates of mineralization and nitrification were measured using the isotope dilution method (Hart et al., 1994). In 2000, intact cores were sampled, as described above, in four blocks of four. Two from each block were treated with 5 μmol of 99% <sup>15</sup>N as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and two treated with a similar concentration of <sup>15</sup>N as KNO<sub>3</sub>. In 2001, five blocks of two cores were taken and treated with 5 μmol of 99% <sup>15</sup>N as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> only. The <sup>15</sup>N treatment was distributed between a depth of 4 and 8 cm by using repeated injections. One core from each treatment was taken apart and extracted in the field and a second core was extracted after about 24 h of incubation at 12 °C in the laboratory. The same horizon used for the bulked sample was sliced from the core, homogenized and extracted with 2 M KCl (120 ml soil:240 ml KCl). Dry weights were determined on separate volumetric samples and these subsamples were ground and analyzed for C and N. The Mason-jar diffusion method of Khan et al. (1998) was used to collect the inorganic N for isotopic analysis. In this procedure, an aliquot of the KCl extract was incubated in a sealed jar with added base (MgO) to convert the NH<sub>4</sub><sup>+</sup> to NH<sub>3</sub>. Acidified paper disks were suspended above the extract to trap the released NH<sub>3</sub>. Separate aliquots of the KCl extract were used for collecting either NH<sub>4</sub><sup>+</sup> or NH<sub>4</sub><sup>+</sup> + NO<sub>3</sub><sup>-</sup>. For the latter, the NO<sub>3</sub><sup>-</sup> was converted to NH<sub>4</sub><sup>+</sup> by addition of 0.2 g of Devarda's alloy (Fluka Chemical). Additional KCl (solid) was added to each jar to bring the final concentration to approximately 4 mol l<sup>-1</sup>. Each aliquot was spiked with 100 μg of N as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> to provide adequate N for analysis by mass spectrometry. The acidified filter paper disks were analyzed for % atom excess <sup>15</sup>N by the <sup>15</sup>N Analysis Service at the University of Illinois. Concentrations of

inorganic N were measured as described above and gross rates were calculated as described in Hart et al. (1994).

### 2.5. Acetylene additions

At five sites in 2001, subsamples of the bulked horizon were incubated with acetylene, the common method that has been shown to block autotrophic but not heterotrophic nitrification (Hynes and Knowles, 1978). Ten-milliliter subsamples were placed in fifteen 100 ml gas-tight glass bottles and 1 ml of acetylene was added through septa (within about 30 min of sampling). Extraction with 2 M KCl was done in triplicate, three times during the first 10 h after sampling; and after 1 day, 2–4 days and 7 days. After returning to the lab, incubation was in the dark at 12 °C. Inorganic N, dry weights and moisture content were measured as described above.

### 2.6. Soil chemical analysis

Soil pH was determined on moist 5 ml subsamples in 10 ml of 1 mmol l<sup>-1</sup> CaCl<sub>2</sub>. This salt concentration was chosen, rather than a water-pH, to minimize the differences between samples caused by increases in solution ionic strength from nitrate accumulation. For soil C and N analysis, the dried subsamples (used to determine water content) were ground to pass through a 0.125 mm sieve and C and N were determined on an elemental analyzer (CE440, Control Equipment, Lowell, MA) using NIST apple leaves and a USGS soil standard as quality control. Using these same finely sieved samples, acid-insoluble organic matter (OM) was determined by the lignin procedure of Van Soest (1963) using an automated agitation system (Ankom Technology, Fairport, NY). The sample was treated with a detergent solution, followed by 12 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and the remaining OM determined by weight loss on ignition. The percent acid-insoluble OM was calculated assuming the total OM = 1.724 × C. The effective cation exchange capacity (CECe) was determined by the BaCl<sub>2</sub> method of Hendershot and Duquette (1986) using air-dried 2 mm-sieved samples. Weighed 2 ml subsamples were used rather than 2 g and the resulting solution:soil ratio varied between 11:1 and 60:1. Exchangeable cations (Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Fe<sup>2+</sup> and Mn<sup>2+</sup>) were determined

by inductively coupled plasma atomic emission spectrometry, using standard conditions, and exchangeable H<sup>+</sup> was estimated from the pH of the extract.

## 3. Results and discussion

### 3.1. Patterns of N accumulation (net rates)

The repeated subsampling of bulked horizon samples revealed three distinct patterns of net mineralization (ammonification) and nitrification (Figs. 2 and 3). In Pattern 1, the soils from Brush Brook (Figs. 2 and 3a), Buck Creek South (Fig. 3h), Lye Trailsite and Mansfield Ranch Brook (not shown) all had large net increases in NO<sub>3</sub><sup>-</sup> only. In 9 of the 10 of these samples, the NH<sub>4</sub><sup>+</sup> concentration was lower after 4 weeks than the initial field-extracted value. Pattern 2 was high net nitrification along with relatively high net increases in NH<sub>4</sub><sup>+</sup>, shown in soils from Neversink (Fig. 3c and d) and Lye Brook Roadsite (Fig. 3b). In these six samples, the net increase in mineralization appeared to lag behind the increase in nitrate. Pattern 3, higher net mineralization than net nitrification, was found in the remaining 16 samples. Soils from Sleepers River (Fig. 3e) and Mansfield Forehead (Fig. 3f) showed relatively high rates of mineralization and low rates of nitrification. Negligible net nitrification was found in the samples from HBEF (Fig. 3i and j) and Cone Pond (Fig. 3k and l). These three patterns were consistent across the two sampling periods (late season 2000 and early season 2001) but overall rates were almost always higher in the early season samples of 2001 (Table 3). Although it is well known that there is high spatial variability in measured N transformation rates, within-site differences (samples taken with 10 m of each other) in patterns were much less than between sites (Figs. 2 and 3).

Similar patterns (high NO<sub>3</sub><sup>-</sup> only, high NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, or NH<sub>4</sub><sup>+</sup> only) were found by Vitousek et al. (1982) in an earlier defining study of N mineralization potential. Identical methods were used in both studies, i.e. subsamples of a composite soil sample extracted over time, except that Vitousek et al. incubated their samples at 20 °C in aerated plastic cups, maintained the water content at -10 kPa, and sampled weekly. We incubated our bulked samples at 12 °C in sealed plastic bags and subsampled more

