Nitrogen Cycling in the Upland Boreal Shield Forest: Response to an Experimental Addition of Nitrate

by

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A thesis
presented to the University of Waterloo
in fulfilment of the
thesis requirement for the degree of
Doctor of Philosophy
in
Earth Sciences

Waterloo, Ontario, Canada, 1998

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Abstract. Nitrogen Cycling in the Upland Boreal Shield Forest: Response to an Experimental Addition of Nitrate

The emission of N gases by industrial and agricultural activity has increased the load of N by several-fold to many forested ecosystems during this century. Following a long-term elevated N input, the demand for N by plants and soil microorganisms may be satisfied and the terrestrial ecosystem may reach a state of "N saturation". One of the main features of N saturation is an increase in net nitrification rates in soils. Nitrification is a strong acidifying process because both acidity (2 moles of H^+ per mole of NH_4^+ nitrified) and a mobile anion (NO_3^-) replace the soil-bound NH_4^+. Nitrogen saturation can cause freshwater acidification and forest decline. Presently, boreal and temperate Shield catchments efficiently retain mineral N inputs (NH_4^+ and NO_3^-) and buffer downstream acid-sensitive freshwaters from N-based acidification. However, the mechanisms responsible for N retention are not well understood. These retention mechanisms must be defined to evaluate the long-term potential of Shield catchments to mitigate the acidification of freshwaters.

The objectives of this study were 1) to describe the N cycle in small upland boreal Shield catchments at the Experimental Lakes Area (ELA), northwestern Ontario, and 2) to study the processes involved in N retention in this system using an experimental addition of NO_3^- to one catchment. The ELA Upland catchments are representative of sparsely vegetated rocky ridges common throughout acid-sensitive areas of the Canadian Precambrian Shield. As is typical of the boreal forest, this landscape is a vegetation mosaic where thin forested soils (or "forest islands") are scattered among bedrock outcrops covered with discontinuous mats of lichens, mosses, and grasses (or "lichen patches"). In the first part of the study, the emphasis was on the comparison of the N cycle between forest islands and lichen patches. The information gathered was used to make predictions on the behavior of the landscape following an increased N input. During the second part of the study, 40 kg N ha^{-1} yr^{-1} as $NaNO_3$ was added to one catchment (U3; 0.40 ha) for two years. This N input was similar to the highest level of N deposition presently observed in North America. The mechanisms of N retention and their efficiencies were evaluated using a combination of mass-balance

budgets, soil N mineralization assays, the recovery of a ^{15}N label added with the NO_3^-, plant growth, and plant nutrient content.

Under unmanipulated conditions, several aspects of the Upland catchments N cycle contradicted the traditional view for the boreal forest. As was expected for an unproductive conifer forest, mineral N inputs were efficiently retained. However, overall the catchments leaked more N than expected because of the export of dissolved organic N (DON). There was a striking contrast in internal N cycling in the different components of the landscape. Forest islands were N-limited, as indicated by an efficient mineral N retention, a low net N mineralization, the absence of net nitrification, and a low plant N content. On bedrock surfaces, the export of NH_4^+ and NO_3^- in runoff was not related to precipitation inputs but to net mineralization and nitrification rates in lichen patches, demonstrating that this component of the boreal Shield ecosystem was unexpectedly close to N saturation.

The response of U3 to the $NaNO_3$ treatment indicated a variable potential in time and space to retain the elevated N input. Nitrate retention was limited during the snowmelt period when biological retention mechanisms were less active. However, during the growing season N retention by U3 remained similar to reference catchments. Forest islands and lichen patches responded in opposite ways to the increased NO_3^- input. On bedrock surfaces, net nitrification rates doubled in lichen patches and by the second year of addition N was no longer retained. Although fast hydrological flushing and low biomass must have limited N retention on bedrock surfaces, the intrinsic N saturation of lichen patch soil microorganisms was determinant in preventing NO_3^- retention. In contrast, in forest islands N retention remained similar to the reference because soil microorganisms directly and indirectly contributed to N retention. Forest island soil microorganisms directly mediated NO_3^- retention by immobilizing N during the decomposition of litter with a high C:N. In addition, nitrogen retention was indirectly mediated by the tendency to convert NO_3^- inputs into NH_4^+ during internal cycling. This indirect retention occurred because assimilatory NO_3^- reduction decreased the demand on the soil NH_4^+ pool, allowing for NH_4^+ to accumulate in the soil instead of NO_3^-. Unlike NO_3^-, NH_4^+ can be retained in catchments by a variety of abiotic immobilization mechanisms and is less likely to be lost in runoff. Based on the recovery of

the ^{15}N label added with the $NaNO_3$ treatment, N was retained by plant and lichen uptake in lichen patches and by both plant uptake and microbial immobilization in forest islands. Thus, in lichen patches the intrinsic N saturation of the soil microbial community left the onus of N retention on plants and lichens.

On the short-term, the upland boreal Shield landscape has a limited potential to prevent N-based acidification of downstream ecosystems because of a weak potential for N retention during a part of the year and the intrinsic N saturation of a portion of the landscape. Although forest islands were not N-saturated on the short term, the increased N load from upslope bedrock surfaces may accelerate the onset of N saturation following an increased N input. Because the different components of the boreal Shield landscape are hydrologically connected, N saturation may occur as a cascading effect in this system. The role of lichen patches at the head of the cascade had been hitherto unrecognized.

Acknowledgements

This thesis has considerably benefited from the support of many individuals and funding agencies. I thank them all.

Several summer and co-op students from the University of Waterloo have provided logistical support both in the field (Katie Peebles & Jennifer Adams) and in the laboratory (John Spoelstra, Heather Houghton, Sandra Hearney, Shelley Shain-Delanghe, & Adria Kukk). Bill Mark ran most of the samples for stable isotope analyses at the Environmental Isotope Laboratory of the University of Waterloo. Richard J. Elgood coordinated the laboratory work in Waterloo and was instrumental in method development for several aspects of the study.

The logistical scale of the field work at the ELA would not have been possible without the considerable support provided by the Freshwater Institute in Winnipeg. Eva Schindler was responsible for the storage and handling of water samples throughout the study. Mike Stainton supervised chemical analyses and accommodated an array of requests and inquiries. Ken Beaty and Mark Lyng provided support and advice for the hydrological aspect of my work. Ticia Lyng ably performed the soil analyses for the N mineralization assays. Bob Hecky and Ray Hesslein provided both logistical support and advice during the planning and execution of the experiment. I warmly thank my other friends at the ELA for a most enjoyable stay.

I received financial support from Le Fonds pour la Formation de Chercheurs et l'Aide à la Recherche from the government of Québec, an Ontario Graduate Scholarship, and a grant from the Ontario Federation of Anglers and Hunters. Research funds principally came from a NSERC Strategic Grant and from the Department of Fisheries and Oceans Canada.

I am especially indebted to Dr. C.J. Allan who originally set-up the 'Upland' catchments at the ELA and was extremely generous in accommodating numerous requests throughout the study.

Last, I would like to thank my co-supervisors, Dr. Sherry L. Schiff and Dr. Ramon O. Aravena for their support throughout this work. I also thank the input from members of my supervisory committee (Drs. R. Gillham, D. Rudolph and M. English).

Dedication

Pour Michel et Lise,

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List of Abbreviations

AGB	above-ground biomass
AES	Atmospheric Environment Service
BP	bulk precipitation
C:N	carbon to nitrogen ratio
CPN	coarse particulate nitrogen
CSSC	Canadian Soil Survey Committee
CWD	coarse woody debris
DAYS	number of days since the last rain event
DBH	diameter at breast height
DOC	dissolved organic carbon
DOM	dissolved organic matter
DON	dissolved organic nitrogen
E	evapotranspiration
ELA	Experimental Lakes Area
F	nitrogen export in runoff
G	groundwater recharge
H	hydraulic head, or stage
MIN_{net}	net nitrogen mineralization
NAPAP	National Acid Precipitation Assessment Program
$NO_3^-{}_{net}$	net nitrification
P, RAIN	precipitation
PC	particulate carbon
PN	particulate nitrogen
Q	discharge
R	runoff
R_{TN}	total nitrogen retention coefficient
s, SD	standard deviation
s^2	variance
SE	standard error
T	treatment NO_3^-
TDIN	total dissolved inorganic nitrogen
TDN	total dissolved nitrogen
TN	total nitrogen
UKRGIAN	United Kingdom Research Group on Impacts of Atmospheric Nitrogen
ΔNH_4^+	change in NH_4^+ concentration
ΔS	change in water storage

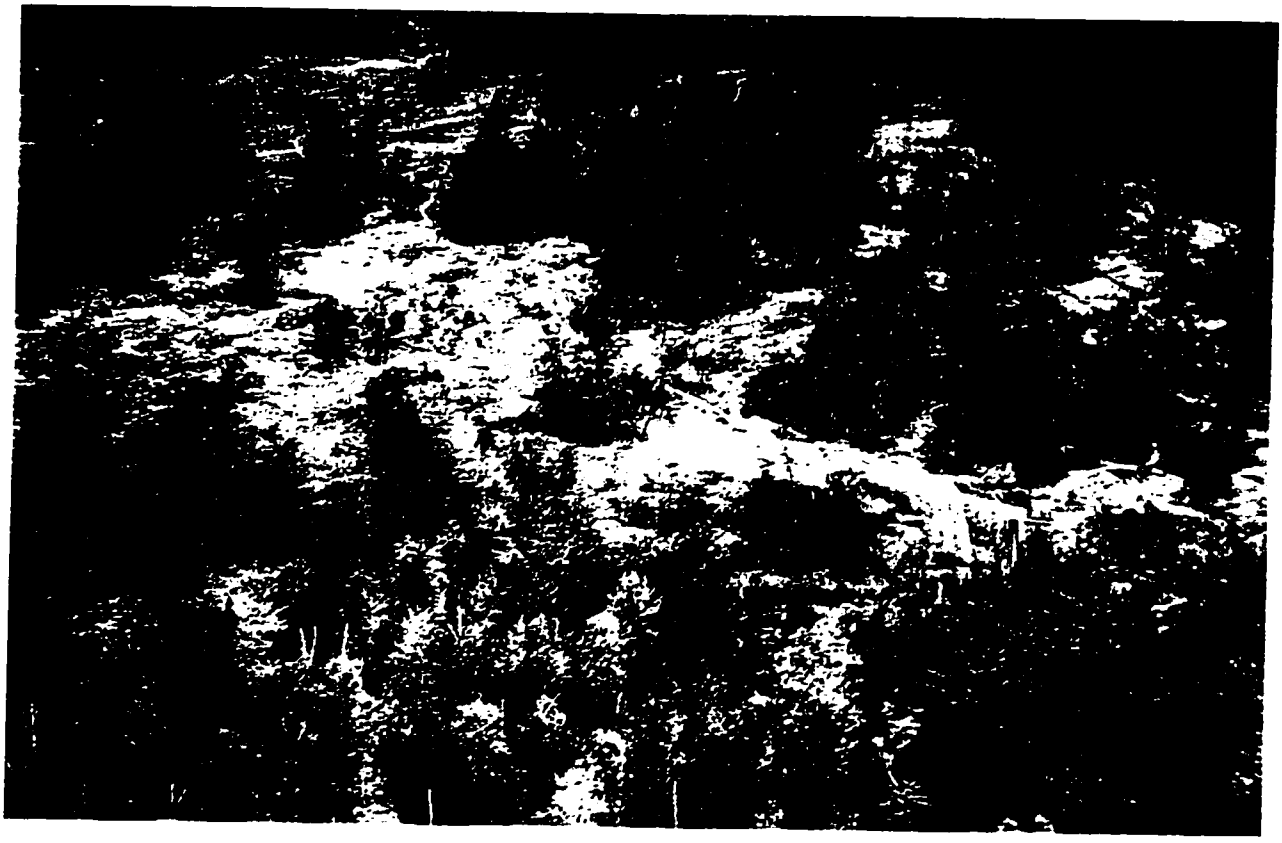


Plate 1. Upland catchment U2 (0.47 ha) at the Experimental Lakes Area in northwestern Ontario. The catchment consists of several small forested soil pockets interspersed among moss- and lichen-covered bedrock outcrops. Overland flow leaving the catchment is re-directed to a V-notch weir (in the green box) using epoxy-covered concrete deflector walls. The pink granodiorite bedrock is best exposed near the U2 outflow because the lichens are scraped-off by ice lenses occasionally forming during the snowmelt period. A portion of catchment U3 is visible in the upper left corner, including the U3b bedrock surface sub-catchment and the U3f forest island sub-catchment. This landscape is representative of rocky ridges commonly found in acid-sensitive areas of the Precambrian Shield.

Introduction

The ongoing problem of acid rain

Nitrogen (N) compounds are increasingly recognized as a source of acid rain in North America (National Acid Precipitation Assessment Program [NAPAP] 1992; RMCC 1997a,b,c). When the problem of acid rain was first recognized, sulphuric acid (H_2SO_4) was the primary source of acidity and efforts were primarily invested in reducing the emission of its precursor, SO_2 gases (Likens & Bormann 1974). In eastern Canada, SO_2 emissions have declined from ~4 400 kilotons (kt) in 1976 to <2 000 kt in 1994 (RMCC 1997a). Partial recovery in some acidified ecosystems has been observed, especially in areas previously affected by smelter emissions such as Sudbury (Gunn & Keller 1990; RMCC 1997b; Mallory et al. 1998). However, in general the acidity of rainfall has not improved because the decrease in SO_4^{2-} concentration was matched by a decrease in base cation concentration (Hedin et al. 1994).

In parallel to the decline in SO_2 emissions, emissions of acid-generating N gases, NO_x and NH_3, have grown. Increased fossil fuel combustion, especially from vehicles, has increased the emissions of NO_x gases, one of the precursors for nitric acid (HNO_3) in rain (NAPAP 1992). Ammonia (NH_3) emission has almost certainly increased because of the spectacular rise in fertilizer use and in livestock farming over the last 30 years (Bowman et al. 1997). In some areas of Europe (especially the Netherlands), NH_3 emission from areas with intensive livestock farming yield N deposition to nearby forests in excess of 75 kg N ha^{-1} yr^{-1} (van Breeman et al. 1982; Dise & Wright 1995). To put these European N deposition levels in perspective, they occasionally exceed the recommended fertilizer application guidelines for some crops in southern Ontario (Ontario Ministry of Agriculture, Food, and Rural Affairs 1994). N deposition to forests in Canada is much lower than in Europe and ranges from <5 kg N ha^{-1} yr^{-1} in pristine areas to >13 kg N ha^{-1} yr^{-1} in some parts of eastern Canada (Jeffries 1995; Arp et al. 1996). However, N deposition to Canadian forests is probably underestimated because detailed measurements of the different pathways of N deposition have not been made (RMCC 1997c).

On a global basis, the acidification potential of N compounds emitted in the atmosphere is much greater than the one for S (Galloway 1995). Since the emission of N gases will remain high in the next century (NAPAP 1992; Galloway 1995), acid rain will continue to be an important environmental problem in both the short- and long-term.

The biogeochemistry of elevated N deposition

The biogeochemistry of elevated N deposition is more complex than the one for elevated S inputs. Sulphuric acid deposition is a powerful agent of catchment acidification because of its efficient consumption of soil acid neutralizing capacity. During catchment acidification, base cations on soil exchange sites are released in soil pore water by exchange with the incoming H^+ and then lost from the system through leaching with the mobile SO_4^{2-} anion (Reuss & Johnson 1986). Acidification by H_2SO_4 can be neutralized by SO_4^{2-} adsorption in soils (Seip et al. 1985; Johnson et al. 1991), by plant uptake, or by reduction of SO_4^{2-} to FeS_2 and other inorganic S forms in anoxic environments (Anderson & Schiff 1987; Devito 1995). Large areas of Canada, including much of the Precambrian Shield (Arp et al. 1996), are sensitive to H_2SO_4 acidification because of the combination of thin soils, the absence of carbonate minerals, the limited potential for soil SO_4^{2-} adsorption, and the low biological demand for S. The mechanisms neutralizing SO_4^{2-} acidity may not be permanent because acidity is regenerated by SO_4^{2-} desorption (Johnson et al. 1991) or the oxidation of mineral and organic S (LaZerte 1993; Yan et al. 1996).

Unlike S, N is one of the most important nutrients in forests and has a complex and tight cycle. In most forested ecosystems, the demand for N by plants usually exceeds the new N inputs and most of the N required by plants is obtained through recycling from the soil organic matter pool (Clark & Rosswall 1981). Regardless of the form or the amount of N entering a catchment, *as long as N inputs are retained no loss of alkalinity or export of acidity caused by N compounds occurs* (Fig. A). In many acid-sensitive environments, the efficient retention of N by forests is presently buffering downstream ecosystems from acidification by N inputs (Dillon & Molot 1990). However, the capacity of forests to retain N inputs is not unlimited (Ågren and Bosatta 1988). Upon long-term exposure to elevated N inputs, forests may become 'saturated' with N. 'N saturation' is defined as a supply of N in excess of

ecosystem requirements (Ågren and Bosatta 1988; Aber et al. 1989; Stoddard 1994). During N saturation, the pool of soil NH_4^+ builds-up, nitrification rates increase, and NO_3^- is exported in groundwater and surface runoff. The onset of nitrification is the key acidifying process during N saturation because both acidity and a mobile anion (NO_3^-) are generated (Aber et al. 1989). In a process similar to elevated SO_4^{2-} deposition, the increased NO_3^- export results in the loss of base cations from soils and the acidification of the catchment (Galloway et al. 1987). Under acute long-term deposition, N can cause forest decline (Nihlgard 1985; Aber et al. 1989).

Elevated N deposition may cause eutrophication as well as acidification in some ecosystems. The increased N inputs to estuaries and coastal waters has been linked to the recurrence of noxious algal blooms (Pearl 1993; 1997). In terrestrial ecosystems, long-term elevated N inputs may lead to plant community changes towards species that are better competitors in nutrient-rich environments (van Breeman and van Dijk 1988). Nutrient-poor ecosystems, such as ombrotrophic bogs, may be especially sensitive to species change under long-term elevated N inputs (Gorham et al. 1984; Aerts et al. 1992).

Scope of the thesis

The objectives of this thesis were 1) to describe the N cycle in small upland boreal Shield catchments and 2) to study the mechanisms of N retention in this system using an experimental addition of NO_3^- to one catchment. As for the N cycle, where the product of one reaction is invariably the substrate for another, each chapter was written to stand-alone but they are still strongly interrelated. Chapter 1 provides a description of the N cycle in the Experimental Lakes Area 'Upland' catchments, the site chosen for the study. Material from this chapter provides much background information useful for later chapters. A small digression from the Upland catchments was taken in Chapter 2, where the ELA long-term bulk deposition record for N is reviewed. This record is probably the longest one anywhere for N deposition in the boreal forest. Chapter 3 reviews the dynamics of N mineralization in the 'forest island' and 'lichen patch' component of the Upland catchments.

Chapters 4 and 5 are the core of the thesis. An experiment was designed to test the efficiency of N retention mechanisms in the Upland landscape under an elevated N input. Forty kg N ha^{-1} yr^{-1} as $NaNO_3$ was applied for two years to catchment U3. This treatment was 8-fold background N deposition at the ELA and was of similar magnitude as the highest N input to forests in North America (at high elevations in the Adirondack Mountains in the U.S.) The response of U3 through nutrient export, N mineralization, and plant growth is summarized in Chapter 4. The $NaNO_3$ treatment contained a ^{15}N tracer to aid in determining the fate of N retained by the catchment. In Chapter 5, the patterns in the recovery of the ^{15}N tracer and their implications for the mechanisms of N retention in the upland boreal Shield forest are addressed.

Finally, a detailed methodology to estimate uncertainty in element flux through runoff is presented in Chapter 6.

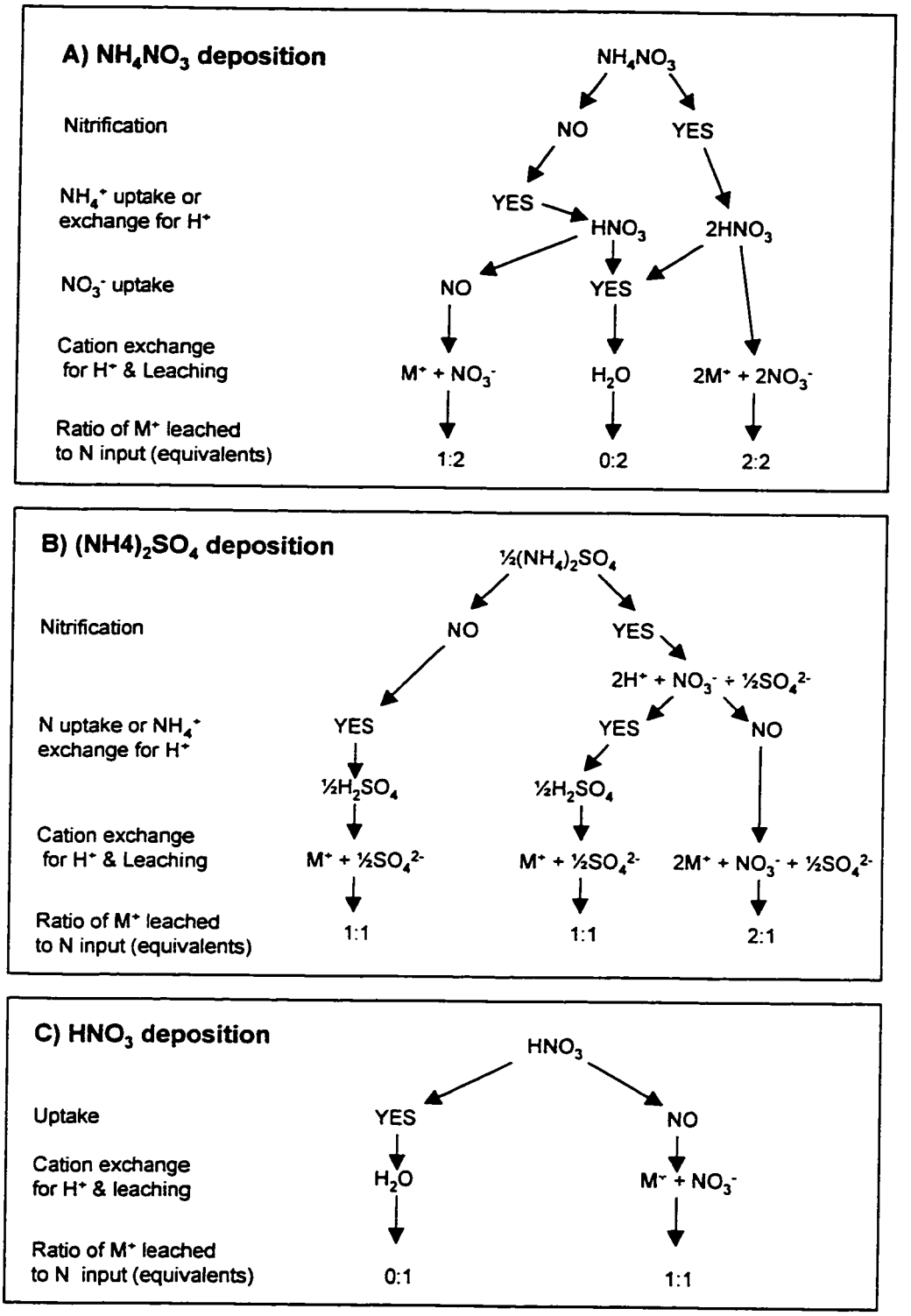


Fig. A. Export of base cations from catchments as a function of the form and internal transformations of N inputs. Modified from Reuss & Johnson (1986) and UKRGIAN (1994). In (B), some alkalinity is lost under all scenarios because of the SO_4^{2-} anion. N inputs do no result in the loss of alkalinity when N is retained.

Chapter 1. An Overview of Nitrogen Cycling in Heterogeneous Upland Boreal Shield Catchments

Introduction

The boreal forest is one of the largest biomes on Earth, covering ~12 million km^2 or ~11% of the land surface, encompassing most of northern Canada, Siberia and Scandinavia (Kimmins & Wein 1986; Bonan & Shugart 1989). Although a wide variety of ecosystems occur over this area, a defining characteristic of the biome is the tendency for nutrients to accumulate in large soil pools because the prevailing cold climate limits organic matter decomposition (Van Cleve et al. 1986; Bonan & Shugart 1989). Often, the slow rates in nutrient recycling result in plant growth that is nutrient limited, especially for N (Weetman & Fournier 1984a,b; Shaver & Chapin 1986; Vitousek & Howarth 1991). Site characteristics, such as slope and aspect, influence the soil temperature regimes and the nutrient recycling rates (Van Cleve et al. 1991). Different plant communities tend to become established along site-induced productivity gradients, yielding the typical mosaic in plant cover characteristic of the boreal forest (Viereck et al. 1986).

Plants themselves tend to reinforce the tendencies in site productivity induced by geomorphic features by producing different types of litter (Van Cleve et al. 1983; Chapin 1986). Fast-growing species, such as birch (*Betula* spp.), produce a labile litter that decomposes rapidly, while slow-growing species, such as black spruce (*Picea mariana* Mill. B.S.P.), produce a refractory litter that decomposes slowly (Flanagan & Van Cleve 1983; Flanagan 1986). The type of litter produced by a given plant is adapted to maintain the nutrient status of the environment within the range where the plant is most competitive (Chapin 1986; Northup et al. 1995a). Overall, the kind of organic matter supplied to decomposers may be more important than climatic factors in regulating nutrient recycling rates in boreal and tundra soils (Hobbie 1996).

The cycles of C and N in boreal regions have received considerable attention because of their strong feedback on the global C cycle (Gorham 1991; Houghton et al. 1998). Storage

of C in boreal ecosystems may be a part of the 'missing' terrestrial sink for the global atmospheric CO_2 budget (Peterson & Melillo 1985; Schindler & Bayley 1993). Schindler & Bayley (1993) and others have hypothesized that an increase in the deposition of N compounds to boreal regions may increase plant productivity, resulting in increased storage of atmospheric CO_2 in boreal biomass, soil, and peat. Thus, N fertilization of the boreal forest may partially mitigate CO_2-induced climate warming by lowering the concentration of CO_2 in the atmosphere. On the other hand, elevated N inputs can be a source of acid rain to the boreal forest (Ågren & Bossata 1988; Aber et al. 1989; Schindler & Bayley 1993). The outcome of simultaneous changes in N deposition and in climate is difficult to predict because the feedbacks between climate and nutrient cycling are complex in the boreal forest (Houghton et al. 1998). For example, small changes in soil temperature may strongly increase organic matter decomposition rates and produce a net return of CO_2 to the atmosphere (Houghton & Woodwell 1989). Temperature increases may bring about changes in plant communities towards species that are less efficient in tying-up C and N in soil organic matter (Hobbie 1996).

Although nutrient cycling in the boreal forest has received much attention (Tamm 1976, Wein & MacLean 1983; Wein et al. 1983; Van Cleve et al. 1986), there exist many gaps in our knowledge of the internal cycling of nutrients like N (Näsholm et al. 1998; Houghton et al. 1998). For example, although it is known that the boreal forest efficiently retains nutrients, especially following disturbances such as clear-cutting (Vitousek 1981; Nicholson et al. 1982) or forest fires (Bayley et al. 1992), the mechanism mediating retention are not always understood (Vitousek & Melillo 1979). Understanding the mechanisms of nutrient retention in the boreal forest will be necessary to predict and mitigate the impact of present and future environmental changes on this ecosystem.

The upland boreal Shield forest of the ELA

In this chapter, the N cycling properties of an upland boreal Shield forest will be described, with an emphasis on the contrasts between different plant/soil communities within the system. The Upland catchments of the Experimental Lakes Area (ELA) are a set of small 0- or 1-order watersheds used to study the processes controlling element exports to Shield

lakes (Allan et al. 1993; Allan & Roulet 1994a,b). This system offers several advantages to study the N cycle on both a mass-balance and an internal cycling point of view. The Upland catchments are practical for traditional input-output element budgets because all runoff exits the system as overland flow, which can be easily gauged (Chapter 6). Two distinct plant communities with contrasting internal N cycles occur within the system (Chapter 3), which enables comparative studies of changes in internal nutrient recycling following disturbances (Chapter 4 and 5). The small size of the watersheds (0.2 – 7 ha) is amenable to whole-catchment manipulations at a reasonable cost. The area is typical of sparsely vegetated rocky ridges in acid-sensitive areas of the Precambrian Shield, which makes the Uplands especially suitable for topics relevant to catchment acidification. Whole-catchment manipulation studies have taken place in similar landscapes in Scandinavia (Wright et al. 1988, 1993, 1995a,b). Overall, the goal of summarizing the available information about the N cycle in the Uplands was to help formulate predictions on the response of this system following a disturbance, such as an increased input of N (Chapters 3 & 4).

Methods

Study Site

The ELA (northwestern Ontario) is a group of 58 small lakes and watersheds set aside for whole-ecosystem research (Johnson & Vallentyne 1970; Fig. 1.1). Climate at the ELA is continental, with long, cold winters (mean 1970-95 January temperature = -17.3°C) and short but warm summers (mean July temperature = 19.2°C). Between 1970 and 1995, the area received an average of 673 mm of precipitation, with approximately 30% as snow (Beaty & Lyng 1989; K.G. Beaty unpublished data). With the exception of some logging and camping in the region, the area is pristine. Forest fires are common in the region (Bayley et al. 1992) but the last fire in the Upland catchments occurred over 130 years ago.

The 0-order watersheds (U1 to U4) range in size between 0.17 and 0.56 ha and the 1-order watershed (U8) covers 7.2 ha (Table 1.1). The catchments are located on a topographic high and are composed of patches of thin, forested soils ('forest islands') interspersed among lichen and moss-covered bedrock outcrops (Fig. 1.2). Catchments U1 and U3 contain two

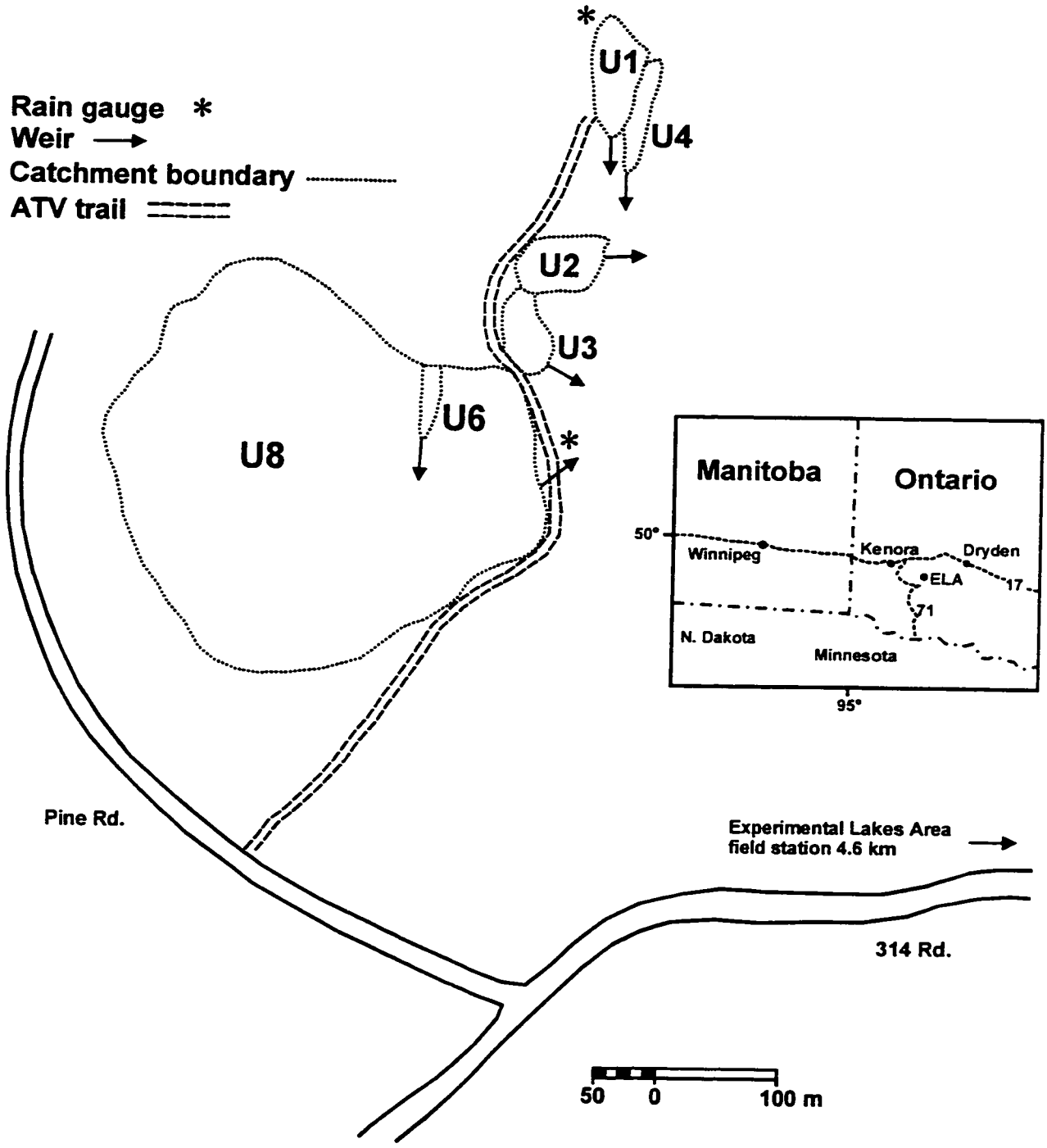


Fig 1.1. Location of the Experimental Lakes Area Upland catchments. Catchments U1 to U6 are 0-order and range in size between 0.2 to 0.6 ha. The 1-order catchment U8 contains more abundant soil deposits, including a ~ 1 ha wetland near its center.

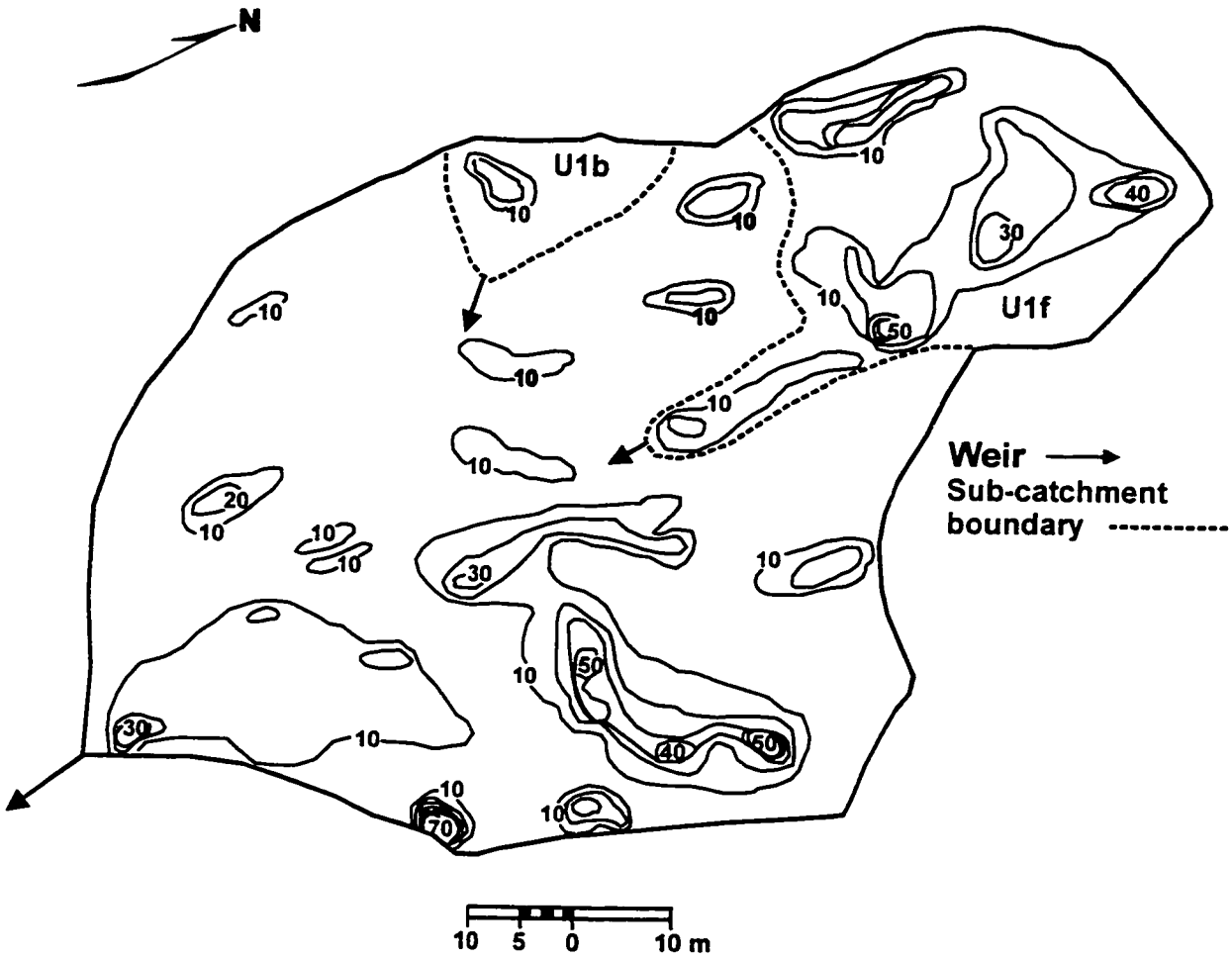


Fig. 1.2. Catchment U1 at the Experimental Lakes Area, northwestern Ontario (0.56 ha). Contour lines indicate soil depth (in cm). "Forest islands" occur where soil is at least 10 cm. Bedrock surfaces are either covered with crustose lichens or with "lichen patches".

sub-catchments, either draining small bedrock surfaces (U1b and U3b) or one or two forest islands (U1f and U3f). It should be noted that forest island sub-catchments are more like 'miniature' versions of whole catchments because they contain both bedrock surfaces and forested areas. However, the proportion of the forest island sub-catchments covered by trees is larger than for whole catchments (Table 1.1). In addition, water was sampled immediately downstream from forest island sub-catchments, whereas outflow from whole catchments was a mix of bedrock surface and forest island runoff.

Table 1.1. Physiographic characteristics of the ELA Upland catchments. From Allan et al. 1993.

	Area (m^2)	Mean slope	% Bedrock surface	% Forest islands	Mean soil depth (cm)
U1	5553	0.177	73	27	8
U1b	172	0.205	98	2	3
U1f	1102	0.093	62	38	11
U2	4694	0.178	65	35	11
U3	4006	0.169	79	21	8
U3b	266	0.187	100	0	4
U3f	381	0.053	60	40	13

In general, forest islands cover approximately 30% of catchment area. Jack pine (*Pinus banksiana* Lamb.) occurs where soils are thinner and black spruce (*Picea mariana* (Mill.) B.S.P.) and occasionally white pine (*Pinus strobus* L.) where soils are thicker. The shrub cover consists of *Juniper communis* L., *Vaccinium* spp., and occasionally the fern *Pteridium aqualinum* L. Kuhn. The moss cover is variable and usually composed of *Pleurozium schreberi* (Brid.) and *Dicranum* sp. The forest floor in forest islands is 5 to 25 cm thick and composed of L, F, and H horizons. The mineral soil, when present, is 10 to 40 cm thick and limited from one to several Ah horizons, and occasionally a C or Cg horizon. Soils are classified as truncated orthic humic regosols and sombric brunisols (Canadian Soil Survey Committee 1978; Allan et al. 1993), are texturally in the silt loam size range, and are composed of aluminosilicate minerals (Allan et al. 1993). Carbonates are absent. Bedrock is mostly slow-weathering pink granodiorite (McCullough and Campbell 1973).

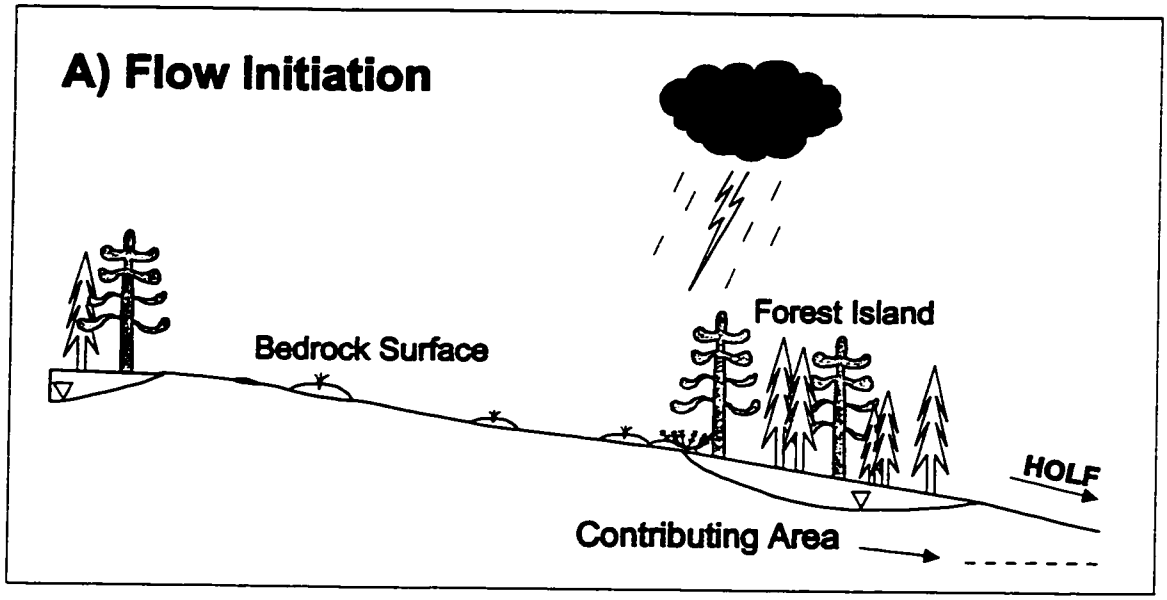
Bedrock outcrops cover approximately 70% of the catchment surface and are composed of two features. About 65% of the bedrock surface is covered with crustose lichen such as *Rhizocarpon geographicum* (L.) DC and some foliose lichens. The remaining bedrock surface is covered by 'lichen patches' – clumps of the fruticose lichen *Cladina* spp. and *Cladonia* spp., the mosses *Polytrichum* spp, *Andreaea rupestris* Hedw., and *Racomitrium microcarpon* (Hedw.), some grasses (*Poa* spp.), and occasionally *Juniper*. Lichens and *Poa* are predominant in upslope areas while mosses are more common in seepage areas downslope from forest islands. One to 10 cm deposits are found under lichen patches ('nonsoil' under the

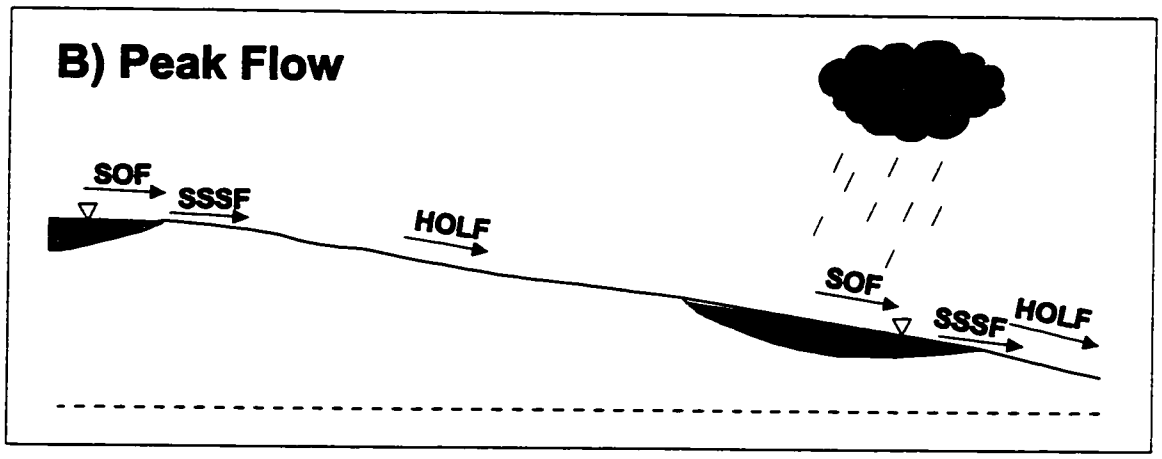
Canadian Soil Survey Committee 1978). The composition of lichen patch 'nonsoil' is variable but consistent between areas covered by different organisms (Chapter 5). Noticeable features include a S horizon (mostly from *Polytrichum* stems), an occasional thin horizon of decomposing lichen ('DL'), and an occasional F horizon of grass litter flattened by the snowpack. All lichen patches are underlain by a more mineral-rich but strongly humified layer ('H').

The original impetus to set-up small experimental catchments at the ELA was to complement whole-lake (Schindler et al. 1985) or wetland acidification studies (Bayley et al. 1987). The element input-output budgets for the Uplands for the 1987-1990 period were summarized in Allan (1993) and Allan et al. (1993). Allan and Roulet (1994b) studied the hydrological properties of the Uplands, with an emphasis on flow-generating mechanisms during storms (Fig. 1.3). Allan and Roulet (1994a) investigated the biogeochemistry of Al in the different landscape units and Allan (1995) summarized the response of catchments U3 and U4 to a low-level NH_4NO_3 and H_2SO_4 addition to the snowpack. Vitt (1991) studied the growth of the moss *Racomitrium microcarpon* in the vicinity of the catchments.

In- and out-fluxes

Precipitation depth has been measured on site using two standard AES rain gages. Bulk precipitation chemistry has been monitored continuously at the ELA meteorological station (~3 km from the catchments) since 1970 (Chapter 2). In the spring, snowpack water equivalents and N content were measured prior to snowmelt. Water budgets and element flux through runoff were measured using 60° or 90° V-notch weirs. Detailed procedures for measuring element flux (including the magnitude of the error) are outlined in Chapter 6. The concentration of NH_4^+, NO_3^-, particulate-N (PN), and TDN in precipitation, snow, and runoff were determined following Stainton et al. (1977). Dissolved organic N was estimated as TDN $- NH_4^+ - NO_3^-$. The export of coarse particulate N (i.e., particles $\leq$1 mm) was estimated by installing a 1 mm screen downstream from the U1 and U2 weirs, but was an insignificant loss of N (Chapter 4).





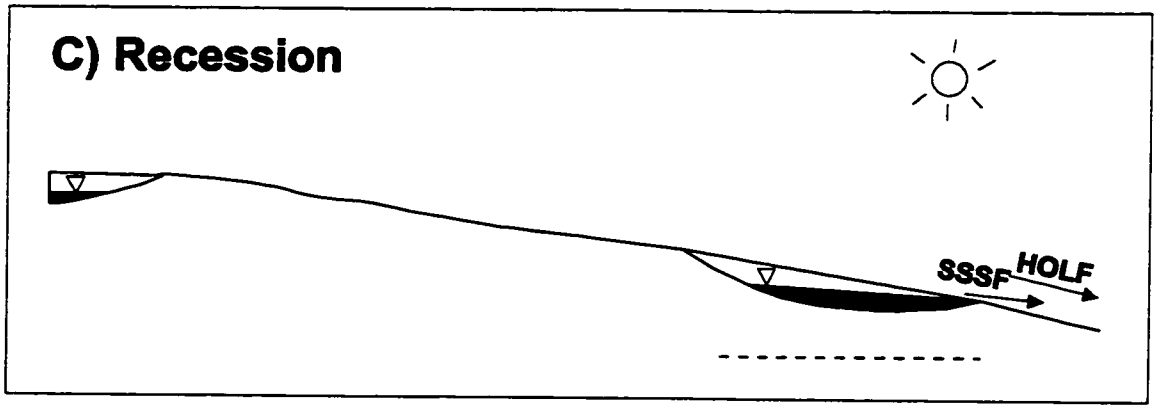


Fig. 1.3. Runoff generation mechanisms in 0-order boreal Shield catchments during different phases of a storm hydrograph. (A) flow initiation, (B) peak flow, and (C) recession phase. HOLF – Horton overland flow, SSSF – sub-surface storm flow, and SOF – saturated overland flow. From Allan & Roulet (1994b). The inverted triangles show the position of the perched water tables in each forest islands.

N Pools

The detailed procedures used to measure the size of the different N pools in U1 and U3 are outlined in Chapter 5. Briefly, ground cover biomass and soil pools were measured separately for forest islands and lichen patches using quadrats and soil cores. Tree diameter at breast height (DBH) was measured for all the trees in the catchments and biomass was estimated using published allometric relationships for each species (Allemdag 1983). The N content for different tree components were either measured (needles, wood) or estimated from the literature (roots, branches, and bark).

Litter production

The input of above-ground litter in forest islands was measured in 1995-96 in forest islands using 12 - 0.25 m^2 litter traps. Litter was removed in the spring and fall, dried, homogenized with a Wiley and a ball mill, and the C and N content determined with an elemental analyzer.

N mineralization

N mineralization was measured using buried bag incubations in forest islands and in lichen patches (Chapter 3). Briefly, soil N mineralization was estimated by observing the changes in NH_4^+ and NO_3^- concentration during monthly three-week incubations in buried soil bags. Incubations were performed from May to October in 1995 and 1996 and for the 1995-96 overwinter period. Net mineralization (MIN_{net}) was defined as the change in NH_4^+ + NO_3^- concentration and net nitrification ($NO_3^-{}_{net}$) as the change in NO_3^- concentration over time. Mineralization rates obtained with the buried bag technique were similar to the ones obtained using *in-situ* core incubations (Raison et al. 1987; Chapter 3).

Plant growth and nutrients

In 1994, 20 *Pinus*, 20 *Picea*, and 20 *Picea* saplings were permanently marked with aluminum tags in catchments U1, U2, and U3. DBH (or height for saplings) was measured in fall 1994-96. Ten colonies of the moss *Racomitrium microcarpon* were permanently marked in U1, U2, and U3 by painting references on the bedrock. The lateral expansion of the colonies during the growing season was measured by taking photographs in the spring and fall

(Vitt 1991). The nutrient status of Upland trees was assessed from the N, P, Ca, Mg, and K content of *Picea* and *Pinus* needles collected in fall 1996.

Results & Discussion

In the following, the patterns in N export, pool sizes, and internal cycling will first be reviewed for bedrock surfaces and forest islands. An interesting insight in the processes regulating N fluxes and internal cycling in each unit was obtained by comparing patterns during a relatively dry (1995) and wet year (1996). In 1995, precipitation was near the average for the ELA (603 mm), but prolonged droughts occurred in the spring and fall. In contrast, 1996 was the wettest year in the ELA record (>1 000 mm at the meteorological station). The N cycle at the landscape level will be summarized based from the contribution from each unit. Later parts of the discussion will explore the mechanisms responsible for generating the contrasting N cycles in the landscape.

Bedrock surface N cycle

Nitrogen distribution, cycling, and export on bedrock surfaces was unusual and dynamic. Despite a sparse plant and lichen cover, a large amount of N was stored on bedrock surfaces (700 kg N per hectare of bedrock surface [ha_b]). Most of this N was the 'H' horizon (~620 kg N ha_b^{-1}), with smaller pools in the different litter layers (~53 kg N ha_b^{-1}) and in biomass (~24 kg N ha_b^{-1}; Fig. 1.4). Approximately 4% (or 22 kg N ha_b^{-1}) of the 'H' pool N was in live and dead *Poa* roots and in moss rhizoids. No estimates of primary productivity are available at the moment. Patterns in biomass may not reflect primary production because organisms with a high biomass (mosses and especially lichens) grow slowly. In contrast, primary production by grasses was probably larger than its proportion of the biomass would suggest (~10%).

Net N mineralization and net nitrification were surprisingly high underneath lichen patches (Fig. 1.4). Net N mineralization rates ranged between 9 to 16 kg N ha_b^{-1} yr^{-1} and were higher in 1995, mostly because of higher rates during a warm and dry period in May and June (Chapter 3). Although net nitrification is usually nil in boreal soils, net nitrification occurred in lichen patches and represented 43% - 55% of the net N mineralization.

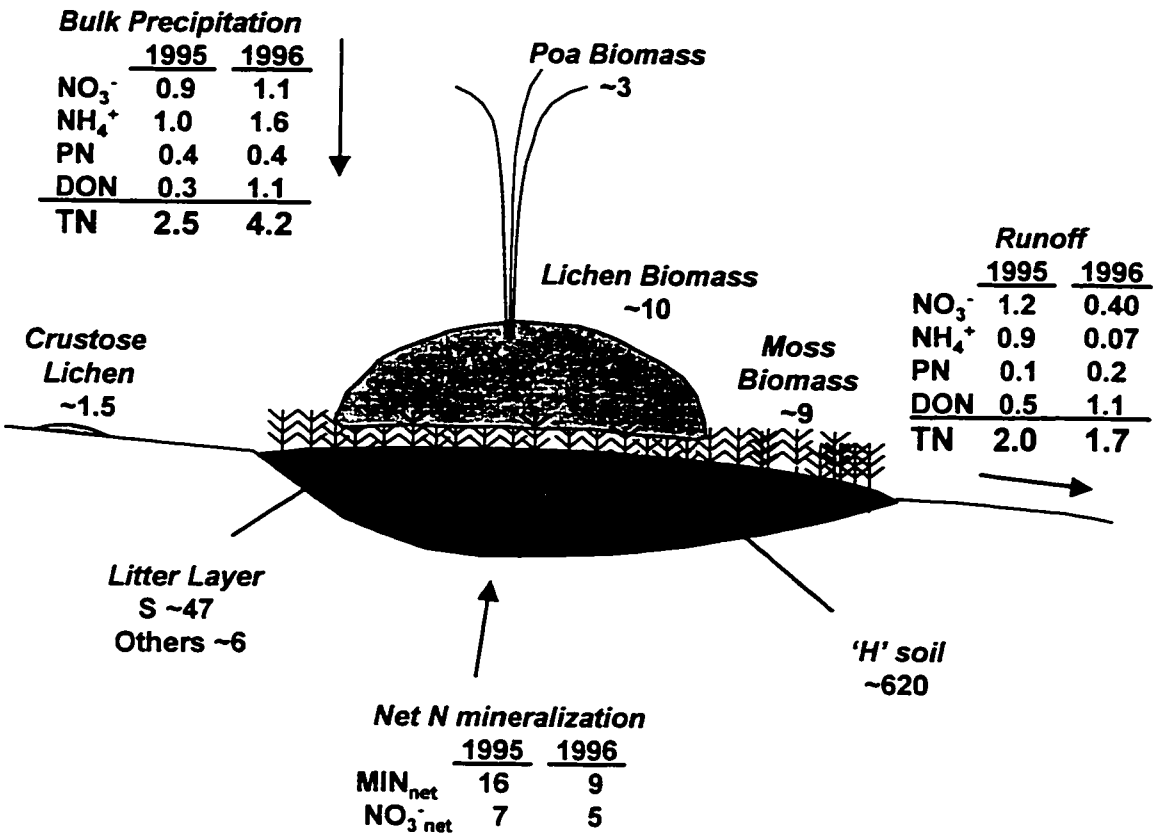


Fig. 1.4. Nitrogen pools and fluxes on boreal Shield bedrock surfaces. Fluxes are for the growing season only (May – September). Pools and fluxes expressed as kg N per ha of bedrock surface.

The pattern in N export from bedrock surfaces varied considerably from year to year (Fig. 1.4). Bulk precipitation input was 3 - 4 kg N ha^{-1} per growing seaon (gs). Additional N inputs may have occurred from N fixation by free-living cyanobacteria growing on mosses (Alexander & Billington 1986; Chapter 3) and from pollen from surrounding forest islands. N retention and the main form of N exported were variable from year-to-year. During the dry year (1995), N retention was only 20% of inputs because of a net export of DON (0.52 kg N ha^{-1} gs^{-1}) and NO_3^- (1.2 kg N ha^{-1} gs^{-1}). However, despite a larger precipitation input, N retention was larger and similar to forest islands (60%) during the wet year (1996). The main form of N exported in 1996 was DON (1.1 kg N ha^{-1} gs^{-1}). However, unlike in 1995, a net

export of DON did not occur because a similar amount had entered the catchment in precipitation.

Mineral N export may have been larger in 1995 because of the higher input from N mineralization underneath lichen patches and a decreased potential for uptake by frequently dehydrated mosses and lichens. Although mosses and lichen quickly become active following rehydration (Ahmadjian & Hale 1973; Richardson 1981), cellular damage during wetting and drying cycles results in a delay before full activity is restored (Richardson 1981). Even a small delay to recover full physiological activity could impair nutrient uptake on bedrock surfaces because most of the flux of water occurs within a few hours during typical summer storms (Lechowicz 1981; Allan & Roulet 1994b). During wet years, the main form of N exported from bedrock surfaces (PN and DON) suggests that most of the N entering bedrock surfaces was incorporated and recycled instead of simply flushed through the system.

The export of coarse particulate N from bedrock surfaces is probably larger than the PN exports tend to indicate (Fig. 1.4). Significant amounts of soil and debris accumulated in the holding pond area at the bedrock surface weirs. Most of this sediment appeared to originate from overturned or disintegrating lichen patches. When dehydrated, small lichen patches can be overturned by sudden storms, strong winds, or by wildlife. Overturned lichen patches can travel significant distances downslope before resettling. The 'H' soil and the grus (coarse, gravel-size material resulting from bedrock weathering) exposed by lichen patch overturning becomes susceptible to erosion during storms. Occasional small depressions with well-weathered rock but no crustose lichen growth suggest that even large (<1 m diameter) lichen patches can be completely lost through erosion. The 'death' of a lichen patch may result from the tendency of some organisms, such as *R. microcarpon*, to grow in an outward fashion while the center of the colony dies. Vitt (1991) used the diameter of *R. microcarpon* 'rings' to estimate the age of colonies and suggested that some dated back to the last fire (>130 yrs B.P.)

Although only a small part of the biomass (~1.5 kg N ha_b^{-1}), crustose and foliose lichens probably play a significant role in the element flux from bedrock surfaces. Crustose

and foliose lichens contribute to the physical weathering of the bedrock by the extension-contraction of the thallus during wetting-drying cycles, or by sending rhizines (lichen equivalent to roots) in fractures or the weak planes of minerals (Syers & Iskandar 1973). Lichens contribute to the chemical weathering of the bedrock by keeping the substrate wet for longer periods of time, by generating CO_2, and by producing a variety of organic acids (Syers & Iskandar 1973; Allan & Roulet 1994b, Easton 1995). Lichens retain atmospheric particles (Syers & Iskandar 1973) and probably participate in the conversion of mineral-N inputs to DON in runoff.

In summary, bedrock surfaces contain a relatively large amount of N and this N has a dynamic cycle. At least during wet years, total N retention is as efficient as forest islands. However, large net N mineralization, the occurrence of net nitrification, and a relatively high export of NH_4^+ and NO_3^- suggest that this system is not strongly N-limited.

Forest islands N cycle

At the whole-catchment scale, the biomass of the *P.banksiana – P. mariana* forest was very low compared to other similar boreal ones (Table 1.2). However, at the scale of forest islands, the size of N pools was similar to other boreal conifer forests (Table 1.2). Overall, ~3 400 kg N was stored per ha of forest island (ha_f). Most of the N was in soil pools (~3 250 kg N ha_f^{-1}) with smaller amounts in understory (9 – 24 kg N ha_f^{-1}) and tree biomass (~166 kg N ha_f^{-1}). Live and dead fine roots accounted for ~163 kg N ha_f^{-1} of the soil N mass. The largest difference between Upland forest islands and other *P. banksiana* forests was the larger forest floor mass in the Uplands. An independent estimate of the N mass in the forest floor using Allan & Roulet's (1994a) soil pit data (1 710 kg N ha_f^{-1}) was similar to the estimate obtained in this study (1 660 kg N ha_f^{-1}). In part, a different definition of 'forest floor' between studies may result in the higher estimate in the Uplands. On the other hand, the Upland *P. banksiana – P. mariana* forest is possibly the oldest of its kind studied to date (i.e. *P. banksiana* >100 years-old have less commercial value). Thus, a large accumulation of N in the 'old' Upland forest is not inconsistent with the tendency for nutrient accumulation in unproductive boreal conifer forest floors.

Table 1.2. Distribution of N in some North American boreal conifer forests. Pools in kg N ha^{-1}, fluxes in kg N ha^{-1} yr^{-1}. Upland data expressed per ha of forest island.

Forest Type	Black spruce	White spruce	Jack pine	Jack pine	Black spruce	Upland
Location	Alaska	Alaska	Minnesota	Ontario	Ontario	NW Ontario
Age			40	20 – 65		>130
Trees	120	274	296	133 – 205	482 - 547	166
Understory	-	-	17	6	0.7 - 40	9 – 24
Litterfall	3	9	-	21	20 - 30	10 – 18
Forest Floor	630	570	689	234 - 430	1050 – 1375	1660
Mineral Soil	3070	2400 - 4000	2312	3729	695 - 1423	1590
Source	Van Cleve et al. 1983	Van Cleve et al. 1983	Alban et al. 1978	Foster & Morrison 1976	Gordon 1983	this study

The form of N exported by forest islands was less variable from year-to-year than on bedrock surfaces (Fig. 1.5). In both 1995 and 1996, DON was the main form of N lost in runoff (~80%). DON export was probably hydrologically driven, with fluxes 3-fold higher during the wetter 1996. PN export was also larger (2-fold) in 1996, but NH_4^+ and NO_3^- exports remained the same. The potential for mineral-N retention by forest islands is larger than what bulk precipitation alone suggests. For forest islands located lower in the landscape, additional N is provided through runoff from upslope bedrock surfaces and forest islands. The combination of input from precipitation, bedrock surfaces, and from upslope forest islands is unique for each forest island.

The internal N cycle in forest islands does not seem to balance. In mature forests, litterfall is an estimate of above ground tree demand for N (10 – 18 kg N ha_f^{-1} yr^{-1}). As a first approximation, an equivalent demand for N can be assumed for fine root turnover (Ruess et al. 1996), yielding a total demand for N between 20 – 36 kg N ha_f^{-1} yr^{-1}. Including some N retention during the snowmelt period, bulk precipitation and bedrock surface inputs represent ~10 kg N ha_f^{-1} yr^{-1}, while N-mineralization is ~5 kg N ha_f^{-1} yr^{-1}. Thus, the yearly N supply apparently only represented 40% to 70% of the annual N demand.

The 'missing' N was probably derived from recycling, but was missed because of a methodological artifact in the buried bag assay or an uncounted form of N. A drawback of the N mineralization assay is that roots are cut-off by soil coring and may provide a fresh

source of organic matter to decomposing microorganisms (Schlesinger 1997). In forest islands, the C:N of fine roots was higher (36 – 71) than the bulk soil organic matter (14 – 33; Chapter 5). The implication for the N mineralization assay is that N tends to be immobilized (i.e., to accumulate) during the decomposition of organic matter with a high C:N (see *N mineralization-immobilization* in Chapter 5). Thus, the buried bag incubation assay provided a minimum estimate of soil N mineralization in forest islands because some of the mineralized N may have been subsequently immobilized on decaying roots. The opposite situation may have occurred in lichen patches because *Poa* roots have a low C:N (20) that will favor a net mineralization during decomposition.

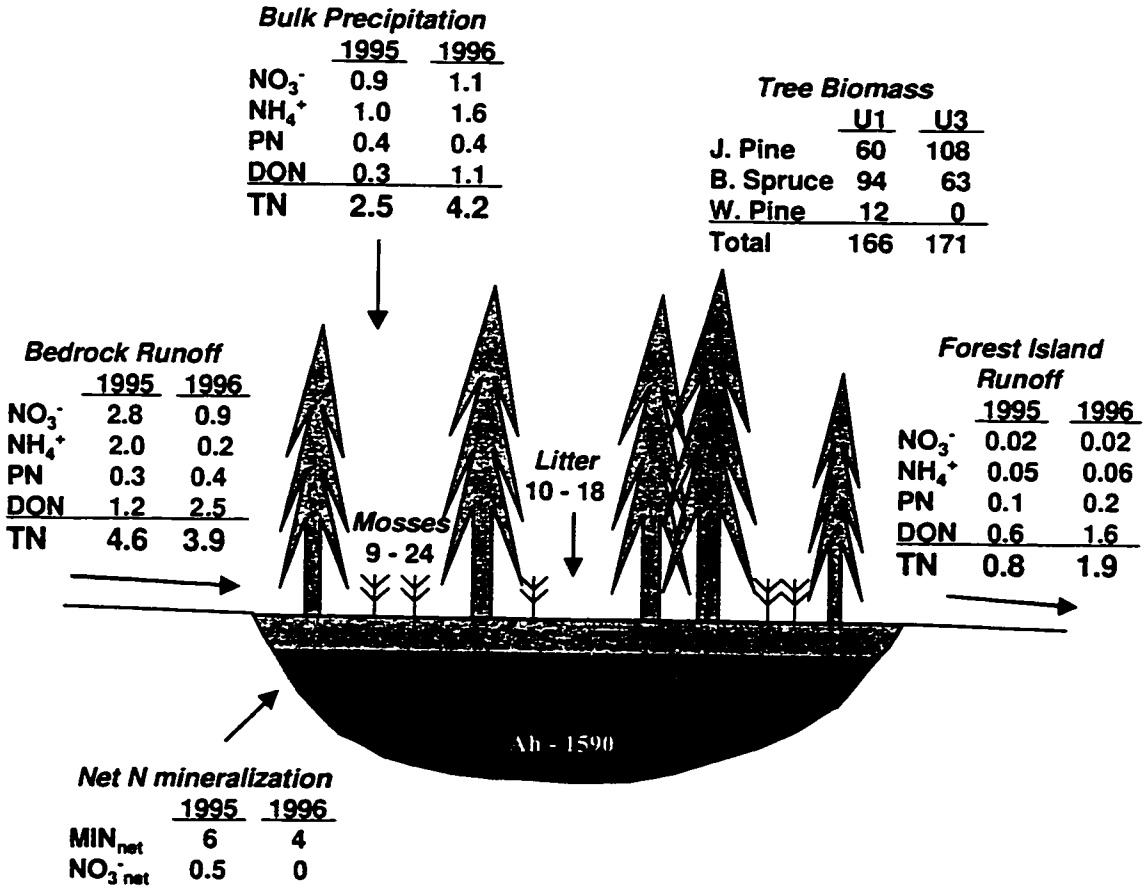


Fig. 1.5. Nitrogen pools and fluxes in forest islands. Fluxes for the growing season only (May – September). Pools and fluxes expressed as kg N per ha of forest island. Contribution from bedrock surfaces estimated using the average ratio of 2.7 ha of bedrock surfaces per ha of forest island.

A possibly unaccounted source of N for forest islands could be DON (Ruess et al. 1996). DON was the most important form of soluble N in Upland soils and was produced in large amounts during decomposition (Chapter 3). Boreal and tundra plants can utilize simple organic N compounds as a source of N for growth (Kielland 1994; Schimel & Chapin 1996; Raab et al. 1996; Näsholm et al. 1998), especially through mycorrhizae (i.e., symbiotic association between roots and fungi; Allen 1991; Finlay et al. 1992). There are examples from other unproductive conifer forests where the internal N cycle may be short-circuited at the DON stage. Under extremely N-limiting conditions, *Pinus muricata* pygmy forests in California produce a litter enriched in polyphenols (Northup et al. 1995a), which inhibits decomposition past the DON stage (Northup et al. 1995b). It is suspected that *P. muricata* can take up DON through mycorrhizae. Thus, producing a litter rich in polyphenols could provide a competitive advantage to *P. muricata* over other plants that cannot use DON (Chapin 1995). Whether a similar mechanism could occur in the Uplands will require further experimentation.

Overall, the analysis of the N budget in forest islands suggests that the N demand is high relative to the N supply. The biological retention mechanisms for N appear strong because the export of mineral N is nearly independent of the supply or hydrological conditions during the growing season. Particulate N and DON are the main form of N exported because physical and geochemical processes are more important in regulating their loss than biological ones (McDowell & Wood 1984; Hedin et al. 1995; Houle et al. 1995).

Catchment scale N cycle

The pattern in N export at the catchment scale was closer to the one of forest islands than bedrock surfaces (Fig. 1.6). As for forest islands, mineral N inputs were efficiently retained, but TN export was variable from year-to-year because DON losses varied 2.5-fold. Forest islands leave a stronger imprint on whole catchment runoff because most of the water must transit through at least one before leaving the landscape (Fig. 1.7). Only a small contributing area immediately upslope of the weirs yields bedrock surface runoff directly to the catchment outflows (Allan & Roulet 1994b; Fig. 1.3). Bedrock surface runoff is enriched in mineral N and is a net source of base cation nutrients (Ca^{2+}, K^{+}, and Mg^{2+}) relative to

precipitation (Allan et al. 1993). In contrast, runoff from forest islands is more acidic (pH 3.9 - 4.1 vs. 4.3 - 4.7 for bedrock surfaces), depleted in base cations, and enriched in dissolved organic matter. Similarly, in the sub-alpine environment the strategic location of small patches of forest along preferential flow paths strongly influences the geochemistry of runoff (Baron 1991). However, upslope bedrock surfaces are also important for downstream systems because they produce a larger volume of runoff per unit area and export nutrients.

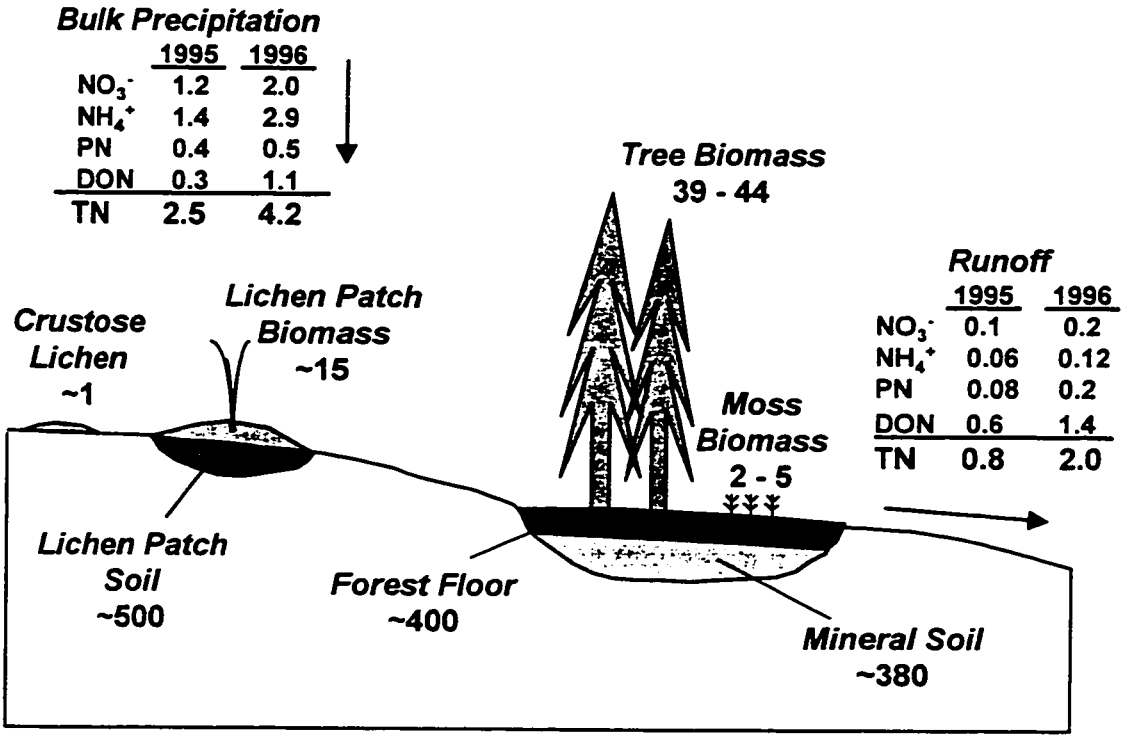


Fig. 1.6. Upland catchment N pools and fluxes. Pools in kg N ha^{-1} and fluxes in kg N ha^{-1} yr^{-1}.

The element export from the 0-order Upland catchments has some similar and some divergent properties from larger catchments at the ELA (Table 1.3). Across the range in catchment size at the ELA, mineral N inputs are efficiently retained and DON is exported (Table 1.3). However, the amount and timing of runoff is different between large and small catchments. Areal runoff is lower in the larger catchments, especially when a larger proportion of precipitation occurs during summer months when evapotranspiration is elevated. Runoff from the 0-order catchments is more acidic (Table 1.3). Relative to bulk

precipitation, the Rawson Lake North West inflow (56 ha) is a sink for H^+ while U1 (0.56 ha) and the small 1-order U8 (7.1 ha) are net sources. U1 and U8 are sinks or weak sources for base cations like Ca^{2+}, while base cations are exported from larger catchments even during dry years (Table 1.3). In the small catchments, acidity generated by the biological uptake of NH_4^+ and base cations is not neutralized by geochemical weathering because the mineral soil is thin and the water residence time is short. The Upland catchments should be more vulnerable to acidification by elevated N and S inputs than catchments containing thicker overburden deposits because of a limited potential for geochemical buffering.

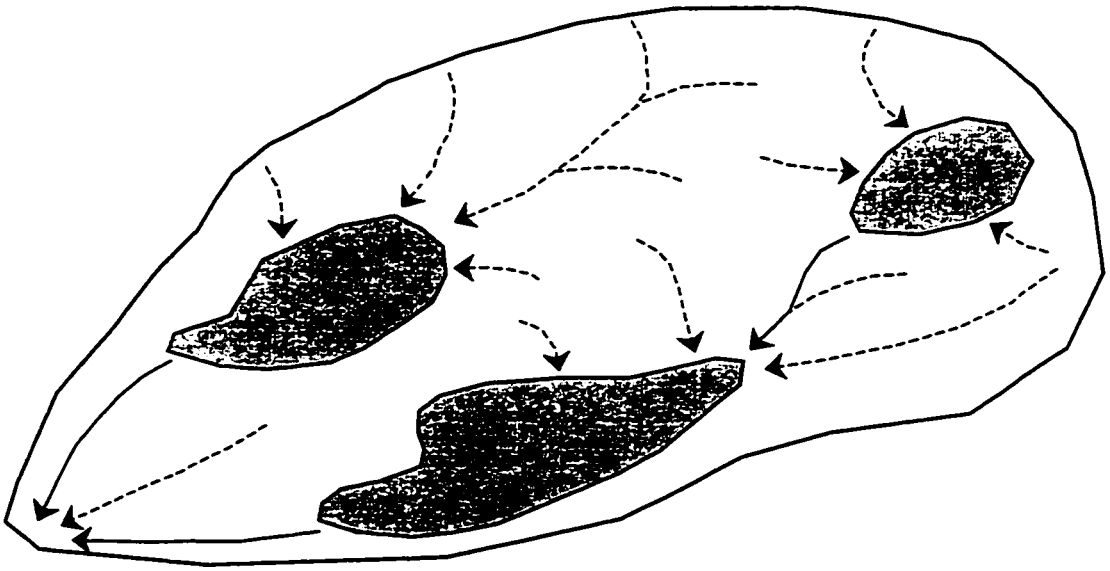


Fig. 1.7. Conceptual representation of bedrock surface and forest island flowpaths in the upland boreal Shield landscape.

Table 1.3. Bulk precipitation input and element export from 0- and 1-order catchments at the Experimental Lakes Area. A comparison is made between years with **(A)** high runoff (1989) and **(B)** low runoff (1990). Fluxes are in kg ha^{-1} yr^{-1} or equivalent ha^{-1} yr^{-1} (for charged species). Data from Allan et al. (1993) and D.W. Schindler & B.R. Parker pers. comm.

(A) 1989

	Bulk Precipitation	U1 (0.56 ha)	U8 (7.1 ha)	Rawson NW inflow (56 ha)
NO_3^- (kg N ha^{-1} yr^{-1})	2.1	0.11	0.01	0.13
NH_4^+ "	2.2	0.08	0.07	0.02
PN "	0.55	0.19	0.09	0.14
DON "	1.9	1.0	0.95	1.3
TN "	6.8	1.4	1.1	1.6
TP (kg ha^{-1} yr^{-1})	0.094	0.039	0.025	0.031
DOC "	16.7	43.4	46.6	35.3
H^+ (eq ha^{-1} yr^{-1})	52	107	92	19.2
Ca^{2+} "	98	101	113	193
Mg^{2+} "	30	62	95	126
Na^+ "	19	52	70	71
K^+ "	8	14	13	34
Cl^- "	11	14	22	16
SO_4^{2-} "	130	133	191	195
Si (kg ha^{-1} yr^{-1})	0.08	5.23	8.0	6.7
DIC "	2.02	5.0	6.9	3.1
Water Flux (mm)	601	340	318	198

(B) 1990

	Bulk Precipitation	U1 (0.56 ha)	U8 (7.1 ha)	Rawson NW inflow (56 ha)
NO_3^- (kg N ha^{-1} yr^{-1})	1.5	0.01	0.01	0.10
NH_4^+ "	1.6	0.06	0.04	0.04
PN "	0.69	0.08	0.06	0.05
DON "	0.90	0.74	0.65	0.55
TN "	4.7	0.89	0.76	0.74
TP (kg ha^{-1} yr^{-1})	0.11	0.023	0.017	0.012
DOC "	15.1	32	32	21
H^+ (eq ha^{-1} yr^{-1})	37	66	57	11
Ca^{2+} "	115	61	73	125
Mg^{2+} "	42	39	61	78
Na^+ "	15	34	50	48
K^+ "	7	7	11	8
Cl^- "	12	7	10	14
SO_4^{2-} "	141	76	126	121
Si (kg ha^{-1} yr^{-1})	0.09	4.0	6.6	4.5
DIC "	2.03	3.3	3.5	2.2
Water Flux (mm)	559	196	197	92

Plant growth and nutrients

The growth of plants may be controlled by different factors in forest islands and lichen patches. In forest islands, N was a probable growth-limiting nutrient for trees. An estimate of nutrient limitation in *P. banksiana* and *P. mariana* was made by comparing needle nutrient content and ratios to the critical values for *Picea abies* seedlings (Rosengren-Brinck & Nihlgård 1995). This comparison is qualitative because different conifer species and developmental stages may have different nutrient requirements. The foliar N content in *P. mariana* (10 mg N g_{dw}^{-1}) and *P. banksiana* (11 mg N g_{dw}^{-1}) needles was below the suggested threshold for N limitation in *P. abies* (13 mg N g_{dw}^{-1}; Fig. 1.8). Although foliar P in both species and K for *P. banksiana* were also at the nutrient limitation threshold, the ratio of these elements relative to N indicated primarily N limitation (Fig. 1.8). According to Weetman and Fournier (1984a), the 'optimum' foliar N content for *P. banksiana* is 14 mg N g_{dw}^{-1}, which is consistent with N limitation in Upland trees.

Tree growth may have been influenced by climate because of its control on nutrient mineralization rates in the soil (Chapin 1986; Van Cleve et al. 1990). *Picea* growth was highest in 1995 (Fig. 1.9) when soils were warmer, drier, and net N mineralization rates more elevated (Chapter 3). Increased growth during droughts has been observed in *P. mariana* growing in bogs (Gorham et al. 1984), presumably through increased rates of peat N mineralization following the lowering of the water table. In Alaska, the needle nutrient content and the photosyntethic activity of *P. mariana* were increased by experimentally heating a forest floor by 9°C (Van Cleve et al. 1983), although no increased growth resulted on the short-term. Although limited to 2 years of measurements, the pattern in tree growth in the Upland catchments illustrates the complex feedbacks between climate and nutrient cycles in the boreal forest.

Climatic factors may also control the growth of lichens and mosses on bedrock surfaces, but not through its effect on nutrient recycling rates. Unlike trees, *R. microcarpon* grew more during the wetter 1996 (Chapter 4). Vitt (1991) also found a positive correlation between *R. microcarpon* growth and precipitation during the growing season. Similar relationships are common in boreal lichens (Hale 1973) and other boreal mosses (Busby et al.

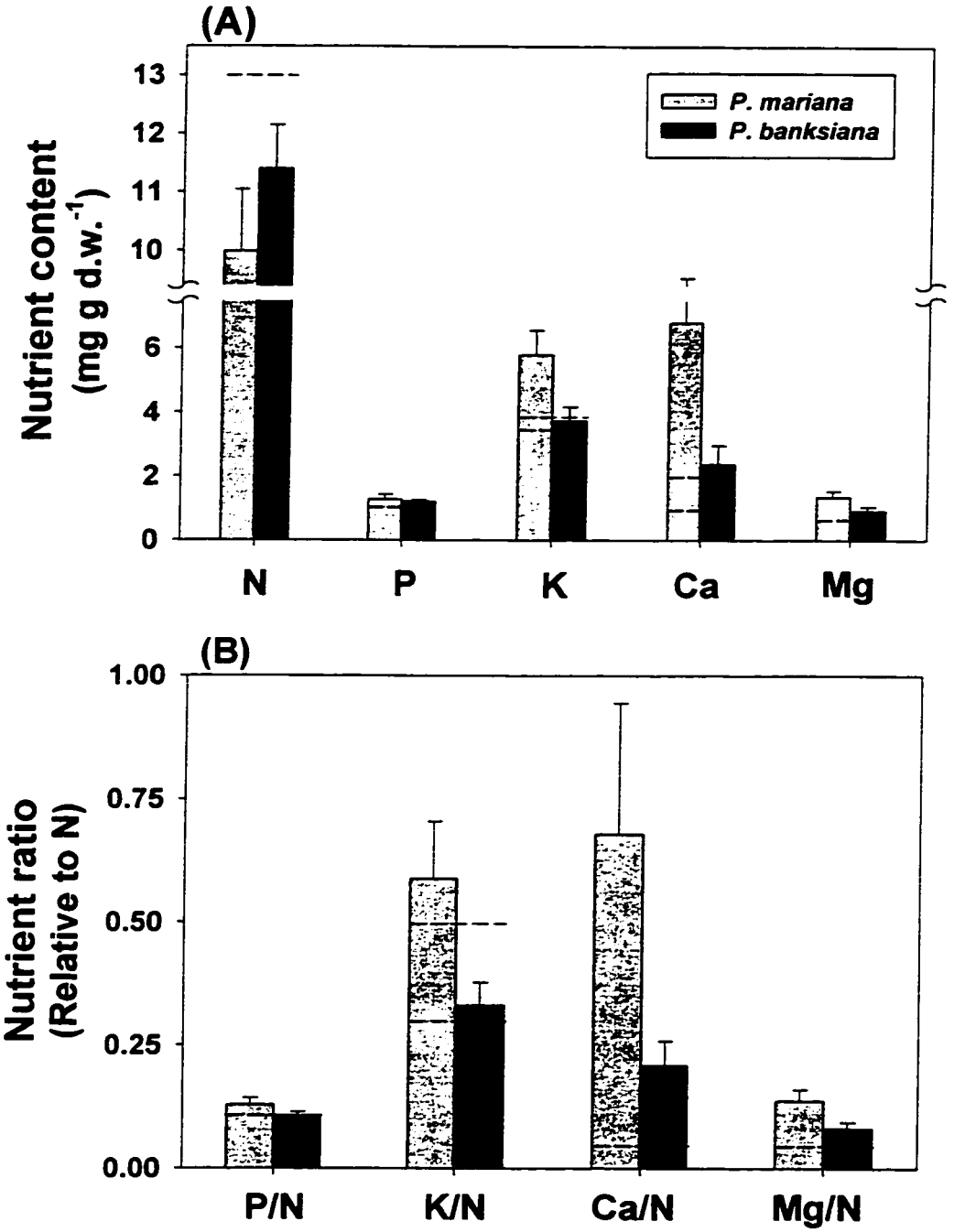


Fig. 1.8. Nutrient content (**A**) and ratios relative to N (**B**) in *P. mariana* and *P. banksiana* 0+ year needles in U1 in September 1996. The range in 'critical' concentrations and ratios for *Picea abies* seedlings (summarized by Rosengren-Brinck & Nihlgård 1995) are showed with dashed lines.

1978). Precipitation is related to moss and lichen growth because of its effect on their energy balance. Relative to vascular plants, mosses and lichens have limited means to prevent water losses and undergo long periods of time under water stress (Blum 1973). The balance between C obtained by photosynthesis and C lost through respiration is negative (i.e. C is lost) when mosses and lichens have a low moisture content or are in a dormant, desiccated state (Richardson 1981). In addition, respiration rates are elevated and photosynthetic rates depressed for several hours following re-wetting (Lechowicz 1981; Richardson 1981). Thus, a smaller proportion of energy can be allocated to growth in 'dry' relative to 'wet' years. However, especially during wet years, nutrients may also limit growth. Boreal lichens and mosses sprayed with dilute nitric acid tend to have higher growth rates or photosynthetic activity on the short term (Bayley et al. 1987; Lechowicz 1987; Scott et al. 1989). At the present, there is more evidence for water rather than nutrient-limitation of growth for Upland mosses and lichens.