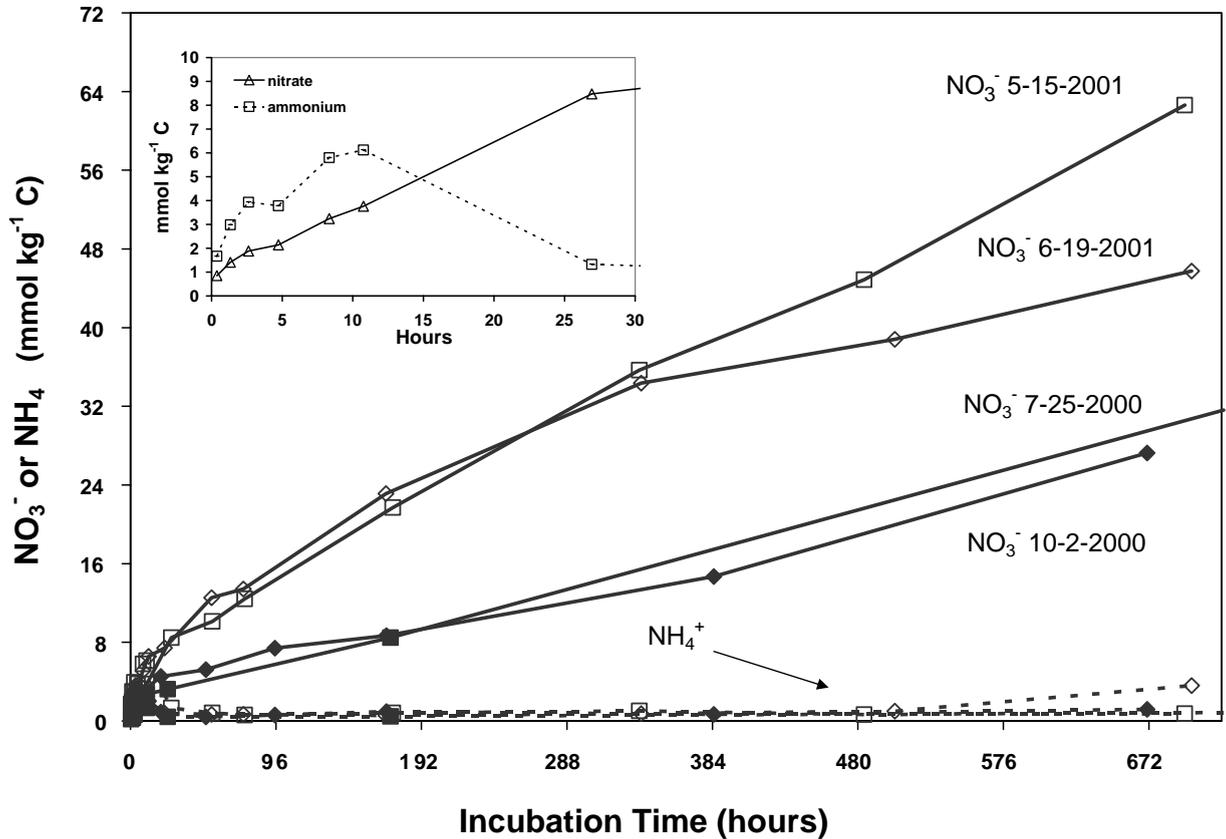


Fig. 2. Net mineralization (ammonification) and nitrification in bulked horizon samples taken from Brush Brook, watershed G. Inset shows the pattern over the first day of incubation.

frequently, especially during the first few days of incubation. In samples from some western US forest types, Vitousek et al. (1982) observed NO<sub>3</sub><sup>-</sup> accumulation only after an initial lag period. We observed no such lag period in any of our samples that accumulated NO<sub>3</sub><sup>-</sup> but our study did not encompass as many forest types or as wide a geographical region.

In our samples that had substantial increases over 4 weeks in either NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup>, there was always a higher rate of increase over the first 10–30 h (most apparent in Fig. 3e–g). This increase was linear over the first 10 h with differences detectable within 1 h of sampling. Those samples that showed rapid NO<sub>3</sub><sup>-</sup> accumulation (Patterns 1 and 2) consistently had increases in NH<sub>4</sub><sup>+</sup> over the first 10–30 h followed by a decline (see inset in Fig. 2 and Ross and Hales (2003) for more examples). As discussed above, many samples remained low in NH<sub>4</sub><sup>+</sup> for the remainder of

the incubation period (Pattern 1) but others had increases following a lag period (Pattern 2). As a result, the Pattern 1 samples switched from having a higher concentration of ammonium in the field to higher nitrate in the incubation, with the change usually occurring within the first 48 h (Fig. 2 inset).

The amount of either NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup> that accumulated in the intact cores was related to the concentrations in bulked samples (Figs. 4 and 5). In the Pattern 1 samples, the intact core NH<sub>4</sub><sup>+</sup> was always higher than in the 4-week bulked sample. The mixing apparently stimulated greater conversion of the available NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup>, possibly by reducing spatial heterogeneity (Davidson and Hackler, 1994). If sampling-induced disturbance stimulates net N transformations, intact cores should provide a closer estimate of in situ rates than bulked sample measurements. However, there is still a degree of disturbance in the cores; roots are

severed and plant uptake ceases. These conditions may increase the  $\text{NH}_4^+$  supply to microorganisms (through a decrease in plant consumption) and cause net nitrification increases that would not be observed in situ yet would still be lower than found in bulked samples.

### 3.2. Gross rate measurements

Gross mineralization rates, measured with the isotope dilution method (Hart et al., 1994) in intact cores, also showed differences between the two sampling periods, late season 2000 or early season 2001 (Fig. 6).

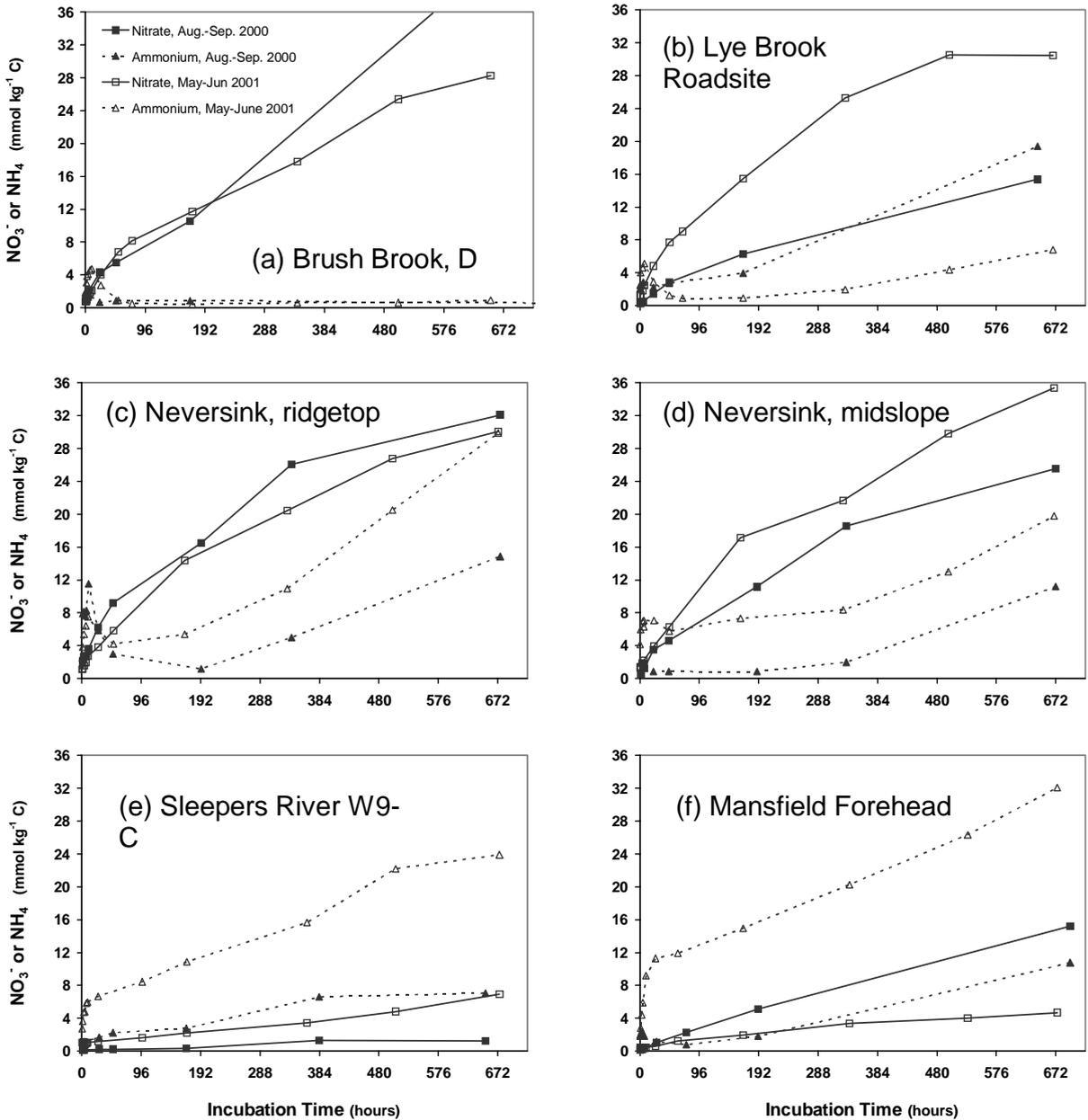


Fig. 3. Net mineralization (ammonification) and nitrification in bulked horizon samples from 12 locations in 8 research sites.

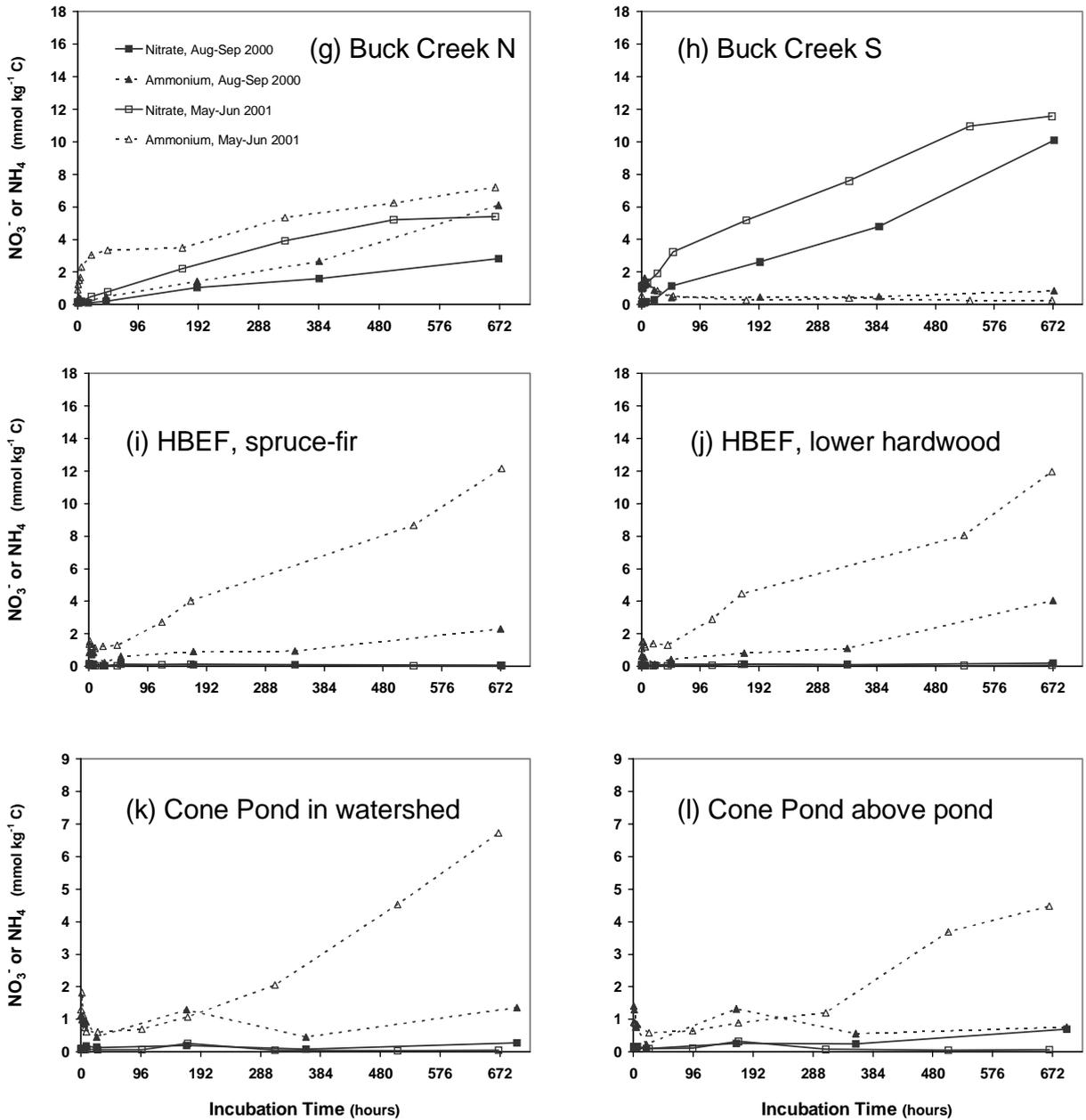


Fig. 3. (Continued).

Although there was considerable variability, higher gross rates were found at lower C:N ratios. The variability generally increased with increasing rates and probably reflects the intrinsic variability often found in forest soils. Gross consumption of ammo-

nium closely followed the gross mineralization rates with the exception of both sites at HBEF and Cone Pond in 2000, which had low mineralization but relatively high consumption. The difference between years (or seasons) at these sites was reflected both in

Table 3  
Net nitrification and mineralization rates in composite samples and gross mineralization rates in intact cores

Site	Sampling date	Soil temperature (°C)	Net nitrification ( $\mu\text{mol kg}^{-1} \text{C h}^{-1}$ )			Mineralization ( $\mu\text{mol kg}^{-1} \text{C h}^{-1}$ )		
			10 h rate <sup>a</sup>	24 h rate	4-Week rate	Net 24 h rate	Net 4-week rate	Gross 24 h rate
Brush Brook, D watershed	9 August 2000	15	272	155	64	-50	-1.6	122
	8 May 2001	5	149	132	42	37	-1.4	248
Brush Brook, G watershed	25 July 2000	13	248	124	43	-31	-1.6	55
	2 October 2000	7	ns <sup>b</sup>	108	37	-41	-0.8	nd <sup>c</sup>
	25 May 2001	14	266	283	89	-13	-1.3	266
Buck Creek, north watershed	19 June 2001	11	353	223	62	-34	2.9	277
	13 September 2000	nd	ns	12	15	-8.8	-0.3	93
Buck Creek, south watershed	23 May 2001	9	29	31	16	12	-0.4	102
	13 September 2000	15	ns	-0.7	4.0	-9.3	8.5	46
Cone Pond, in watershed	23 May 2001	8	ns	14	7.9	98	9.4	76
	31 August 2000	nd	ns	2.0	0.3	-26	0.4	15
Cone Pond, above pond	31 May 2001	6	ns	-0.8	-0.1	-25	8.1	64
	31 August 2000	15	0.9	-0.6	0.8	-56	-0.9	66
Hubbard Brook, lower hardwood WS6	31 May 2001	6	ns	-2.4	-0.1	-13	5.4	53
	27 September 2000	nd	ns	-1.6	0.2	-24	5.1	nd
Hubbard Brook, spruce-fir WS6	26 June 2001	13	ns	-0.6	0.0	16	16	67
	27 September 2000	nd	ns	-4.3	-0.1	-25	2.2	nd
Lye Brook Trailsite	26 June 2001	11	-5.9	-2.9	-0.1	-5.8	16	85
	2 August 2000	16	70	47	19	-44	-1.2	nd
Lye Brook Roadsite	2 August 2000	15	47	53	23	6.5	27	97
	12 June 2001	10	189	162	44	18	6.5	336
Mt. Mansfield, Ranch Brook	31 July 2000	nd	ns	98	52	-12	-2.0	270
Mt. Mansfield, forehead	31 July 2000	13	25	33	22	-25	13	118
	21 June 2001	9	ns	13	6.3	161	45	230
Sleepers River, W9-C	25 October 2000	10	ns	2.8	1.7	30	9.6	75
	17 May 2001	8	ns	6.1	8.7	150	31	170
Neversink, ridgetop Maple A	20 September 2000	13	139	156	44	-78	10.3	nd
	6 June 2001	8	168	104	43	129	41	364
Neversink, midslope Maple C	20 September 2000	15	ns	137	37	-50	13.8	nd
	6 June 2001	9	139	114	51	128	23	845

<sup>a</sup> Calculated from least squares fit. All other rates calculated from two points.

<sup>b</sup> Not significant.

<sup>c</sup> Not determined.

the gross and net rates of mineralization, with both being much higher in the 2001 samples.