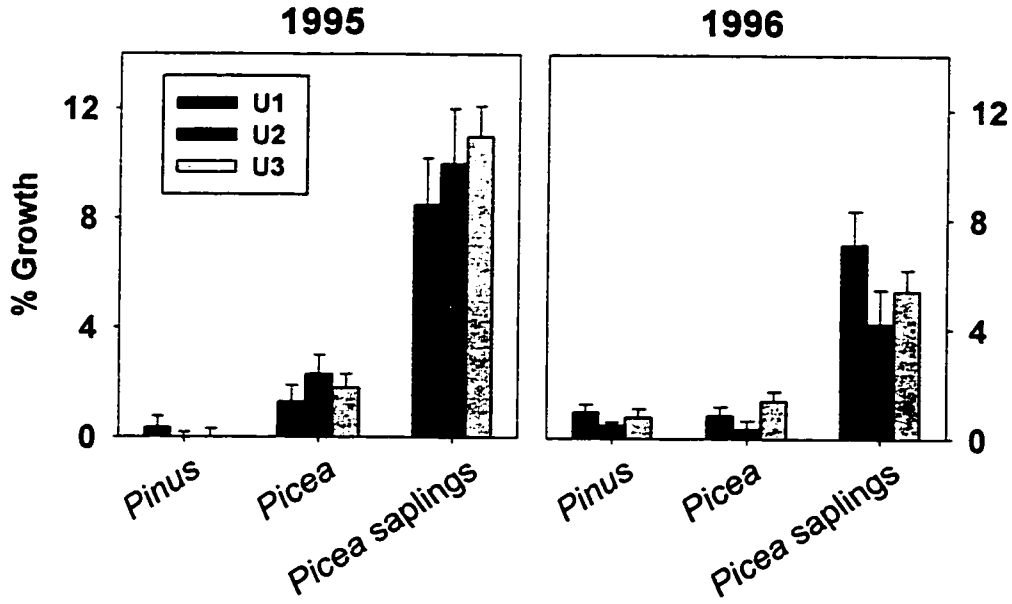


Fig. 1.9. *Pinus banksiana* and *Picea mariana* growth in catchment U1, U2, and U3 in 1995-96. Growth is expressed as the relative increase in tree diameter for mature trees and the relative increase in tree height for saplings. The growing season of 1995 (May – September) was warmer (average air temperature = 16°C) and drier (367 mm of precipitation) than 1996 (15°C and 557 mm).

Gas fluxes

In the preceding discussion, the term 'retention' was defined as the input minus the output of N, and 'retained' N implied N stored somewhere in the catchment. As is typical in catchment-scale studies (Wright et al. 1995b), the in- and out-flux of gases were either assumed to be small or to cancel one another. Within the framework of catchment acidification by N compounds, N gaseous losses have a similar effect as storage of N within catchments. The production of many gases, for example N_2 and N_2O during denitrification, involves the consumption of H^+ (Anderson & Schiff 1987). Thus, in general, acidity is neutralized whether N is 'retained' by storage within the catchment or 'retained' by gaseous N loss. However, unlike with gaseous N losses, acidity neutralized during storage can be regenerated under some conditions (Yan et al. 1996; Burns et al. 1998). In addition, the accumulation of N may bring about significant changes in the plant community and the internal N cycle on the long-term (van Breeman & van Dijk 1988). Presently, only sparse information is available about N gas fluxes in the Upland catchments.

Nitrogen fixation was the most probable gaseous N influx to the Uplands. Allan et al. (1993) hypothesized that N fixation by lichens could be a source of N to lichen patches. In the Uplands, moist and desiccated lichens had no N-fixing activity during acetylene-reduction incubations (Chapter 3). Unlike in lichens, N fixation by free-living cyanobacteria associated with mosses such as *Polytrichum* and *P. schreberi* could be significant (Richardson 1981; Alexander & Billington 1986; Chapter 3). In the Uplands, stable N isotope ratios suggests that mosses obtain some of their N from N fixation (Chapter 3), but this will require further confirmation. Free-living N fixation may also occur in soils and in decaying wood (Harmon et al. 1986). N fixation ranges between 0.1 to 17 kg N ha^{-1} yr^{-1} in boreal and tundra ecosystems (Van Cleve & Alexander 1981), but is generally ~1 kg N ha^{-1} yr^{-1} in old-growth boreal conifer forests (Alexander & Billington 1986).

Several N gases could be produced in the Uplands. N_2 and N_2O could be generated by denitrification (Knowles 1981). However, denitrification is usually negligible in pristine boreal conifer forests because the internal N cycle does not favor the production of NO_3^- (Blew & Parkinson 1993; Chapter 4). Some loss of N oxides is likely because they are

necessary intermediates in many reactions within the N cycle. For example, 1% to 3% of nitrified NH_4^+ is lost as NO and N_2O (Firestone & Davidson 1989). NH_3 volatilization could occur in lichen patches because of greater NH_4^+ production rates and a lower potential for canopy recycling of emitted NH_3 (Denmead et al. 1976). However, the low soil pH in forest islands (~4.1) and lichen patches (~4.4) will not favor the conversion of NH_4^+ to NH_3 (pK_a ~9) and should prevent large volatilization losses. Ammonia losses may occur in 'hotspots'. For example, on bedrock surfaces a pungent NH_3 smell was detectable when ant colonies under flat rocks were exposed. Gaseous N losses are important during forest fires (Wein & MacLean 1983; Bonan & Shugart 1989; Lobert et al. 1990), and possibly following clear-cutting (Vitousek & Melillo 1979; Vitousek et al. 1979). Additional work is required to clarify the importance of N fixation and gaseous N losses in the Upland catchments.

Water stress: the mechanism generating lichen patches and forest islands?

The potential to store water may be a determinant factor in generating the occurrence of lichen patches and forest islands in the Upland landscape. The Uplands can be seen a continuum of small soil deposits left by eolian inputs following deglaciation. At present, there would be a threshold in soil patch volume where enough moisture can be stored to sustain trees during periods of drought. Patches too small to be permanently colonized by trees are occupied by organisms more tolerant of drought conditions. Some of the largest lichen patches contain dead saplings that may have been established during relatively wet periods but perished during droughts. At the regional scale, grassland paleosoils (chernozem) can be found under presently forested areas, suggesting that grassland vegetation may have been more common under a past, milder and drier climate (Zoltai 1965; Brunskill & Schindler 1971). Thus, the proportion of the Upland landscape covered by forest islands or lichen patches could vary as a function of long-term climatic variability.

Once trees invade a lichen patch, they may outcompete other organisms by shading and by changing the nature of the internal N cycle. Boreal conifer tree litter is refractory to decomposition (Flanagan & Van Cleve 1983) and will tend to increase the competition for soil N between plants, heterotrophic microbes, and nitrifiers (Bossata & Berendse 1984; Johnson 1992). Organisms requiring an abundant NH_4^+ supply or NO_3^- as a source of N

would be most strongly affected because a likely outcome of increased competition for soil N is decreased net N mineralization and net nitrification rates (Kirby 1981; Van Vuuren et al. 1992). The large variability in N mineralization, net nitrification, and the type of organisms present between lichen patches may in part reflect past plant cover history. Following a change in plant cover, a transition period will be necessary for the N cycle to adjust to the new source of litter because of the relatively large store of soil organic matter underneath lichen patches.

Implications for elevated N deposition to the Upland boreal forest

In summary, the ELA Upland catchments are composed of two landscape units with different internal N cycles and patterns in nutrient export. Over bedrock surfaces, the production of NO_3^- underneath lichen patches and the relatively large loss of mineral N in runoff suggest that N is not limiting. In contrast, the combination of a low net N mineralization, plant N content, and mineral N export indicate that forest islands are N-limited.

Forest islands and lichen patches will probably react differently to an elevated N input. In forest islands, several mechanisms are available to favor the retention of N. The availability of tree litter with a high C:N will favor the immobilization of N inputs by soil microorganisms (Berg & Staaf 1981). Although net N mineralization in forest islands should increase following an increased N input (Bossata & Berendse 1984), the onset of net nitrification would be required to induce increased N losses (Stoddard 1994). N-limited trees may take up the excess N mineralized.

In contrast, bedrock surfaces are less likely to retain an elevated N input because of a low plant biomass (Johnson 1992), a low potential for N immobilization during moss and grass litter decomposition (Hobbie 1996), and a soil microbial community that may be intrinsically N-saturated (Aber et al. 1989). Following an increased N input, the rapid N saturation of bedrock surfaces may increase the N load to downslope forest islands. Although forest islands may be able to retain the excess N on the short term, the increased N input from bedrock surfaces may reduce the period of time needed for forest islands to become N-

saturated. This process may repeat itself at larger scales as N saturation would cascade down the boreal Shield landscape.

Chapter 2. A 26-Year Record of Mineral and Organic Nitrogen Deposition in the Central Boreal Forest

Introduction

Cultural activity has dramatically increased the input of N to forested ecosystems in many areas of the world (Vitousek 1994; Vitousek et al. 1997). In the boreal forest, the outcome of a long-term increase in N deposition is controversial (Houghton et al. 1998). On one hand, the growth of plants in boreal ecosystems is often N-limited and increased N inputs may boost forest productivity (Peterson & Melillo 1985; Schindler & Bayley 1993). This increase in CO_2-fixation, coupled with the tendency for the boreal biome to accumulate C, may partially mitigate the potential for 'global warming' induced by the rising concentration of atmospheric 'greenhouse' gases like CO_2 (Schindler & Bayley 1993). On the other hand, long-term elevated N inputs may lead to catchment acidification (Dise and Wright 1995) and plant community change in sensitive areas such as wetlands (Gorham et al. 1984; van Breeman & van Dijk 1988). In Canada, some areas of the Laurentian Great Lakes forest located on the Canadian Precambrian Shield show symptoms of excessive N loading (Jeffries 1995; Arp et al. 1996). Although N deposition is probably low throughout most of the boreal forest in Canada (<5 kg N ha^{-1} yr^{-1}; Jeffries 1995) N deposition in combination with sulphur (S) inputs could contribute to catchment acidification in some acid-sensitive regions (Arp et al. 1996). Presently, acid rain is not considered an important environmental problem in the central boreal forest because it is remote from large sources of SO_2 and NO_x emissions (Jeffries 1995; Manitoba Environment 1997).

Ongoing increases in livestock farming and in fertilizer use in the Prairie provinces (Fig. 2.1) and in the U.S. mid-west (Matthews 1994) may increase N inputs to parts of the boreal forest where 'traditional' acidic inputs (nitric and sulphuric acid) are not considered a problem. In Europe, ammonia (NH_3) emission from areas with intensive livestock farming and subsequent NH_3 and ammonium (NH_4^+) deposition to forests is an important cause of catchment acidification (van Breeman et al. 1982; United Kingdom Research Group on the Impact of Atmospheric Nitrogen (UKRGIAN) 1994; Galloway 1995). Because of the

efficient removal of atmospheric NH_3 by forest canopies, the transition zones between forests and farmlands are especially susceptible to elevated N deposition (Allen et al. 1988; UKRGIAN 1994). The excessive deposition of N compounds can result in catchment acidification through the process of 'N saturation' (Ågren & Bossata 1988; Aber et al. 1989). In pristine boreal ecosystems, the competition for soil nutrients between plants and microorganisms is strong and the low availability of NH_4^+ suppresses nitrification (Van Cleve et al. 1983; Johnson 1992). However, upon long-term elevated N deposition, the demand for N by plants and heterotrophic microorganisms may be satisfied and a greater proportion of the soil NH_4^+ pool may be utilized by nitrifiers (Johnson 1992). Nitrification is a strong acidifying process because both acidity (2 H^+ per mole of NH_4^+ nitrified) and a mobile anion (NO_3^-) are generated (Reuss & Johnson 1986). The displacement of base cations from soil exchange sites by H^+ followed by the loss of base cation from the catchment mediated by NO_3^- leaching can result in lower forest productivity (Likens et al. 1996), catchment acidification (Reuss & Johnson 1986), and eventually forest decline (Aber et al. 1989).

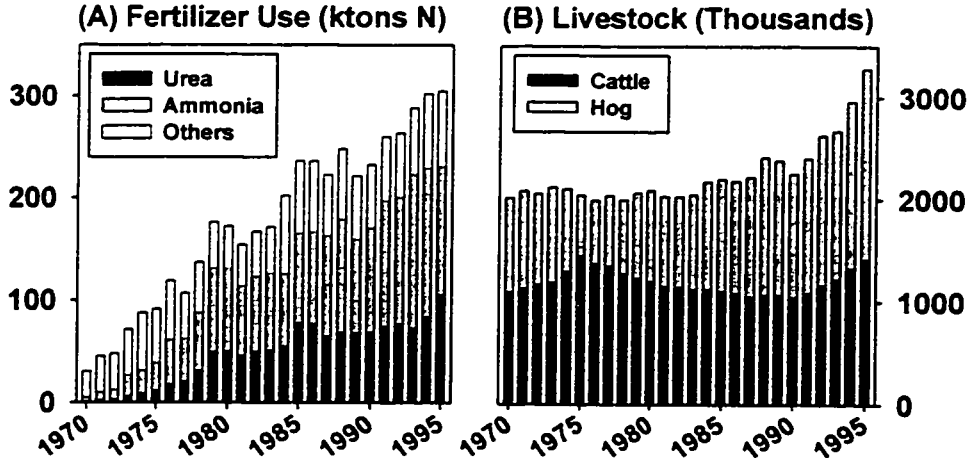


Fig. 2.1. (A) Nitrogen fertilizer use and (B) Heads of cattle and hogs in the Province of Manitoba between 1970 – 95. The ongoing increase in livestock farming is a result of the loss of grain export subsidies to western Canadian farmers (Manitoba Environment 1997)

The bulk deposition of NH_4^+, NO_3^-, particulate N (PN) and dissolved organic N (DON) has been measured continuously since 1970 at the Experimental Lakes Area (ELA) in northwestern Ontario. This record is one of the longest for mineral N deposition in North America and possibly the longest record anywhere for dissolved organic N. The ELA is situated in the south-central boreal Shield forest, over 250 km east from the nearest area of intensive farming in southern Manitoba (Fig. 2.2) and approximately 400 km north from the U.S. mid-west, the area of highest NH_3 emission in North America (Bouwman et al. 1997). Thus, the ELA record is a unique opportunity to evaluate whether recent agricultural and economic development in the Prairies had an impact on N deposition to the boreal forest. The first objective of this study was to review the ELA bulk N deposition record for the 1970-1995 period. The record up to 1982 has been published previously (Linsey et al. 1987) but will be included here for consistency. In addition, the deposition of DON had not been evaluated and will be presented here.

The period covered by the record was characterized by decadal-scale climatic variability and by important changes in the landscape surrounding the ELA. The 1970-1990 period was characterized by a 1.6°C warming and drying trend at the ELA (Schindler et al. 1990; 1996) which was in part due to a drought throughout central North America (Webster et al. 1996). In addition, a windstorm (1973) and two forest fires (1974; 1980) considerably modified the landscape at the ELA. Deforestation and the regional drought may have acted synergistically to generate a warmer and drier climate at the ELA during the 1980's (Schindler et al. 1990). Thus, in a second objective, the bulk deposition record was compared to climatic variables at the site (windspeed, temperature, and precipitation) to evaluate the impact of landscape changes and climatic variability on bulk N deposition.

The input of N to forested catchments is complex because deposition may occur through a variety of 'wet' and 'dry' deposition mechanisms (Hanson and Lindberg 1991; Lovett and Lindberg 1993; Lovett 1994). In a third objective, the wet and dry deposition of N compounds was evaluated for the 1986 - 1991 period, when the ELA also operated a wet-only collector. The difference in deposition between the bulk collector (which always remains

open to the atmosphere) and the wet-only collector (which is unshielded only when wetted) was used here as a minimal estimate of dry deposition. Bulk and wet-only depositions were compared on a seasonal and annual basis. Event-by-event N deposition was also compared to Ca^{2-} deposition, an element expected to have a strong, long-range, dry deposition component as Prairie dust.

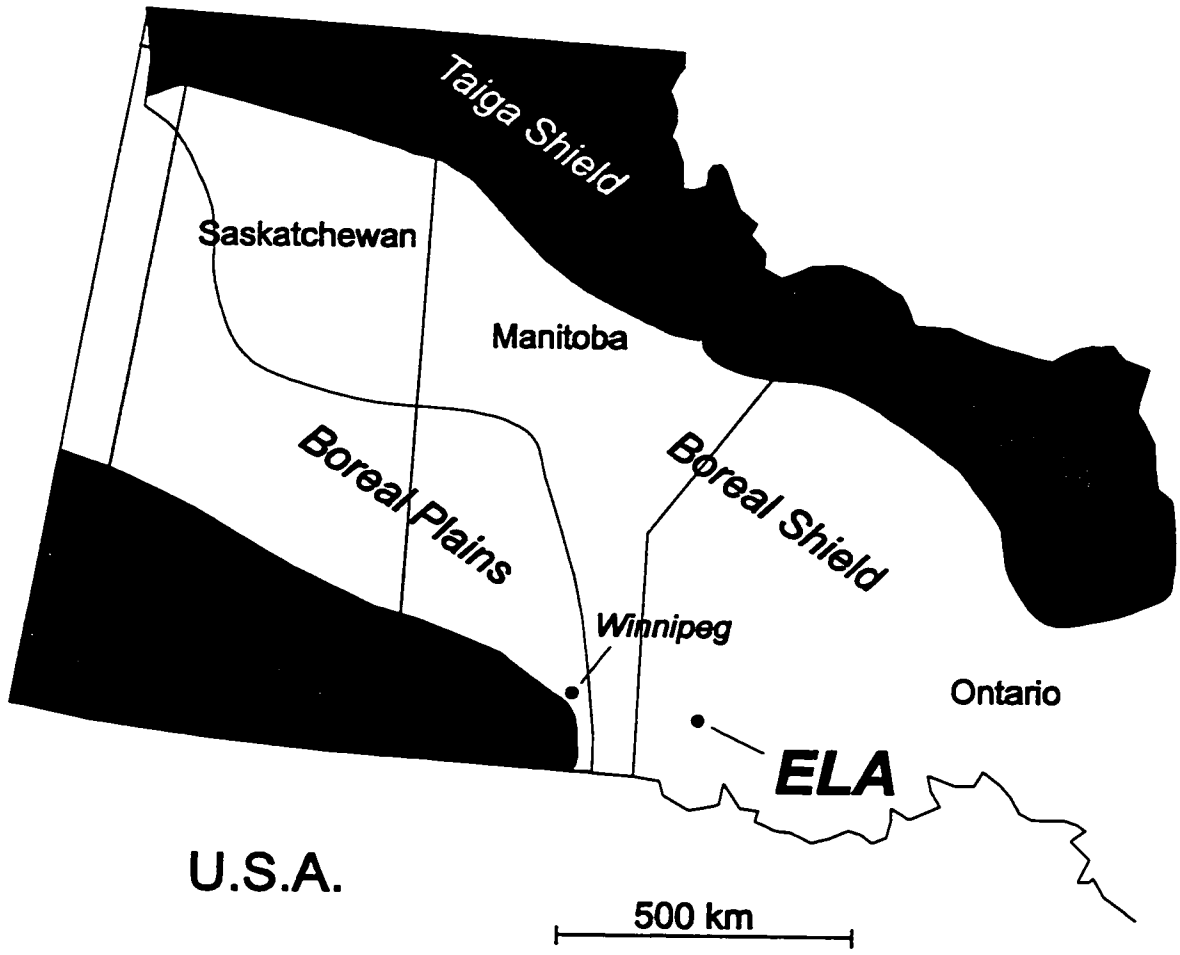


Fig. 2.2. Location of the Experimental Lakes Area and the ecozones of central Canada. A more detailed map of the ecozones of Canada and background information can be found at the Environment Canada Green Lane site http: //www1.ec.gc.ca/ ~vignettes/terr.html.

Methods

Study area

The ELA is a set of 58 lakes and watersheds set aside for long-term monitoring and whole-ecosystem research in a pristine area of northwestern Ontario (Johnson and Vallentyne 1971). Climate at the ELA is humid continental, with mean average temperature of 2.3°C and a mean annual precipitation of 673 mm (27% of which occurs as snow; Beaty and Lyng 1989). Soils at the ELA are generally thin (<1 m) and exposed bedrock outcrops (pink granodiorite) are common (Brunskill and Schindler 1971; McCullough and Campbell 1993). The topography is gently rolling hills, with thicker overburden deposits, wetlands and lakes occurring in valleys. In upland areas, the forest is predominantly composed of jack pine (*Pinus banksiana* Lamb.) and black spruce (*Picea mariana* Mill B.S.P.) Wetlands are predominantly *Sphagnum* bogs or poor fens. Wildfires are common in the area, with a return time of 50-100 years (Schindler et al. 1996). The forest cover in the catchments of Lakes 239 and 240 was damaged by a windstorm in 1973, severly burned by a fire in 1974, and nearly completely destroyed by a large fire in 1980 (Bayley et al. 1992; Schindler et al. 1996). Forest regrowth was slower following the second fire (Bayley et al. 1992). Canopy height in 1995 was approximately 5 m. The maximum height before fires was about 30 m.

The original design of the ELA precipitation monitoring network was for nutrient mass-balance calculation for lakes (Schindler et al. 1976). A bulk collector was installed on a small island on Lake 239 (1970-1982) or Lake 240 (1983-1995) to estimate direct deposition to lake surfaces. The bulk collector was a 0.25 m^2 screened acrylic collector 1.5 m from the ground surface emptying into a 20-L polyethylene carboy. During the winter months, rain and snow samples were collected with a modified collector emptying into a polyethylene bag located at the ELA meteorological station. Snow was pushed into the bag on a daily basis using a polyethylene shovel. Rainfall and water equivalent of snowfall were estimated using Canadian standard rain gauges and shielded Nipher snow collectors at the ELA meteorological station (Beaty and Lyng 1989). The wet-only collector was also located at the ELA meteorological station.

Rain water samples were collected on an event basis throughout the record. During continuous rain events, samples were taken every 24 hours. Samples were kept at 4°C and usually analyzed between 12 to 48 hours following collection. During winter months, samples were collected when enough snow had accumulated in the collector, which varied from 1 day to a month. Snow samples were sealed in plastic bags and kept frozen until analysis. Analyses were made on site during the open water season and either on site or at the Freshwater Institute, Winnipeg, during winter months. Samples obviously contaminated by bird droppings, insects, or terrestrial debris were discarded.

Particulate-N was determined by filtering a sub-sample on a pre-combusted GF/C filter (nominal pore size 1 μm) and the N content was measured using an elemental analyzer. Ammonium, NO_3^-, and NO_2^- were determined colorimetrically following Stainton et al. (1974). Nitrite concentrations were usually low to non-detectable and were pooled with NO_3^-. Total dissolved nitrogen (TDN) was estimated using a UV-persulphate digestion, followed by a reduction of the mineralized N to NH_4^+ by elution through a zinc column (Stainton et al. 1977). DON was estimated from TDN - NH_4^+ - NO_3^-. Analytical detection limit was 1 μg L^{-1} for NH_4^+ and NO_3^-, and ~1 μg N L^{-1} for PN. Precision of duplicate or triplicate samples was ±5% (SD/mean*100) for NO_3^-, NH_4^+ and TDN. Precision for PN was more variable and occasionally as high as 50% during the winter period when PN concentrations were low.

The annual bulk deposition of N compounds was compared to precipitation, temperature, windspeed, and potential evapotranspiration measurements collected at the ELA meteorological station using standard methodology (Beaty & Lyng 1989). Average precipitation, temperature, and windspeed were calculated for the whole-year and for the summer period only (June – August). Patterns between N deposition and environmental variables were evaluated with graphs and a Pearson correlation matrix (with and without Bonferroni-adjusted probabilities; Wilkinson 1990).

Location of the bulk collector

Only one important methodological change occurred over the record. In 1983, the bulk collector was moved from an island on Lake 239 to another on nearby Lake 240 because of concern for occasional contamination by throughfall at the former location. The patterns in DOC and DON deposition before and after relocation were used to infer potential throughfall contamination at the former location. Throughfall contamination would be apparent because it is quite enriched in DOC (~30 mg C L^{-1}) relative to bulk deposition (~ 2-3 mg C-DOC L^{-1}; Allan et al. 1993). Throughfall also tends to have a high DOC:DON ratio (40 – 70 Lamontagne unpublished data).

Patterns in wet and dry N deposition

The deposition of different N forms between collectors between 1986 and 1991 was compared on an annual and seasonal basis. In addition, the patterns in dry and wet N deposition were further investigated using event-by-event variations in N concentration in both collectors (only summer events were used to minimize seasonal variability). Event N concentration was related to the number of days since the last rain event (DAYS) and precipitation depth (RAIN). N concentration was expected to be positively correlated with DAYS (because of dry deposition to the bulk collector and the accumulation of particles in the atmosphere during dry periods) and negatively with RAIN (because of dilution of dry deposition and the gradual washout of atmospheric particles during prolonged rain events). In addition to the different N forms, event Ca^{2-} concentration was also analyzed in a similar fashion because it provided a reference for an element with a strong dry deposition component as dust (Linsey et al. 1987; Lovett & Lindberg 1993).

Uncertainties in DON estimates

Dissolved organic N concentrations have the highest uncertainty because they accumulate the errors of TDN, NH_4^+, and NO_3^- analyses (Gorzelska et al. 1997). The uncertainty is largest when the difference between TDN and mineral N is small, as is often the case in rainwater. Twelve percent of samples did not have a DON value because one of the N analyses was missing. Missing DON values were usually from small rain events (mean = 5.5

mm) where not enough water was collected for all analyses. An examination of the frequency distribution of DON concentrations revealed a subset of samples with extremely low (<-500 μg N L^{-1}; 1.0%) or extremely high (>2 000 μg N L^{-1}; 1.3%) DON values (Fig. 2.3). Extremely low DON values may have resulted from an unrecorded analytical error. Extremely high values could have resulted either from an analytical error or an unrecorded contamination of the sample. Samples with DON concentration below -500 μg N L^{-1} or above 2 000 μg N L^{-1} were removed from further analyses. DON concentrations were negative in 11.3% of the remaining samples (Fig. 2.3). Negative DON values were kept to avoid introducing a systematic bias in the data set. In other words, assuming a normal error distribution for TDN, NH_4^+ and NO_3^- analyses, negative DON values counterbalanced randomly high DON values. Thus, when averaged over the year, DON deposition was probably an unbiased but unprecise estimate of the 'true' mean value.

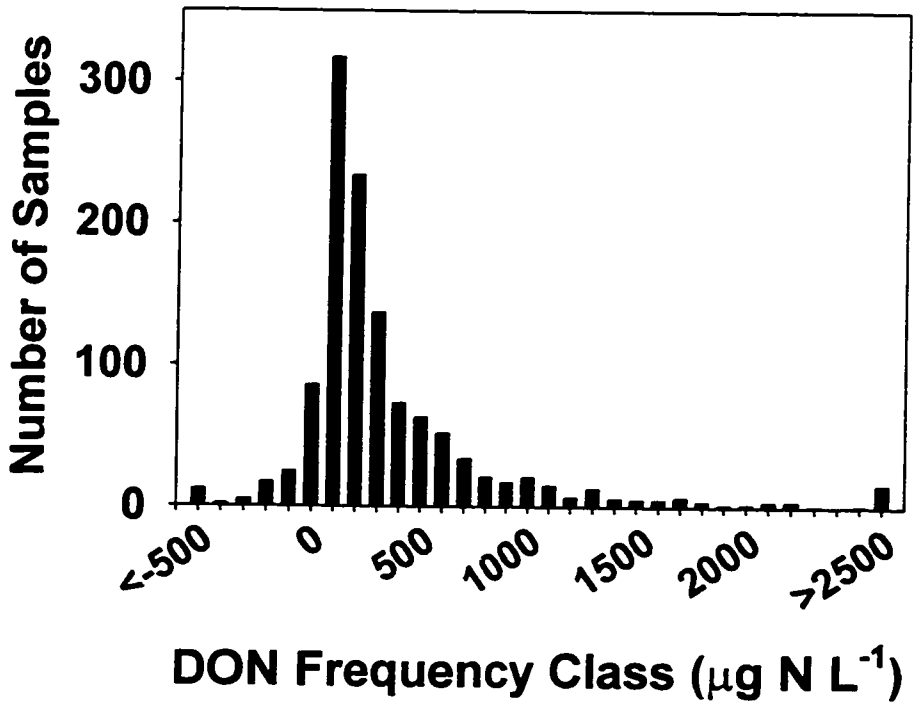


Fig. 2.3. Frequency distribution for DON concentration in bulk precipitation at the ELA, 1970-1995.

The UV-persulphate oxidation may underestimate DON concentration. In an inter-laboratory comparison of DOC standards, Koprivnkjak et al. (1995) found that the UV-persulphate oxidation (without Pt catalyst) yielded good recovery of DOC in specific standards but underestimated DOC in natural mixtures by 20-24%. It is suspected that the UV-persulphate oxidation underestimates DON as well (Cornell et al. 1995; Scudlark et al. *in press*). However, all current methods to estimate TDN have shortcomings and a thorough intercalibration of techniques has not been made for rainwater (Gorzelska et al. 1997). The recovery of DON standards is excellent with our procedure (M.P. Stainton unpublished data) but occasional runoff samples with high NO_3^- concentrations have consistently yielded negative DON concentrations upon reanalysis (S. Lamontagne unpublished data). Some DON may have been lost to the polyethylene buckets (Scudlark et al. *in press*).

Results

Long-term N bulk deposition

The deposition of N at the ELA has varied from 4 to 10 kg N ha^{-1} yr^{-1} between 1970 and 1995 (Fig. 2.4). The deposition of PN shows a slight linear decreasing trend through the record, from a high of 2 kg N ha^{-1} yr^{-1} in the early 1970's to 0.5 to kg N ha^{-1} yr^{-1} in the 1990's (Pearson $r = -0.40$; $P < 0.05$). However, this downward trend is not statistically significant when two high values in the early 1970's are removed (Fig. 2.4). The deposition of NH_4^+ and NO_3^- was near stoichiometric ($r = 0.85$; $P < 0.001$), each varying between 1.2 to 3 kg N ha^{-1} yr^{-1}. Mineral-N deposition peaked slightly in the early 1970's when precipitation was high and in the early 1980's following the second wildfire. Dissolved organic N deposition was the most variable, with a gradual rise and a peak in deposition (3.5 kg N ha^{-1} yr^{-1}) in the late 1980's, followed by a decrease in the 1990's. A large part of the increase in N deposition in the late 1980's was attributable to increased DON deposition.

Peak N deposition corresponded with a relatively warm, dry, and windy period at the ELA (Fig. 2.4). The synergistic effects of increased air temperature and windspeed on the local climate in the late 1980's can be readily seen from the increase in potential evaporation

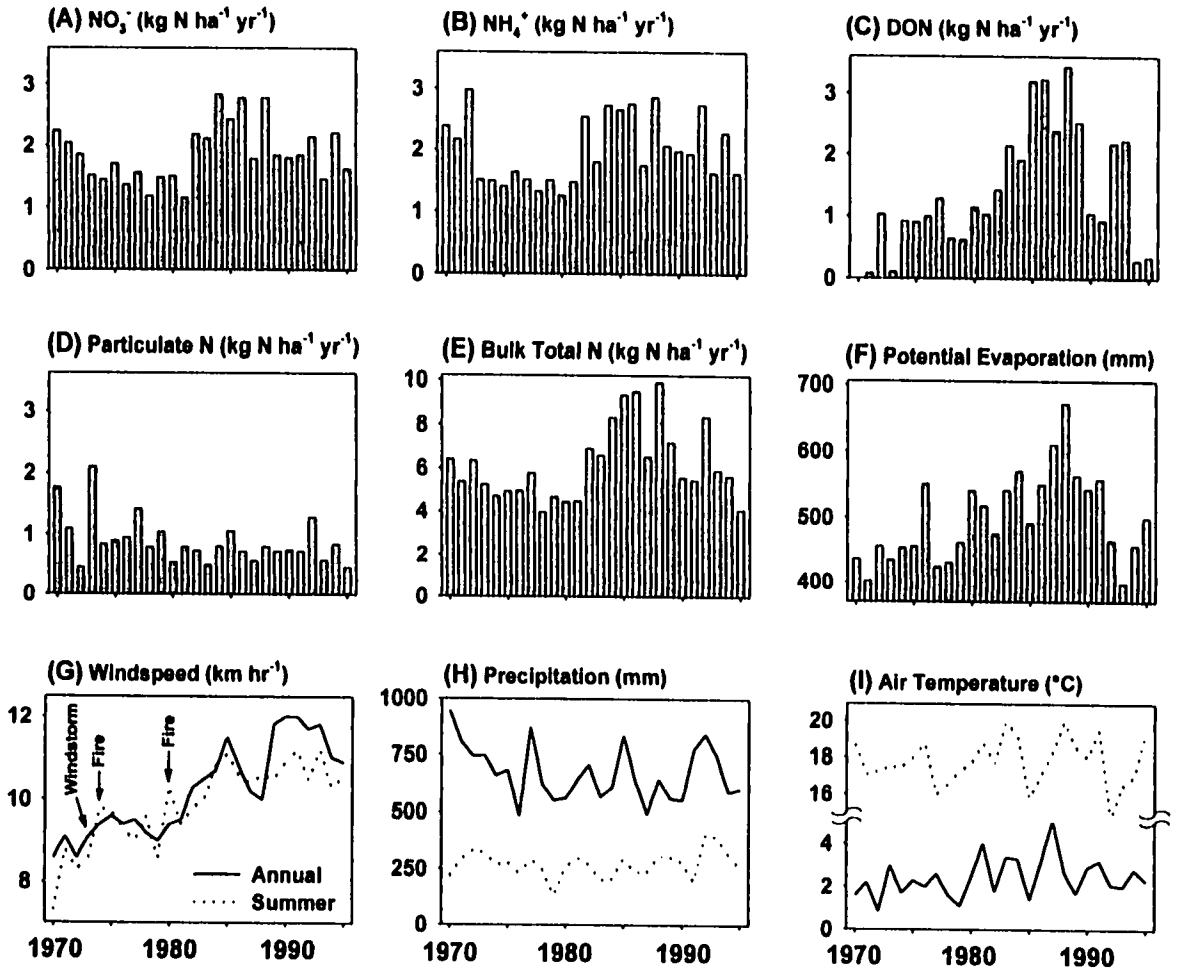


Fig. 2.4. Bulk N deposition and related environmental variables at the ELA, 1970-1995.

Table 2.1. Pearson correlation matrix for the annual bulk deposition of N compounds and related environmental variables. The probabilities shown are not Bonferroni-corrected. Generally, when P<0.001 the Pearson correlation coefficient was also signifiicant (at P<0.05 or better) when Bonferonni-corrected. Year = temporal trends; Precip = annual precipitattion; SumPr = summer precipitation; Pevapo = potential evaporation (Class A pan); Temp = annual air temperature; SumTp = summer air temperature; Wind = annual windspeed; SumWind = summer windspeed.

	NO_3^-	NH_4^+	PN	DON	TN	Year	Precip	SumPr	Pevapo	Temp	SumTp	Wind	SumWd
NO_3^-	1.0												
NH_4^+	0.85***	1.0											
PN	0	-0.02	1.0										
DON	0.528**	0.46*	-0.33	1.0									
TN	0.87	0.83***	-0.03	0.81***	1.0								
Year	0.25	0.18	-0.45*	0.45*	0.29	1.0							
Precip	0.19	0.31	0.58*	-0.11	0.22	-0.27	1.0						
SumPr	-0.04	0.21	0.11	0.17	0.18	0.21	0.37	1.0					
Pevapo	0.39	0.25*	-0.41*	0.58**	0.44**	0.40*	-0.55**	-0.30	1.0				
Temp	0.10	-0.14	-0.13	0.20	0.07	0.31	-0.33	-0.12	0.51**	1.0			
SumTp	0.12	-0.07	-0.30	-0.02	-0.07	0.06	-0.43*	-0.51**	0.63***	0.37	1.0		
Wind	0.30	0.25	-0.32	0.49*	0.38	0.88***	-0.08	0.25	0.30	0.21	-0.04	1.0	
SumWd	0.27	0.12	-0.55*	0.60***	0.35	0.84***	-0.31	0.17	0.48*	0.33	0.05	0.86***	1.00

* = P<0.05
** = P<0.01
*** = P<0.001

during this period (Fig. 2.4). Particulate N and DON deposition were the only forms of N with strong relationships to environmental variables (Table 2.1), but in an opposite fashion. While DON deposition was positively correlated to potential evaporation ($r = 0.58$) and summer windspeed ($r = 0.60$), PN deposition was negatively correlated to both ($r = -0.41$ and $r = -0.55$ respectively). Surprisingly, PN and DON deposition were not significantly correlated to one another ($r = 0.33$; $P>0.05$). Overall, climatic variability was strongly related to the deposition of organic-N but not mineral-N forms.

The bulk collector was relocated from an island on Lake 239 to another in Lake 240 in 1983 because of concerns for occasional contamination by throughfall at the former location (Fig. 2.5). The average DOC:DON ratio before and after relocation decreased from 28 to 19, consistent with some throughfall contamination at the former location. On the other hand, high DOC deposition also occurred at the Lake 240 location, suggesting that the change in DOC:DON ratio could also be due to other factors.

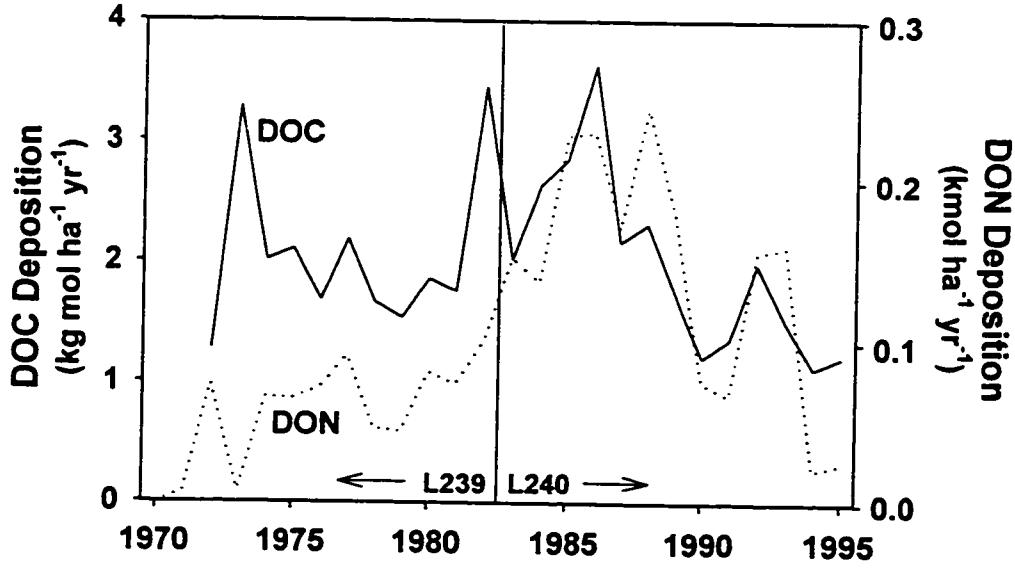


Fig. 2.5. DOC and DON bulk deposition at the ELA, 1970 –1995. The bulk collector was moved from an island in Lake 239 to one on Lake 240 in 1983.

Comparison of bulk and wet-only N deposition

The bulk and wet-only deposition rates were similar for the mineral-N forms but not for the organic-N ones. Between 1986 and 1991, the deposition of NO_3^- and NH_4^+ was 25% and 2% higher in the bulk collector respectively. However, PN (two-fold) and DON (five-fold) inputs were substantially higher in the bulk collector (Table 2.2 and Fig. 2.6). The deposition of all N forms was highest during summer months, but especially for DON (Fig. 2.6). For mineral-N, deposition was enriched in NO_3^- during winter (NH_4^+:NO_3^- = 0.71 and 0.70 in the bulk and wet-only collector respectively) and enriched in NH_4^+ during summer (1.1 and 1.5). Overall, the similarity in mineral N deposition between collectors suggests that NH_4^+ and NO_3^- were mostly wet deposited, while PN and DON inputs had a strong dry deposition component.

Event-by-event patterns in N deposition

In both types of collector, the event-by-event concentration of most N forms was positively correlated with the number of days since the last rain and negatively correlated with the size of the event (Table 2.3). In other words, N concentration was highest for small rain events following a drought period. However, the increase in concentration with event interval and the decrease in concentration with event size was less than proportional (Fig. 2.7). In other words, for a two-fold increase in event size, concentrations decreased by less than two-fold. In the bulk collector, DON concentration had the largest negative loading factor with RAIN (Table 2.3). In contrast, DON concentrations in the wet-only collector were not related to either DAYS or RAIN and were generally low. Thus, DON was mostly dry deposited and was strongly diluted by precipitation. The pattern in DON concentration relative to DAYS and RAIN was different than the one for calcium concentration (Table 2.3), suggesting that DON inputs were from a different pathway than dust. Event NH_4^+ concentration was poorly related to either DAYS or RAIN in both collectors. Post-depositional artifacts (such as NH_3 volatilization or influx) may have introduced noise in the NH_4^+ concentration data.

Table 2.2. Relationships between the concentration of C and N compounds in bulk and wet-only precipitation on an event basis (1986 - 91). All least-square regressions significant at $P<0.001$. Data in $\mu mol\ L^{-1}$.

	r^2	Standard Error
$Log\ NO_3^-{}_{WET} = 0.095 + 0.804\ Log\ NO_3^-{}_{BULK}$	0.55	0.246
$Log\ NH_4^+{}_{WET} = 0.228 + 0.802\ Log\ NH_4^+{}_{BULK}$	0.73	0.216
$Log\ DON_{WET} = 0.212 + 0.301\ Log\ DON_{BULK}$	0.12	0.457
$Log\ PN_{WET} = -0.070 + 0.614\ Log\ PN_{BULK}$	0.34	0.393
$Log\ DOC_{WET} = 0.931 + 0.487\ Log\ DOC_{BULK}$	0.57	0.188
$Log\ PC_{WET} = 0.449 + 0.630\ Log\ PC_{BULK}$	0.10	0.303
$Log\ Ca^{2-}{}_{WET} = -0.126 + 0.862\ Log\ Ca^{2-}{}_{BULK}$	0.65	0.264

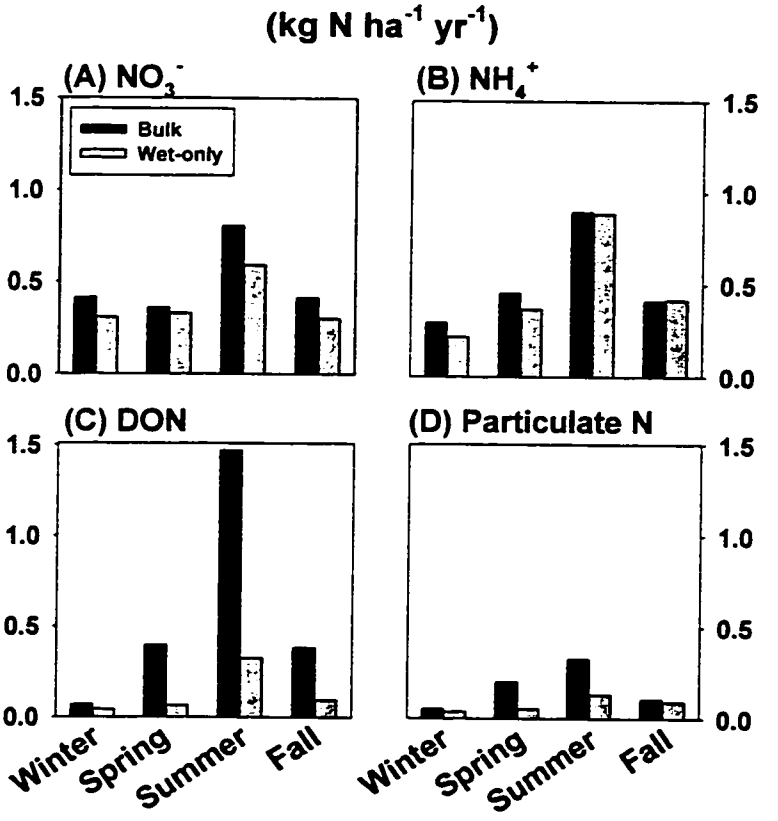


Fig. 2.6. Average seasonal N deposition in the bulk and wet-only collectors, 1986-1991.