Gross nitrification rates were measured in 2000 only and were relatively low compared to other reports (Stark and Hart, 1997; Stottlemeyer and Toczydlowski, 1999; Verchot et al., 2001). Consumption of  $\text{NO}_3^-$  was also relatively low and usually close to the gross nitrification rate (Table 4). The low consumption suggests low abiotic fixation of the added nitrate. The gross nitrification rates were often similar to the net rates measured in intact cores (Fig. 7a,

Table 4) and usually much lower than the net rates measured in the bulked samples over the same time period (Fig. 7b). The latter is obviously not possible unless there was either an error in the measurement or a change in rates induced by homogenizing the sample. Large sampling-induced increases in net nitrification have been shown to occur in the Brush Brook watershed (Ross and Hales, 2003) and samples from that watershed show the highest net rates reported in this study. All samples that had high rates of net nitrification (Pattern 1 or 2) also had greater

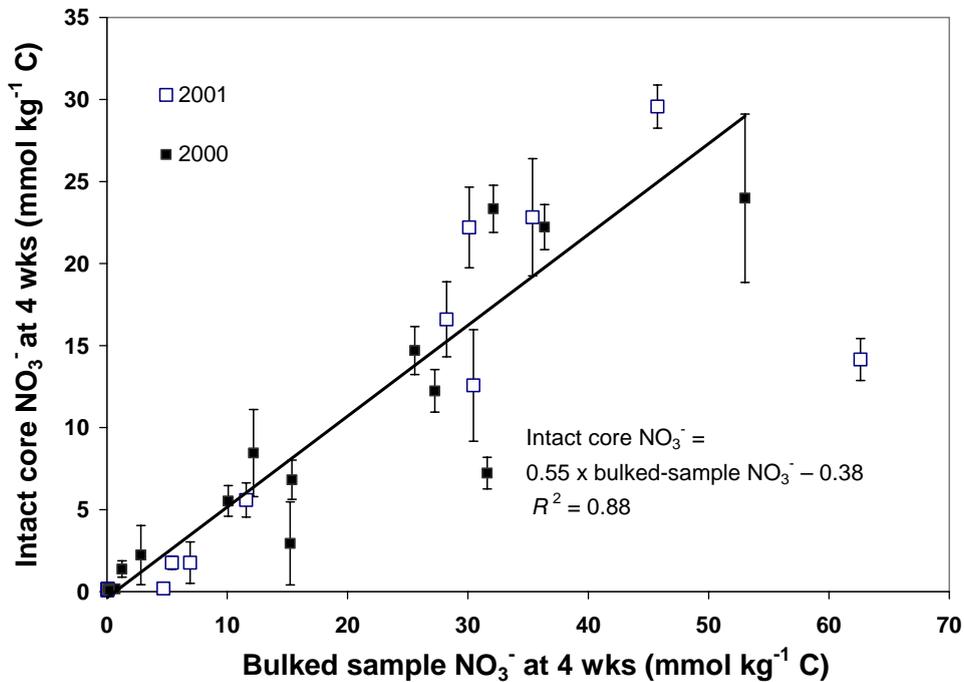


Fig. 4. Comparison of nitrate concentrations after 4 weeks of incubation in bulked horizon samples and the same horizon from intact cores. The outlier (bulk sample  $\text{NO}_3^-$  above  $60 \text{ mmol kg}^{-1}$ ) was from the Brush Brook G watershed in April 2001 and had the highest  $\text{H}_2\text{O}$  content (relative to C content) of any sample ( $>3$  standard deviations above the mean), suggesting possible anaerobiosis in the intact cores. Error bars represent  $\pm$  the standard error.

bulk-sample net nitrification than intact-core gross nitrification. Thus it is likely that bulked-sample rates are often much higher than actual in situ rates and need to be strictly used as potential rate estimates.

It is instructive to compare the gross rates of mineralization in intact cores with the combined net rates of mineralization and nitrification in bulked samples (Fig. 8). The similarity in the rates, although offset from a 1:1 relationship, suggest that bulking the samples induced a switch from  $\text{NH}_4^+$  consumption (other than nitrification) to nitrification. The decrease in consumption may also have caused the high initial rates of net mineralization in many of the bulked samples, discussed above. The increase in  $\text{NH}_4^+$  combined with a decrease in spatial heterogeneity could cause a rapid response in the ammonia oxidizing community. This adds support to the hypothesis that in situ rates of nitrification may be much lower than those measured, in either intact cores or bulked samples. The measurement of mineralization and nitrification potential is possible by many methods and results

show a good relationship between two common sampling procedures. However, comparisons among studies will not be valid unless similar methods were used. The bulked-sample method is somewhat easier to perform and the homogenization reduces variability. It is important to obtain an initial extraction as soon as possible after disturbance and it is critical to express the results as potential rates only.

### 3.3. Acetylene inhibition of nitrification

There has been debate as to whether ammonia oxidation in acid soils is carried out primarily by chemoautolithotrophic bacteria (e.g. *Nitrosospira* species) or heterotrophic bacteria (see De Boer and Kowalchuk (2001) for a recent review). In the 2001 sampling, we incubated bulked subsamples from each watershed that showed net nitrification (Patterns 1 and 2) in an atmosphere of 1% acetylene. This technique continues to be used to differentiate the different oxidation pathways (De Boer and Kowalchuk, 2001). No detectable change

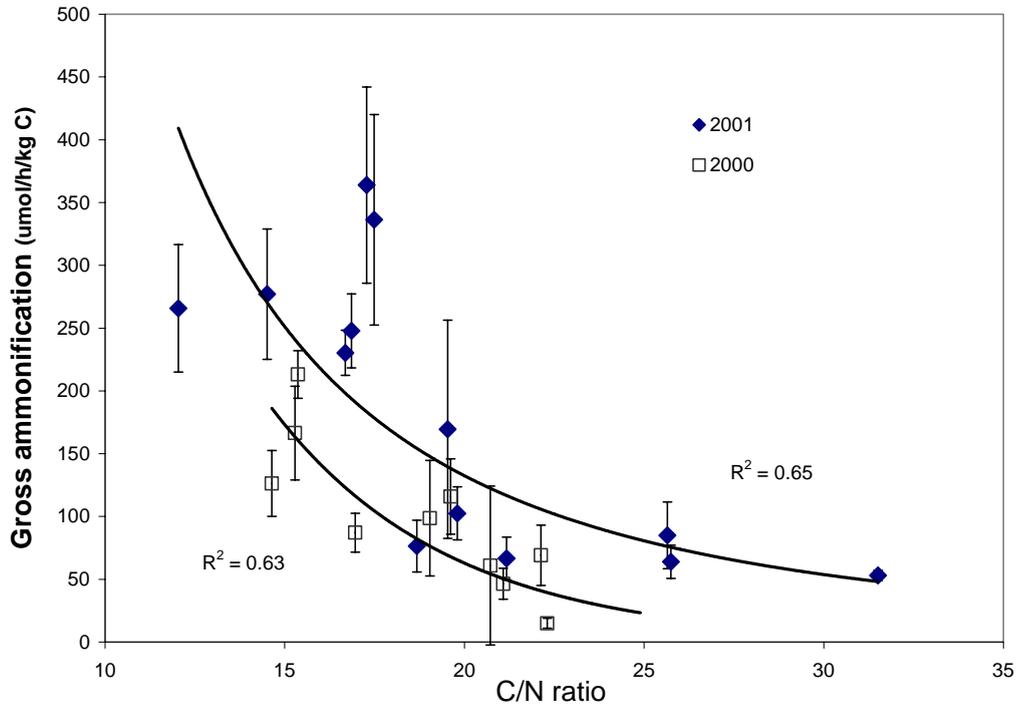


Fig. 5. Comparison of ammonium concentrations after 4 weeks of incubation in bulked horizon samples and the same horizon in intact cores. Error bars represent  $\pm$  the standard error.