Table 2.3. Nitrogen and calcium concentration in **A)** a bulk collector and **B)** a wet-only collector as a function of precipitation depth (RAIN; mm) and the number of days prior to the last event (DAYS). Data pooled from the summer period (June to August) for 1986-1991.

A) Bulk

	r^2	n
log NO_3^- (μmol L^{-1}) = 1.484 + 0.161 log DAYS* − 0.239 log RAIN***	0.13	117
log NH_4^+ (μmol L^{-1}) not significant		
log PN (μmol L^{-1}) = 1.113 + 0.273 log DAYS*** − 0.318 log RAIN***	0.29	117
log DON (μmol L^{-1}) = 2.150 + 0.199 log DAYS** − 0.613 log RAIN***	0.48	98
log Ca^{2+} (μmol L^{-1}) = -1.729 + 0.328 log DAYS*** − 0.434 log RAIN***	0.30	114

B) Wet-only

	r^2	n
log NO_3^- (μmol L^{-1}) = 1.154 + 0.290 log DAYS** − 0.170 log RAIN$^{P=0.09}$	0.09	98
log NH_4^+ (μmol L^{-1}) not significant		
log PN (μmol L^{-1}) = 0.571 + 0.303 log DAYS* − 0.263 log RAIN***	0.08	90
log DON (μmol L^{-1}) = not significant		
log Ca^{2+} (μmol L^{-1}) = -1.58 + 0.272 log DAYS** − 0.336 log RAIN*	0.10	85

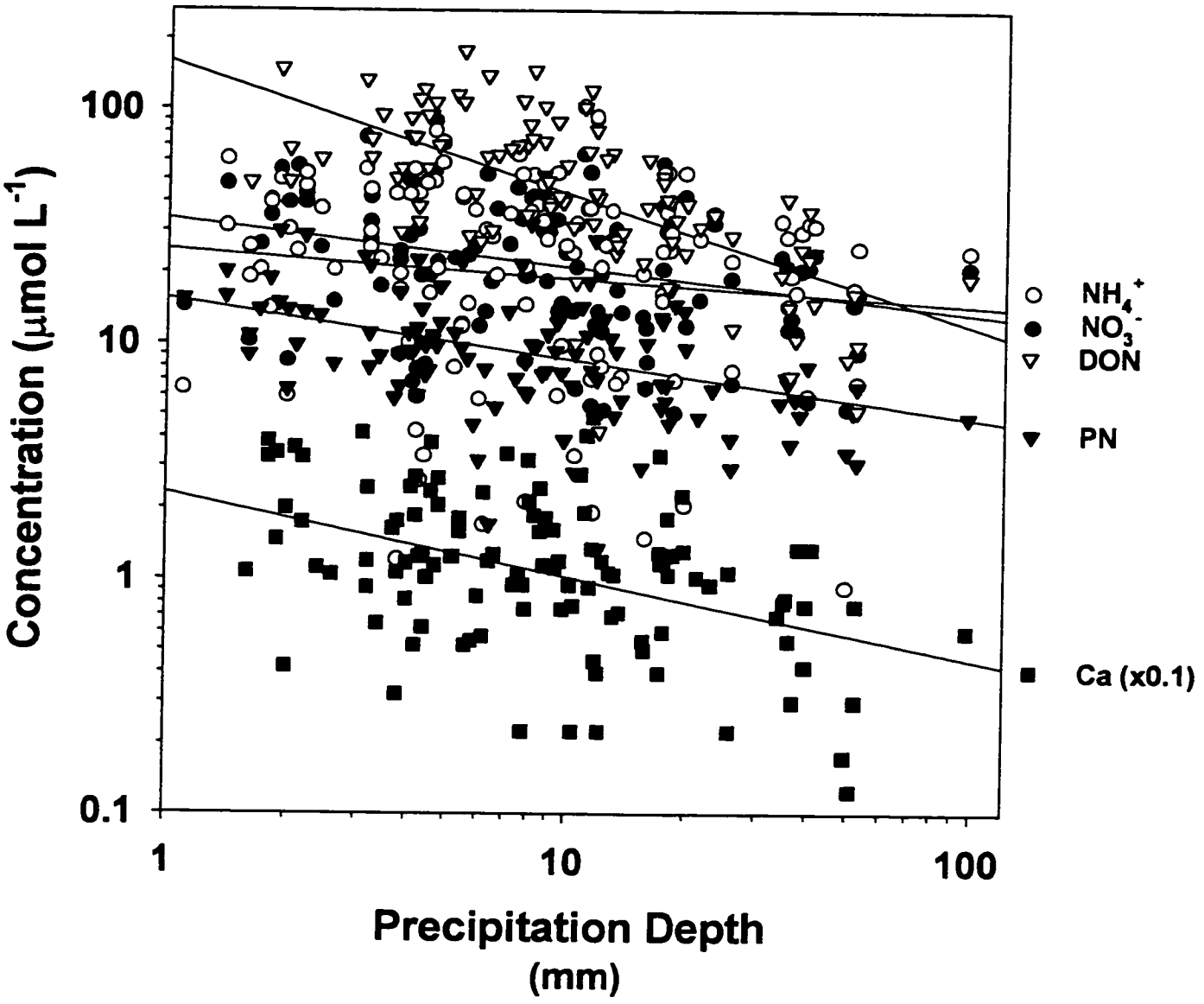


Fig. 2.7. Event N and Ca concentration for the ELA bulk collector during the summers of 1986-91. Calcium concentrations were decreased by a factor of 10 for clarity.

Discussion

The bulk deposition of N has varied from 4 to 10 kg N ha^{-1} yr^{-1} over a 26-year period at the ELA. The peak in N deposition corresponded with a relatively warm, dry and windy period in the late 1980's and was due in large part to increased DON deposition. Dissolved organic N had a strong dry deposition component, but the source of emission (local vs. long-range) is unclear at the present. Although DON in bulk collectors is often assumed to originate by leaching from particles such as pollen, there was no significant correlation between PN and DON deposition over the record. The input of NH_4^+ and NO_3^- was mostly through wet deposition and was near stoichiometric throughout the record, suggesting that they were transported to the ELA by a common process.

In general, the deposition of N at the ELA is intermediate between levels measured in remote areas (<1 - 5 kg N ha^{-1} yr^{-1}; Galloway et al. 1982; Jeffries 1995) and regions heavily affected by anthropogenic activity, such as in parts of eastern Canada (~13 kg N ha^{-1} yr^{-1}; Jeffries 1995). In North America, the highest N deposition occurs at high elevations in New England (~40 kg N ha^{-1} yr^{-1}), where acidic cloud water deposition is significant (Lovett et al. 1982). Nitrogen deposition in some parts of Europe (i.e. the Netherlands) occasionally exceeds 75 kg N ha^{-1} yr^{-1} (Dise and Wright 1995). Although low, N deposition at the ELA is within the range of hypothesized long-term critical loads for some sensitive components of the boreal ecosystem. Sensitive areas include ombrotrophic bogs (5 –10 kg N ha^{-1} yr^{-1}; Bobbink et al. 1992), shallow soft-water bodies (5 – 15 kg N ha^{-1} yr^{-1}; Bobbink et al. 1992), and lake littoral communities (3 – 7 kg N ha^{-1} yr^{-1}; Nilsson and Grennfelt 1988). Generally, inorganic N inputs are efficiently retained by forested catchments when deposition is below 9 kg N ha^{-1} yr^{-1} (Dise and Wright 1995). At the ELA, Allan et al. (1993) observed an efficient retention of mineral N inputs across a range of catchment size during the period of peak N deposition.

Whether present levels of N deposition at the ELA are different than pre-European settlement levels is difficult to determine. Historically, forests located near the Prairie grasslands may have received a higher N load than similar areas located closer to the center of

the Precambrian Shield. The alkaline and seasonally dry soils of the Prairies could have favored NH_3 (Dawson 1977; Schlesinger & Hartley 1992) and probably particulate emissions even prior to European settlement. In addition, the pre-settlement populations of large ruminants may have promoted the emission of NH_3 (Woodmansee 1978; Bowden 1986; but see Schimel et al. 1986). Dry deposition of N is much more efficient on forest canopies than on grasslands (Hanson and Lindberg 1991). Thus, historically and in the present, the transition between the Prairies and the boreal forest may have 'filtered' N from air masses from the Prairies. Presently, this situation occurs in Europe where the interface between agricultural and forested areas receives the highest N loads (van Breeman et al. 1982; Allen et al. 1988).

What part of total N deposition do bulk collectors represent?

At the Integrated Forest Study sites, where standardized and detailed wet and dry deposition measurements were made, bulk deposition was 17% to 78% of wet + dry deposition (Lovett and Lindberg 1993). Bulk collectors underestimate total N deposition because they sample wet deposition (excluding fog and cloudwater inputs) and only a portion of dry deposition. Wet deposition results from the incorporation of atmospheric particles and gases into cloud droplets, and the scavenging of particles and gases by raindrops or snowflakes as they fall (Lovett 1994). Dry deposition is a 'catch-all' term for a variety of gaseous and particulate deposition mechanisms. Bulk collectors are not efficient at sampling dry deposition because particles smaller than 5 μm and gaseous inputs are poorly represented (Lovett 1994; Hanson & Lindberg 1991). In general, dry N deposition is more important close to sources of emission and less important in remote areas (Boring et al. 1988). Thus, dry N deposition at the ELA is undoubtedly underestimated but is probably less than wet deposition.

Organic-N deposition

Similar to the ELA, bulk organic-N inputs range from 1 to 4 kg N ha^{-1} yr^{-1} at other sites in North America and Europe and represented from 13% to 30% of the total bulk N input (Table 2.4). At Harp Lake (Ontario), where both bulk and wet-only organic-N deposition was

measured, wet deposition of organic-N was 69 to 89% of bulk organic-N deposition (Table 2.4), a higher proportion than at the ELA. Most studies did not separate organic-N inputs into a DON and PN component. At two Czech sites where PN and DON were also operationally defined using a 1 μm filter, DON represented a similar proportion of organic-N deposition (68% to 82%; Kopácek et al. 1997). In most studies, organic-N inputs were assumed to be mostly local in origin (from pollen, dust, spores or others).

Table 2.4. Inorganic and organic N deposition at various sites in Europe and North America.

	NO_3^-	NH_4^+	Organic N	TN	Reference
ELA, northwestern Ontario					
Bulk	1.2 - 2.8	1.3 - 3.0	0.8 - 4.3	4.0 - 9.9	this study
Wet	1.0 - 1.9	1.4 - 2.5	0.5 - 1.1	2.4 - 4.4	
Marcell Experimental Forest, Minnesota					
Wet	2.0	2.9	0.5	5.4	Urban &
Dry	~2	1.2	-	-	Eisenrich 1988
Wet+Dry	~4	4.1	0.5	8.6	
Harp Lake, Ontario					
Bulk	3.5 - 4.7	3.5 - 3.9	2.2 - 3.3	10 - 11	Scheider et al.
Wet	2.9 - 3.7	2.8 - 3.0	1.9 - 2.1	7.9 - 8.5	1979
Narrow Lake, Alberta					
Bulk				4.2	Shaw et al. 1989
IFS sites					
Bulk	2.0 - 4.4	0.17 - 4.6	-	-	Lovett &
Wet	1.7 - 3.7	1.0 - 4.3	0.10 - 0.61	2.8 - 10	Lindberg 1993
Wet+Dry	3.3 - 17	1.5 - 9.8	0 - 1.7	4.9 - 28	
Czech Republic					Kopácek et al.
Bulk	2.9 - 5.5	3.0 - 7.1	1.3 - 4.7	10 - 14	1997
Various U.S. Sites					Boring et al.
Bulk			1.7 - 4.3	1.1 - 12.4	1988

Particles are a known source of DON prior to and following deposition to bulk collectors. Prior to deposition, DON tends to be generated by leaching and breakdown of particles in the harsh atmospheric environment (Saxena & Hildemann 1996). As found for

other nutrients, leaching from atmospheric particles could be especially important in precipitation passing through the plumes of soot particles generated by forest fires (Maclean et al. 1983). Many particles, especially pollen, leach DON following deposition to bulk collectors (Nicholls & Cox 1978; Likens et al. 1983; Kopácek et al. 1997).

Microbial activity or the emission of volatile organic N compounds from plants, soils, or wetlands are alternative sources for DON in the bulk collector. The uptake of mineral N by microorganisms in the bulk collector would be observed as 'DON' because most bacteria would pass through a 1 μm GF/C filter. However, the rapid analysis of samples and the good agreement between event NH_4^+ and NO_3^- concentrations between the bulk and the wet-only collector suggests that conversion of mineral N into DON by microorganisms was not the primary source of DON. Plant emission (Sharkey et al. 1991), organic matter decay (Graedel 1978), and forest fires (Lobert et al. 1990) are known sources of volatile organic N compounds to the atmosphere. The ocean surface has been identified as a source of atmospheric organic N (Wilson 1959a,b; Timperley et al. 1985), although whether this also occurs in lakes is unknown. Additional work is needed to characterize organic-N inputs at the ELA.

Co-deposition of NH_4^+ and NO_3^-

The stoichiometric input of NH_4^+ and NO_3^- suggests that they were transported to the ELA by a common process. NH_3 emitted from soils usually does not travel long distances because it is very reactive with surfaces (Bowman et al 1997). On the other hand, if the emitted NH_3 encounters an air mass containing acidic substances, the following reactions can take place:

$$NH_3 + H^+ \leftrightarrow NH_4^+$$

$$2\,NH_4^+ + SO_4^{2-} \leftrightarrow (NH_4)_2SO_4$$

$$NH_4^+ + NO_3^- \leftrightarrow NH_4NO_3$$

Unlike NH_3, NH_4^+ and its sulphate and nitrate salts are much less readily removed from the atmosphere and can be distributed to remote areas by long-range transport (Allen et al. 1988;

Bowman et al. 1997). Throughout the record, the deposition of NH_4^+ in the bulk collector was strongly related to NO_3^- deposition ($r = 0.85$; $P<0.001$) but almost completely uncorrelated to SO_4^{2-} deposition ($r = -0.02$; $P<0.88$). This is consistent with NH_4NO_3 formation being favored in relatively non-polluted environments (Graedel 1977). Transport as $(NH_4)_2SO_4$ tends to occur closer to sources of SO_2 pollution (Hedin et al. 1990). Although NH_3 emissions are a potentially important source of acidity to forests, constraints on long-range transport will tend to favor redeposition in the vicinity of the sources of emission. At the ELA, the higher deposition of NO_3^- relative to NH_4^+ during winter months suggests that urban and industrial sources of emissions are more important during that period (Treloar 1993). In contrast, a relatively higher NH_4^+ deposition during summer months indicates a stronger rural component to the N input for that period (Linsey et al. 1987; Treloar 1993).

NH_4^+ and NO_3^- bulk deposition peaked in the early 1970's and 1980's, but the mechanisms involved may have been different. The first peak in deposition corresponded with a wet period, where increased precipitation probably favored the atmospheric washout of mineral-N. On the other hand, the second peak in deposition corresponded with deforestation and drought conditions in the area. Increased emission of N gases from the Prairies, forest soils, and wetlands during the drought may have favored increased NH_4^+ and NO_3^- deposition at the ELA. Alternatively, decreased canopy interception of dry deposition because of deforestation could have favored downwind mineral-N deposition without any changes in the rates of N emission.

Conclusion and Recommendations

Bulk N deposition at the ELA has varied between 4 to 10 kg N ha^{-1} yr^{-1} between 1970 and 1995. The peak in N deposition corresponded with a relatively warm, dry, and windy period, and a large part of the increase was due to elevated DON deposition. Nitrogen deposition at the ELA is intermediate between levels expected in 'pristine' areas and regions more heavily affected by anthropogenic activity.

It is not clear at the present what proportion of the PN and DON deposited at the ELA is from local or long-range sources. Bulk collectors are deemed not suitable when studying N deposition to forests because of the likelihood of organic contamination from local sources (Lovett 1994). On the other hand, in the Shield landscape, organic-N deposition has important implications whether or not it is of local or long-distance origin. Assuming a local terrestrial origin, organic-N deposition is a more important transport of N from drainage basins to lakes than runoff (usually <1.5 kg N ha^{-1} yr^{-1} at the ELA). The potential for long-range transport of organic-N should not be underestimated either. The abundance of montmorillonite in ELA lake sediments (a common clay mineral in the Prairies but not on the Shield; Brunskill et al. 1971) suggests that long-range particulate inputs are significant at the ELA. Neglecting organic-N inputs may underestimate the N load to sensitive ecosystems by 10% – 40%.

Although N deposition at the ELA shows signs of anthropogenic influence, N inputs have not paralleled the 10-fold increase in fertilizer use in the Prairies during the record. However, agricultural activity in the Prairies may have a stronger impact on N deposition to nearby forests in the future because of an ongoing increase in livestock farming. Livestock production is a more important source of atmospheric NH_3 than fertilized agricultural land (Schlesinger & Hartley 1992; Bowman et al. 1997). While livestock farming was fairly constant from 1970 to 1990 (Fig. 2.1), many Canadian Prairie farmers are currently switching to livestock production because of the recent loss of grain export subsidies (Manitoba Environment 1997). Increased livestock production may result in increased emission of N gases from the Prairies and higher N deposition to surrounding forests in the future. Thus, it is important to maintain precipitation monitoring programs such as the one at the ELA to assess future N deposition trends to the central boreal forest.

The ELA precipitation monitoring program could be upgraded to better evaluate the input of N and other nutrients to the region in the future. The present design is susceptible to error (such as the ones that occur when the area surrounding the collector is de- or afforested) because only one collector is used. In other research areas similar to the ELA (such as

Hubbard Brook in New Hamsphire or Dorset in southern Ontario) bulk deposition is measured using several collectors. Samples from different collectors can be pooled to reduce analytical cost, but more detailed studies could also be undertaken by monitoring samplers separately for selected time periods. The wet-only collector formerly in operation at the meteorological station should be reactivated. Process-based studies should be undertaken to evaluate the origin (and magnitude) of wet and dry N deposition to the area. The hypothesis that a gradient in N deposition exists at the prairie/boreal forest interface could be tested at a sharp transition between these ecosystems in southeastern Manitoba.

Chapter 3. Nitrogen Mineralization in Upland Precambrian Shield Catchments: Contrasting the Role of Lichen-Covered Bedrock and Forested Areas

Lamontagne, S. 1998. *Biogeochemistry* **41**: 53-69
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Introduction

In the boreal forest, nitrogen is often a limiting nutrient for plant growth because low soil temperature, low soil pH, and refractory litters limit N-recycling through mineralization of the forest floor (Van Cleve & Yarie 1986; Bonan & Shugart 1989; Van Cleve et al. 1990). Frequently, nutrient storage and primary production are higher in the lichen and moss mats covering the forest floor than in trees (Rencz & Auclair 1978; Oechel & Van Cleve 1986). Lichen and moss mats are generally thought to promote nutrient deficiency in trees by successfully competing for nutrient inputs in rain, by generating refractory litter, and by cooling the forest floor (Oechel & Van Cleve 1986).

However, it is possible that lichen and moss mats are not always a strong sink for nutrients. Upland Precambrian shield catchments at the Experimental Lakes Area are a mozaic of forest islands interspersed within lichen and moss-covered bedrock outcrops (Fig. 3.1). Allan et al. (1993) have demonstrated that while forest islands and bedrock surfaces exported similar quantities of dissolved organic N (DON), mineral N retention was larger in forest islands. Allan et al. (1993) hypothesized that the higher mineral N export from bedrock surfaces was caused by fast hydrological flushing limiting the retention of N in precipitation and N fixation by lichen providing a source of mineralizable N. Alternatively, N mineralization may be higher under lichen and moss patches because of a different composition of soil organic matter (Nadelhoffer et al. 1991), warmer and drier conditions (Van Cleve & Yarie 1986), and a low immobilization of mineral N through root uptake (Johnson 1992).

As a part of a whole-catchment study of N-cycling, net mineralization (MIN_{net}) and net nitrification rates ($NO_3^-{}_{net}$) were measured in forest islands and lichen patches of an upland boreal forest. The main objective was to determine whether there were differences in N mineralization rates on a seasonal and annual basis between lichen patches and forest islands. In addition, the potential for warmer soil temperature and lichen N fixation to promote higher mineralization rates in lichen patches was tested. Mineralization rates were estimated using buried bag incubations (Eno 1960) and validated with two experiments. First, the buried bag assay was compared to *in-situ* core incubations (Raison et al. 1987), another common method used to estimate field N mineralization. Second, the assumption of the linearity of mineralization rates during incubations was tested in both soil types (Adams et al. 1989). The latter experiment also explored the possibility of measuring DON production rates from buried bag incubations.

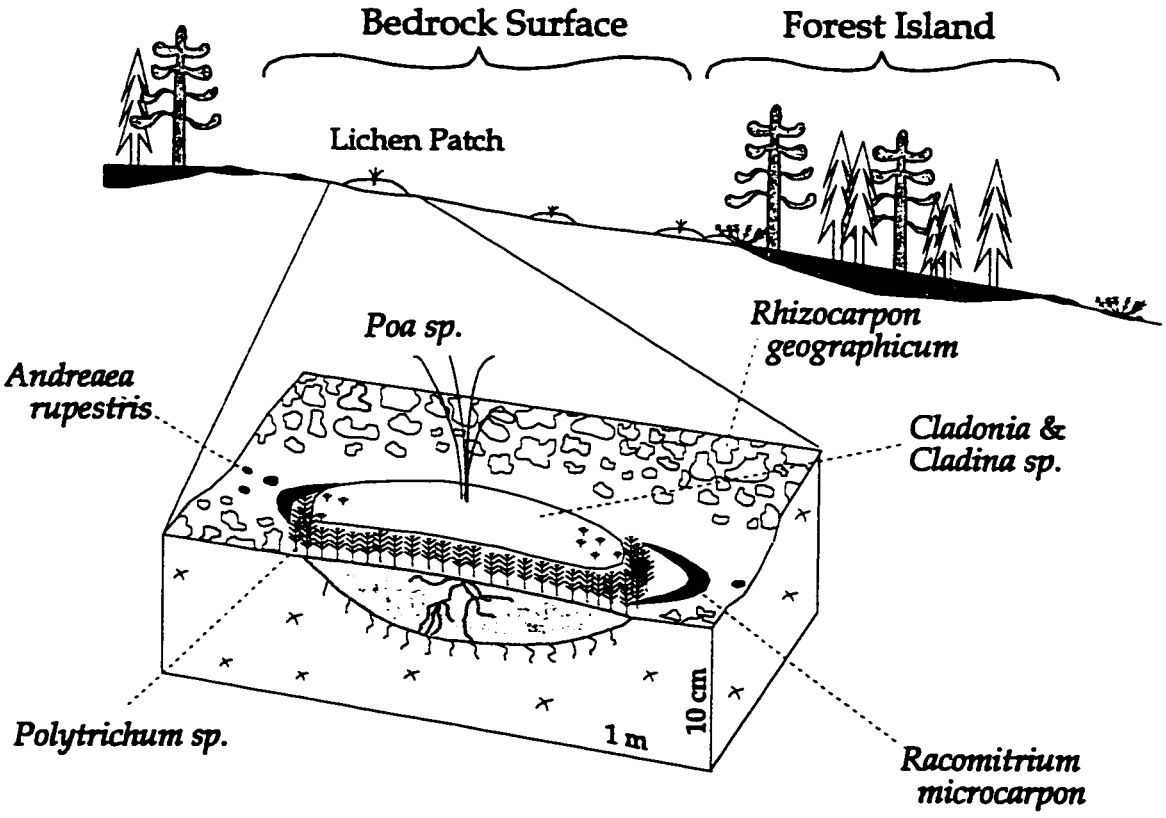

Fig. 3.1. Cross-section of the upland boreal forest landscape at the Experimental Lakes Area, northwestern Ontario. Jack pine and black spruce occur in forest islands with soils 10 to 50 cm deep. Deposits between 1 to 10 cm thick are found under lichen patches. On topographic highs, exposed bedrock often covers 70% of the landscape in this region.

Methods

Site Description

All experiments were performed in the upland catchments of the Experimental Lakes Area, a set of small watersheds used to study processes controlling element export to shield lakes (Allan et al. 1993; Allan & Roulet 1994a,b; Allan 1995). Climate at the ELA is humid continental, with a mean average temperature of 2.3°C and a mean annual precipitation of 673 mm (27% of which occurs as snow; Beaty & Lyng 1989). Soils at the ELA are thin and classified as truncated orthic humic regosols and sombric brunisols (Canadian Soil Survey Committee 1978; Allan & Roulet 1994a). Mineral soils within the Upland catchments fall in the silt loam size-range and are probably of eolian origin. Bedrock is mostly slow weathering pink granodiorite (McCullough & Campbell 1993). Wildfires are frequent in the area (Bayley et al. 1992) and the last fire in the Upland catchments occurred approximately 120 years ago.

The distribution of vegetation within the catchments is heterogeneous but follows a characteristic pattern (Fig. 3.1). Trees occur in small depressions with 10 to 50 cm of organic and mineral soil (approximately 30% of catchment area). Jack pine (*Pinus banksiana* Lamb.) is common on the thinner soil while black spruce (*Picea mariana* Mill. B.S.P.) and a few white pine (*Pinus strobus* L.) occur where soils are deeper. Most trees were probably regenerated following the last wildfire. Currently, the fall of senescent Jack pine creates openings that are colonized by pin cherry (*Prunus pensylvanica* L.f.), red maple (*Acer rubrum* L.) and black spruce, the latter through vegetative growth. The understory comprises the shrub *Juniper communis* L., the lichen *Cladina mitis* (Sandst.) Hustich and the moss *Pleurozium schreberi* (Brid.) Mitt. The forest floor is 5 to 25 cm thick and composed of L, F, and H horizons (Table 3.1). Locally, a S horizon composed of undecayed moss stems is present. The mineral soil is 10 to 40 cm thick and limited to one to several Ah horizons, and occasionally a C or Cg horizon (Allan et al. 1993; Allan & Roulet 1994a).

Table 3.1. Forest island and lichen patch organic soil characteristics. Replicates (n = 4) were obtained by pooling samples from several stations in each soil type (n = 8 for lichen patch %C and %N). Soil pH was obtained by mixing 5 g of homogenized, 2 mm sieved, dried soil to 10 mL of distilled water or 0.1M $CaCl_2$. Mean ± SE. Volume weighed runoff pH from Allan et al. 1993. Carbon to N ratios are expressed on a molar basis.

	Lichen Patches L & 'H'	Forest Islands LFH
pH (H_2O)	4.38 ± 0.14	4.08 ± 0.13
pH (0.1M $CaCl_2$)	3.86 ± 0.15	3.55 ± 0.12
Volume Weighed runoff pH	4.66	4.01
%C	15 ± 3.0	31 ± 6.0
%N	0.86 ± 0.16	1.0 ± 0.2
C:N	15	27

Bedrock outcrops cover approximately 70% of the catchments and are composed of two features (Fig. 3.1). About 65% of the bedrock outcrops is covered with crustose lichen such as *Rhizocarpon geographicum* (L.) DC. and some foliose lichen. The remaining bedrock surface is covered by clumps of the fruticose lichens *Cladina* spp. and *Cladonia* spp., the mosses *Polytrichum*.spp., *Andreaea rupestris* Hedw.and *Racomitrium microcarpon* (Hedw.), some herbs and grasses, and the shrub *Juniper communis* (L.) These organisms occur together in well-stratified units - hereafter referred to as lichen patches for simplicity (Fig. 3.1). One to 10 cm deposits are found under lichen patches (nonsoil under the Canadian Soil Survey Committee 1978). In general, lichen patch 'nonsoil' can be divided into a S horizon of standing, undecayed moss stems and grasses, a L horizon of flattened and slightly decomposed mosses, lichens and grasses, and a mineral-rich H or Ah horizon ('H' hereafter). Lichens are predominant in upslope areas while mosses are more common in seepage areas downslope from forest islands (Vitt 1991). The diameter of lichen patches ranges from 30 cm to 3 m. Based on the lateral growth rate of *R. microcarpon* moss colonies, Vitt (1991) estimated that extant moss colonies could date from as far back as the last fire.

Monthly N mineralization assay

Three-week buried bag incubations where carried-out in May to October 1995 and 1996 in catchment U1. Ten forest floor stations and five lichen patches were monitored in 1995, and eight stations in each soil type in 1996. Soil cores were collected using a 2 cm dia. steel soil corer. Soil cores for initial extractable N concentrations were kept at 4°C until processing (usually within 24 h). The soil cores to be incubated were placed into polyethylene bags (Nasco Whirl-Packs 7.5 x 16 cm for cores shorter than 10 cm and 11 x 21 cm for longer cores), sealed tightly, and returned to the soil. In forested areas, most cores collected were 15 cm or shorter. When longer cores were obtained, only the top 15 cm portion was retained. At most sites, this would encompass the LFH organic layer and the upper part of the Ah mineral horizon. When present, the S horizon was excluded. Soil cores obtained in lichen patches were 2.5 to 7 cm long and included the complete profile with the exception of the S horizon. Soil temperature was monitored weekly at mid-day at 5 cm depth in two lichen patches and two forest islands.

The effect of location on N mineralization rates was tested with a reciprocal transplant experiment in May 1996, a period when the temperature difference between the forest floor and lichen patches is maximum. Eight lichen patch and forest floor soil bags were transplanted. This experiment was run concurrently with the monthly N mineralization assay.

Validation of buried bag incubations

In July and August 1994, buried bag N mineralization estimates in forest islands were compared to *in-situ* core incubation estimates (Raison et al. 1987). For *in-situ* core incubations, one core for initial N concentration was taken at each sampling station. Two additional cores were inserted in the soil, one open to the atmosphere and the other covered with a plastic film. At the end of the incubation, a final core was taken. The rational behind the *in-situ* core incubation is that the open core monitors mineralization minus leaching losses, the covered one measures mineralization without leaching losses, and the final core estimates mineralization minus leaching losses and minus plant uptake (Raison et al. 1987). For *in-situ* core incubations, cores were made of PVC (5.2 cm dia. x 17 cm long) and buried to a depth

of 15 cm. Twelve buried bags and ten sets of cores were incubated in both catchment U1 and in nearby U3 for 28 days. Upon retrieval, soil in the PVC cores was extruded by 5 cm intervals and analyzed separately. To reduce the labour involved, sets of PVC cores were pooled to give six replicates. In June and July 1996, the linearity of mineralization rates obtained with buried bags was tested in both soil types. Twenty-eight bags were placed in a 5 m^2 area of forest floor and in a 2 m^2 lichen patch. Four bags were retrieved from each area after 0, 1, 2, 3, 4, 6 and 8 weeks.

N fixation by lichen

Lichen N-fixation was estimated using acetylene-reduction incubations and by comparing the ^{15}N signature of lichen to the one of non N-fixing plants. For acetylene reduction assays, six ca. 10 g wet weight composite *Cladina* and *Cladonia* lichen samples were incubated on three occasions in May and June 1995. Samples were placed in 160 mL serum bottles and capped. Ten percent of the headspace was replaced with acetylene. Bottles were incubated in the shade to prevent overheating. Ten mL gas samples were collected after 1, 8 and 24 hours using the double-syringe technique and stored in evacuated 10 mL blood serum tubes. Lichen samples free of acetylene and air blanks were included with all incubations. On one occasion with dry antecedent conditions, triplicate lichen samples were soaked in local runoff water for an hour prior to the incubation. Acetylene and ethylene concentrations were determined by flame ionization detection using a Hewlett-Packard model 5750 gas chromatograph at the Freshwater Institute, Winnipeg, Manitoba (detection limit 0.02 $\mu M\ C_2H_2\ L^{-1}$).

N-fixers tend to have a ^{15}N signature closer to atmospheric N_2 ($\delta^{15}N = 0‰$) compared to non-N-fixing plants (Peterson & Fry 1987). Six composite samples of the lichen *Cladina mitis*, and the mosses *R. microcarpon* and *Polytrichum* spp. were collected in August 1994. *Cladina mitis* and *Polytrichum* spp. occur on top of the patches and presumably obtain most of their N from precipitation. *Racomitrium microcarpon* is a creeping moss and probably receives N from precipitation and seepage from lichen patches. Moss and lichen samples were freeze-dried, and ball milled. Isotopic ratios were determined using a VG continuous

flow mass-spectrometer connected to a Carlos Erba elemental analyzer at the University of Waterloo Environmental Isotope Laboratory.

Analytical procedures for extractable soil N

Soil samples were kept at 4°C in the dark until extraction and analysis (usually within 24 h of collection). Cores were weighed and live plants, large roots, twigs and gravel were removed by hand. The soil was then thoroughly homogenized. Five g sub-samples were collected for water content determination and for N extraction. Soil water content was determined gravimetricaly by drying for 24 hours at 60°C. Soil moisture content was expressed relative to the saturated water content of the soil, determined by letting thoroughly wetted soil sub-samples drain on a filter paper for 12 hours. N was extracted by shaking the soil sub-sample vigorously for 1 h in 50 mL 2M KCl. The soil extracts were pre-filtered on combusted and washed Whatman GF/C filter and filtered on combusted and washed Whatman GF/F filter (nominal pore size 0.7 μm). The extracts were stored in tightly sealed glass vials at 4°C until analysis.

Total dissolved N, NH_4^- and NO_3^-/NO_2^- concentrations were determined colorimetricaly following a procedure modified from Stainton et al. (1977). Nitrite concentrations were always low to non-detectable and were pooled with NO_3^- concentrations. Dissolved organic N was estimated as TDN (by UV-persulphate digestion) minus NH_4^- and NO_3^- concentrations. Brine extracts were diluted at least 10X with distilled deionized water prior to TDN analysis. Volumetric N concentrations were converted to μg N per g soil dry weight, and then to g N ha^{-1} by multiplying by the average dry mass of the initial and final cores divided by the core area.

Only net rates of mineralization can be measured with the incubation techniques used (Nadelhoffer et al. 1984; Stark & Hart 1997). Net nitrification ($NO_{3\,net}^-$) was estimated as the change in NO_3^- concentration (or areal mass) over time and net mineralization (MIN_{net}) as the change in $NH_4^- + NO_3^-$ over time. An added complication when estimating DON production rates is determining the proportion of mineralized N originating from particulate N or DON

(Eviner & Chapin 1997). A high DON production estimate (DON_{max}) can be made by assuming all mineral-N produced originates from DON, and a low estimate (DON_{min}) by assuming all mineral-N originates from particulate N. Errors on monthly mineralization rates were calculated using first-order error propagation, assuming no covariance between terms (Meyer 1975). Annual net mineralization budgets were calculated by summing monthly mineralization estimates.

Results

Validation of the buried bag assay

During the 8-week period where one site of each soil type was intensively sampled, the increase in exchangeable N concentration was roughly linear over time for mineral-N species but not for DON (Fig. 3.2). In lichen patches, there was a large accumulation of NO_3^- over time but little net change in NH_4^+ concentration. Net mineralization rates in the forest island site were lower than in the lichen patch site, with only NH_4^+ concentration having a significant increase over time (Fig. 3.2 & Table 3.2). A spike in DON occurred in both soil types at the beginning of incubations, probably due to disturbance and root cutoff during core collection (Hendrickson & Robinson 1984; Clarholm et al. 1981). Most of the excess DON appears to have been consumed after one week of incubation, and DON concentrations tended to increase thereafter (Fig. 3.2). Qualitative estimates of DON production were calculated using DON concentration *after one week of incubation* as the initial concentration (Table 3.2). Dissolved organic nitrogen production (as DON_{max}) was 2-fold higher than MIN_{net} in the lichen patch site, and 2.5-fold MIN_{net} in the forest island site. Dissolved organic nitrogen production rates in the other experiments could not be corrected for a potential initial DON spike, therefore they will not be presented here.

Net mineralization rates were not significantly different between *in-situ* cores and buried bags (MIN_{net} : 105 vs 89 g N ha^{-1} d^{-1} respectively; Table 3.3) However, $NO_3^-{}_{net}$ was significantly lower in cores when rates are expressed on an areal basis (-3.8 vs 1.9 g N ha^{-1} d^{-1}; Table 3.3). Leaching of NO_3^- from both open and covered cores probably occurred when

the water table rose to the surface in low-lying areas during large storms (Lamontagne pers. obs.) Consequently, it was not possible to estimate leaching losses using the difference in N concentration between covered and open cores (not significantly different than 0 for both MIN_{net} or $NO_{3\ net}^-$; P>0.05). Therefore, the 'plant uptake' term (covered - final core) represent both plant uptake and leaching losses during incubations (Table 3.3). The loss of mineral N through runoff is very small in forest islands (ca. 0.02 kg N ha^{-1} yr^{-1}; Allan et al. 1993), therefore the plant uptake terms are probably accurate. The amount of mineral N produced through mineralization was similar to plant uptake during the incubation (Table 3.3). Most of the N mineralization occurred in the top 10 cm of the forest island soil profile (Table 3.3).

Table 3.2. Average mineralization rates over an 8-week period in one intensively sampled forest island and one lichen patch in June-July 1996. Organic matter content estimated from loss on ignition. Mineralization rates were assumed linear as a first approximation and were estimated using least-square regression. Dissolved organic nitrogen production estimates were calculated using the concentration of DON after one week of incubation as the initial concentration.

	DON_{min}	DON_{max}	MIN_{net}	$NO_{3\ net}^-$
		$\mu g\ N\ g^{-1}\ d^{-1}$		
Lichen Patch	0.61*	1.3*	0.73*	0.70*
Forest Island	0.11	0.18	0.078*	0
		$\mu g\ N\ g\ organic\ matter^{-1}\ d^{-1}$		
Lichen Parch	1.3	2.5	1.4*	1.4*
Forest Island	0.11	0.21	0.093	-0.002
		$g\ N\ ha^{-1}\ d^{-1}$		
Lichen Patch	165*	331*	166*	167*
Forest Island	72	114	42*	-1.4

* slope significantly different from 0 (P<0.05)

Lichen patch and forest island N mineralization

On an annual basis, MIN_{net} was 7-fold and $NO_{3\ net}^-$ 40-fold higher in lichen patches than forest islands (Fig. 3.3). In forest islands, peak MIN_{net} occurred in June and July, while

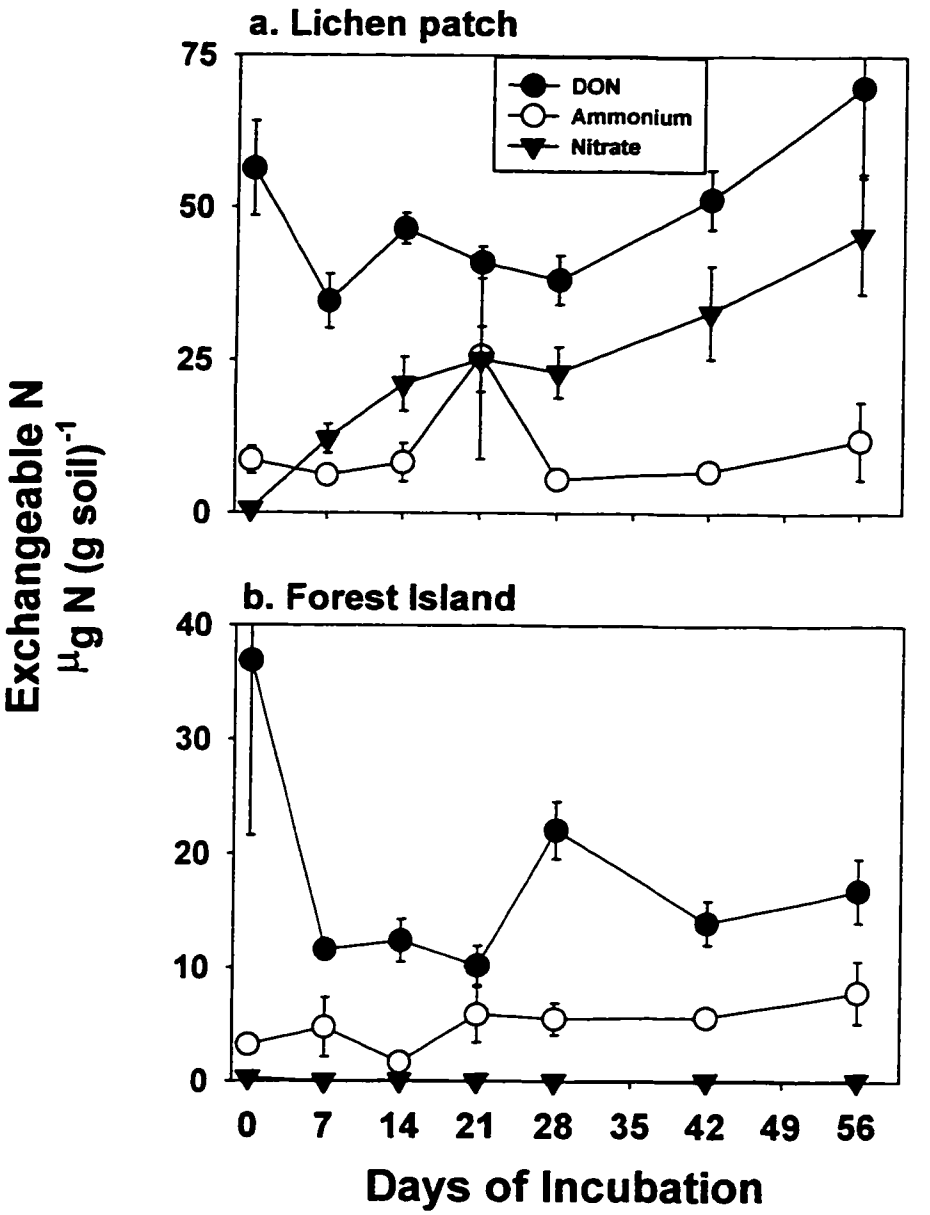

Fig. 3.2. Change in DON, NH_4^+, and NO_3^- concentrations in buried bags incubated in one intensively sampled **a)** lichen patch and **b)** forest island in June and July 1996. Weekly, mid-day, soil temperature varied in a non-systematic fashion between 16 to 21°C in the lichen patch and 13 to 17 °C in the forest island.