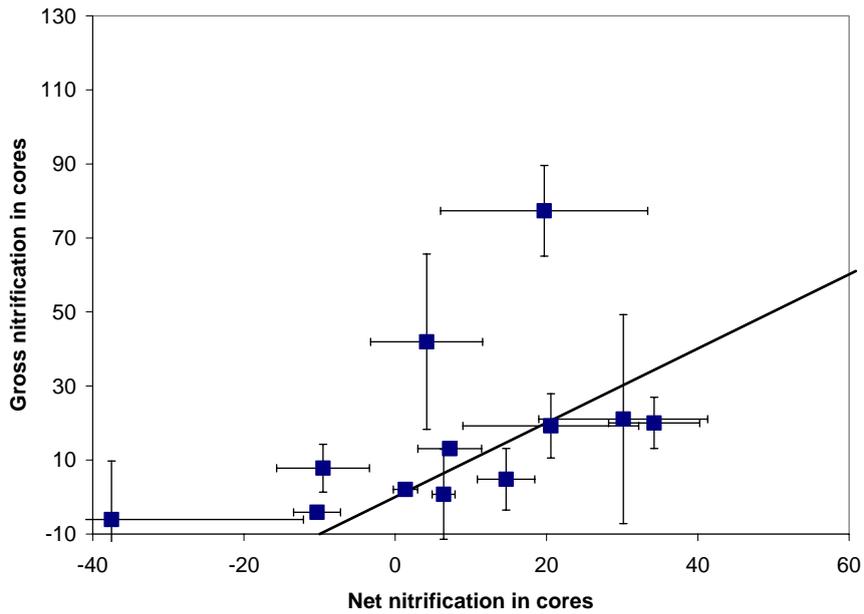


Fig. 6. Gross mineralization (ammonification) rates in intact cores vs. the C:N ratio. Error bars represent  $\pm$  the standard error.

Table 4  
Gross and net nitrification rates in intact cores from the 2000 sampling period

Site	Sampling date	Gross nitrification, 24 h rate ( $\mu\text{mol kg}^{-1} \text{C h}^{-1}$ )		Gross $\text{NO}_3$ consumption ( $\mu\text{mol kg}^{-1} \text{C h}^{-1}$ )		Net nitrification in the intact cores ( $\mu\text{mol kg}^{-1} \text{C h}^{-1}$ )	
		Mean	S.E.	Mean	S.E.	Mean	S.E.
Brush Brook, D watershed	9 August 2000	21.1	28.2	-1.8	35.8	30.1	11.2
Brush Brook, G watershed	25 July 2000	42.0	23.7	37.8	25.2	4.1	7.4
	2 October 2000	25.6	14.2	16.5	14.2	9.0	11.6
Buck Creek, north watershed	13 September 2000	0.7	12.1	-5.6	13.0	6.4	1.5
Buck Creek, south watershed	13 September 2000	2.1	1.5	0.7	0.3	1.3	1.6
Cone Pond, in watershed	31 August 2000	7.8	6.5	12.3	5.5	-9.6	6.1
Cone Pond, above pond	31 August 2000	-6.1	15.8	31.4	13.1	-37.5	25.4
Hubbard Brook, lower hardwood WS6	27 September 2000	-1.3	0.6	-0.2	0.8	-1.2	1.1
Hubbard Brook, spruce-fir WS6	27 September 2000	-1.3	2.8	-1.3	2.5	0.0	1.4
Lye Brook Trailsite	2 August 2000	13.1	1.3	8.1	2.7	7.2	4.2
Lye Brook Roadsite	2 August 2000	19.2	8.7	-1.3	10.9	20.6	11.6
Mt. Mansfield, Ranch Brook	31 July 2000	4.8	8.3	-9.8	10.4	14.7	3.8
Mt. Mansfield, forehead	31 July 2000	-4.1	1.4	6.2	4.5	-10.3	3.1
Sleepers River, W9-C	25 October 2000	-2.1	11.6	0.7	2.9	-2.7	13.1
Neversink, ridgetop Maple A	20 September 2000	77.4	12.2	57.7	16.5	19.7	13.7
Neversink, midslope Maple C	20 September 2000	20.0	6.9	-12.9	7.2	34.2	6.0

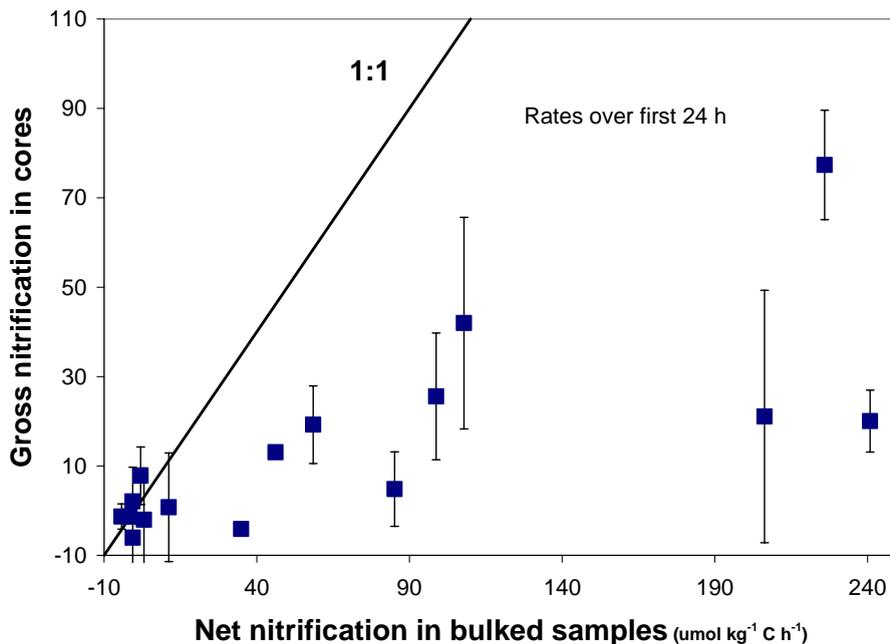


Fig. 7. (a) Comparison of gross and net nitrification rates in the intact cores from the 2000 sampling; (b) gross nitrification rates in intact cores vs. the net nitrification rates in bulked, composite samples taken from around the cores. Error bars represent  $\pm$  the standard error.

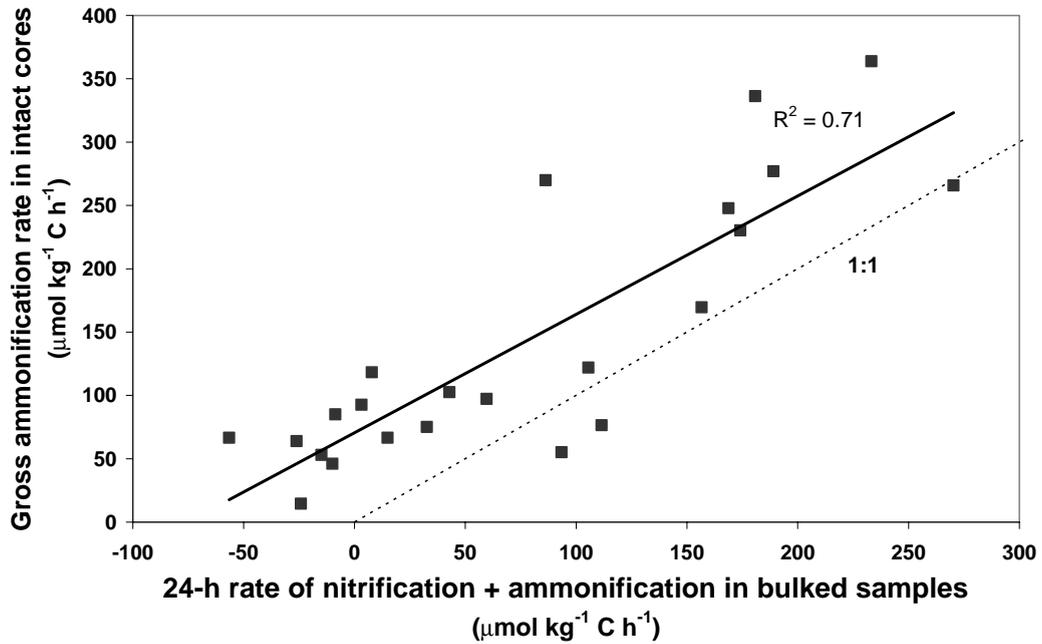


Fig. 8. Gross mineralization (ammonification) in intact cores vs. the sum of the net nitrification and mineralization in composite samples taken from around the cores.