Table 3.3. Nitrogen mineralization estimates obtained with buried bag and *in-situ* core incubations in July-August 1994 in forest islands. In the *in-situ* core incubation, the plant uptake term also includes leaching losses because the latter could not be accurately estimated. Total mineralization estimates in cores are weighed by the average soil mass in the core section when expressed on a per gram of soil basis, and added between section when expressed on an areal basis. Total mineralization estimates obtained with both buried bags and cores are not significantly different (t-tests), except for $NO_{3\,net}^-$ when expressed on an areal basis ($P<0.05$).

a) MIN_{net}

		$\mu g\ N\ (g\ soil)^{-1}\ d^{-1}$		$g\ N\ ha^{-1}\ d^{-1}$	
Method	Depth	MIN_{net}	Plant Uptake	MIN_{net}	Plant Uptake
Core	0-5 cm	0.33 ± 0.18	0.40 ± 0.15	57 ± 33	68 ± 32
	5-10 cm	0.14 ± 0.07	0.14 ± 0.08	41 ± 21	41 ± 20
	10-15 cm	0.02 ± 0.013	0.04 ± 0.02	7.3 ± 3.1	13 ± 7
	Total	0.12 ± 0.08	0.14 ± 0.08	105 ± 39	121 ± 39
Bag	Total	0.21 ± 0.07		89 ± 24	

b) $NO_{3\,net}^-$

		$\mu g\ N\ (g\ soil)^{-1}\ d^{-1}$		$g\ N\ ha^{-1}\ d^{-1}$	
Method	Depth	$NO_{3\,net}^-$	Plant Uptake	$NO_{3\,net}^-$	Plant Uptake
Core	0-5 cm	-0.02 ± 0.004	-0.001 ± 0.003	-2.02 ± 0.49	-0.13 ± 0.09
	5-10 cm	-0.002 ± 0.006	0.003 ± 0.003	-0.654 ± 1.6	0.60 ± 0.75
	10-15 cm	-0.004 ± 0.014	0.002 ± 0.003	-1.1 ± 2.3	0.78 ± 0.65
	Total	-0.005 ± 0.006	0.002 ± 0.003	-3.8 ± 2.8	1.25 ± 1.0
Bag	Total	0.004 ± 0.002		1.9 ± 0.9	

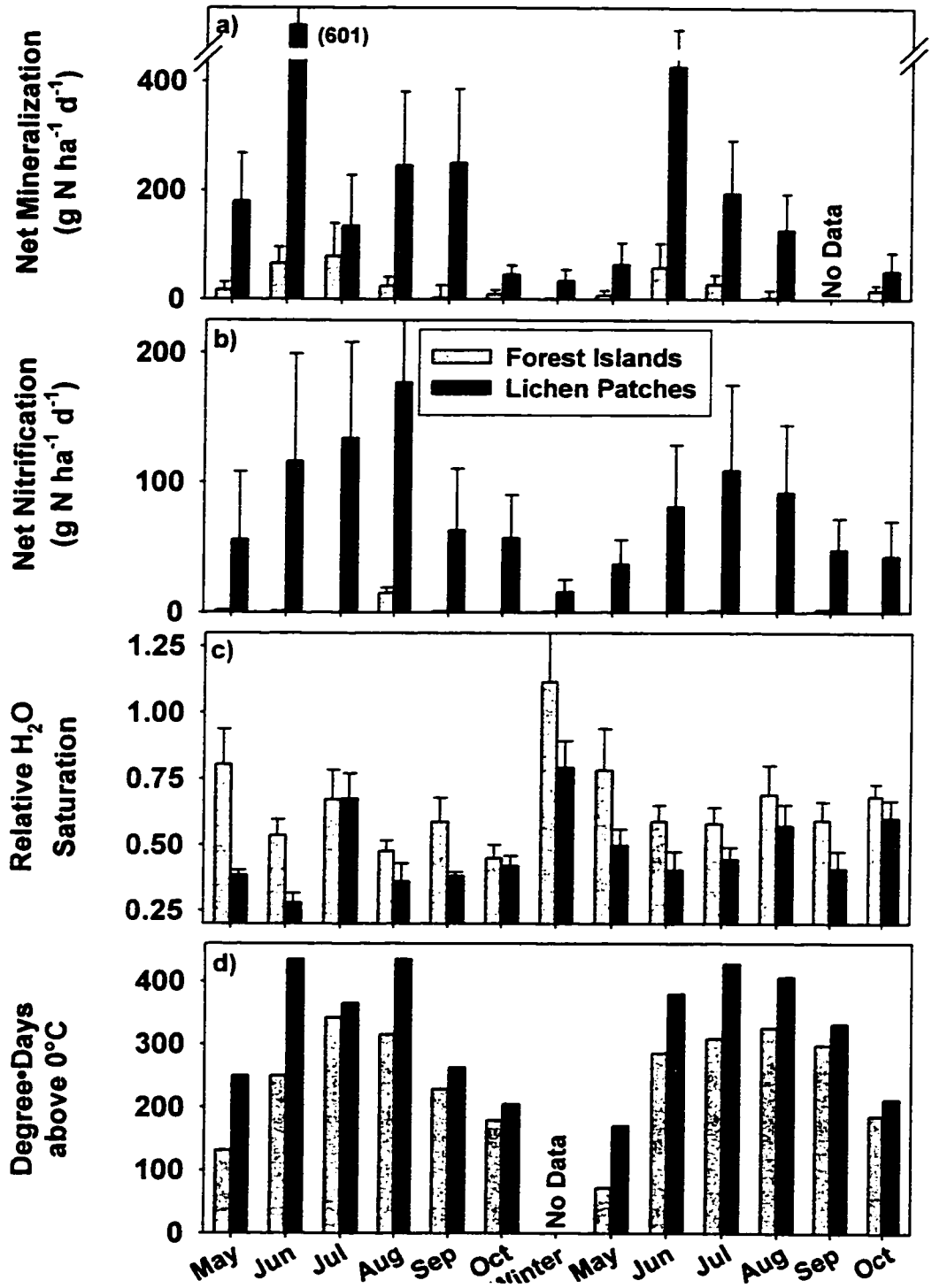

Fig. 3.3. Average monthly **a)** MIN_{net}, **b)** $NO_3^-{}_{net}$, **c)** relative soil moisture content of initial bags, and **d)** cumulative degree-days above 0°C (during the 21 days of incubation) for catchment U1 in 1995-1996.

significant $NO_3^-_{net}$ was only measured in August '95 when soil moisture was low. In lichen patches, peak MIN_{net} occurred in June and peak $NO_3^-_{net}$ in July and August (Fig. 3.3). Overall, lichen patches were only slightly warmer than forest islands. The average May to October soil temperature at 5 cm was 11.6 ± 4.0°C in the forest islands and 15.4 ± 4.7°C in lichen patches. Temperature differences were largest during spring and summer, and smallest in fall (Fig. 3.3). Geothermal heat exchange with bedrock probably moderates the influence of declining average air temperature and lower solar insolation in fall. Both soils were usually unsaturated during summer months (Fig. 3.3).

In lichen patches, monthly MIN_{net} and $NO_3^-_{net}$ were positively related to cumulative degree-days above 0°C during incubations ($r = 0.61$, $P < 0.05$ and $r = 0.84$, $P < 0.001$ respectively), but were weakly correlated to relative saturation ($r = -0.34$, $P > 0.05$; $r = -0.48$, $P > 0.05$). Monthly forest floor mineralization rates were poorly correlated to both cumulative degree-days and relative saturation. During the reciprocal transplant experiment, the average soil temperature was 3.4°C in forest islands and 8.1°C in lichen patches. Transplanted soil from lichen patches behaved similarly to controls (Table 3.4). The comparison of mineralization rates between control and transplanted forest island soil was inconclusive because rates were very low and variable (Table 3.4).

Table 3.4. Buried bag mineralization rates (in g N ha^{-1} d^{-1}) for forest floor and lichen patch soil incubated in their location of origin and transplanted in the other area in May 1996. Mean ± 1 SE, n = 8, ns = P > 0.05.

	Control	Transplant	t-test
	Lic→Lic	*Lic →For*	
MIN_{net}	65 ± 39	83 ± 44	0.1 ^{ns}
$NO_3^-_{net}$	37 ± 19	49 ± 33	0.09 ^{ns}
	For →For	*For→Lic*	
MIN_{net}	7 ± 9	2 ± 18	0.06 ^{ns}
$NO_3^-_{net}$	0 ± 0	0.1 ± 0.1	1.0 ^{ns}

Lichen N fixation

No N-fixation by desiccated or moist lichen was detected during acetylene- reduction incubations (data not shown). The absence of ethylene was verified by adding small amounts to samples (Len Hendzel, Freshwater Institute, Winnipeg, Manitoba, pers. comm.) The lichen *Cladina mitis* was more depleted in ^{15}N ($\delta^{15}N$ = -4.08 ± 0.40‰; mean ± SE) than the mosses *Polytrichum* spp. and *R. microcarpon* (-1.70 ± 0.24‰ and -3.4 ± 0.5‰ respectively). Thus, N-fixation by lichen is not an important source of N in this system.

Discussion

Differences in soil organic matter composition are probably more important than temperature in generating the patterns in N mineralization between forest islands and lichen patches. In laboratory incubations of six tundra soils, Nadelhoffer et al. (1991) found that the composition of soil organic matter was more important than soil temperature in controlling rates of N mineralization, especially at temperature below 9°C. Similarly, Hobbie (1996) suggested changes in vegetation community structure brought by future warming in the tundra may have a stronger influence on N recycling rates than changes in soil temperature.

Forest island N mineralization

Either low gross mineralization rates or strong immobilization of mineral N can account for low MIN_{net} and $NO_3^-{}_{net}$ in forest islands. The C:N of the soil organic matter in forest islands is high (27), which should favour the immobilization of mineral N by microorganisms (Janssen 1996). On the other hand, conifer litter from acidic and nutrient-poor sites tends to be enriched in compounds refractory to mineralization such as polyphenols (Davies 1971; Northup et al. 1995a). The low availability of labile C has also been shown to limit decomposition rates in *P. banksianna* litter (Foster et al. 1980). Although soil pH (4.08) was lower in forest islands, it was probably not low enough to prevent autotrophic nitrification (Tietema et al. 1992; Persson & Wirèn 1995). Denitrification may have also lowered MIN_{net} by removing NO_3^- from soil solution. However, under pristine conditions, denitrification tends to be low in boreal forests and wetlands because of rapid removal of NO_3^-

from soil solution by plants and microorganism (Bowden 1987; Urban et al. 1988; Blew & Parkinson 1993). Net N mineralization in forest islands is low when compared to Alaskan conifer forests (MIN_{net} 12-20 kg N ha^{-1} yr^{-1}; Van Cleve et al. 1983; Van Cleve & Yarie 1986), although comparisons are difficult as methodology varies greatly between studies.

Lichen patch N mineralization

Higher MIN_{net} and $NO_{3\ net}^-$ in lichen patches is consistent with a lower potential for N immobilization because of the low C:N (15) of the soil organic matter. Although moss and lichen litter decomposes slowly (Heal & French 1974; Moore 1981), rates can increase when the litter is exposed to wetting and drying cycles (Chapin et al. 1988; Belyea 1996). Lichen patches have rapid and frequent wetting and drying cycles because of the absence of canopy interception of precipitation, low water storage capacity, and lateral flow of runoff over bedrock surfaces (Allan & Roulet 1994b). The presence of fast-decomposing graminoid litter (Hobbie 1996) and higher exposure to visible and UV-light (Gehrke et al. 1995) may also increase mineralization rates in lichen patches. Net N-mineralization in lichen patches is of similar magnitude as MIN_{net} in boreal wetlands. However, $NO_{3\ net}^-$ is usually nil in the latter ecosystem (Urban & Eisenreich 1988; Bowden 1987).

N fixation

N fixation by lichens is not a significant source of N to lichen patches. The most abundant lichen species (*Cladina* and *Cladonia* spp.) are not strong N-fixers (Millbank 1976; Alexander & Billington 1986). On the other hand, N fixation by free-living cyanobacteria associated with mosses has been shown to be more important than lichen N fixation in the Alaskan taiga (Alexander & Billington 1986). The ^{15}N signature of the mosses *Polytrichum* spp. and *R. microcarpon* was closer to atmospheric N than the lichen *C. mitis*, suggesting that N-fixation may be a source of N to moss growth in lichen patches. The moss *P. schreberi* is common in forest islands and has also been shown to have N-fixing activity (Alexander & Billington 1986). Thus, moss-associated N fixation may represent a significant input of N in both lichen patches and forest islands.

Bedrock surfaces and forest islands contribution to catchment N export

Despite small biomass and soil volume, bedrock surfaces account for 87% of net N mineralized on a yearly basis in the upland catchments (Table 3.5). Patterns in N mineralization are in agreement with N export through runoff from bedrock surfaces and forest islands. Allan et al. (1993) showed that bedrock surfaces export more NO_3^-, NH_4^-, and particulate N than forest islands. Higher N export from bedrock surfaces is probably a combination of lower retention of N input in precipitation and leaching of mineralized N from lichen patches. Thus, upslope bedrock surfaces are a source of N to forest islands, and forest islands are better at N retention than estimated from atmospheric input alone because of the downslope translocation of nutrients.

Table 3.5. Contribution of different landscape units to annual net N mineralization budgets in catchment U1 for 1995 and 1996. Forest islands cover 27%, lichen patches 24%, and bedrock with only crustose lichen 49% of catchment area. 'Bedrock surfaces' is the combination of lichen patches and crustose lichen-covered bedrock. It was assumed that net N mineralization is nil over crustose lichen-covered bedrock areas. Overwinter bags were only incubated in the winter of 1995-96 but were used in the annual budget calculations for both years.

Year	MIN_{net}	$NO_{3\ net}^-$
	kg N (ha of unit)$^{-1}$ yr^{-1}	
	Lichen patches	
1995	50 ± 12	21 ± 5
1996	33 ± 7	15 ± 3
	Bedrock surfaces	
1995	16 ± 4	6.9 ± 1.6
1996	8.9 ± 2.0	4.9 ± 1.0
	Forest Islands	
1995	6.3 ± 2.3	0.45 ± 0.18
1996	3.9 ± 1.6	0.01 ± 0.10
	Catchment U1	
1995	13 (90%)*	5.2 (97%)
1996	7.6 (85%)	3.6 (99%)

* Percent contribution from lichen patches

In many areas of the Precambrian Shield, exposed bedrock can represent a significant proportion of lake perimeter. These areas are seldom gauged because they tend to occur on steep or unfocussed concave slopes. Because of higher water yields (Allan & Roulet 1994b) and lower immobilization of nutrients, neglecting the contribution of bedrock surfaces may underestimate nutrient load to Shield lakes.

Chapter 4. Response of an Upland Boreal Shield Forest to a Short Term NO_3^- Addition

Introduction

The increase in N deposition to forests resulting from the emission of N gases from industrialized and agricultural regions is one of the most important aspects of global change (Galloway 1995; Vitousek et al. 1997). The outcome of increased N deposition to the boreal forest is controversial because it may bring both beneficial and detrimental effects. At early stages of elevated N deposition, plant productivity may increase in regions of the boreal forest where plant growth is N-limited (Aerts et al. 1992). Increased plant productivity may serve as a sink for atmospheric CO_2 and ameliorate global warming through storage of C in biomass, soil, and peat (Schindler & Bayley 1993). On the other hand, elevated N deposition is a source of acid rain (Likens & Bormann 1974; van Breeman et al. 1982) and it is estimated that large areas of northern Europe, Scandinavia and North America are undergoing N-based acidification (Aber et al. 1989; Dise & Wright 1995; Arp et al. 1996).

The biogeochemistry of increased N deposition is more complex than the one of elevated S inputs. The potential for N-based acidification of a catchment is dependent on the load (Dise & Wright 1995), the form (Reuss & Johnson 1986), and especially the internal cycling of the added N (Ågren & Bosatta 1988). Increased N inputs occur through a variety of gaseous, dissolved, and particulate forms, and from several wet and dry deposition mechanisms (Hanson & Lindberg 1991; Lovett 1994). However, regardless of the form of N added, as long as N inputs are retained N-based acidification does not occur (Reuss and Johnson 1986). Presently, the retention of N by forested catchments is buffering downstream acid-sensitive freshwaters from N-based acidification (Dillon & Molot 1990).

On the long-term, the response of the forest internal N cycle following increased N deposition is pivotal in controlling the extent of acidification. On an annual basis, the amount of N added to forests (even under elevated deposition) is usually small relative to what is recycled internally (Gosz 1981; Melillo 1981). Strong competition for soil mineral N between

plants, heterotrophic microorganisms, and nitrifiers prevents the accumulation of a large NH_4^+ pool and the production of NO_3^- by nitrification (Johnson 1992). However, upon chronically elevated N inputs, the accumulation of N in the ecosystem decreases competition for soil N, resulting in a larger pool of NH_4^+ available to nitrifiers. Nitrification is an important acidifying process because both acidity (2 moles of H^+ produced per mole of NH_4^+ nitrified) and a mobile anion (NO_3^-) are produced (Reuss & Johnson 1986; Aber et al. 1989). Following the onset of nitrification, catchment acidification occurs because H^+ displaces base cations from soil exchange sites and cations are lost with NO_3^- in runoff. The long-term load of N needed to induce 'N saturation' in forests is a current topic of research (Dise & Wright 1995; Jeffries 1995; Arp et al. 1996).

The response of an upland boreal Shield forest to an increased N input was studied with a 2-year addition of 40 kg N ha^{-1} yr^{-1} as $NaNO_3$ to a small catchment at the Experimental Lakes Area (ELA), northwestern Ontario. The system chosen for the experiment had several inherent features that aided in understanding the processes involved in N retention by the boreal forest. The ELA Upland catchments are a set of small watersheds (0.4 – 7.1 ha) composed of a mosaic of small forested soil pockets ('forest islands') interspersed among lichen- and moss-covered exposed bedrock outcrops (Allan et al. 1993). In forest islands, the internal N cycle, soil, and N biomass pools are typical of an unproductive and N-limited boreal conifer forest (Chapter 1). On bedrock surfaces, plant biomass is much smaller than in forest islands (~22 kg N ha^{-1} vs. ~180 kg N ha^{-1}). However, a surprisingly large amount of N (~670 kg N ha^{-1}) is stored in the thin organic deposits found under patches of lichen, moss, and grasses ('lichen patches' hereafter). The N cycle in lichen patches is a startling contrast to the one in forest islands. While net mineralization rates are low (~5 kg N ha^{-1} yr^{-1}) and net nitrification rates nil in forest islands, both net N mineralization (~40 kg N ha^{-1} yr^{-1}) and net nitrification rates (~18 kg N ha^{-1} yr^{-1}) are high in lichen patches (Chapter 3). One of the mechanisms hypothesized to generate the diverging N cycles between forest islands and lichen patches is the production of a refractory litter with a high C:N in forest islands. The poor quality of conifer litter slows down mineralization (Flanagan & Van Cleve 1983; Van Cleve & Yarie 1986), while its high C:N (36 - 505 instead of 20 - 30 in lichen patches) favors

a net immobilization over a net mineralization of N during early stages of decomposition (Berg & Staff 1981). Thus, the addition of N to one of the Upland catchments combined two experiments in one because it provided detailed information on the response of two contrasting plant/soil communities to a perturbation in their N cycle.

The choice of $NaNO_3$ as the source of N was a tradeoff between the different goals of the study. One goal was to examine the internal cycling of NO_3^- using a source enriched in both ^{15}N ($\delta^{15}N$ = +320‰) and ^{18}O ($\delta^{18}O$ = +30‰). Nitric acid was not a practical source of N because it would have required an extensive irrigation network to apply the HNO_3 in a sufficiently diluted form to prevent direct damage to organisms. Addition of NH_4NO_3 would have included a potential source of acidity (NH_4^+), but would have interfered with the isotopic tracer aspect of the work because of the two different forms of N. $NaNO_3$ was chosen because sodium is not a limiting nutrient for forest growth and $NaNO_3$ could be applied inexpensively in dissolved form using a back-pack sprayer. Thus, the experiment was an 'alkalization' of the system because any NO_3^- retained by biological activity (or denitrified) consumed an equivalent amount of acidity (Reuss & Johnson 1986; Schiff & Anderson 1987). The load of N added was ~8-fold the background total N deposition at the ELA and was similar to the highest N load observed in North America, at high elevations in New England (40 kg N ha^{-1} yr^{-1}; Lovett et al. 1982). However, the treatment was much lower than levels of N deposition occasionally observed in Europe (>75 kg N ha^{-1} yr^{-1}; Dise & Wright 1995) and especially in short-term fertilizer application to similar *Pinus banksiana* forests (200 – 500 kg N ha^{-1} yr^{-1}; Morrison & Foster 1977; Weetman & Fournier 1984a).

In this chapter, the hydrochemical and internal N cycling response of one Upland catchment (U3) following an increased N load will be described. Clues about the mechanisms of N retention will be investigated by comparing the response of forest islands and lichen patches to the N addition. These hypotheses will be further tested in Chapter 5 using the recovery of the ^{15}N label.

Methods

Study site

The ELA (northwestern Ontario) is a group of 58 small lakes and watersheds set aside for whole-ecosystem research (Johnson & Vallentyne 1970). Climate at the ELA is continental, with long, cold winters (mean 1970-95 January temperature = -17.3°C) and short but warm summers (mean July temperature = 19.2°C). Between 1970 and 1995, the area received an average of 673 mm of precipitation, with approximately 30% as snow (Beaty & Lyng 1989; K.G. Beaty unpublished data). Soils at the ELA are thin and classified as truncated orthic humic regosols and sombric brunisols (Canadian Soil Survey Committee 1978; Allan & Roulet 1994a). Mineral soils within the Upland catchments fall in the silt loam size-range and are probably of eolian origin. Bedrock is mostly slow weathering pink granodiorite (McCullough & Campbell 1993). Wildfires are frequent in the area (Bayley et al. 1992), with the last fire in the Upland catchments occurring approximately 130 years ago.

Catchment U3 (Fig. 4.1) was selected as the manipulated system and U1 and U2 were used as references. The catchments are 0-order and have similar hydrochemical properties (Allan et al. 1993). Runoff is episodic and ephemeral, lasting for about a month during snowmelt and from hours to a few days following summer storms. Runoff is naturally acidic (pH 4.01 – 4.72) due to the strong contribution of organic acids with a low pK_a and low mineral weathering rates. Catchment U3 has been the site of a low-level addition of H_2SO_4 (18 kg SO_4^{2-} ha^{-1} yr^{-1}; 2-fold background) and NH_4NO_3 (2.62 kg N ha^{-1} yr^{-1}; 50% background) on the snowpack in 1989-90 (Allan 1995). Runoff chemistry returned to background by 1994.

Forest islands occur in small depressions with 10 to 50 cm of organic and mineral soil (approximately 30% of catchment area). Jack pine (*Pinus banksiana* Lamb.) is common on the thinner soil while black spruce (*Picea mariana* Mill. B.S.P.) and a few white pine (*Pinus strobus* L.) occur where soils are deeper. The understory is variable between forest islands and composed of the shrub *Juniper communis* (L.), the fern *Pteridium aqualinum*, and various mosses (*Pleurozium schreberi* (Brid.) Mitt and *Dicranum* spp.) The forest floor is 5 to 25 cm

thick and composed of L. F. H horizons. A S horizon (decaying moss stems) is locally present. The mineral soil is 0 to 40 cm thick and limited to one to several Ah horizons and occasionally a C or Cg horizon.

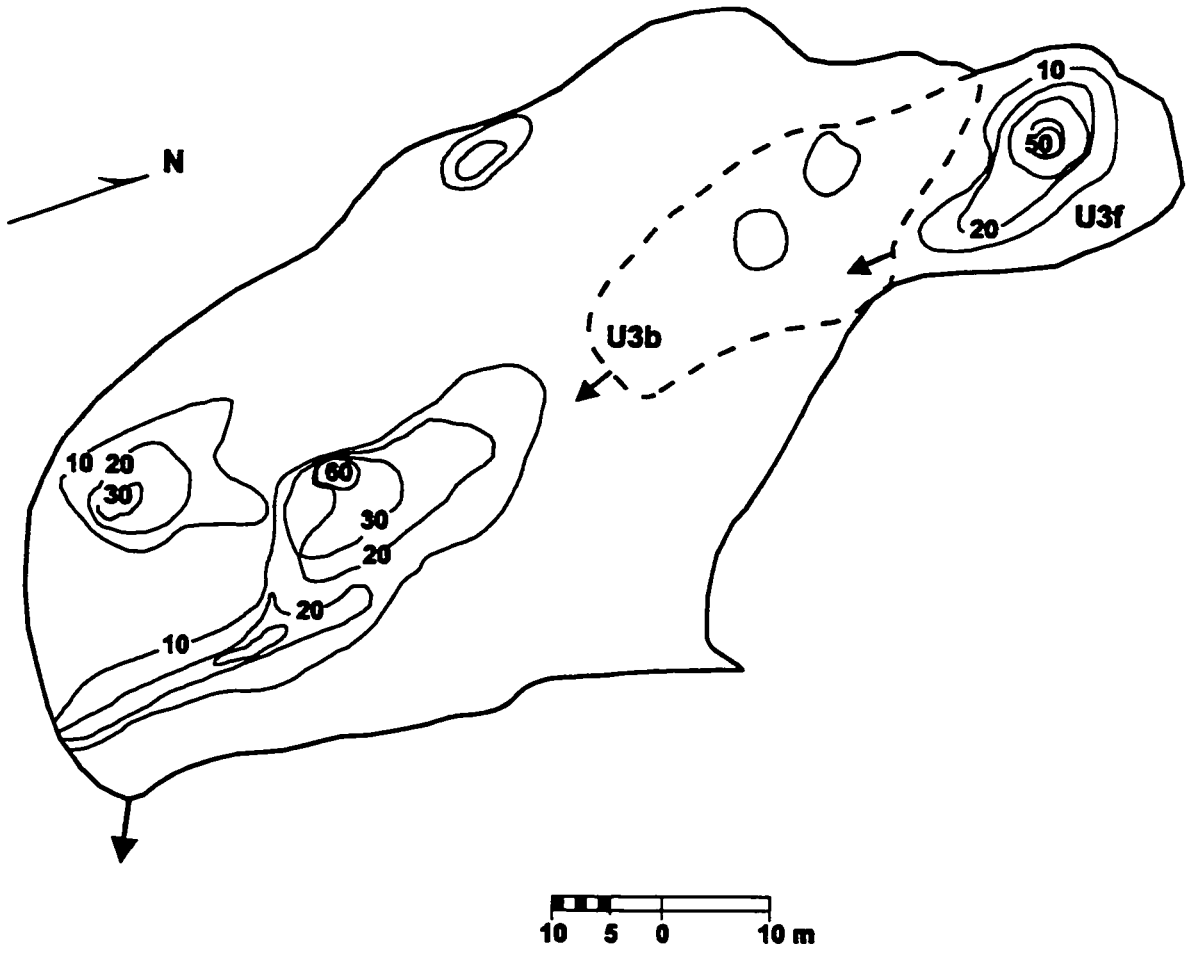

Fig. 4.1. U3 soil depth contour map (in cm), including the approximate location of the U3b and U3f sub-catchments.

Bedrock outcrops cover approximately 70% of the catchments and are composed of two features (Chapter 3). About 65% of the bedrock surface is covered with crustose lichen such as *Rhizocarpon geographicum* (L.) DC. and some foliose lichens. The remaining bedrock surface is covered by lichen patches composed of the fruticose lichens *Cladina* spp.

and *Cladonia* spp., the mosses *Polytrichum*.spp., *Andreaea rupestris* Hedw. and *Racomitrium microcarpon* (Hedw.), some grasses (*Poa* spp.), and occasionally the shrub *Juniper communis* (L.) One to 10 cm deposits are found under lichen patches (nonsoil under the Canadian Soil Survey Committee (CSSC) 1978). The organic content of the deposits (23 - 31%) is intermediate between a 'mineral' and 'organic' soil according to CSSC (1978). For simplicity and to denote that they have different properties than corresponding soils in forest islands, lichen patch deposits will be referred as an 'H' horizon hereafter. Lichens are predominant in upslope areas while mosses are more common in seepage areas downslope from forest islands (Vitt 1991). The diameter of lichen patches ranges from 30 cm to 3 m. Based on the lateral growth rate of *R. microcarpon* moss colonies, Vitt (1991) estimated that extant moss colonies could date from as far back as the last fire.

Treatment application

The period of the study covered the summer of 1994 (June – August), most of 1995 (i.e., an early but small snowmelt was missed), and the complete hydrograph for 1996. The $NaNO_3$ treatment was applied to U3 from the end of April 1995 to mid-August 1996 (36 kg N ha^{-1} yr^{-1} in 1995 and 40 kg N ha^{-1} yr^{-1} in 1996), with U1 and U2 used as reference. The N treatment was applied as 38 applications per year of a 2M $NaNO_3$ solution using a back-pack sprayer. One application was made for approximately every 15 mm of precipitation received at the catchment. An effort was made to apply the treatment during rain events or on the snowpack prior to snowmelt to mimic the natural rhythm of N deposition. Boardwalks were installed in forest islands to allow spraying on the forest floor while minimizing trampling of the ground cover. The treatment was applied as evenly as possible and the boundaries of the watershed were marked to avoid spraying outside the catchment.

Hydrochemical monitoring

Precipitation depth was measured at the highest and lowest elevation within the Uplands (~50 m relief) using standard AES rain gauges. Precipitation chemistry was measured with a bulk collector located either at the ELA meteorological station or on an island on Lake 240 (approximately 3 km away from the catchments). In 1996, water

equivalents and the chemical content of the snowpack were measured in U1 and U3 prior to snowmelt. Each catchment was instrumented with an insulated 90° V-notch weir. Concrete deflector walls covered with epoxy paint redirected overland flow towards the weirs. During snowmelt, a propane lantern was left burning overnight in the weir enclosure to prevent freeze-up. From May to September, outflow from bedrock surface and forest island sub-catchments were monitored in U1 (U1b and U1f) and U3 (U3b and U3f; Fig. 4.1). Note that U3f flows into U3b. The contribution from the U3b bedrock surface was estimated by subtracting the U3f input from the U3b export, although this will not take into account biological reactions involving U3f water within U3b. However, the larger proportion of runoff originating on the bedrock surface minimizes the bias. In addition, water from U3f rapidly leaves U3b along one preferential flow path and does not interact with most of the U3b surface. U1b and U1f are not connected to one another (Allan et al. 1993).

The detailed procedures for the calculation of element flux through runoff (including uncertainty) have been described elsewhere (Chapter 6). Briefly, runoff chemistry was sampled for every runoff event using either an autosampler or grab samples. None of the sampling schemes were perfectly flow-integrated, but the bias introduced was small (Chapter 6). Following collection, runoff samples were kept at 4°C in the dark until analysis. During the snowmelt period, samples were analyzed at the Freshwater Institute (Winnipeg) within a week of collection. Otherwise, samples were analyzed on site within 48 hours.

Analysis for particulate N (PN), total dissolved N (TDN), NH_4^+, NO_3^-, NO_2^-, pH and DOC followed standard ELA procedures (Stainton et al. 1977). PN was determined by filtering a known volume of water through a pre-combusted GF/C filter (1 μm nominal pore size). The PN content of the filter was determined with an elemental analyzer. A correction was added in U3 samples to account for the high residual TDN in the filter pore-water. TDN was measured by UV-mediated persulphate oxidation followed by reduction to NH_4^+ by elution through a zinc column. NH_4^+, NO_3^- and NO_2^- were determined colorimetrically using an autoanalyzer. Nitrite concentrations were usually at or near the detection limit (0.07 μmol

L^{-1}) and were pooled with NO_3^-. Dissolved organic N (DON) was estimated as the difference between TDN and NH_4^+ plus NO_3^- (i.e., TDN - TDIN).

Coarse particulate N (CPN) export (>1 mm, mostly needles) was quantitatively collected using a 1 mm screen downstream of U2 and U3. CPN samples were collected after every 1 to 3 storms, homogenized with a Wiley mill, and the nutrient content determined with an elemental analyzer.

Analytical error on DON analyses

DON estimates have the largest uncertainty because they accumulate the error of several chemical analyses and are calculated by difference. DON estimates are especially uncertain in water samples having TDN ≈ TDIN (Gorzelska et al. 1997). High TDN to TDIN values were common in bulk precipitation samples (Chapter 2) and in U3 runoff in the spring of 1996, where 6 out of 17 samples had negative DON concentrations. Random analytical error was included in the estimation of DON exports (Chapter 6). Thus, if the error on the different analyses needed to estimate DON is truly random, individual DON concentration measurements may be imprecise but DON fluxes over the whole year will be accurate because many samples were taken (>30 per year). However, for the U3 - 1996 spring runoff, negative DON values may not have been caused solely by random analytical error because some samples with unusually high TDIN (>5 000 μg N L^{-1}) consistently yielded negative DON concentrations upon reanalysis (M.P. Stainton, Freshwater Institute, pers. comm.). The negative DON spring values were replaced by the volume-weighed DON concentration for non-negative samples for that period. Most of the DON export occurred during the summer period when analytical uncertainty was smaller (i.e. TDN >> TDIN).

Water balance

The water balance for the Upland catchments was defined as:

$$R = P - E - G \pm \Delta S$$

where R is runoff (mm), P the precipitation, E the evapotranspiration, G the groundwater recharge and ΔS the change in soil water storage. G is assumed to be insignificant through the granodiorite bedrock. Seepage from fractures is not observed on exposed bedrock surfaces in the vicinity of the ELA, including on the cliff separating the Upland catchments from Lake 302. Over the whole year, ΔS is negligible because a permanent water table does not occur and soils are very thin. Thus, the water balances simplifies to:

$$R = P - E$$

The small size of the Upland catchments and the predominance of overland flow facilitate P and R measurements. However, the spatial heterogeneity of the forested cover makes the estimation of E problematic. When needed, E was calculated by difference between P and R (Allan et al. 1993).

Estimation of error on the hydrochemical budgets

The error on bulk precipitation input (s_{BP}) was estimated by first-order error propagation of event precipitation error (s_P) and analytical error (s_C) (Meyer 1975). Event s_P was assumed to be 20% of the mean of the two Upland AES collectors (Winter 1981). Measurements between the two collectors usually agreed within a few percent. However, the collectors may over- or more likely undercatch precipitation under some circumstances (Winter 1981; LaBaugh & Winter 1984). S_C was obtained from replicated measurements (Chapter 6). Error on event bulk precipitation flux was obtained by propagating s_P and s_C:

$$s_{BP} = \sqrt{\frac{s_P^2}{P^2} + \frac{s_C^2}{C^2}} \bullet BP$$

where BP is the event bulk precipitation flux for a given element, P is precipitation depth, and C the element concentration. The error on yearly precipitation flux was estimated by the summing the variances of individual events:

$$S_{BP(year)} = \sqrt{S^2_{BP(1)} + S^2_{BP(2)} + \ldots}.$$

Retention coefficients for TN (R_{TN}) were calculated following:

$$R_{TN} = \frac{BP + T - F}{BP + T},$$

where T is treatment NO_3^- input (for U3) and F the export of TN in runoff. For the calculation of the error on R_{TN}, error on T (s_T) was set at 0% for U3 and 10% for the sub-catchments (i.e. some uneven application was assumed). The error on R_{TN} (s_{RTN}) was estimated from:

$$S_{RTN} = \sqrt{\frac{S^2_D}{D^2} + \frac{S^2_{IN}}{IN^2}} \bullet R_{TN},$$

where IN = BP + T and D = IN – F.

N mineralization

N mineralization was estimated using 21-day buried bag incubations (Eno 1960) in U1 and U3 forest islands and lichen patches. One incubation was made every month from May to October, and one overwinter in 1995-96. In 1994, pre-treatment mineralization rates were estimated in July and August using buried bags and *in-situ* core incubations (Raison et al. 1987) in forest islands only. More information on methodology and a thorough analysis of the U1 data can be found in Chapter 3. Net mineralization (MIN_{net}) was estimated as ΔNH_4^- + ΔNO_3^- and net nitrification ($NO_3^-{}_{net}$) as ΔNO_3^-.

Plant growth

In each catchment, 20 *P. banksiana*, 20 *P. mariana*, and 20 *P. mariana* saplings (i.e., <2 m high) were permanently marked using aluminum tags in the fall of 1994. Diameter at breast height for mature trees and height for saplings was measured each spring and fall. In the fall of 1996, needle samples were collected from half of the marked mature trees. Needles were collected using a tree pruner on a 5 m pole. Needles were collected on the sunny side of the trees and from different heights whenever possible. Needle samples from U1 and U3 were freeze-dried, homogenized using a ball mill, and analyzed for N, P, K, Ca, Mg, and Na content at the Land Resources Science analytical laboratory of the University of Guelph. Critical nutrient concentrations could not be found in the literature for *P. banksiana* and *P. mariana* needles. The range in critical concentrations and critical ratios listed by Rosengren-Brinck & Nihlgård (1995) for *Picea abies* was used as an approximation.

In each catchment, the lateral expansion of 10 *Racomitrium microcarpon* moss colonies growing on bedrock was estimated by taking photographs in the spring and fall (Vitt 1991). Permanent references and colony number were painted on the bedrock (but not on the mosses).

Denitrification

Denitrification was estimated as N_2O evolution in closed chambers. Nitrous oxide was assumed to be the main product of denitrification because of the low soil pH (~4.0, 2:1 H_2O ext.; Knowles 1981). Four 0.056 m^2 collars were installed in U1 and eight in U3 in 1995 to a depth of ~10 cm in the forest floor. Four incubations were made in 1996, one following snowmelt, two following summer storms, and one in the fall. Collars were fitted with a groove where a 8 L chamber could be inserted and sealed with water. Following installation, the chamber was left in place for 1 hour to equilibrate. Gas samples were collected using the double-syringe technique and stored in re-evacuated 10 mL 'Vaccutainers' blood serum tubes. Samples were taken hourly for up to 4 hours. Nitrous oxide concentration was measured by flame ionization detection gas chromatography (Hewlett-Packard Model 5750).

Results

Hydrology

The period of the experiments was characterized by extremes in the hydrological input at the ELA. While June and August 1994 had average to low precipitation, July 1994 was the wettest in the ELA record (180.5 mm). While 1995 had near average precipitation over the whole year (603 mm), month-long droughts occurred in June and September. In contrast, 1996 was the wettest year in the ELA record (<1 000 mm at the meteorological station; K.G. Beaty, Freshwater Institute, Winnipeg, MB, pers. comm.). For the main catchments, runoff coefficients were lowest in 1995 (0.26 - 0.35) and highest in 1996 (0.47 - 0.49; Table 4.1). Runoff coefficients for the bedrock sub-catchments (0.53 - 0.83) were much higher than the forest island sub-catchments (0.27 - 0.54; Table 4.1).

Bedrock surface and forest island N exports under background conditions

Background nutrient export patterns for whole-catchments, forest islands, and bedrock surfaces have been reviewed elsewhere (Chapter 1) and will only be summarized briefly here. Bulk precipitation input to the catchments ranged between 4 – 6 kg N ha^{-1} yr^{-1} and was roughly evenly divided between NH_4^+, NO_3^-, and organic-N. Forest islands and whole catchments had similar patterns in N export. In both cases, mineral N inputs were efficiently retained and most of the export was as DON (Table 4.2). Overall, 68% - 79% of the total N input was retained. However, total N retention was lower during very wet periods, such as the summer of 1994, because higher runoff favored DON losses (Table 4.2).

On bedrock surfaces, the quantity and form of N exported was variable from year-to-year (Table 4.3). During a relatively dry year (1995), R_{TN} was low relative to forest islands (0.20 vs. 0.71) because of significant NO_3^-, NH_4^+ and DON exports (Table 4.3). However, during a wet year (1996) the bedrock surfaces R_{TN} was similar to forest islands (0.60 vs. 0.57) because mineral N inputs were more efficiently retained (Table 4.3). Lower net N mineralization rates underneath lichen patches and a stronger potential for nutrient uptake by

lichens and mosses has been hypothesized to favor increased N retention during wet years (Chapter 1).

Table 4.1. Upland catchments hydrological summary for 1994-96.

	Precipitation (mm)	Runoff (mm)	Runoff coef.
		U1	
14 Jun – 31 Aug 94	335 ± 20.0	131 ± 6.2	0.39
15 March - 31 Oct 95	474 ± 25.6	127 ± 7.9	0.27
1 Nov 95 - 31 Oct 96	856 ± 35.4	408 ± 11.0	0.48
		U2	
14 Jun – 31 Aug 94	335 ± 20.0	147 ± 7.8	0.44
15 March - 31 Oct 95	474 ± 25.6	124 ± 10.5	0.26
1 Nov 95 - 31 Oct 96	862 ± 36.1	403 ± 13.7	0.47
		U3	
14 Jun – 31 Aug 94	335 ± 20.0	178 ± 9.5	0.53
15 March - 31 Oct 95	474 ± 25.6	167 ± 11.3	0.35
1 Nov 95 - 31 Oct 96	867 ± 36.7	426 ± 13.7	0.49
		U1b	
1 May 95 - 30 Sep 95	367 ± 23.7	194 ± 13.8	0.53
1 May 96 - 30 Sep 96	557 ± 18.3	385 ± 35.7	0.69
		U1f	
14 Jun 94 - 31 Aug 94	335 ± 20.0	162 ± 17.5	0.48
1 May 95 - 30 Sep 95	367 ± 23.7	97.9 ± 10.1	0.27
1 May 96 - 30 Sep 96	557 ± 18.3	303 ± 34.7	0.54
		U3b	
1 May 95 - 30 Sep 95	367 ± 23.7	254 ± 22.7	0.69
1 May 96 - 30 Sep 96	557 ± 18.3	460 ± 42.6	0.83
		U3f	
14 Jun 94 - 31 Aug 94	335 ± 20.0	169 ± 18.3	0.50
1 May 95 - 30 Sep 95	367 ± 23.7	126 ± 17.6	0.34
1 May 96 - 30 Sep 96	557 ± 18.3	302 ± 34.6	0.54

Table 4.2. Nitrogen fluxes from catchment U1, U2, and U3 in 1994-96. Mean ± SD. Coarse particulate exports were negligible (<0.015 kg N ha^{-1} yr^{-1}) and are not shown. The sum of the 1996 snowmelt and post-snowmelt fluxes may vary slightly from total 1996 fluxes because of small rounding error and small stoichastic variability during the computer simulations used to estimate the fluxes and their uncertainty (Chapter 6).

	1994	1995	1996 (snowmelt)	1996 (post-snowmelt)	1996 (Total)
			Bulk Deposition (kg N ha^{-1} yr^{-1})		
NO_3^-	0.55 ± 0.039	1.2 ± 0.17	0.53 ± 0.076	1.5 ± 0 11	2.0 ± 0.13
NH_4^+	0.29 ± 0.018	1.4 ± 0.20	0.59 ± 0.069	2.3 ± 0.14	2.9 ± 0.16
DON	0.16 ± 0.074	0.33 ± 0.49	0.038 ± 0.180	1.0 ± 0.09	1.1 ± 0.20
Particulate-N	0.36 ± 0.022	0.42 ± 0.029	0.13 ± 0.023	0.41 ± 0.020	0.54 ± 0.030
Total N	1.4 ± 0.07	3.4 ± 0.40	1.3 ± 0.15	5.2 ± 0.42	6.5 ± 0.45
			U1 (kg N ha^{-1} yr^{-1})		
NO_3^-	0.016 ± 0.0016	0.10 ± 0.014	0.090 ± 0.0076	0.16 ± 0.012	0.25 ± 0.014
NH_4^+	0.036 ± 0.0022	0.058 ± 0.0054	0.055 ± 0.0029	0.061 ± 0.0042	0.12 ± 0.005
DON	0.56 ± 0.033	0.48 ± 0.037	0.40 ± 0.020	0.80 ± 0.033	1.2 ± 0.038
Particulate-N	0.070 ± 0.0054	0.080 ± 0.0089	0.074 ± 0.0039	0.14 ± 0.006	0.21 ± 0.007
Total N	0.68 ± 0.040	0.72 ± 0.050	0.62 ± 0.030	1.2 ± 0.046	1.8 ± 0.054
R_{TN}	0.51 ± 0.063	0.79 ± 0.15	0.52 ± 0.13	0.77 ± 0.10	0.72 ± 0.086
			U2 (kg N ha^{-1} yr^{-1})		
NO_3^-	0.043 ± 0.0054	0.13 ± 0.016	0.040 ± 0.0039	0.074 ± 0.0054	0.12 ± 0.007
NH_4^+	0.054 ± 0.0038	0.074 ± 0.0075	0.060 ± 0.0035	0.060 ± 0.0098	0.12 ± 0.006
DON	0.80 ± 0.058	0.69 ± 0.061	0.50 ± 0.033	1.1 ± 0.05	1.6 ± 0.07
Particulate-N	0.094 ± 0.0080	0.086 ± 0.011	0.090 ± 0.0059	0.14 ± 0.007	0.23 ± 0.009
Total N	0.99 ± 0.072	0.98 ± 0.083	0.69 ± 0.039	1.4 ± 0.07	2.1 ± 0.08
R_{TN}	0.29 ± 0.073	0.71 ± 0.15	0.47 ± 0.13	0.73 ± 0.10	0.68 ± 0.085
			U3 (kg N ha^{-1} yr^{-1})		
Experiment		36.0	15.8	24.2	40.0
NO_3^-	0.022 ± 0.0019	3.5 ± 0.30	10 ± 0.8	3.0 ± 0.20	13 ± 0.8
NH_4^+	0.053 ± 0.0031	0.13 ± 0.011	0.081 ± 0.0056	0.15 ± 0.086	0.23 ± 0.010
DON	0.86 ± 0.052	1.4 ± 0.24	0.78 ± 0.27	3.8 ± 0.28	4.9 ± 0.39
Particulate-N	0.10 ± 0.009	0.14 ± 0.015	0.092 ± 0.0067	0.27 ± 0.015	0.36 ± 0.010
Total N	1.0 ± 0.06	5.2 ± 0.35	11 ± 0.8	7.2 ± 0.36	19 ± 0.9
R_{TN}	0.29 ± 0.067	0.87 ± 0.016	0.36 ± 0.048	0.76 ± 0.022	0.59 ± 0.022

Table 4.3. May to September N fluxes from bedrock surfaces and forest islands sub-catchments in 1995-1996.

	1995 (kg N ha^{-1} yr^{-1})	1996 (kg N ha^{-1} yr^{-1})
	Bulk Deposition	
NO_3^-	0.86 ± 0.053	1.1 ± 0.69
NH_4^+	0.97 ± 0.074	1.6 ± 0.12
PN	0.38 ± 0.027	0.37 ± 0.019
DON	0.29 ± 0.14	1.1 ± 0.43
TN	2.5 ± 0.11	4.2 ± 0.39
	U1b	
NO_3^-	1.2 ± 0.23	0.40 ± 0.074
NH_4^+	0.86 ± 0.014	0.071 ± 0.0054
PN	0.11 ± 0.019	0.18 ± 0.021
DON	0.52 ± 0.089	1.1 ± 0.12
TN	2.0 ± 0.30	1.7 ± 0.20
R_{TN}	0.20 ± 0.13	0.60 ± 0.12
	U1f	
NO_3^-	0.022 ± 0.0044	0.019 ± 0.0017
NH_4^+	0.048 ± 0.0068	0.061 ± 0.0059
PN	0.10 ± 0.016	0.194 ± 0.021
DON	0.55 ± 0.076	1.6 ± 0.14
TN	0.72 ± 0.099	1.8 ± 0.17
R_{TN}	0.71 ± 0.067	0.57 ± 0.11
	U3b	
Experiment	28.4 ± 2.84	24.2 ± 2.42
NO_3^-	17 ± 1.3	24 ± 2.0
NH_4^+	0.31 ± 0.036	0.35 ± 0.047
PN	0.16 ± 0.049	0.31 ± 0.10
DON	1.1 ± 0.32	5.6 ± 1.0
TN	19 ± 1.5	30 ± 2.7
R_{TN}	0.38 ± 0.11	- 0.06 ± 0.13
	U3f	
Experiment	28.4 ± 2.84	24.2 ± 2.42
NO_3^-	2.6 ± 0.67	5.9 ± 0.91
NH_4^+	0.14 ± 0.024	0.26 ± 0.037
PN	0.21 ± 0.042	0.60 ± 0.093
DON	1.3 ± 0.25	5.1 ± 0.81
TN	4.2 ± 0.84	12 ± 1.7
R_{TN}	0.86 ± 0.13	0.58 ± 0.12

Whole-catchment response to N addition

Catchment U3 responded in an immediate and sustained fashion to the increased N input. The concentration of NO_3^- in runoff increased 100-fold and remained high throughout the period of addition (Fig. 4.2). The concentration of other N forms (PN, DON, and NH_4^+) in U3 runoff also increased relative to references, especially during the second year of NO_3^- addition. In general, PN, NH_4^+, and DON concentrations were 1.5- to 3-fold background by 1996. A strong response was observed for runoff pH, which increased by ~0.2 units in 1995 and also in 1996. The relative increase in DOC and DON concentrations appeared to match the change in pH. One exception was a pulse of DON in May 1996 in U3, which was also observed in the sub-catchments (Fig. 4.3). Following the cessation of N addition, NO_3^- concentration quickly returned to background. However, pH, DOC and the other forms of N remained elevated (Fig. 4.2).

The retention of N was high during the first year of NO_3^- addition (R_{TN} = 0.87) but declined during the second year (0.59; Table 4.2). However, in 1996 most of the NO_3^- export occurred during the snowmelt period (10 out of 13 kg N ha^{-1} yr^{-1}) when R_{TN} was low (0.36). In addition, R_{TN} was lower in 1996 because DON export had increased 3-fold relative to reference catchments (Table 4.2). U3 R_{TN} during the 1996 post-snowmelt period (0.76) was similar to the one of reference catchments (0.77 an 0.73 for U1 and U2 respectively). Thus, after two years of addition, NO_3^- was still strongly retained during the growing season when biological retention mechanisms were active.

U3 sub-catchments runoff response

The response of the U3 sub-catchments to the NO_3^- addition was complex and will be reviewed in some detail because it provides insights into the mechanisms mediating N retention in the Upland system. It should be kept in mind that in addition to the NO_3^- treatment, nutrient cycling in the sub-catchments was also influenced by climatic factors from year-to-year (Chapter 1). The contrasts in runoff concentration and N export between and within sub-catchment types will be reviewed below.

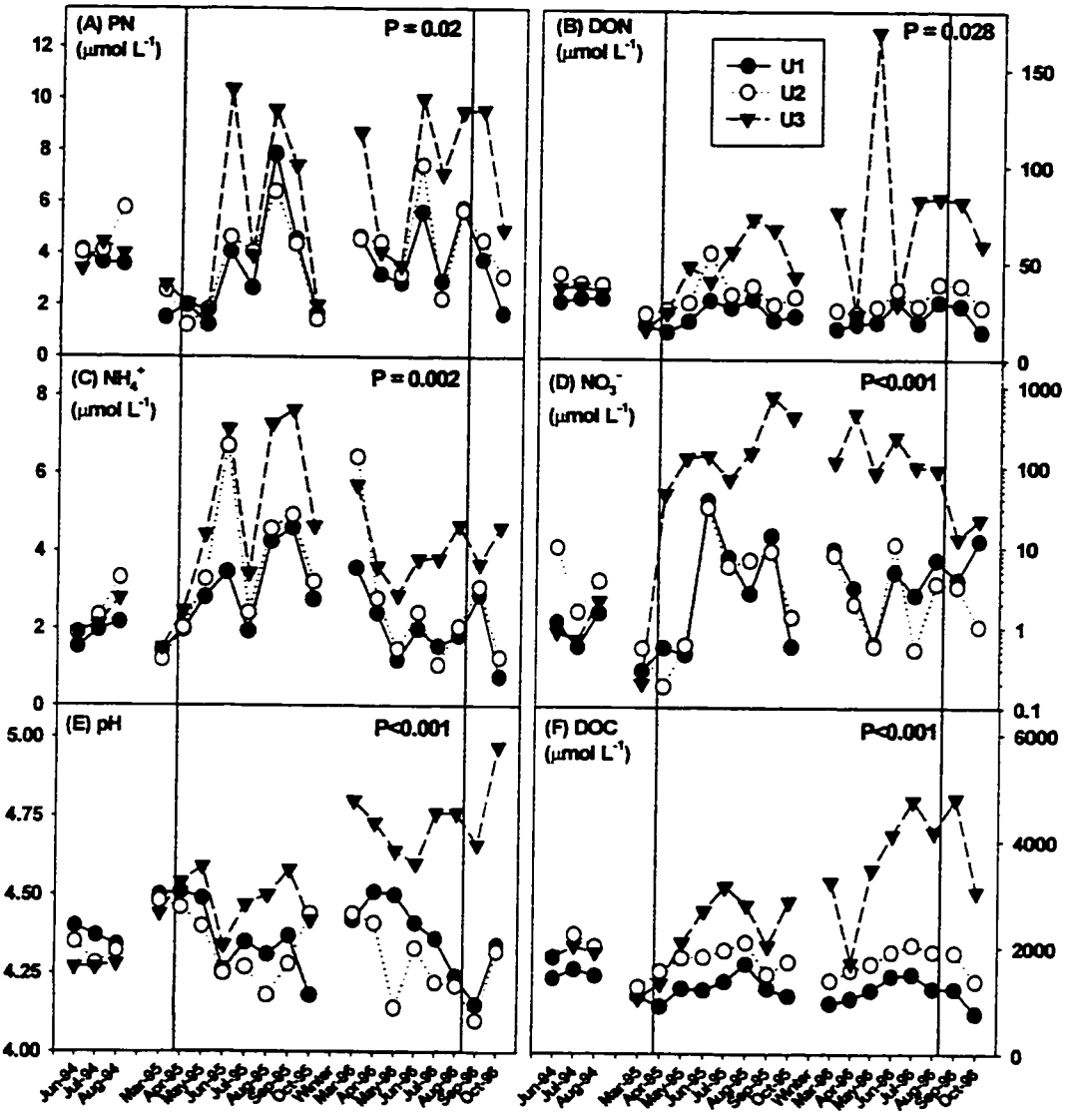

Fig. 4.2. Monthly volume-weighed **(A)** PN, **(B)** DON, **(C)** NH_4^+, **(D)** NO_3^-, **(E)** pH, and **(F)** DOC concentrations from reference catchments U1 and U2 and the NO_3^--amended U3, 1994-1996. Shaded areas represent the period of application of the N treatment. Pre-treatment conditions were similar to the ones reported by Allan et al. (1993). Randomized intervention analysis (Carpenter et al. 1989) was used to determine if there was a significant change in element concentration between U3 and the reference catchments following the addition of NO_3^-.

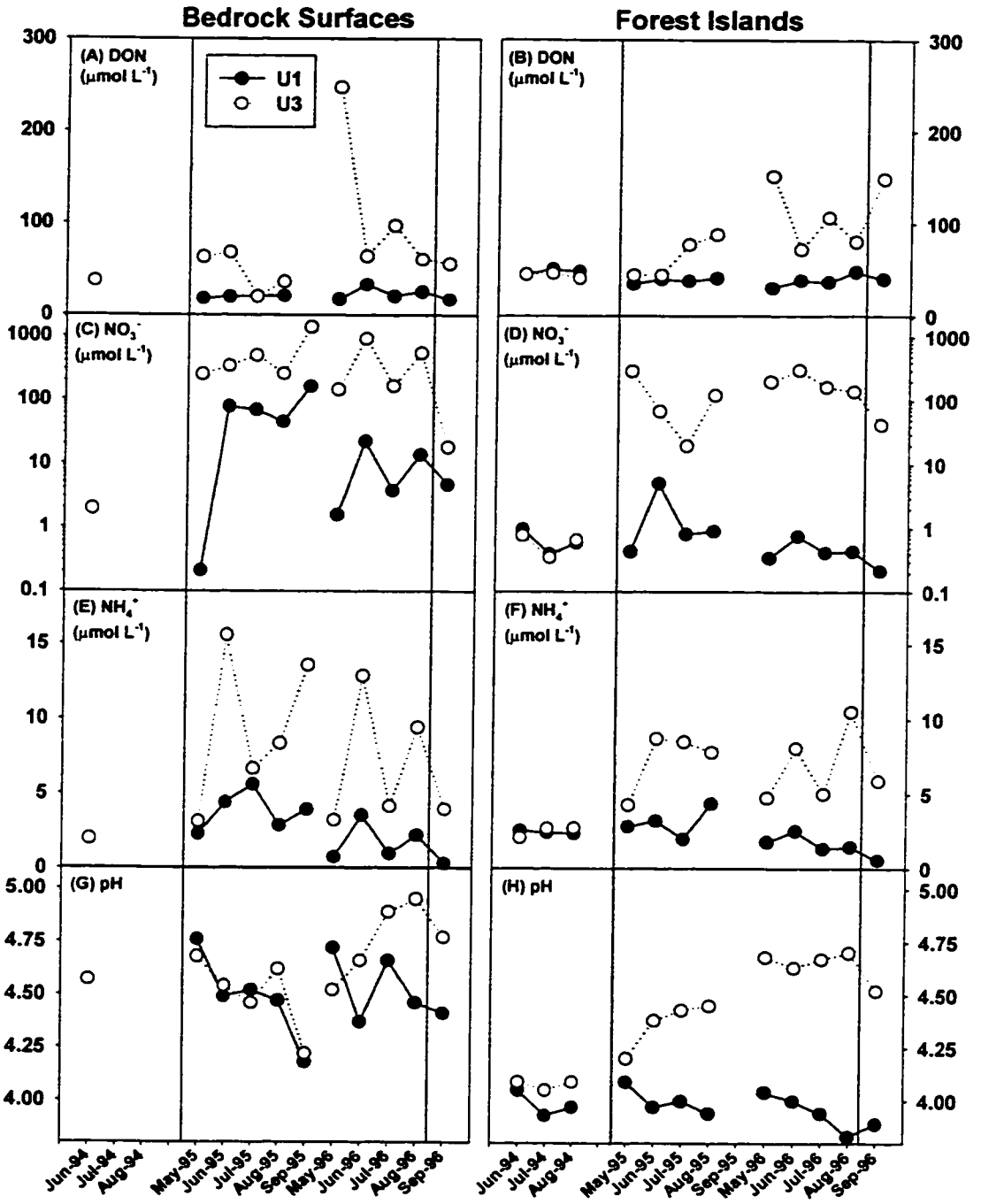

Fig. 4.3. Monthly volume-weighed runoff concentration for **(A &B)** DON, **(C & D)** NO_3^-, **(E & F)** NH_4^+, and **(G & H)** pH from U1 and U3 bedrock surface and forest island sub-catchments, 1994-1996. On average, runoff coefficients are larger for bedrock surfaces and differences in concentrations may not reflect differences in fluxes (Table 4). Shaded areas represent the period when NO_3^- was added to U3.

U1b & U3b

Under background conditions, NO_3^- concentration, NH_4^+ concentration and pH were elevated in bedrock surface runoff relative to forest islands (Fig. 4.3). Runoff pH gradually declined during the growing season, a tendency also observed in forest islands (Fig. 4.3). Following the $NaNO_3$ addition, NO_3^-, NH_4^+, and DON concentrations increased in U3b and were more variable than in U1b. Runoff pH was similar to U1b in 1995 but increased in 1996.

In 1995, both U1b and U3b did not retain N inputs very efficiently (R_{TN} = 0.20 vs. 0.38 respectively). However, retention coefficients are misleading because while only ~0.5 kg N ha^{-1} was stored in U1b, ~12 kg N ha^{-1} was stored in U3b in 1995 (Table 4.3). In contrast, in 1996 U1b retained N inputs more efficiently (R_{TN} = 0.60) but U3b had no net N retention (R_{TN} = -0.06 ± 0.13). In U3b, N losses occurred mostly as NO_3^-, but DON exports (~5.6 kg N ha^{-1} in 1996) were also important.

It may seem puzzling that R_{TN} was lower in U1b in 1995 despite the large input of $NaNO_3$ to U3b. However, the mechanism by which mineral N was delivered to each sub-catchment was different and may have affected to potential for retention by plant and lichen uptake. In 1995, the input of N from N mineralization underneath lichen patches in U1b was large relative to precipitation inputs (see *N mineralization* below). Mosses and lichen may be better adapted to use N in precipitation than N originating from recycling in soils (Chapter 1). Thus the NO_3^- treatment added as 'rain' in U3b may have been better retained than NO_3^- originating from nitrification in U1b. The potential for moss and lichen uptake was probably diminished in U3b in 1996 because of the loss of moss biomass during the experiment (see *plant growth* below).

U1f & U3f

Forest islands retained the NO_3^- treatment more efficiently than bedrock surfaces (Table 4.3). As for bedrock surfaces, R_{TN} was higher in U3f than in U1f in 1995 (0.86 vs. 0.71). However, unlike on bedrock surfaces, R_{TN} were similar for U1f and U3f in 1996 (0.57

vs. 0.58). As for U3b, the efficient retention of NO_3^- in U3f was partially offset by increased DON exports (Table 4.3). Overall, at least 43 kg N ha^{-1} was retained by forest islands during the experiment, ~3.5 times more than on bedrock surfaces.

Soil N concentration

Under background conditions, the concentration of NH_4^+ on soil exchange sites is ~5 μg N g_{soil}^{-1} in the forest floor and ~10 μg N g_{soil}^{-1} in the lichen patch 'H' (Fig. 4.4). In both U1 and U3, soil NH_4^+ concentrations doubled in the summer of 1995 following a drought in late May and June. Under background conditions, soil NO_3^- concentrations were usually undetectable in forest islands (<0.025 μg N g_{soil}^{-1}) and 1 – 5 μg N g_{soil}^{-1} in lichen patches.

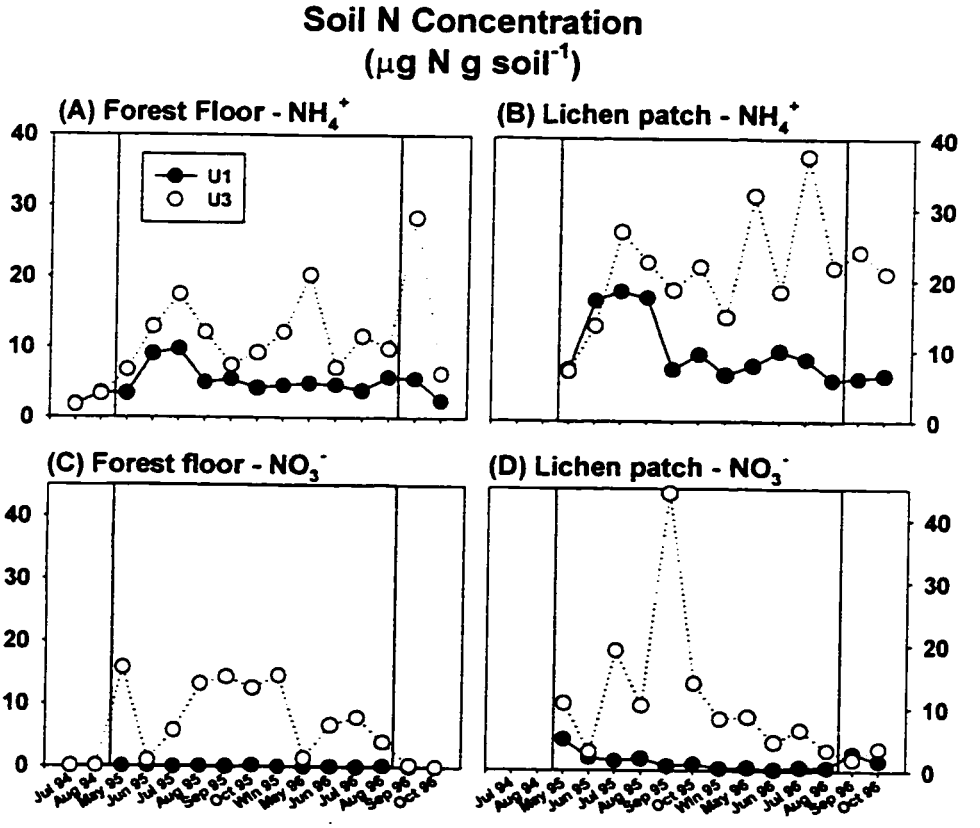

Fig. 4.4. Exchangeable soil N concentrations in the forest LFH and lichen patch 'H' in U1 and U3, 1994-1996. Concentrations obtained from 2 M KCl extracts.

Following the addition of NO_3^- to U3, soil NH_4^+ concentrations doubled in the forest floor and tripled in lichen patches (Fig. 4.4). Unlike in the reference soil, a pool of NO_3^- was present in the forest floor (~10 μg N g_{soil}^{-1}) and NO_3^- concentrations increased in lichen patches (1 – 40 μg N g_{soil}^{-1}). Although NO_3^- quickly returned to background following the cessation of NO_3^- addition, NH_4^+ remained high.

Changes in net N mineralization and nitrification rates

There was a striking contrast between the internal N cycle response of U3 forest islands and lichen patches to the N addition (Table 4.4). In 1994, net mineralization rates (MIN_{net}) were identical and net nitrification rates ($NO_{3\,net}^-$) nil in U1 and U3 forest islands during two summer incubations (Table 4.4). No background data (i.e. 1994) was available for lichen patches, so it has to be assumed that rates between catchments were similar prior to the experiment. During the addition of $NaNO_3$ to U3, *$NO_3^-_{net}$ increased in lichen patches but NO_3^- was consumed (i.e. negative $NO_3^-_{net}$) in forest islands* (Table 4.4). MIN_{net} probably increased in both forest islands and lichen patches, but the large variability of the forest islands estimates prevents establishing this with certainty. Mineralization rates tended to be higher in both catchments in 1995, probably because of warmer and drier soils (Chapter 3). For U3 as a whole, the combination of increased $NO_{3\,net}^-$ in lichen patches and NO_3^- consumption in forest islands yielded a catchment-scale $NO_{3\,net}^-$ similar to U1 (Table 4.4).

Denitrification

Very small N_2O fluxes were measured in 1996 in U3. The largest flux (0.37 μmol N_2O m^{-2} h^{-1}) was measured in May, at the end of the snowmelt period when soils had been saturated for a month (Table 4.5). Even by extending the largest N_2O flux measured to the whole year and the whole catchment, this only represented a loss of 0.9 kg N ha^{-1} yr^{-1} from U3. The small N_2O fluxes measured during summer months may arise from N_2O generated during nitrification or NO_3^- reduction (Firestone & Davidson 1989). With the possible exception of under the snowpack when anoxic conditions were most likely to develop, denitrification does not appear to have been a significant loss of N from U3.

Table 4.4. Nitrogen mineralization in catchment U1 and U3, 1995-96 (mean ± SE). Net N mineralization rates were similar in U1 and U3 forest islands in the summer of 1994 (MIN_{net} = 89 ± 33 and 89 ± 37 g N ha^{-1} d^{-1}) and $NO_3^-{}_{net}$ was low (1.0 ± 0.8 and 2.7 ± 1.5 g N ha^{-1} d^{-1}). Mineralization rates obtained with buried bags and *in-situ* core incubations were comparable (Chapter 3).

		MIN_{net}	ΔNH_4^+	$NO_3^-{}_{net}$
		kg N (ha of unit)$^{-1}$ yr^{-1}		
		Lichen Patches		
U1	1995	50 ± 12	29 ± 12	21 ± 5
	1996	33 ± 7	17 ± 5	15 ± 3
U3	1995	93 ± 29	57 ± 19	35 ± 13
	1996	65 ± 9	28 ± 6	36 ± 8
		Bedrock Surfaces		
U1	1995	16 ± 4	9.6 ± 4.0	6.9 ± 1.6
	1996	8.9 ± 2.0	5.6 ± 1.7	4.9 ± 1.0
U3	1995	31 ± 10	19 ± 6	12 ± 4
	1996	21 ± 3	9.0 ± 2.0	12 ± 3
		Forest Islands		
U1	1995	6.3 ± 2.3	5.9 ± 2.3	0.45 ± 0.18
	1996	3.9 ± 1.6	4.0 ± 1.6	0.01 ± 0.1
U3	1995	6.7 ± 6.3	20 ± 6	-14 ± 3
	1996	17 ± 13	36 ± 30	-19 ± 8
		Catchment		
U1	1995	13 ± 4	8.6 ± 3.5	5.2 ± 1.2
	1996	7.6 ± 1.9	5.2 ± 1.7	3.6 ± 0.8
U3	1995	26 ± 9	19 ± 6	6.5 ± 3.8
	1996	20 ± 5	15 ± 8	5.5 ± 4.0

Table 4.5. N_2O emission rates in static chambers in forest islands in 1996. The May measurements were made following snowmelt while soils were still saturated. Summer and fall measurements were made following rainstorms. The main product of denitrification was assumed to be N_2O. Mean ± SE. n = 4-8.

	U1		U3	
	μmol N_2O m^{-2} h^{-1}	kg N ha^{-1} yr^{-1}	μmol N_2O m^{-2} h^{-1}	kg N ha^{-1} yr^{-1}
15 May 96	-0.01 ± 0.02	0	0.37 ± 0.04	0.9
6 Jun 96			0.07 ± 0.03	0.2
25 June 96	0.08 ± 0.07	0.2	0.17 ± 0.08	0.4
25 Sep 96			-0.03 ± 0.16	0

Plant growth and needle nutrient content

In the short-term, the addition of NO_3^- to U3 did not result in increased tree growth (Chapter 1). However, the nutrient status of trees was different between U1 and U3 in the fall of 1996. In U1, needle N concentration was low in both *P. mariana* and *P. banksiana* (~10 and ~11 mg N g_{dw}^{-1} respectively). In addition, the P content for both species and K for *P. banksiana* were low (Fig. 4.5). After two years of N addition to U3, the needle N content was near the N-limitation threshold (~12 mg N g_{dw}^{-1}) for *P. abies* but was still below the 'optimal' level suggested by Weetman & Fournier (1984b) for *P. banksiana* (~14 mg N g_{dw}^{-1}). Nutrient ratios suggest that trees may have been more P- or K-limited in U3 in 1996 (Fig. 4.5).

An unexpected effect of the experiment was the loss of a part of the moss and lichen community in U3. While *R. microcarpon* colonies grew by 2 – 12% per year in the reference catchments, U3 lost ~5% of the surface area covered by the colonies in 1995 and ~20% in 1996 (Fig. 4.6). Browning (loss of green tissue or discoloration) was evident in 1996 on *Polytrichum* spp. mosses and on some of the *Cladina* spp. lichen. The mechanism responsible for the loss of a part of the moss cover is not known at the moment. Observations during a survey in the spring of 1997 (9 months following the cessation of the NO_3^- addition) indicated that moss growth had resumed in some previously damaged colonies (i.e., new green biomass had appeared).

Discussion

Forests islands and lichen patches represent distinct status in the N cycle of a terrestrial community. In forest islands, low net N mineralization, the absence of net nitrification, a low N content of plant tissue, and the efficient retention of mineral-N inputs indicate a community where the availability of N can limit plant productivity. In contrast, in lichen patches high net mineralization and nitrification rates and the leaching of mineral-N in runoff during dry years indicate a system that is closer to N saturation.

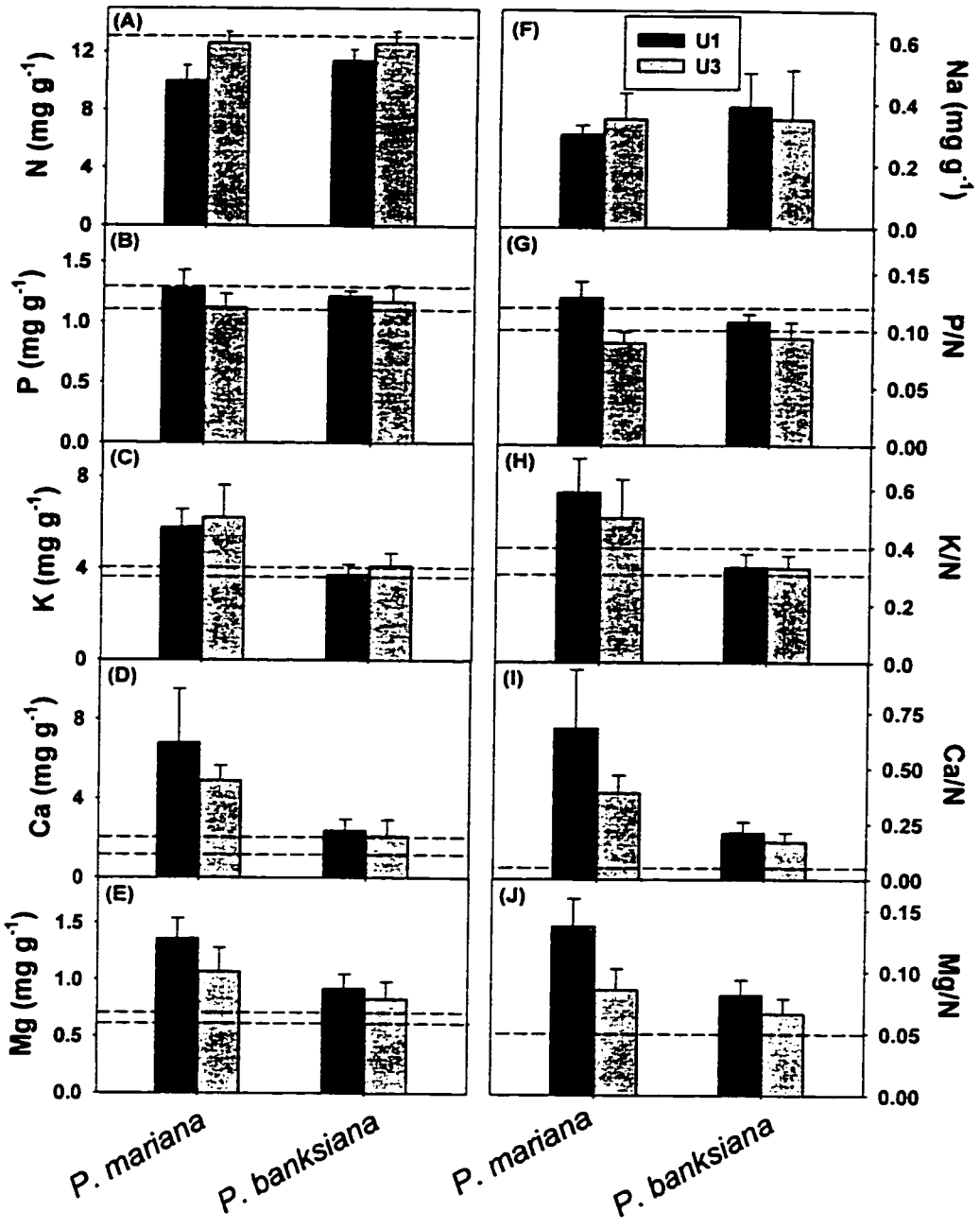

Fig. 4.5. September 1996 needle-of-the-year nutrient content in *Picea mariana* and *Pinus banksiana* from U1 and U3. The range in critical nutrient concentrations or ratios for *Picea abies* listed in Rosengren-Brinck & Nihlgård (1995) was used as a proxy for *P. mariana* and *P. banksiana*.(dashed lines).

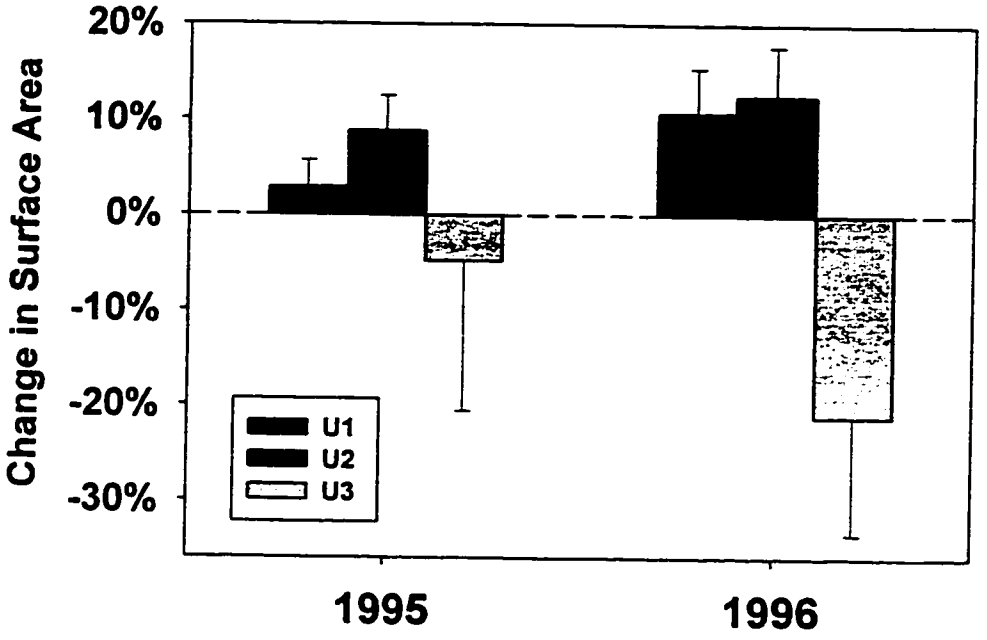

Fig. 4.6. Changes in the surface area covered by the creeping moss *Racomitrium microcarpon* colonies in U1, U2, and U3 in 1995-1996.

Consistent with their N cycle under background conditions, lichen patches and forest islands responded oppositely to an increased N input. In lichen patches, net nitrification rates increased and by the second year of addition N was not retained anymore. Thus, lichen patches are intrinsically N-saturated and have a limited potential to retain an increased N input. In contrast, in forest islands there was a net consumption of NO_3^- by soil microorganisms and N retention remained similar to reference systems. Considering the increased N input from both the treatment and upslope bedrock surfaces, forest islands have demonstrated a strong potential to retain N.

For catchment U3 as a whole, the pattern in N retention was variable in time. Nitrate retention was poor during snowmelt. Unlike NH_4^+, NO_3^- usually does not have abiotic immobilization mechanisms and retention must be biologically mediated (Vitousek & Melillo 1979). A pulse of NO_3^- export during spring runoff is frequently observed in areas receiving

elevated N inputs (Galloway et al. 1987; Stoddard 1994). Low NO_3^- retention during snowmelt is probably driven by low plant and soil microorganism activity during that period. During the growing season, whether catchment U3 reached N saturation following the increased NO_3^- load may be a matter of definition. One definition of N saturation is an input of N in excess of ecosystem requirements (Aber et al. 1989), with the excess N leaching as NO_3^- (Stoddard 1994). Following this definition, U3 became N saturated even during the growing season because NO_3^- export increased. However, Aber et al. (1989)'s definition may not be practical in catchments were surface runoff flowpaths are important. In hydraulically responsive systems such as Shield catchments, rapid routing of water through preferential flowpaths may prevent NH_4^+ and NO_3^- uptake by plants and microorganisms. Thus, 'hydrologic' NO_3^- export (Wright et al. 1995a) is fundamentally different than 'N saturation' NO_3^- because it is independent of the N status of the ecosystem. In the Upland catchments, the small contributing area of bedrock surface in the vicinity of the weirs may be a source of 'hydrological' NO_3^- originating from precipitation (Allan & Roulet 1994b).

A better definition for N saturation applicable to Shield catchments has been put forward by Dillon & Molot (1990). In this case, N saturation is defined as a decreased retention of N inputs in response to an increase in N deposition. This definition better accounts for 'hydrological' NO_3^-, which should remain a constant proportion of the NO_3^- input. During the growing season, N retention by U3 was similar to (or better than) reference catchments, even though the N load was 8-fold background. Thus, at least during the growing season, on the short-term U3 was not saturated by a 40 kg N ha^{-1} yr^{-1} load.

The dynamics of the soil microbial community in lichen patches is especially indicative that a true state of N saturation occurred in that system. Unlike in forest islands where net nitrification does not occur, NO_3^- production increased underneath lichen patches, further increasing the burden of NO_3^- retention on plants and lichens. Most mosses and lichens probably had a limited potential to use N from soil recycling because they either have no roots or only coarse equivalents (Ahmadjian & Hale 1973; Richardson 1981). Small creeping mosses (*Andreaea rupestris* and *R. microcarpon*) in the path of seepage from lichen

patches could have assimilated some of the mineralized NO_3^-. However, most of the bedrock surface biomass occurs on top of the 'H' soil where NO_3^- is produced. Thus, NO_3^- produced by increased net nitrification may have been more difficult to retain than NO_3^- added to bedrock surfaces as 'precipitation'. Increased NO_3^- export from bedrock surfaces may have been induced as much by changes in internal N cycling in lichen patches than the increased N input per se. A parallel can be made with forests undergoing N saturation, where the onset of nitrification below the rooting zone may be the most efficient mechanism to export NO_3^- and acidity to groundwater (Stoddard 1994; Persson & Wirén 1995).

Mechanisms generating the net conversion of NO_3^- to NH_4^+ in forest islands

Assimilatory NO_3^- reduction coupled with a decreased NH_4^+ uptake rate were the probable mechanisms responsible for the net consumption of NO_3^- and the increased net production of NH_4^+ in forest islands during the experiment. Net nitrification is usually low in conifer forest floors because gross nitrification rates are low, or the potential for NO_3^- immobilization is larger than gross nitrification rates (Stark & Hart 1997). The increased net production of NH_4^+ in forest islands was an indirect consequence of assimilatory NO_3^- reduction. Regardless of whether soil microorganisms are C- or N-limited, adding N to soils usually increases net N mineralization rates (Bossata & Berendse 1984). This occurs because in undisturbed soils the strong competition for N between plants, heterotrophic microorganisms and nitrifiers usually yields no net change in NH_4^+ and NO_3^- concentration over the year (Nadelhoffer et al. 1984; Johnson 1992). However, during buried soil bag incubations roots are severed, the competition for soil N is relaxed, and mineral-N usually taken up by roots accumulates over time. Thus, in U3 forest islands the consumption of treatment NO_3^- relaxed the need for soil microorganisms to utilize NH_4^+ as a source of N for growth, and the NH_4^+ immobilization rate decreased (Fig. 4.7a). This combination of processes implies that the nitrogen in the excess NH_4^+ produced did not necessarily originate from the NO_3^- that was consumed.

Dissimilatory NO_3^- reduction to NH_4^+ could be an alternative mechanism for net NO_3^- consumption and increased net NH_4^+ production in forest islands during the experiment

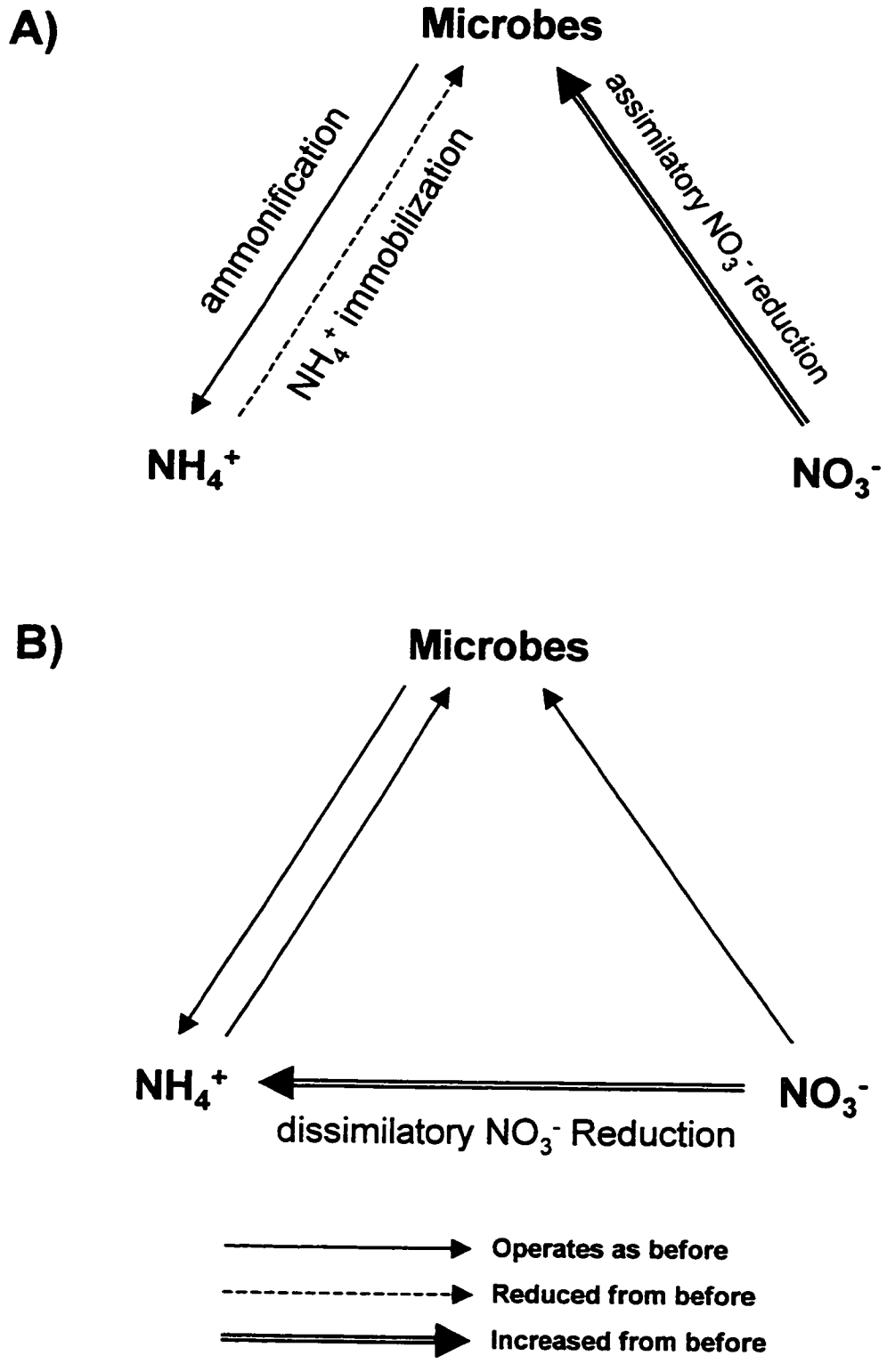

Fig. 4.7. Hypothesized scenarios for the response of soil microorganisms in U3 forest islands following the addition of NO_3^-. **(A)** Assimilatory NO_3^- reduction. **(B)** Dissimilatory NO_3^- reduction.