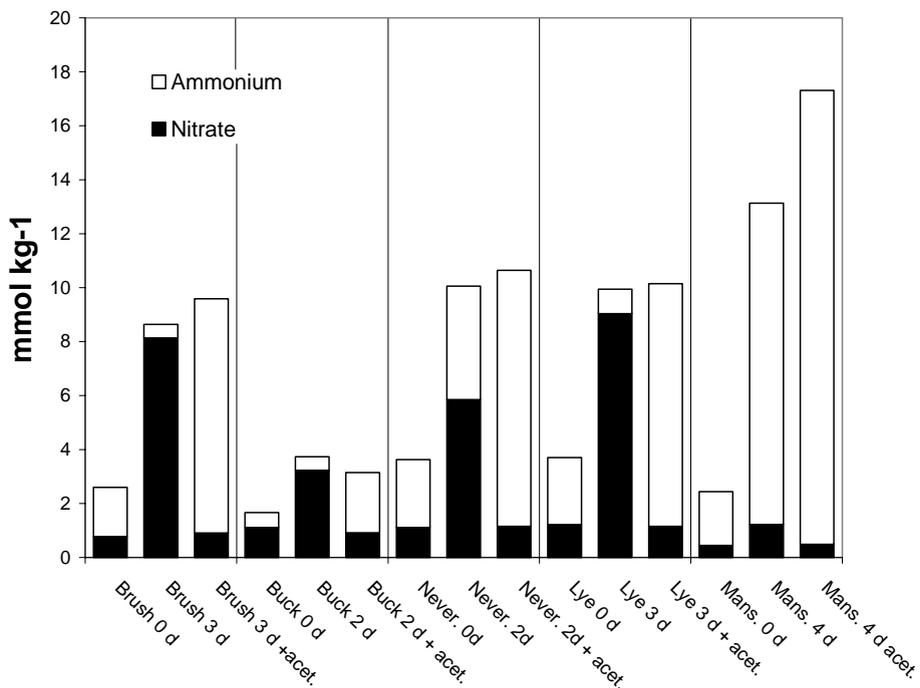


Fig. 9. Net accumulation of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in composite samples from five of the research sites incubated with and without 1% acetylene.

occurred in the concentration of  $\text{NO}_3^-$  in samples incubated with acetylene (Fig. 9). In each case, six measurements were made over a 7-day period and the average concentration of the five sites was  $0.93 \text{ mmol kg}^{-1}$  at the time of sampling and  $0.92 \text{ mmol kg}^{-1}$  after 7 days of incubation. It is interesting to note that the sum of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  stayed relatively constant during the incubation, regardless of treatment. Also, the  $\text{NO}_3^-$  concentration did not decrease in the acetylene-treated samples, i.e. there was either no consumption or remarkably similar rates of consumption and production. Additional evidence, mainly from molecular studies, is accumulating to show that autotrophic oxidation is the primary mechanism of nitrification in acid forest soils (De Boer and Kowalchuk, 2001). Our acetylene treatments support this hypothesis.

#### 3.4. Relationship of rates to soil and site properties

The propensity for forest soils to exhibit net nitrification has been linked to the C/N ratio by many researchers (Persson et al., 2000; Goodale and Aber, 2001; Aber et al., 2003). Low to negligible net

nitrification rates have been found above a C/N ratio between 22 and 25. A linear relationship with relative nitrification (the fraction of net inorganic N that is  $\text{NO}_3^-$ ) has been found below this C/N ratio, but often with considerable scatter. We obtained similar results using either the absolute rate of nitrification in the bulked samples (Fig. 10) or relative rates (not shown). The relative rates did not give as strong a relationship because the Pattern 1 soils all had nearly 100%  $\text{NO}_3^-$  in the bulked sample incubations. The samples that showed the highest nitrification rates all had *Acer saccharum* as either the dominant or co-dominant overstory tree within a 5 m radius of the sampling site (Table 1). The impact of *A. saccharum* species on nitrification rates has been shown in a number of studies (Boerner and Koslowsky, 1989; Finzi et al., 1998; Lovett et al., 2000, 2002, in press; Christ et al., 2002; Mitchell et al., 2003). In our study, the separation into *A. saccharum* and non-*A. saccharum* sites showed two different relationships between nitrification and C/N ratio (although it could be argued that there is only one scattered relationship below a C/N of 25). Lovett et al. (in press), in a study of species effect on nitrification rates in the Catskills

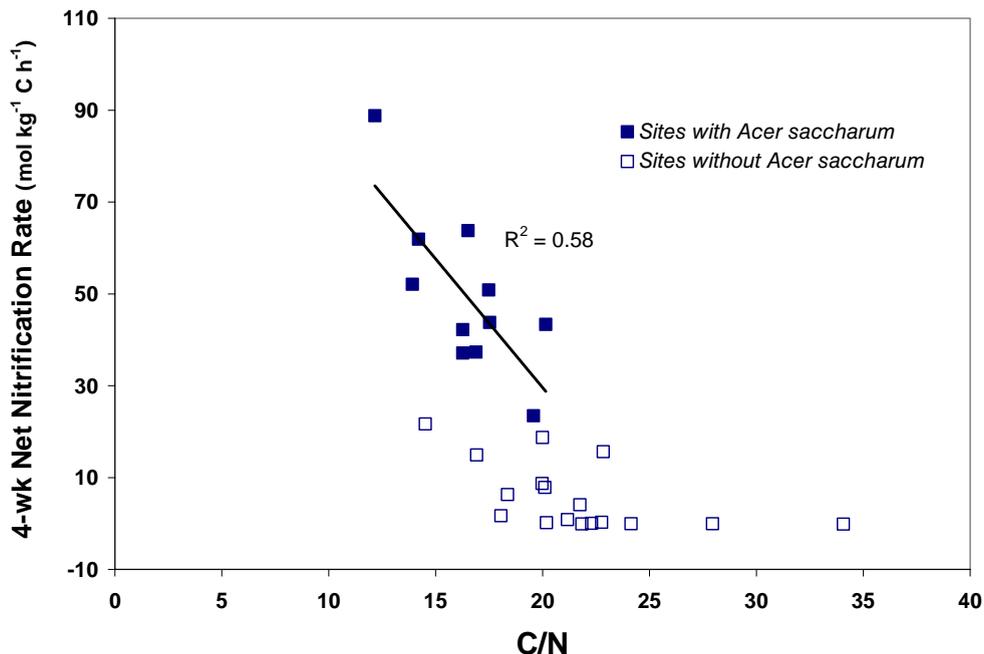


Fig. 10. The relationship between the soil C:N ratio and the 4-week nitrification rate in bulked samples.

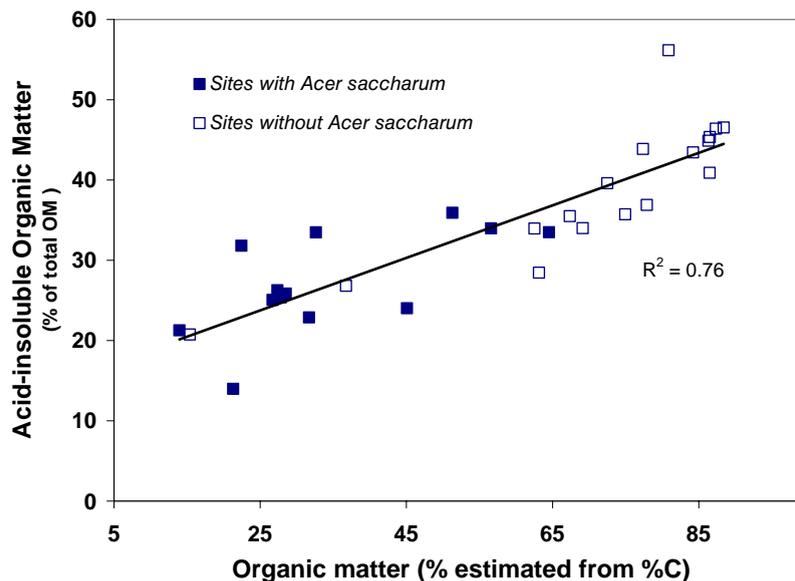


Fig. 11. Soil OM vs. the acid-insoluble OM (expressed as a percent of the total C). The acid-insoluble amount was determined by the standard “lignin” procedure.