(Fig. 4.7b). Dissimilatory NO_3^- reduction is a fundamentally different process than assimilatory reduction because NO_3^- is used as an electron acceptor and is directly released as NH_4^+ (Tiedje et al. 1981). However, several lines of evidence suggest that dissimilatory NO_3^- reduction was not important. Dissimilatory NO_3^- reduction requires anoxic conditions (Tiedje et al. 1981), which are unlikely to develop in forest islands during the summer period because a permanent water table does not occur. In addition, denitrification (dissimilatory NO_3^- reduction to N_2O or N_2) is more common in temporarily anoxic environments because it can be mediated by facultative aerobes (Tiedje et al. 1981; Højberg et al. 1994). However, the very low rates of N_2O evolution during static chamber incubations in 1996 indicate that denitrification was not important either in forest islands during the growing season. Thus, assimilatory NO_3^- reduction appeared to have been the main process mediating the net consumption of NO_3^- and increased net production of NH_4^+ in U3 forest islands during the experiment.

Under the context of elevated N deposition to the boreal forest, there are important implications for assimilatory NO_3^- reduction by soil microorganisms in U3 forest islands. Nitrate is the form of mineral-N most difficult to retain within catchments because abiotic immobilization typically does not occur (Vitousek & Melillo 1979). In addition, old-growth conifer species may have a limited potential to utilize NO_3^- as a source of N (Kronzucker et al. 1997). Thus, soil microorganisms will be mostly responsible in preventing NO_3^- loss through leaching. Soil microorganisms can *directly* mediate NO_3^- retention when they immobilize N during the decomposition of sources of organic matter with a high C:N ratio (Chapter 5). In addition, N retention will also be *indirectly* favoured by the net tendency of soil microorganisms to convert NO_3^- to NH_4^+ during internal cycling. Ammonium is more easily retained within catchments because it may be a preferable form of N for some plants (Kronzucker et al. 1997) and can be immobilized abiotically (Vitousek & Melillo 1979). Abiotic immobilization mechanisms for NH_4^+ include ion exchange (Vitousek & Melillo 1979), substitution for K^+ in the interlayer of some clay minerals (Nômmink 1981), and chemical incorporation into humus (Nômmink 1970; Schimel & Firestone 1989).

Loss of the U3 moss cover

An effort was made to apply the $NaNO_3$ treatment as numerous small doses during rain events or on the snow to dilute the treatment as much as possible. However, visible damage was done to lichens and especially mosses by the second year of $NaNO_3$ addition. At the present, it is not known whether mosses were damaged by the salinity of the spray (~2M), a toxic intracellular level for some N compound, or some other process. Unlike vascular plants, which have leaves covered with waxy cuticles to minimize water and gas exchange, many mosses and lichens can absorb water to several times their body weight in a few minutes (Blum 1973). Thus, directly spraying mosses and lichens even during rain events may have caused intracellular Na^+ and NO_3^- levels to rise sharply. Boreal Shield lichens and mosses are adapted to interact with dilute waters low in nutrients and may have limited means to cope with toxic nutrient concentrations.

Important loss of moss cover has been observed in other experiments simulating the effect of acid deposition on the boreal forest (Hutchinson & Scott 1988). At relatively high pH (>4.0), the HNO_3 component of simulated acid rain inputs can promote moss and lichen growth on the short term (Lechowicz 1987; Scott et al. 1989). On the other hand, the fertilization effect is overriden under acute deposition, especially when S is also added with N (Lechowicz 1982; Hutchinson & Scott 1988). The experiment by Hutchinson and Scott (1988) with the common Shield moss *Pleurozium schreberi* is especially illuminating because 'acid rain' was applied at several pH levels (in a 2:1 molar ratio as H_2SO_4:HNO_3) for a relatively long period of time (5 years). At pH 5.6 and 4.0, a gradual increase in the moss cover occurred during the five years of addition. Moss growth may have been favored both by the addition of water and the addition of NO_3^-. However, at pH 3.5 and 3.0, 16% to 24% of the moss cover was lost after 5 years and remaining fronds were brown or blackened. At the acute pH 2.5 treatment, the *Pleurozium* cover was lost by the second year of addition. Scott & Hutchinson (1988) hypothesized that the partial loss of the moss cover had a negative feedback effect on the quality of the habitat for remaining mosses. As more bare ground was left exposed, the site became warmer, drier and consequently less favorable to moss growth. The sensitivity of mosses and lichens to simulated acid rain is consistent with field

observations that they are among the most sensitive organisms to atmospheric pollution (Gilbert 1973; Richardson 1981). Simulated acid rain experiments may underestimate the sensitivity of lichens and mosses to atmospheric pollution because physiological damage from toxic gases, such as ozone or SO_2, and from heavy metals is not taken into account (Richardson 1981).

If the moss and lichen cover is reduced following long-term chronic N inputs (Gorham et al. 1984; van Breeman & van Dijk 1988), important feedback mechanisms may affect the internal N cycle in boreal forest floors. The potential for direct uptake of NH_4^+ and NO_3^- in precipitation will be diminished and will have to be compensated by increased N retention in soils. However, as happen following forest fires, the loss of the insulating moss and lichen cover will lead to warmer and drier soils and higher N mineralization rates (MacLean et al. 1983; Oechel & Van Cleve 1986; Van Cleve et al. 1990). Nutrients retained by mosses and lichens may be immobilized for long periods of time because their litter is refractory and decomposes slowly (Heal & French 1974). On the long-term, the decreased input of moss and lichen litter may switch the soil internal N cycle towards a system where nutrients are recycled more rapidly. This tendency will be magnified if mosses and lichens are replaced by faster-growing plants producing faster- decomposing litters (Hobbie 1996).

Increased DOM exports in U3

One of the strongest responses of U3 to the addition of NO_3^- was an increase in the export of dissolved organic matter (DOM). In catchments, DOM is produced by biological activity in the forest canopy and in organic soils, where concentrations are highest (McDowell & Likens 1988). During downward transport through the soil profile, DOM is removed from solution by sorption to reactive surfaces such as Al- or Fe-sesquioxides in the mineral soil (McDowell & Wood 1984; Moore et al. 1992) and consumed by microorganisms (Qualls & Haines 1992). Consequently, because of more contact with organic soils, surface flowpaths are more enriched in DOM than groundwater (Houle et al. 1995; D'Arcy & Carignan 1997; Hinton et al. 1997).

Both geochemical and biological processes might be responsible for the increased DOM flux from U3 during the NO_3^- addition. An important geochemical effect of $NaNO_3$ addition was that runoff pH increased because of NO_3^- reduction. Change in soil pH could have affected the solubility of DOM because it is composed in part of organic acids with a low pK_a (Oliver et al. 1983). Organic acids in forest floor humus will tend to buffer pH change following NO_3^- reduction by releasing H^+ in the soil solution. As the experiment progressed, humus became more soluble (i.e. had a higher charge) because organic acids were increasingly deprotonated. A parallel can be made between the $NaNO_3$ addition to U3 and the application of urea to *P. banksiana* forest floors. Following urea addition, urease activity in the forest floor increases soil pH ($CO(NH_2)_2 + 3\ H_2O \rightarrow 2\ NH_4^+ + HCO_3^- + OH^-$), and promotes the dissolution of forest floor humus (Camiré & Bernier 1980; Foster et al. 1980). If geochemical processes controlled DOM exports from U3, increased DON export would be less likely with forms of N common in elevated N deposition (HNO_3, NH_4NO_3 and $(NH_4)_2SO_4$) because runoff pH would be more likely to decrease (Reuss & Johnson 1986).

Alternatively, stimulation of organic matter decomposition by N addition could have increased the production of DOM. However, microbial decomposition was more likely C-limited in the forest floor and N addition probably did not increase organic matter decomposition rates (Foster et al. 1980; Bossata & Berendse 1984). On the other hand, leaching of photosynthate from injured mosses and lichens may have contributed to the increased DOM export (Richardson 1981). Similarly, the peak in DOM export from U3 in May 1996 may reflect an increase input of labile organic matter caused by the death of mosses, fine roots or microbes over winter. This process may have been aided by a soil freezing-thawing cycle shortly following the melt of the snowpack in late April. Soil freezing can generate a nutrient flush by killing fine roots and microbes (Boutin & Robitaille 1995). Overall, the relative importance of geochemical and biological processes cannot be determined at the present, but the pH effect was probably very important in favoring increased DOM losses.

The increased concentration of DOM in soil solution adds a complicating factor to the interpretation of the soil N mineralization dynamics in U3. Instead of just N being supplied to soil microorganisms, both C and N were added. During the addition of urea to *P. banksiana* forest floors, it has been suggested that increased C availability brought by humus dissolution favors the microbial immobilization of urea-derived NH_4^+ (Camiré & Bernier 1980). The effect of humus dissolution on microbial activity will depend in part on how labile this C is. For example, sugar addition to forest floors are much more efficient in inducing microbial N immobilization than wood chips (Yarie & Van Cleve 1996). It is likely that humus-derived C was a poor source of C for microorganisms. Because the input of N was much larger than the input of humus-C (8- vs. 2 or 3- fold) and that this C was probably refractory, the U3 experiment can still be considered primarily as a N addition. From the point of view of N retention, the input of humus-C may have increased the potential for N immobilization by soil microorganisms.

Unlike in U3, large changes in DOM export have not been observed in catchments undergoing experimental or cultural acidification (Wright et al. 1993; Norton et al. 1994; Wright et al. 1995), or recovering from acidification (LaZerte & Dillon 1984; Wright et al. 1993). The relatively small size of the soil pools in U3 may have resulted in a more limited potential to buffer pH change following NO_3^- reduction relative to other systems. In addition, in U3 the release of DOM from the forest floor would be less likely to be sequestered by sorption in the mineral soil. The mineral soil is thin and frequently by-passed during storms (Allan & Roulet 1994b; Fig. 1.2).

The importance of the form of N added, forest floor processes, and mineral soil processes in controlling DOM exports can be seen when DOM fluxes from U3 are compared to the ones of fertilized pine plots at the Harvard forest (Currie et al. 1996). At the Harvard forest, the flux of DON from the forest floor had increased after 7 years of NH_4NO_3 addition. However, this increased DON flux was mediated by a decrease in the C:N ratio of DOM, not by an increased DOM export. The excess DON exported from the forest floor was retained in the mineral soil. Thus, no net change in DOC and DON export occurred at the Harvard forest.

While the C:N of DOM also decreased in U3 (from 50 – 60 under background conditions to ~42) both DOC and DON exports increased.

The mechanisms generating the changes in DOC and DON export in U3 are complex and not fully understood at the moment. However, it is clear that DON is the most important form of N exported under pristine conditions (Allan et al. 1993; Hedin et al. 1995; Kortelainen et al. 1997). However, increased N losses during the process of N saturation occur primarily as NO_3^- (Norton et al. 1994; Dise & Wright 1995; Wright et al. 1995a,b).

Comparison to other whole-catchment N additions

The increased N export from U3 after only two years of N addition is consistent with the response of a variety of forested catchments subjected to similar experimental or anthropogenic N inputs. Across a range of sites in Europe, N is efficiently retained when deposition is <10 kg N ha^{-1} yr^{-1}, but above 25 kg N ha^{-1} yr^{-1} N exports are usually substantial (Dise & Wright 1995). At the Sogndal catchment in Norway (which is similar to U3), 90% of a 10 kg N ha^{-1} yr^{-1} input was retained over a nine year period and most of the NO_3^- export also occurred during snowmelt (Wright et al. 1995a). In northeastern America, the response of forested catchments to elevated N inputs is consistent with European findings. At the Bear Brook Watersheds of Maine, runoff from West Bear Brook showed a decline in pH and an increase in NO_3^- and SO_4^{2-} concentration within 3 years of the addition of 50 kg N ha^{-1} yr^{-1} as $(NH_4)_2SO_4$ (Norton et al. 1994).

The factors predisposing catchments to N saturation are not clear at the present. In general, N export is some function of the N input (Dise & Wright 1995). However, at a given deposition level, N exports are variable between systems. The age and type of forest, climate, geological features, and previous site history probably all contribute to define the potential for N retention for a given system (Aber et al. 1993; Dise & Wright 1995; Magill et al. 1997). The onset of N saturation may occur when some environmental threshold is reached. For example, the negative correlation between soil pH and N retention (Dise & Wright 1995) may be related to a decreased root uptake of N caused by increased Al^{3+} toxicity at pH <4.2 (Ulrich 1986; Persson et al. 1995). Whether N will be allowed to accumulate within forests or will be

removed (by fires or harvesting) will be important in determining long-term patterns in N export (Ågren & Bossata 1988; van Breeman & van Dijk 1988).

Conclusion

The upland boreal Shield landscape contains communities with contrasting N cycles, and these communities reacted oppositely to an experimentally elevated NO_3^- input. Forest islands are naturally N-limited and were able to retain an 8-fold increase in N on the short-term. On bedrock surfaces, the natural N saturation of lichen patches prevented the retention of the elevated N input. Although a lower above-ground biomass probably contributed to a lower N retention on bedrock surfaces, the different characteristics of the litter supplied to soil microorganisms may be the most important factor determining the efficiency of N retention between the two communities. In forest islands, the input of refractory conifer litter with a high C:N maintains conditions where the competition for mineral N remains high between plants and microorganisms. Although plant may suffer from the reduced availability of N on the short-term, the efficient retention of transient N inputs may benefit them on the longer-term. In lichen patches, the low C:N of litter fosters conditions where competition for soil mineral N is not as strong, and transient N inputs are not retained by soil microorganisms. Thus, in forest islands both plants and soil microorganisms contribute to N retention, while on bedrock surfaces the onus of retention is solely on plants and lichens.

The different components of the upland boreal Shield landscape are hydrologically connected. Thus, the N load to forest islands originating from upslope bedrock surfaces is increased by the rapid N saturation of lichen patches following an increased N input. Although forest islands could retain this elevated N load on the short-term, the lateral export of N from bedrock surfaces may accelerate the process of N saturation in forest islands. This process may repeat itself at larger scales, resulting in N saturation "cascading" down the boreal Shield landscape.

Chapter 5. Evaluation of the Mechanisms of N Retention in the Upland Boreal Forest Using the Recovery of a ^{15}N-NO_3^- Source

Introduction

The elevated deposition of N compounds is an important source of acid rain in many areas of North America, Scandinavia, and Europe (Aber et al. 1989; Dise & Wright 1995; Galloway 1995). The biogeochemistry of elevated N deposition is complex because whether acidification occurs depends on the internal cycling of N within catchments (Ågren & Bossata 1988; Aber et al. 1989; Stoddard 1994). Presently, forests on the acid-sensitive Precambrian Shield are buffering downstream freshwaters by efficiently retaining N inputs from precipitation (Dillon & Molot 1990; Jeffries 1995). The mechanisms involved in N retention are not well understood (Vitousek & Melillo 1979; Northup et al. 1995b), yet will have to be determined to assess the long-term potential of Shield catchments to retain N. Mechanisms of N retention cannot be inferred from input-output budgets alone (Vitousek et al. 1979; Vitousek 1981) but must be determined by understanding the internal N cycle within catchments. One powerful tool to study the internal cycling of N inputs is to follow the movement and storage of ^{15}N tracers added to forests (Peterson & Fry 1987; Nadelhoffer & Fry 1994).

The response of an upland boreal Shield landscape to an elevated N input was studied during a two-year addition of 40 kg N ha^{-1} yr^{-1} as $NaNO_3$ to catchment U3 at the Experimental Lakes Area (ELA) in northwestern Ontario. This system had several features that made it especially attractive for the study of the effect of elevated N deposition to acid-sensitive areas of the boreal Shield. Two distinct plant/soil communities occur within this system. "Forest islands" are scattered through the landscape and are surrounded by moss- and lichen-covered bedrock outcrops. On bedrock surfaces, stratified clumps (or "lichen patches") of several moss (*Polytrichum* spp., *Racomitrium microcarpon*), fruticose lichen (*Cladina* spp.), and grass species (*Poa* spp.) occur. Bedrock surfaces store almost as much N as forest islands because of a large accumulation of N in thin organic deposits underneath lichen patches (Chapter 1). Forest islands and lichen patches have contrasting N cycles. In forest islands, N mineralization rates are low, there is no net nitrification, and mineral-N inputs are efficiently

retained. In contrast, in lichen patches net N mineralization and net nitrification rates are high and the retention of mineral-N is low during dry years. Thus, forest islands appeared to be N-limited under natural conditions while lichen patches were close to 'N saturation' (Aber et al. 1989). During the experimental addition of NO_3^- to catchment U3, lichen patches quickly became N-saturated and did not efficiently retain the elevated N input. In contrast, forest islands were able to retain the N from both the treatment and the increased downslope transport from bedrock surfaces.

The goal of the experiment was to understand the mechanisms involved in the retention of NO_3^- in this landscape. As a part of this study, the NO_3^- input was labeled with ^{15}N ($\delta^{15}N$ = 320‰) to help determine its storage within the catchment. Two hypotheses were being tested using the recovery of the label. Firstly, it was expected that moss and lichen biomass would become rapidly labeled with ^{15}N because they specialize in utilizing N from precipitation, while trees mostly utilize N originating from soil recycling. Secondly, it was hypothesized that the amount of label stored within a given pool of soil organic matter would be positively related to the C:N ratio of that pool. This latter hypothesis has important implications for the contribution of soil microorganisms in the retention of N inputs. It has been hypothesized that during the process of N saturation, the soil component of a forested ecosystem must saturate before the above-ground biomass component (Ågren & Bossata 1988). In other words, in system approaching N saturation, the onus of the retention of elevated N inputs will be on plants and lichen because soil microorganisms will not contribute to N retention. The C:N ratio of soil and litter is one of the factor that will determine whether N inputs will be retained by soil microorganisms.

N mineralization-immobilization

To understand the potential for the retention of elevated N inputs by soil microorganisms and the type of information provided by the recovery of the ^{15}N label, the concept of N mineralization-immobilization will be briefly reviewed. During the decomposition of litter in soils, N is simultaneously produced (i.e., mineralized) and taken up (i.e., immobilized) by microorganisms (Paul & Juma 1981; Emmett & Quarmby 1991; Downs et al. 1996). Whether the net balance will be towards net N mineralization or net N

immobilization will depend on the C:N of organic matter (Berg & Staaf 1981), its decomposability (Jansson 1958; Janssen 1996), and the type of microorganism utilizing the carbon (i.e., fungi or bacteria; McGill et al. 1981; Tietema 1998).

Generally, the N content of litter during decomposition follows three stages (Fig. 5.1). Initially, the translocation of N prior to leaf or needle abscission and the leaching of soluble organic matter following shedding yields a litter depleted in N. If the C:N is very high, during the second stage of decomposition the N content of litter will *increase* because N-limited microorganisms will tend to sequester N originating from deposition or mineralization elsewhere in the soil profile. Over time, the C:N of litter gradually decreases as C is respired away and N accumulates (McClaugherty et al. 1985; Melillo et al. 1989). Eventually, a 'critical' C:N threshold is reached where the balance between N mineralization and immobilization is zero. The range in critical C:N varies from 20 in labile litter such as hay (Jansson 1958) to over 50 in some refractory conifer litter (Berg & Staaf 1981). Not all litter types have an accumulation phase for N (Berg & Staaf 1981; Hobbie 1996; Fig. 5.1). Past the critical C:N, the net tendency is towards N mineralization, resulting in the accumulation of NH_4^+ in the soil and its utilization by plants. It must be emphasized that the soil environment is complex and that N immobilization and mineralization always occur simultaneously. Some label will be incorporated in pools of organic matter with a tendency towards net N mineralization because mineralization – immobilization reactions will not be at steady-state relative to the new isotopic input (Fig. 5.2).

Although immobilization is thought to be primarily microbially-mediated in coniferous forest floors (Schimel & Firestone 1989), abiotic immobilization also occurs. Examples of abiotic immobilization include NH_4^+ retention on soil particles by cation-exchange (Vitousek & Melillo 1979), the sequestration of NH_4^+ into the interlayer of some clay minerals (Nômmink 1981; Drury et al. 1989), or the chemical incorporation of NH_4^+ or amino-N in humus (Nômmink 1970; Schimel & Firestone 1989). N immobilized in microorganisms on the short-term can be physically and chemically integrated in soil organic matter on the long-term (Houghton et al. 1998). In the context of the Upland experiment, it must be emphasized that NO_3^- generally does not have abiotic immobilization mechanisms

(Vitousek & Melillo 1979). Thus, the NO_3^- addition to catchment U3 was a strong test for the potential for biologically-mediated retention of an elevated N input because all retained N had to have been transformed into NH_4^+ or organic N.

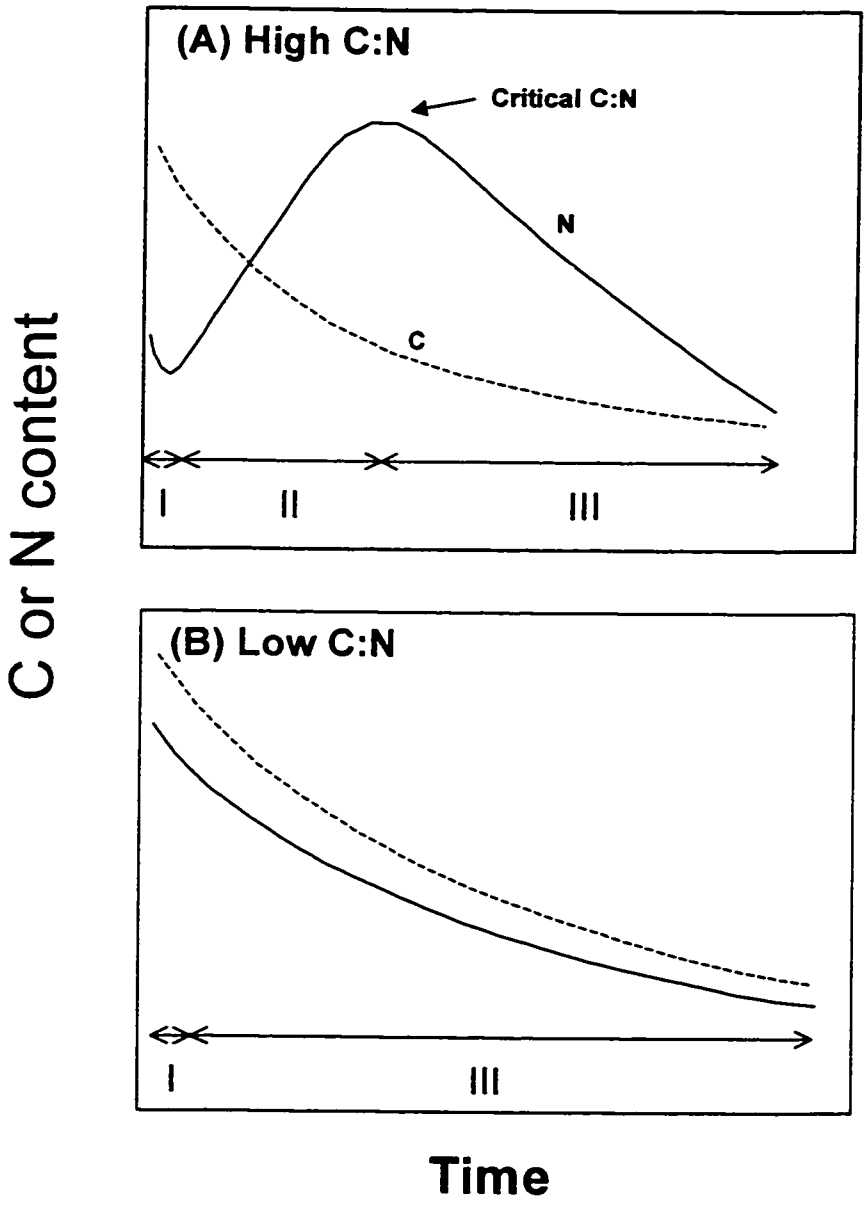

Fig. 5.1. Nitrogen content during the decomposition of soil organic matter in (A) a pool with a high initial C:N and (B) a pool with a low initial C:N. During stage I, some N is lost by leaching from the fresh litter. During stage II, N-limited microorganisms translocate N from other sources to aid in the decomposition of the organic matter. With time, the N content of litter builds-up while the C content decreases. At a 'critical' C:N threshold, the balance between net N mineralization and net N immobilization is zero. As the litter further decomposes (stage III), the net tendency is to release mineral N. Modified from Berg & Staff (1981). Carbon and N content are at different scales.

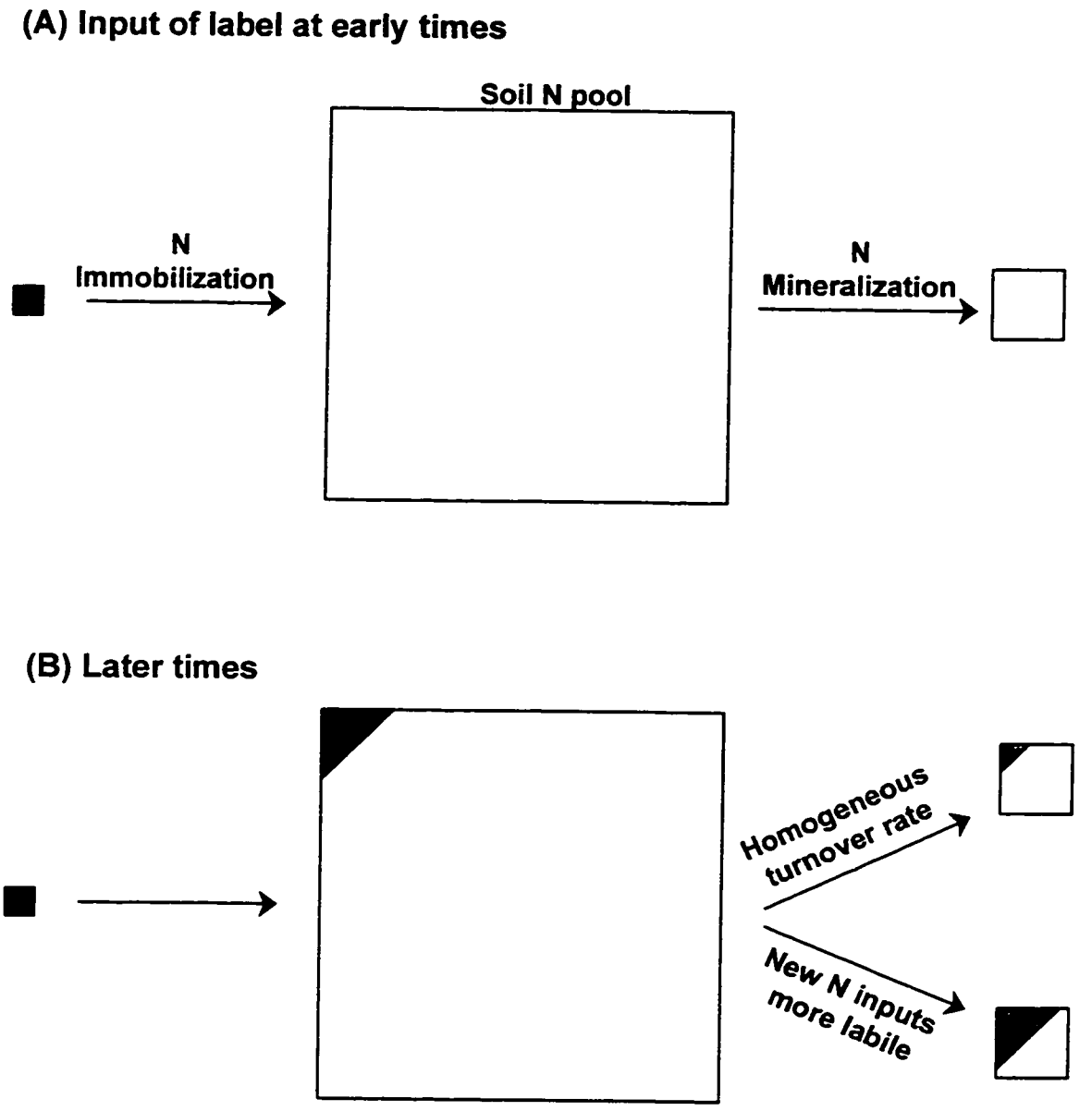

Fig. 5.2. Conceptual representation of the dynamics of a ^{15}N label incorporation into a soil organic matter pool with a net N mineralization. The size of the boxes is proportional to the size of the pool or the flux.

Methods

Site Description

The ELA is located at the southern edge of the boreal Shield forest in central Canada (Brunskill & Schindler 1971). The study catchment is one of six small watersheds (0.2 – 7.1 ha) that has been used for whole-catchment manipulation and nutrient export studies (Allan et al. 1993; Allan & Roulet 1994b). Climate at the ELA is continental, with long, cold winters (mean 1970-95 January temperature = 19.2°C) and short but warm summers (mean July temperature = 19.2°C). Between 1970 and 1995, the area received an average of 673 mm of precipitation, with approximately 30% as snow (Beaty & Lyng 1989; K.G. Beaty unpublised data). Soils are thin and classified as truncated orthic humic regosols and sombric brunisols (Canadian Soil Survey Committee 1978; Allan & Roulet 1994b). Mineral soils within the Upland catchments fall in the silt loam size-range and are probably of eolian origin. Bedrock is mostly pink granodiorite (McCullough & Campbell 1993). Wildfires are frequent in the area (Bayley et al. 1992); the last occurred in the Upland catchments <130 years ago.

The distribution of vegetation within the catchments is heterogeneous but follows a characteristic pattern. Forest islands occur in small depressions which contain 10 to 50 cm of organic and mineral soil (approximately 30% of catchment area). Jack pine (*Pinus banksiana* Lamb.) is common on the thinner soil while black spruce (*Picea mariana* Mill. B.S.P.) and a few white pine (*Pinus strobus* L.) occur where soils are deeper. Most trees were probably regenerated following the last wildfire. Currently, the fall of senescent jack pine creates openings that are colonized by pin cherry (*Prunus pensylvanica* L.f.), red maple (*Acer rubrum* L.) and black spruce, the latter through vegetative growth. The understory is comprised of the shrub *Juniper communis* L., the lichen *Cladina mitis* (Sandst.) Hustich and the mosses *Pleurozium schreberi* (Brid.) Mitt and *Dicranum* spp. The forest floor is 5 to 25 cm thick and composed of L, F, and H horizons. Locally, a S horizon is present. The mineral soil is 0 to 40 cm thick and limited to one to several Ah horizons, and occasionally a C or Cg horizon (Allan et al. 1993; Allan & Roulet 1994).

Bedrock outcrops cover approximately 70% of the catchments and 2/3 of this surface contains only crustose lichen such as *Rhizocarpon geographicum* (L.) DC. and some foliose lichen. The remaining bedrock surface is covered by 'lichen patches', clumps of the fruticose lichens *Cladina* spp. and *Cladonia* spp., the mosses *Polytrichum* spp., *Andreaea rupestris* Hedw. and *Racomitrium microcarpon* (Hedw.), some grasses (*Poa* spp.), and occasionally the shrub *Juniper communis* (L.) One to 10 cm organic deposits are found under lichen patches (nonsoil under the Canadian Soil Survey Committee 1978). The composition of the organic soil layers is variable yet consistent between lichen patches covered by different organisms (Fig. 5.3). Notable features include an S horizon (mostly from *Polytrichum* stems), an occasional thin horizon of decomposing lichen ('DL'), and an occasional F horizon composed of grass litter flattened by the snowpack. All lichen patches are underlain by a more mineral-rich but strongly humified soil layer ('H'). Lichens and grasses are predominant in upslope areas while mosses are more common in seepage areas downslope from forest islands (Vitt 1991). The diameter of lichen patches ranges from 30 cm to 3 m. Based on the lateral growth rate of *Racomitrium microcarpon* moss colonies, Vitt (1991) estimated that extant moss colonies may date to the last fire.

Application of the ^{15}N-NO_3^- label

The $NaNO_3$ treatment was applied to U3 from mid-April to September 1995 and from March to mid-August 1996 (36 kg N ha^{-1} yr^{-1} in 1995 and 40 kg N ha^{-1} yr^{-1} in 1996). The $NaNO_3$ treatment was applied as 34 (1995) or 38 (1996) applications of a ~2M $NaNO_3$ solution using a backpack sprayer. One application was made for approximately every 15 mm of precipitation received at the catchment. In 1995, an early (but small) snowmelt was missed. In 1996, the snowpack water equivalent was measured and the proportional N load applied prior to snowmelt. During the growing season, the treatment was applied during rain events. Each application was sprayed as evenly as possible throughout the catchment. Boardwalks were constructed in forest islands to minimize damage to the forest floor by trampling. The bulk N source was labeled with 10% ^{15}N-$NaNO_3$ (Isotec) for a final tracer signature of $\delta^{15}N$-NO_3^- = +320‰. The $\delta^{15}N$ is defined as the part per thousand difference between the $^{15}N/^{14}N$ ratio (R) of a sample relative to a standard (atmospheric N_2; Peterson & Fry 1987):

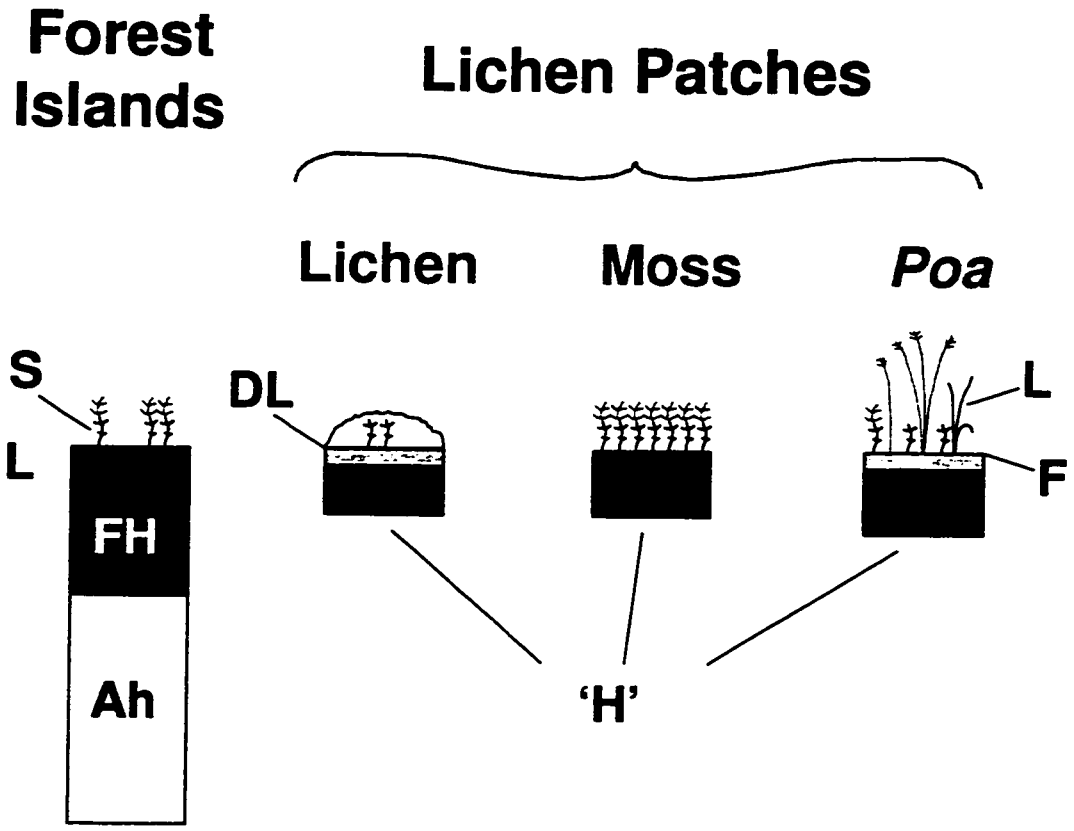

Fig. 5.3. Conceptual representation of soil horizons in forest islands and lichen patches from upland boreal Shield catchments. The S horizon is composed of the brown portion of moss stems, the 'DL' of decomposing lichen litter, and the 'H' is a mineral-rich but strongly humified soil underlying all types of lichen patches. Solum thickness varies between 10 – 50 cm in forest islands and 1 – 10 cm in lichen patches.

$$\delta^{15}N = [(R_{sample} - R_{standard}) - 1] \cdot 10^3 \quad (5.1)$$

^{15}N budgets

The fate of label added to U3 was determined by estimating ^{15}N losses through runoff throughout the period of application and by measuring the amount of label stored in various biomass and soil pools after the experiment was completed. The procedures used to estimate N export in runoff have been described elsewhere (Chapters 4 and 6). The loss of label through runoff was estimated using the $\delta^{15}N$ of total dissolved N (TDN), with an emphasis on periods with high flows (snowmelt and large summer storms). Runoff samples (2 – 4 L) were filtered on pre-combusted GF/F filters (nominal pore size 0.7 μm), frozen, and shipped in insulated coolers to the Environmental Geochemistry Laboratory at the University of Waterloo. In the laboratory, TDN sub-samples (~500 mL) were freeze-dried and analyzed for $\delta^{15}N$ following procedures outlined below. The export of coarse particulate N was also measured using a 1 mm screen immediately downstream from the U3 weir (Chapter 4), but was not significant (both in terms of mass flux and label loss).

Biomass and soil pools

From 1994 to 1996, bulk samples for *Cladina* spp., *Polytrichum* spp., and *R. microcarpon* were collected on bedrock surfaces in U1 and U3 to follow the changes in N content and $\delta^{15}N$ enrichment during the experiment. Samples were collected from several colonies and pooled to yield three replicates per catchment. In forest islands, *P. mariana* and *P. banksiana* 0+ needles were also collected each fall (Chapter 4). Samples were frozen until analysis. In fall 1996, *Picea* and *Pinus* needle litter inputs were collected in 6 litter traps in both U1 and U3. Litter from each tree species was pooled to yield three samples per species per catchment.

The storage of the label in U3 was estimated by measuring label accumulation in tree biomass in the fall of 1996 (~1 month after the end of the experiment) and in ground cover and soils in late May - early June 1997. In comparison to other pools, storage of the ^{15}N label in trees was less precise because of spatial heterogeneity in tree shape and the impossibility to

measure ^{15}N in all tree parts. For biomass determination, the diameter at breast height (DBH) for all *Picea* and *Pinus* was measured in U1 and U3. A relationship between DBH and tree height was estimated for a range in tree sizes for each species, and tree biomass determined using Alemdag's (1983) allometric equations. The applicability of these equations to Upland trees is uncertain because trees had a variety of growth forms depending on their location within forest islands. For example, *P. banksiana* were slender with fewer lower branches in the center of forest islands but stouter near edges (Hosie 1990). Current-year and older age-classes of foliage were sampled for 10 *P. mariana* and *P. banksiana* in U1 and U3 (Chapter 4). Wood samples were taken by drilling small holes at breast height for numerous trees and by pooling the wood chips to yield three samples for each species for each catchment. The nutrient content from unsampled tree parts (branches, bark, and large roots) was estimated from the literature (Morrison 1973, 1974; Alban et al. 1978) and was assumed to contain no ^{15}N label. *Picea* saplings (trees with DBH <5 cm) were enumerated and above ground-biomass estimated by the destructive sampling of one average-height individual (in June 1997). *Juniper communis* biomass was estimated by measuring the area covered by each individual. Areal cover was converted to biomass using the wood and needle biomass of sacrificied individuals (n = 4).

1997 soil survey – Bedrock surfaces

The lichen patch sampling scheme was designed to enable the comparison of ^{15}N storage patterns between lichen patches composed of different organisms (i.e., lichens, mosses, or *Poa*). Four 20 m transects were established in U3. One station with a cover containing mostly lichens, mosses, or *Poa* was sampled per transect. At each station, the ground cover and organic horizons were sampled using a 68 cm^2 quadrat. The 'H' horizon was sampled in the middle of the ground cover quadrat using a 24 cm^2 core. Horizons were identified and separated in the field. While it is acknowledged that the brown portion of the moss stem is composed of live and dead cells (Richardson 1981), the boundary between the biomass and S horizon was operationally set at the green to brown leaves transition. The four transects were also used to estimate the areal cover of lichen patches over bedrock surfaces and the volume of the 'H' horizon. The presence of a lichen patch (lichen or moss at least 1 cm in height), the dominant organism by cover (lichen, moss, or *Poa*), and the thickness of

the 'H' horizon was measured at 50 cm intervals. The background ^{15}N signatures and N concentrations for biomass and soil horizons were obtained by sampling similar lichen patches in U1 (three for each vegetation type).

Forest island soil

Two to six stations were selected at regular intervals along the longitudinal axis of all U3 forest islands (18 cores in total). At each station, a 24 cm^2 core was taken and the horizons separated in the field. The ground cover was scattered (mostly *Pleurozium schreberi* and *Dicranum* spp.) and the S horizon was pooled with the L. At most stations, the F and H could not be reliably separated and were collected as one unit. With the exception of a few deeper soil pockets, the mineral soil (if present) was seldom deeper than 10 cm and was separated by 5 cm intervals (0+, 5+, and 10+ cm). Roots were common throughout the soil profile, including at the mineral soil – bedrock interface. Background samples for ^{15}N and N content were obtained in a similar fashion in U1 (n = 8). Soils were set to air-dry within a day of collection.