of New York, also found high rates and low C/N under *A. saccharum*. In their study, *Quercus rubra* (not found at our study sites) soils showed a poor relationship between C/N and nitrification. The C/N ratio is an indicator of the relative amount of N available for microbial transformations, and other factors, such as the relative availability of C, obviously should have some influence. The Van Soest (1963) procedure for the determination of lignin content of plant tissue (or more properly the acid-insoluble organic content) was used to examine the recalcitrance of the OM in our soil samples. We found a significant relationship between this relatively crude measurement and the soil %OM (Fig. 11). The *A. saccharum* sites did not show a different relationship but Fig. 11 illustrates that they did have a lower average %C (20.1%) than the non-*A. saccharum* sites (41.5%), consistent with previous findings (Finzi et al., 1998). This confounds the interpretation of species effect somewhat because the N transformation rates are all normalized to the C content. However, net nitrification does appear to be affected by an interaction between soil properties and tree species.

The effect of tree species has not always been found. Bohlen et al. (2001) sampled four sites each

at four elevations outside of W6 at HBEF. Two of our sampling sites were adjacent to two of their plots, one each at the lowest and the highest elevation. Their sampling included plots containing *A. saccharum* species (our two had none) and they found that nitrification rates were not related to the presence of *A. saccharum* but were the greatest at the highest elevation, which was dominated by *Fagus grandifolia*. Verchot et al. (2001) also did not find a consistent relationship between tree species and N transformation rates, whereas Christ et al. (2002), Lovett and Rueth (1999), and Lovett et al. (2002, in press) did find an influence of *A. saccharum* species on net nitrification. It is clear from the literature that large variations in nitrification rates may be found between watersheds dominated by similar tree species (Creed and Band, 1998; Schiff et al., 2002). Topographical position (Garten et al., 1994), land-use history (Goodale and Aber, 2001), and soil type (Reich et al., 1997) have all been shown to affect rates. The microbial processes are influenced by a number of factors most of which also influence the character of the soil. The relationship of nitrification rates to the soil C/N ratio is probably the most robust across different watersheds. Development of other tests of C and N availability may provide better indices of nitrification potential.

#### 4. Conclusions

The cross-site comparison of different methodologies yielded a number of conclusions:

1. Three different temporal patterns of mineralization and nitrification (high  $\text{NO}_3^-$  only, high  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , or  $\text{NH}_4^+$  only) were found across these research sites. Samples from 2 different years within a site usually had similar patterns and net rates.
2. In the first day after sampling, gross rates of mineralization in intact cores were similar to the sum of the net rates of mineralization and nitrification in bulked samples. Gross rates of nitrification and nitrate consumption were low. Both these observations suggest that sampling increased overall nitrification rates.
3. The 4-week net rates in intact cores were about half that of the rate in bulked samples but were closely related. Both methods represent degrees of disturbance and both are appropriate for potential rate measurements.
4. Inhibition by acetylene confirmed that nitrification is likely carried out by an autotrophic pathway.
5. As found by other researchers, the C:N ratio was related to the magnitude of net nitrification. Additionally, there was an association of *A. saccharum* with high net nitrification.

As pointed out by Hart et al. (1994), measuring N transformation rates may invariably alter the rates. Additional work is needed to establish the relationship between the potential rate measurements and in situ rates. Only then will we be able to accurately model the effects of nitrogen additions. Future investigations into the microbial community structure and its spatial arrangement may help elucidate the exact nature of N transformations in these soils.

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#### References

- Aber, J.D., Goodale, C.L., Olinger, S.V., Smith, M.-L., Magill, A.H., Martin, R.A., Hallett, R.A., Stoddard, J.L., 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? *Bioscience* 53, 375–390.
- Andersson, P., Berggren, D., Nilsson, I., 2002. Indices for nitrogen status and nitrate leaching from Norway spruce (*Picea abies* (L.) Karst.) stands in Sweden. *For. Ecol. Manage.* 157, 39–53.
- Bailey, S.W., Driscoll, C.T., Hornbeck, J.W., 1995. Acid–base chemistry and aluminum transport in an acidic watershed and pond in New Hampshire. *Biogeochemistry* 28, 69–91.
- Binkley, D., Hart, S.C., 1989. The components of nitrogen availability assessments in forest soils. In: Stewart, B.A. (Ed.), *Advances in Soil Science* 10. Springer, New York, pp. 57–112.
- Boerner, R.E.J., Koslowsky, S.D., 1989. Microsite variations in soil chemistry and nitrogen mineralization in a beech–maple forest. *Soil Biol. Biochem.* 6, 795–801.
- Bohlen, P.J., Groffman, P., Driscoll, C.T., Fahey, T.J., Siccama, T.G., 2001. Plant–soil–microbial interactions in a northern hardwood forest. *Ecology* 82, 965–978.
- Burns, D.A., Kendall, C., 2002. Sources of  $\text{NO}_3^-$  in drainage waters of two Catskill Mountain watersheds differentiated through dual isotope analysis. *Water Resour. Res.*, 38, p 9/1 to 9/12. 10.1016/S1238410769700225.
- Campbell, J.L., Eagar, C., McDowell, W.H., Hornbeck, J.W., 2000. Analysis of nitrogen dynamics in the Lye Brook Wilderness Area, Vermont, USA. *Water Air Soil Pollut.* 122, 63–75.
- Campbell, J.L., Eagar, C., McDowell, W.H., 2002. Patterns of streamwater acidity in the Lye Brook Wilderness, Vermont, USA. *Environ. Manage.* 30, 234–248.
- Christ, M.J., Peterjohn, W.T., Cumming, J.R., Adams, M.B., 2002. Nitrification potentials and landscape, soil and vegetation characteristics in two Central Appalachian watersheds differing in  $\text{NO}_3^-$  export. *For. Ecol. Manage.* 159, 145–158.
- Creed, I.F., Band, L.E., 1998. Export of nitrogen from catchments within a temperate forest: evidence for a unifying mechanism regulated by variable source area dynamics. *Water Resour. Res.* 34, 3105–3120.
- Davidson, E.A., Hackler, J.L., 1994. Soil heterogeneity can mask the effects of ammonium availability on nitrification. *Soil Biol. Biochem.* 26, 1449–1453.
- De Boer, W., Kowalchuk, G.A., 2001. Nitrification in acid soils: micro-organisms and mechanisms. *Soil Biol. Biochem.* 33, 853–866.
- Fernandez, I.J., Simmons, J.A., Briggs, R.D., 2000. Indices of forest floor nitrogen status along a climate gradient in Maine, USA. *For. Ecol. Manage.* 134, 177–187.

- Finzi, A.C., Van Breemen, N., Canham, C.D., 1998. Canopy tree–soil interactions within temperate forests: species effects on soil carbon and nitrogen. *Ecol. Appl.* 8, 440–446.
- Fisk, M.C., Schmidt, S.K., Seastedt, T.R., 1998. Topographic patterns of above- and belowground production and nitrogen cycling in alpine tundra. *Ecology* 79, 2253–2266.
- Garten, C.T., Huston, M.A., Thoms, C.A., 1994. Topographic variation of soil nitrogen dynamics at Walker Branch watershed, Tennessee. *For. Sci.* 40, 497–512.
- Gilliam, F.S., Yurish, B.M., Adams, M.B., 2001. Temporal and spatial variation of nitrogen transformations in nitrogen-saturated soils of a central Appalachian hardwood forest. *Can. J. For. Res.* 31, 1768–1785.
- Goodale, C.L., Aber, J.D., 2001. The long-term effects of land-use history on nitrogen cycling in northern hardwood forests. *Ecol. Appl.* 11, 253–267.
- Hart, S.C., Stark, J.M., Davidson, E.A., Firestone, M.K., 1994. Nitrogen mineralization, immobilization, and nitrification. In: Weaver, R.L. (Ed.), *Methods of Soil Analysis, Part 2*. Soil Sci. Soc. Am., Madison.
- Hendershot, W.H., Duquette, M., 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Am. J.* 50, 605–608.
- Hornbeck, J.W., Bailey, S.W., Buso, D.C., Shanley, J.B., 1997. Streamwater chemistry and nutrient budgets for forested watersheds in New England: variability and management implications. *For. Ecol. Manage.* 93, 73–89.
- Hynes, R.K., Knowles, R., 1978. Inhibition by acetylene of ammonia oxidation in *Nitrosomonas europaea*. *FEMS Microbiol. Rev.* 4, 319–321.
- Khan, S.A., Mulvaney, R.L., Brooks, P.D., 1998. Diffusion methods for automated nitrogen-15 analysis using acidified disks. *Soil Sci. Soc. Am. J.* 62, 406–412.
- Kneopp, J.D., Swank, W.T., 1998. Rates of nitrogen mineralization across an elevation and vegetation gradient in the southern Appalachians. *Plant Soil* 204, 235–241.
- Lawrence, G.B., 2002. Persistent episodic acidification of streams linked to acid rain effects on soil. *Atmos. Environ.* 36, 1589–1598.
- Lawrence, G.B., Lovett, G.M., Baevsky, Y.H., 2000. Atmospheric deposition and watershed nitrogen export along an elevational gradient in the Catskill Mountains, New York. *Biogeochemistry* 50, 21–43.
- Likens, G.E., Bormann, F.H., 1995. *Biogeochemistry of a Forested Watershed*. Springer, New York, 159 pp.
- Lovett, G.M., Rueth, H., 1999. Soil nitrogen transformation in beech and maple stands along a nitrogen deposition gradient. *Ecol. Appl.* 9, 1330–1344.
- Lovett, G.M., Weathers, K.C., Sobczak, W.V., 2000. Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York. *Ecol. Appl.* 10, 73–84.
- Lovett, G.M., Weathers, K.C., Arthur, M.A., 2002. Control of nitrogen loss from forested watersheds by soil carbon:nitrogen ratio and tree species composition. *Ecosystems* 5, 712–718.
- Lovett, G.M., Weathers, K.C., Arthur, M.A., Schultz, J.C., in press. Nitrogen cycling in a northern hardwood forest: do species matter? *Biogeochemistry*.
- Mayer, B., Boyer, E.W., Goodale, C.L., Jaworski, N.A., Breemen, N.V., Howarth, R.W., Billen, G., Nadelhoffer, K., Dam, D.V., Helling, L.J., Nosal, M., Paustian, K., 2002. Sources of nitrate in rivers draining sixteen watersheds in the northeastern US: isotopic constraints. *Biogeochemistry* 57/58, 171–197.
- McNulty, S.G., Aber, J.D., Boone, R.D., 1991. Spatial changes in forest floor and foliar chemistry of spruce–fir forests across New England. *Biogeochemistry* 14, 13–29.
- Mitchell, M.J., Driscoll, C.T., Inamdar, S., McGee, G.G., Mbila, M.O., Raynal, D.J., 2003. Nitrogen biogeochemistry in the Adirondack Mountains of New York: hardwood ecosystems and associated surface waters. *Environ. Pollut.* 123, 355–364.
- Murdoch, P.S., Burns, D.A., Lawrence, G.B., 1998. Relation of climate change to the acidification of surface waters by nitrogen deposition. *Environ. Sci. Technol.* 32, 1642–1647.
- Ohrui, K., Mitchell, M.J., Bischoff, J.M., 1999. Effect of landscape position on N mineralization and nitrification in a forested watershed in the Adirondack Mountains of New York. *Can. J. For. Res.* 29, 497–508.
- Persson, T., Rudebeck, A., Jussy, J.H., Colin-Belgrand, M., Priemé, A., Dambirne, E., Karlsson, P.S., Sjöberg, R.M., 2000. Soil nitrogen turnover—mineralisation, nitrification and denitrification in European forest soils. In: Schulze, E. (Ed.), *Ecological Studies* 142. Carbon and Nitrogen Cycling in European Forest Ecosystems. Springer, Berlin, pp. 297–340.
- Peterjohn, W.T., Foster, C.J., Christ, M.J., Adams, M.B., 1999. Patterns of nitrogen availability within a forested watershed exhibiting symptoms of nitrogen saturation. *For. Ecol. Manage.* 119, 247–257.
- Reich, P.B., Grigal, D.F., Aber, J.D., Gower, S.T., 1997. Nitrogen mineralization and productivity in 50 hardwood and conifer stands on diverse soils. *Ecology* 78, 335–347.
- Ross, D.S., Bartlett, R.J., 1990. Effects of extraction methods and sample storage on properties of solutions obtained from forested Spodosols. *J. Environ. Qual.* 19, 108–113.
- Ross, D.S., Hales, H.C., 2003. Sampling-induced increases in net nitrification in the Brush Brook (Vermont) watershed. *Soil Sci. Soc. Am. J.* 67, 318–326.
- Ross, D.S., Bartlett, R.J., Magdoff, F.R., Walsh, G.J., 1994. Flow path studies in forested watersheds of headwater tributaries of Brush Brook, Vermont. *Water Resour. Res.* 30, 2611–2618.
- Schiff, S.L., Devito, K.J., Elgood, R.J., McCrindle, P.M., Spoelstra, J., Dillon, P., 2002. Two adjacent forested catchments: dramatically different  $\text{NO}_3^-$  export. *Water Resour. Res.*, 38, pp. 28/1–28/13. 10.1029/2000WR000170.
- Shanley, J.B., Schuster, P.F., Reddy, M.M., Roth, D.A., Taylor, H.E., Aiken, G.R., 2002a. Mercury on the move during snowmelt in Vermont. *Trans. Am. Geophys. Union* 83, 45–48.
- Shanley, J.B., Kendall, C., Smith, T.E., Wolock, D.M., McDonnell, J.J., 2002b. Controls on old and new water contributions to streamflow in some nested catchments in Vermont, USA. *Hydrol. Process.* 16, 589–609.
- Stark, J.M., Hart, S.C., 1997. High rates of nitrification and nitrate turnover in undisturbed coniferous forests. *Nature* 385, 61–64.
- Stottlemeyer, R., Toczydlowski, D., 1999. Nitrogen mineralization in a mature boreal forest, Isle Royale, Michigan. *J. Environ. Qual.* 28, 709–720.

- Van Miegroet, H., 1995. Inorganic nitrogen determined by laboratory and field extractions of two forest soils. *Soil Sci. Soc. Am. J.* 59, 549–553.
- Van Soest, P.J., 1963. Use of detergents in the analysis of fibrous feeds. II. A rapid method for the determination of fiber and lignin. *J. Assoc. Off. Agric. Chem.* 46, 829–835.
- Verchot, L.V., Holmes, Z., Mulon, L., Groffman, P.M., Lovett, G.M., 2001. Gross vs. net rates of N mineralization and nitrification as indicators of functional differences between forest types. *Soil Biol. Biochem.* 33, 1889–1901.
- Vitousek, P.M., Gosz, J.R., Grier, C.C., Melillo, J.M., Anderson, J.M., Reiners, W.A., 1982. A comparative analysis of potential nitrification and nitrate mobility in forest ecosystems. *Ecol. Monogr.* 52, 155–177.
- Walley, F.L., van Kessel, C., Pennock, D.J., 1996. Landscape-scale variability of N mineralization in forest soils. *Soil Biol. Biochem.* 28, 383–391.
- Zak, D.R., Hairston, A., Grigal, D.F., 1991. Topographic influences on nitrogen cycling within an upland pin oak ecosystem. *For. Sci.* 37, 45–53.