Horizon sub-sampling

In the laboratory, the dried soil samples were gently homogenized using a mortar and pestle to break-up mineral or organic clumps. The FH, 'H' and Ah samples were sieved to separate coarse (>2 mm) and fine (2 mm) fractions. Fine roots were removed from each soil fraction for 20 min and separated into two size classes ('coarse' - >2 mm dia. and 'fine' - <2 mm dia.) No effort was made to separate roots into 'live' or 'dead' categories or by tree species. One hour searches on selected samples indicated that fine root fragments could still be found after an hour, but that most of the biomass (96%) was removed after 20 min. Recovery was probably lower in some FH samples which occasionally contained dense mats of roots and fungus. The coarse soil fraction in the 'H' and Ah samples was mostly gravel-size minerals and was not analyzed further. The 'H' samples contained very fine *Poa* roots (<<1 mm dia.) and occasionally *Polytrichum* tomenta (i.e., terminal portion of the stem with rhizoids) that were included in the 'root' fraction. In U1, sub-samples were pooled to yield one replicate per lichen patch type and two replicates for forest islands. In U3, lichen patches stations were analyzed separately (n = 12) while in forest islands cores were pooled by threes

to yield six replicates. Although analyzed separately, the results for the Ah at different depths will be aggregated for brevity in presentation.

^{15}N analysis

Biomass and organic soil (S, L, and FH horizons) were homogenized in a two step procedure by first passing through a Wiley mill, followed by pulverization into dust with a ball mill. To limit the possibility of sample cross-contamination, a small amount of sample was processed and discarded at the beginning of each milling step. Ball mills were thoroughly cleaned and washed with acetone after each sample to ensure that waxy residues were removed. Roots, 'H' and Ah soil fractions were homogenized with the ball mill only. Carbon, N, and ^{15}N content were analyzed on-line using an Isochrom continuous flow mass-spectrometer connected to a Carlo-Erba elemental analyzer at the Environmental Isotope Laboratory of the University of Waterloo. During all procedures, care was taken to process enriched and background samples separately. A duplicate sample was run every seven samples as a standard procedure of the EIL lab. Precision in the $\delta^{15}N$ analyses was ±0.2‰ (or 5% of the mean) for natural abundance samples and ±1.3‰ (or 2% of the mean) in enriched samples. No memory effect in $\delta^{15}N$ was detected in standard organic material analyzed immediately following enriched samples. Additional analyses were made for samples with enriched ^{15}N close to background.

Estimation of label storage

The proportion of the added ^{15}N stored in a given pool was estimated according to a mass-balance equation (Nadelhoffer & Fry 1994):

$$m_{lab} = m_f (\delta^{15}N_f - \delta^{15}N_i)/(\delta^{15}N_{lab} - \delta^{15}N_i) \qquad (5.2)$$

where,

m_{lab} = mass of treatment NO_3^- incorporated into the N pool;

m_f = final mass of the ecosystem N pool;

$\delta^{15}N_f$ = final ^{15}N abundance of the N pool;

$\delta^{15}N_i$ = initial ^{15}N abundance in the N pool (estimated from the same pool in U1);

and

$\delta^{15}N_{lab}$ = ^{15}N abundance of the labeled N addition.

This equation assumes that the initial and final mass of the pools remained constant over the course of the experiment and that there is no significant fractionation effect when $^{15}NO_3^-$ is incorporated. The input of N in precipitation during the experiment was ~10 kg N ha^{-1} and was assumed to have a $\delta^{15}N_{RAIN}$ ~ 0‰. The dilution of the label by N from precipitation resulted in $\delta^{15}N_{lab}$ ~ 283‰. An approximation of the uncertainty in the amount of label stored in a given pool was obtained by first-order error propagation of Eq. 5.1 (Meyer 1975):

$$s_{m_{LAB}} = m_{LAB}\sqrt{\frac{s_A^2}{A^2} + \frac{s_B^2 + s_C^2}{(B-C)^2} + \frac{s_C^2}{(D-C)^2}} \qquad (5.3);$$

With A = m_f, B = $\delta^{15}N_f$, C = $\delta^{15}N_i$, and D = $\delta^{15}N_{lab}$. The standard deviation of m_f (s_A) was estimated in a similar fashion. When not available (trees), s_A was set at 50% of the mean.

Results

N distribution in the Upland catchments

The distribution of N in U3 had some consistent and unusual features for a boreal conifer forest. Within forest islands, the size of N pools was in the range expected for an unproductive boreal conifer forest (Chapter 1; Table 5.1). However, for the catchment as a whole, there was almost as much N stored over bedrock surfaces (576 kg N ha_c^{-1}) as in forest islands (764 kg N ha_c^{-1}) because of the large lichen patch 'H' horizon pool (480 kg N ha^{-1}). Above-ground biomass (AGB) within forest islands (230 kg N per ha of forest islands) was 8-fold larger than in lichen patches (30 kg N ha^{-1} of bedrock surface). In lichen patches, brown moss biomass (i.e. the S horizon) was much larger than green moss biomass (54 vs. 3.5 kg N

ha^{-1}). However, this ratio could have been inflated by the loss of some of the green moss biomass in U3 during the experiment (Chapter 4).

Table 5.1. Nitrogen pools in catchment U3 expressed at different scales. Error on the pool sizes in Tables 5.3 & 5.4. Forest islands cover 21%, bedrock surfaces 79%, and lichen patches 37% of catchment area.

	kg N / ha Forest Islands	kg N / ha Catchment
Forest Islands		
Trees	190	39
Juniper	17	3.5
Mosses	25	5.2
Total Biomass	**230**	**48**
S+L	171	36
FH	1550	325
A_h	1690	355
Total Soil	**3410**	**716**
Tot. Forest Islands	**3640**	**764**

	kg N / ha Lichen Patch	kg N / ha Bedrock Surface	kg N / ha Catchment
Lichen Patches			
Mosses	9.5	4.4	3.5
Lichens	18	8.2	6.5
Poa	3.3	1.5	1.2
Total Biomass	**30**	**14**	**11**
DL	33	15	12
S	146	68	54
LF	57	27	21
'H'	1300	608	480
Total Soil	**1540**	**718**	**567**
Tot. Lichen P.	**1570**	**729**	**576**
Total Upland			**1340**

%N and $\delta^{15}N$ in different pools

With the exception of *Cladina*, the N content of bedrock surface organisms did not increase during the N addition to U3 (Fig. 5.4). Nitrogen concentration in *Cladina* doubled by 1996, but concentrations were almost back to background by early 1997 (Fig. 5.4). In forest islands, the needle N content increased in both *P. mariana* and *P. banksiana* but was still below the 'optimal' level for growth (Chapter 4).

The response in $\delta^{15}N$ enrichment in biomass was stronger than the change in N content (Fig. 5.5). On bedrock surfaces, up to 40% of the N of some organisms was derived from treatment NO_3^- by fall 1996. However, this enrichment had decreased by a factor of two by June 1997 (Fig. 5.5). The $\delta^{15}N$ of foliage increased by 25‰ to 40‰ each year of addition. In contrast, in lichen patches most of the enrichment had occurred by 1995. The variability in $\delta^{15}N$ in vegetation was quite large in U3 (30% to >100% of the mean). This was expected because of the difficulty in evenly applying the treatment throughout the catchment using a backpack sprayer. In addition, the system is hydrologically connected and the downslope portion of the catchment should have been exposed to more $^{15}NO_3^-$.

All N pools in U3 had a significantly higher $\delta^{15}N$ than similar pools in U1 following the two years of label addition (Fig. 5.6). The enrichment was smallest but still significant in the 'H' 2 mm fraction ($\delta^{15}N$ = 4.7‰ ± 1.5‰ in U3 and 3.5‰ ± 0.53‰ in U1; mean ± SD: t-test, $P<0.05$). All other pools were enriched at least two-fold relative to background. The significant enrichment of the larger soil pools allowed the estimation of label recovery for the whole catchment.

Label Recovery

Including storage and losses through runoff, 58% of the label added to U3 could be accounted for (Table 5.2). In decreasing order of importance, sinks for the label were organic soils (23%), biomass (10%), forest island mineral soil (6%), and the lichen patch 'H' horizon (3%). Losses through runoff accounted for 16% of the label. In runoff, the $\delta^{15}N_{TDN}$ ranged from 28‰ to 151‰ during the growing season, when export occurred as both NO_3^- and DON

(Fig. 5.7). In contrast, $\delta^{15}N_{TDN}$ was highest during the 1996 snowmelt period (~230‰) when most of the NO_3^- (61%) and label loss (75%) occurred.

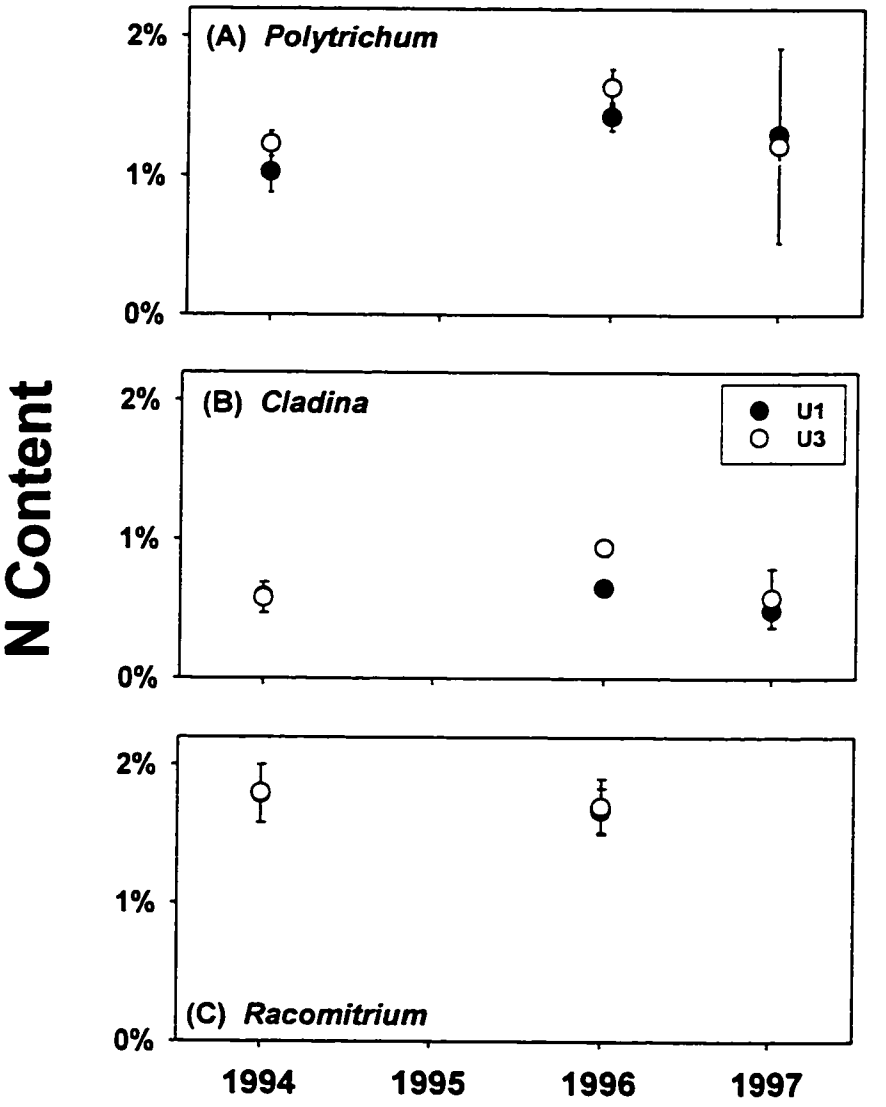

Fig. 5.4. Nitrogen content of bedrock surface organisms in 1994 (reference year), 1996, and 1997 (9 months after the end of N addition to U3). Mean ± SD.

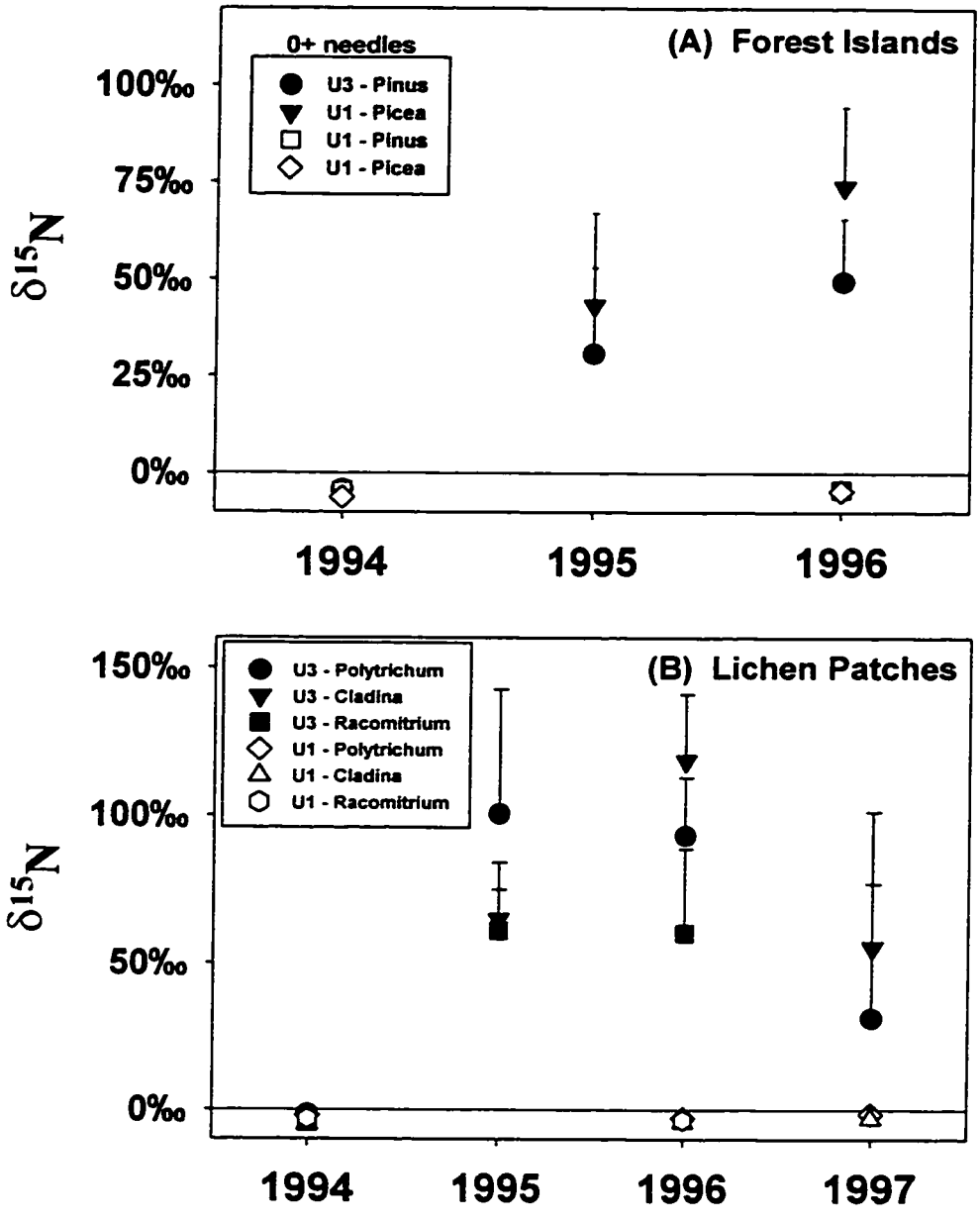

Fig. 5.5. $\delta^{15}N$ from 1994 to 1997 in **(A)** *P. mariana* and *P. banksiana* 0+ needles and **(B)** mosses and lichens from bedrock surfaces. Mean ± SD.

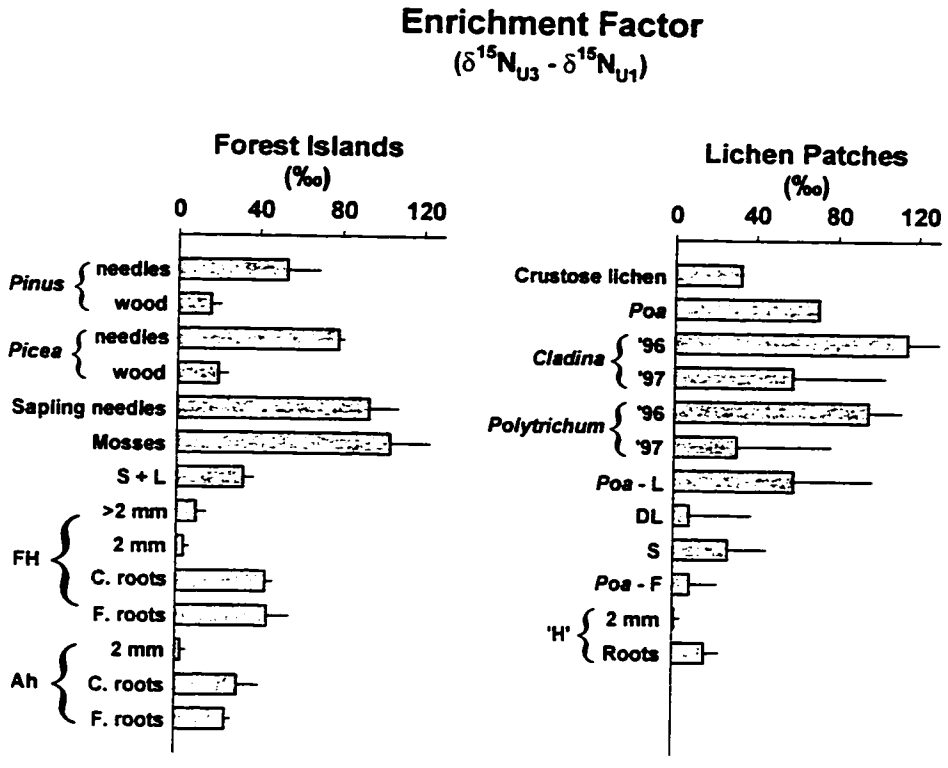

Fig. 5.6. Enrichment factor ($\delta^{15}N_{U3}$ - $\delta^{15}N_{U1}$) for biomass and soil pools in forest islands and lichen patches. Mean ± SD.

Table 5.2. Storage of $^{15}N\text{-}NO_3^-$ added to U3. Mean ±SD.

		N Pool or Flux (kg N ha_c^{-1})	% of added ^{15}N
Biomass		60 ± 16	10 ± 4
Soil	Organic	448 ± 117	23 ± 6
	Ah	356 ± 100	6 ± 2
	'H'	480 ± 106	3 ± 2
Runoff		24 ± 1	16 ± 3
Total Recovery			**58 ± 8**

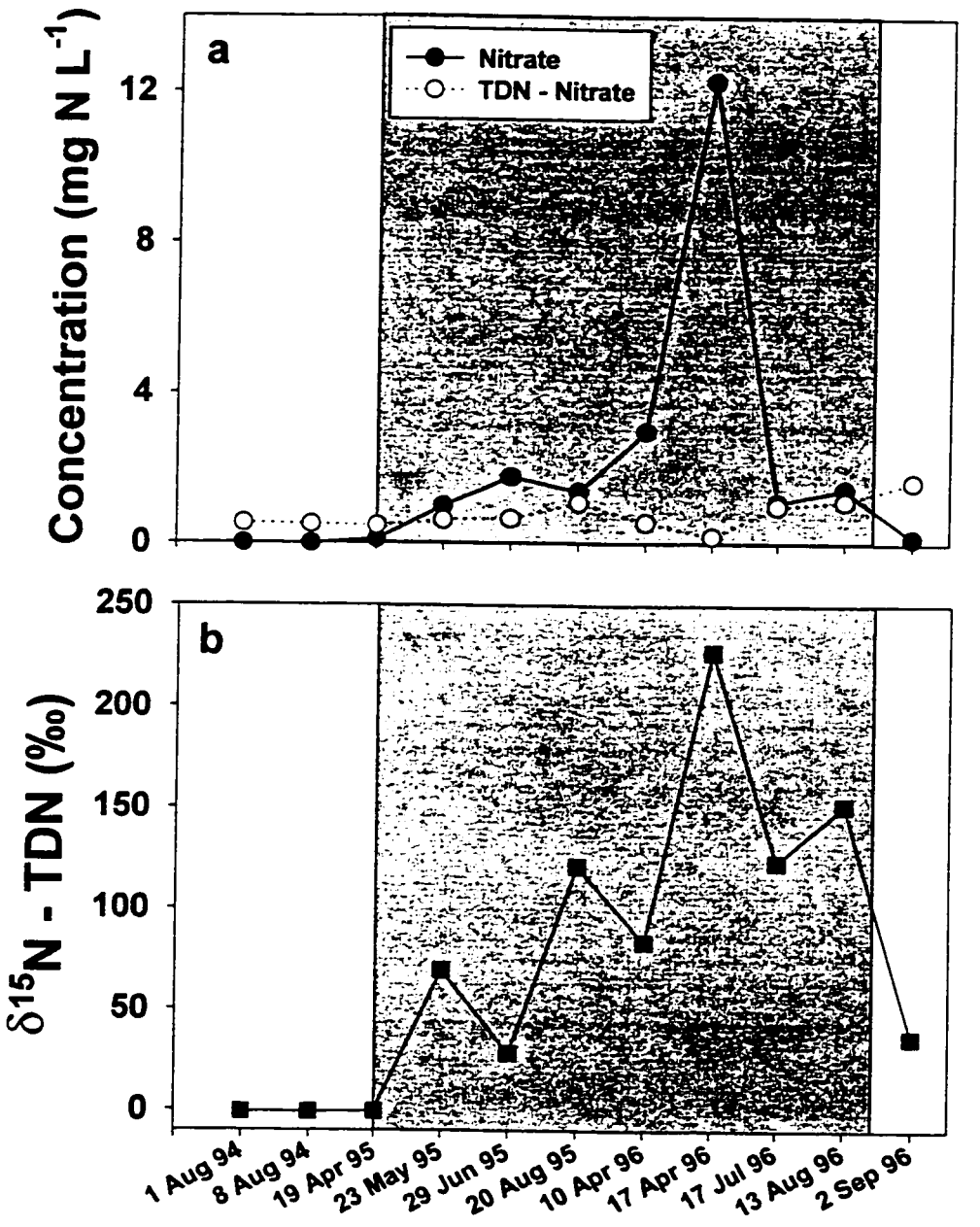

Fig.5.7. **(A)** NO_3^- and TDN - NO_3^- (i.e., DON + NH_4^+) concentrations and **(B)** δ^{15}N-TDN in runoff from U3, 1994-96. Most of the label export in runoff occurred during the 1996 snowmelt when NO_3^- concentration, δ^{15}N-TDN, and runoff were high. The shaded areas represent the period when $Na^{15}NO_3$ was applied to U3. The δ^{15}N of $NaNO_3$ was 320‰.

Forest islands were a larger sink for the label (27%) than bedrock surfaces (14%). In forest islands, 14% of the label was recovered in organic soil, 7% in biomass, and 6% in mineral soil (Table 5.3). In lichen patches, 9% of the label was in the L, S, or F horizons, 2% in biomass, and 3% in the 'H' horizon (Table 5.4). In both lichen patches and forest islands, fine roots were a small proportion of the soil mass (~4%) but a large proportion of the label sink within these pools (~30%). Thus, on the short-term, a disproportionate amount of the label was stored in small pools with a probable fast turnover rate than in the large pools.

In general, the C:N of litter produced in forest islands was larger than in lichen patches (Table 5.5). In forest islands, fresh *Pinus* needle litter inputs ($\delta^{15}N$ = 18‰ ± 1.4‰, mean ± SD, n = 3) and to a lesser extent *Picea* needle inputs ($\delta^{15}N$ = 25‰ ± 4.4‰) in fall 1996 were less enriched than the S+L horizon in spring 1997 ($\delta^{15}N$ = 30‰ ± 5.0‰). In addition, the N content of fresh conifer needle litter (0.49% – 0.66%) was much lower than the N content of the S+L (1.2%). Taken together, the N and $\delta^{15}N$ enrichment of conifer litter decomposing on the forest floor suggests a significant uptake of $^{15}NO_3^-$ by microbial immobilization. In contrast, in lichen patches, biomass and new litter inputs were always more strongly enriched than older litter and had a similar N content (Table 5.4). *Polytrichum* biomass in 1995 – 1996 was more enriched ($\delta^{15}N$ = 93‰ – 101‰) than the lichen patch S horizon in spring 1997 ($\delta^{15}N$ = 27‰ ± 19‰), and more label was stored in the *Poa* – L (1996 stems) then in the *Poa* – F (1995 and older stems; Table 5.4). Thus, in lichen patches, plant uptake of $^{15}NO_3^-$ followed by litter production appears to have been more important than microbial immobilization of $^{15}NO_3^-$ on the litter.

In deeper soil horizons, the storage of label in the root-free component of the FH, Ah, and 'H' horizons is consistent with a greater potential for immobilization in pools of organic matter with a high C:N (Fig. 5.8). The 'H' horizon had the lowest C:N and retained the least label (relative to its size), while the FH had the largest C:N and retained the most. Although it was not possible to clearly distinguish between label retained by plant uptake before the litter was produced or by microbial immobilization following litter production, the available evidence suggests that microbial immobilization was a more important process of N retention in forest islands than in lichen patches.

The error on label storage estimates for individual pools varied between 30% to >100% (Tables 5.3 & 5.4). Several factors affected the magnitude of the error, including 1) pool size uncertainty (e.g., roots); 2) spatial variability in $\delta^{15}N$ in U3 (e.g., mosses); and 3) small enrichment factors (e.g., 'H' horizon). Overall, although the errors on some of the pools were large, sampling error alone cannot account for the 'missing' label (Table 5.2). Thus, unrecorded losses or pools must have been present.

Table 5.3. Nitrogen pools and ^{15}N label storage in U3 forest islands. Mean ± SD.

Horizon	Fraction	%N	C:N	N pool (kg N ha_c^{-1})	^{15}N Storage (%)
P. banksiana				24	1.9
P. mariana				14	2.0
Picea saplings				1.0	0.2
	Total Trees			**39**	**4.1**
Juniper				3.5	0.9
Moss		1.6 ± 0.15	24	5.2 ± 5.8	2.2 ± 2.5
	Total Biomass			**48 ± 20***	**7.2 ± 3.3**
S + L		1.2 ± 0.06	32	36 ± 15	4.8 ± 2.2
FH	2 mm	0.97 ± 0.13	22	254 ± 112	4.3 ± 3.1
	>2 mm	0.82 ± 0.19	33	57 ± 22	2.3 ± 1.4
	C. Roots	0.69 ± 0.066	58	12 ± 3.8	2.2 ± 0.7
	F. Roots	1.0 ± 0.06	40	1.9 ± 0.7	0.4 ± 0.2
	Total FH			**325 ± 114**	**9.2 ± 3.5**
	Total LFH			**361 ± 115**	**14 ± 4.1**
Ah	2 mm	0.36 ± 0.18	14	342 ± 100	4.4 ± 1.8
	C. Roots	0.48 ± 0.17	77	9.7 ± 3.5	1.2 ± 0.5
	F. Roots	0.75 ± 0.42	42	3.5 ± 2.3	0.4 ± 0.3
	Total Ah			**355 ± 100**	**6.0 ± 1.9**
Total Forest Islands*				**764 ± 154**	**27 ± 5.6**

* Assuming a 50% error when SD missing

Table 5.4. Nitrogen pools and ^{15}N label storage in U3 lichen patches. Percent of catchment area covered by each type of lichen patch in brackets. Mean ± SD

Patch	Horizon	Fraction	%N	C:N	Pool Size (kg N ha_c^{-1})	$\%^{15}N$
Lichen	Biomass		0.58 ± 0.21	48	6.5 ± 2.5	1.5 ± 1.3
(9.9%)	DL		1.4 ± 0.4	22	12 ± 6.0	0.5 ± 1.5
	S		1.4 ± 0.8	14	6.5 ± 4.0	0.3 ± 0.2
		Total Org.			**19 ± 7.2**	**0.8 ± 1.5**
	'H'	2 mm	1.6 ± 0.03	11	45 ± 14	0.4 ± 0.4
		Roots	2.0	16	0.15 ± 0.1	0.01± 0.006
		Total 'H'			**45 ± 14**	**0.4 ± 0.4**
	Total Lichen				**70 ± 16**	**2.7 ± 2.1**
Moss	Biomass		1.2 ± 0.70	29	3.5 ± 5.5	0.5 ± 1.0
(16%)	S		1.6 ± 0.34	20	37 ± 18	4.3 ± 3.5
	'H'	2 mm	1.6 ± 0.50	9.8	234 ± 94	0.7 ± 0.9
		Roots*	2.0 ± 0.30	14	8.4 ± 8.2	0.9 ± 1.0
		Total 'H'			**243 ± 95**	**1.6 ± 1.3**
	Total Moss				**284 ± 97**	**6.4 ± 3.8**
Poa	Biomass		2.3	15	1.2	0.34
(11%)	L		1.9 ± 0.25	18	9.6 ± 5.4	2.3 ± 2.0
	S		1.8 ± 0.28	18	10 ± 4.9	1.4 ± 0.7
	F		1.7 ± 0.56	12	11 ± 4.3	0.4 ± 0.6
		Total Org.			**31 ± 8.4**	**4.0 ± 2.2**
	'H'	2 mm	1.4 ± 0.23	9.5	188 ± 46	1.0 ± 1.2
		Roots	1.6 ± 0.34	14	3.0 ± 2.1	0.2 ± 0.2
		Total 'H'			**191 ± 46**	**1.2 ± 1.2**
	Total *Poa*				**222 ± 47**	**5.3 ± 2.5**
	Total Biomass				11 ± 6.0	2.4 ± 1.7
	Total LSF				87 ± 20	9.2 ± 4.3
	'H'	Total 2 mm			468 ± 106	2.1 ± 1.5
		Total Roots			12 ± 8.5	1.1 ± 1.0
	Total 'H'				480 ± 106	3.1 ± 1.8
Total Lichen Patches					**576 ± 109**	**15 ± 5.0**
	Crustose Lichen		2.2	15	~1.2	~0.2
Total Bedrock Surfaces					**577 ± 109**	**15 ± 5**

* Includes moss rhizoids

Table 5.5. Nitrogen content and C:N ratio of litter and soil organic matter in the N-amended U3 and reference U1. Samples collected in September 1996 or early June 1997. Mean ± SD. n = 3 – 10.

	U1		U3	
	%N	C:N	%N	C:N
		Forest Islands		
Picea litter	0.68 ± 0.12	73	0.66 ± 0.13	69
Pinus litter	0.45 ± 0.10	99	0.49 ± 0.003	94
L+S	1.2 ± 0.002	32	1.2 ± 0.06	32
FH - C. roots	0.60 ± 0.072	63	0.69 ± 0.066	58
FH - F. roots	1.0 ± 0.10	36	1.0 ± 0.06	40
Ah - C. roots	0.51 ± 0.10	71	0.48 ± 0.17	77
Ah - F. roots	0.71 ± 0.082	50	0.75 ± 0.42	42
Picea wood	0.08 ± 0.02	505	0.12 ± 0.04	354
Pinus wood	0.09 ± 0.009	463	0.10 ± 0.007	448
		Lichen Patches		
Poa – L	n.a.	n.a.	1.9 ± 0.25	18
Poa – F	1.3	30	1.7 ± 0.56	12
Poa – roots	1.3 ± 0.14	20	1.9 ± 0.31	14
DL	1.4	23	1.4 ± 0.37	22
S	1.6	21	1.6 ± 0.90	19

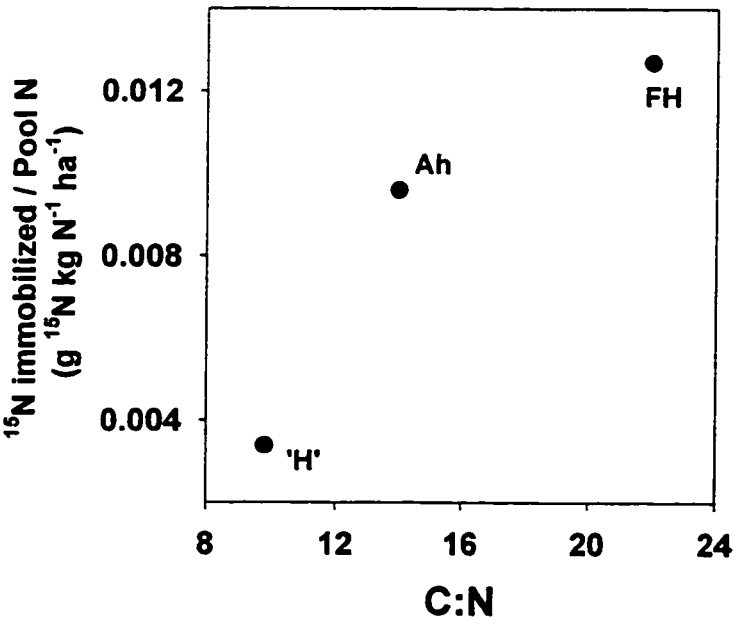

Fig. 5.8. Relationship between the C:N of a soil horizon and ^{15}N label retention (with the label retained by roots excluded).

Distribution of ^{15}N in a *Picea* sapling

The ^{15}N label was relatively evenly distributed in the U3 *Picea* sapling sampled in early June 1997 (Table 5.6). The extremes in $\delta^{15}N$ were between 1 and 5+ needles (28‰ vs. 50‰), with stem and branches at the higher end of enrichment (40‰ – 44‰). The sapling was sampled prior to bud burst. Thus, the high $\delta^{15}N$ of the stem and branches may represent an internal pool containing N translocated from needles in the previous fall, or stored by luxury uptake in the previous year. Although limited to a single tree, the above analysis has demonstrated that the added ^{15}N was not simply accumulating in new growth but circulated rapidly within the whole tree.

Table 5.6. Nitrogen pools and ^{15}N label storage in one 1.3 m high (ca. 20 years old) *P. mariana* sapling from U3 in June 1997.

	Dry Weight (g)	%N	$\delta^{15}N$ (‰)	% of tree ^{15}N	% of tree N
Needles 1 yr	81.05	1.07	49.9	31.5	25.5
2 yrs	47.26	1.06	41.6	15.0	14.8
3 yrs	34.81	0.962	30.5	7.5	9.9
4 yrs	18.59	0.910	30.3	3.7	5.0
5+ yrs	17.31	0.884	28.4	3.2	4.5
Twigs 1 yr	22.57	1.17	46.2	8.7	7.8
2 yr	19.53	0.561	39.3	3.1	3.2
3 yr	15.76	0.511	34.5	2.0	2.4
4 yr	12.14	0.467	33.3	1.4	1.7
5+ yrs	27.19	0.371	34.4	2.5	3.0
Tot. Tw & Ndl	**296.2**			**77.6**	**77.7**
Branches	26.19	0.460	43.6	3.9	3.6
Stem + Bark	159.67	0.302	40.2	14.6	14.2
Misc.	16.68	0.912	34.3	3.9	4.5
Total Woody	**202.5**			**22.4**	**22.3**
Total Sapling	**498.8**				

Discussion

The recovery of a ^{15}N label added to one of the Upland catchments has provided important information about the pathway taken by new N inputs in the forest island and lichen patch communities. Lichen patch biomass was rapidly and strongly labeled, a probable combination of a reliance on N inputs from precipitation and a fast N turnover rate. In contrast, labeling was more gradual in trees. In part, the larger N pool in trees and the tendency for species like *Picea mariana* to efficiently recycle N internally (Flanagan & Van Cleve 1983) should considerably lengthen the turnover time of the tree N pool. In addition, trees had to compete with mosses and soil microorganisms for the new N inputs and probably obtained a larger proportion of their N from a more ^{15}N-depleted recycled N pool. Following the cessation of ^{15}N addition, mosses and lichens $\delta^{15}N$ was rapidly returning to background. In contrast, trees may remain labeled for a longer period of time because of a slower N turnover, and labeled biomass gradually entering the litter pool. A similar situation may occur with *Poa*, the organism probably relying most heavily on recycled N sources in lichen patches. Although mosses and lichens may outcompete *Poa* and trees for N inputs in precipitation on the short-term, *Poa* and trees may have access to this N on the longer term.

The comparison of treatment NO_3^- storage in forest islands and lichen patches by mass-balance (Chapter 4) and ^{15}N-label recovery suggests that forest islands may contain a missing sink for ^{15}N (Table 5.7). In lichen patches, a similar estimate of NO_3^- storage was obtained with both methods (Table 5.7). In contrast, more NO_3^- was retained in forest islands according to the mass-balance analysis. Either an unrecorded loss mechanism or an unmeasured pool may account for the 'missing' ^{15}N in forest islands.

Gaseous efflux of treatment N may be one pathway of label loss from forest islands. However, spot measurements of N_2O efflux from forest islands in 1996 showed that gaseous N loss due to nitrification and denitrification was probably not important (Chapter 4). In addition, the low pH of the forest floor (~4.1; 2:1 v:w H_2O) would not have favored the conversion of NH_4^+ to NH_3 ($pK_a \sim 9$) and prevented NH_3 volatilization. Some loss of label as pollen must have occurred but was not quantified. The lateral export of label outside of the

catchment through roots, rhizomes, or fungal hyphae did not occur because U3 is isolated from the surrounding forest by a granodiorite bedrock ridge. Although some unrecorded gaseous and particulate flux could have occurred, an unrecorded pool within forest islands appears more probable than an unmeasured flux for the missing ^{15}N.

Table 5.7. Nitrogen storage in 1995-96 in U3 forest islands and lichen patches estimated from a mass-balance budget and from the recovery of the ^{15}N label. In the mass-balance, storage is a minimum estimate because N retention during the snowmelt period (i.e., when the sub-catchments were not gauged) is not included.

	Forest Islands (kg N ha^{-1})	Bedrock Surfaces (kg N ha^{-1})
Mass-balance		
Input	59	59
Export	16	49
Storage	43	10
^{15}N recovery	23	13

The storage of label in several biomass pools was not estimated in forest islands, including several tree components (branches, bark, and coarse roots) and a few sparse understory species (*Vaccinium* spp.) In addition, the estimation of storage in some important pools (such as fine roots) was difficult to measure precisely. However, coarse woody debris (CWD) may be the pool of organic matter containing the missing label. Coarse woody debris includes dead branches, cones, fallen trees, and standing dead trees (Harmon et al. 1986) and generally has a high C:N (<100). Microorganisms decomposing CWD tend to be N-limited and will immobilize N inputs (Berg & Staff 1981; Harmon et al. 1986; Downs et al. 1996). For example, fungal hyphae decomposing tree boles can mediate a net translocation of N from lower in the forest floor into the decaying wood (Harmon et al. 1986). In a survey of nutrient immobilization in bole wood from several common southern boreal tree species, Alban & Pastor (1993) found that *P. banksiana* bole wood had the lowest initial N content and the highest potential for N immobilization. Coarse woody debris was abundant in forest islands because *P. banksiana* were at a 'mature' to 'overmature' stage. In addition, during the study period several trees were snapped by strong winds or were killed by lightning. Because of its

heterogeneity and various degrees of decomposition, estimating ^{15}N storage in CWD would be difficult but will be attempted in future studies. Thus, the missing label from U3 forest islands may be a combination of gaseous and particulate fluxes, sampling error, and unrecorded pools. Among unrecorded pools, CWD is the most likely missing sink because its high C:N should have favored the immobilization of NO_3^- inputs.

Although much emphasis is usually given to litter inputs on top of the soil profile, fine root turnover may be important for the retention of N inputs (Magill et al. 1997). Fine root production will be especially significant in the boreal forest because it is a larger input of organic matter to soils than litterfall (Vogt et al. 1986; Ruess et al. 1996). The production of new fine roots probably resulted in $^{15}NO_3^-$ retention in U3, but additional label may have been immobilized on dead roots because some have a high C:N (36 – 77). Fine root turnover may be especially important lower in the soil profile because the low C:N of the bulk soil organic matter will not favor N immobilization, while fine roots C:N is highest there (Table 5.5).

^{15}N recovery in other forested ecosystems

The pattern in storage of ^{15}N labels added to forests is strongly dependent on the form of N added (Table 5.8). When $^{15}NH_4^+$ is added, the tendency is for a larger proportion of the label to be recovered in the forest floor. This is consistent with the availability of abiotic retention mechanisms for NH_4^+ in forest floor humus (Vitousek & Melillo 1979; Schimel & Firestone 1989). With $^{15}NO_3^-$, relatively more label is found in the mineral soil, losses through runoff are higher, and total recovery tends to be lower (Table 5.8). This illustrates the paucity of abiotic retention mechanisms for NO_3^- (Vitousek & Melillo 1979) and the possibility that NO_3^- is a less desirable form of mineral-N for some tree species (Kronzucker et al. 1997). The fate of urea applied to *P. banksiana* forests is similar to NH_4^+ application, with the exception that NH_3 volatilization losses are more important because the ammonification of urea increases forest floor pH (Morrison & Foster 1977).

Nitrogen retention by the understory was variable between studies but can be large on the short-term (Table 5.8). At one extreme, less than 2% of the ^{15}N added to a spruce bog in Alberta was recovered in trees, with most of the label tied up in moss biomass or moss litter

Table 5.8. Recovery of ^{15}N labels added to various conifer forests in Europe and North America.

Forest	Form of N added	Trees	Understory	Soil		Runoff	Total	Reference
				Organic	Mineral			
Beech – maple - birch – spruce	$H^{15}NO_3$	11 – 12%	-	8 – 14%	3 – 4%	-	22 – 30%	Nadelhoffer et al. 1995
Douglas fir	[^{15}N]urea	6%	11%	34%		-	50%	Preston et al. 1990
Lodgepole pine	[^{15}N]urea	10%	2%	81%		-	93%	"
"	$^{15}NH_4NO_3$	5%	3%	87%		-	95%	"
"	$NH_4{}^{15}NO_3$	2%	3%	39%		-	44%	"
Spruce bog	$^{15}NH_4Cl$	<2%	42%	42%		-	86%	Li & Vitt 1997
Douglas fir	$(^{15}NH_4)_2SO_4$	29%	-	15%	22%	32%	99%	Koopmans et al. 1996
Picea abies	$^{15}NH_4Cl$	3%	9%	63%	25%	-	100.5%	Buchman et al. 1996
"	$K^{15}NO_3$	7%	15%	46%	33%	-	104%	"
Picea sitchensis	$^{15}NH_4{}^{15}NO_3$	32%	-	47%	20%	25%	105%	Tietema et al. in press
"	$Na^{15}NO_3$ (35 kg N ha^{-1})	32%	-	17%	11%	35%	99%	"
"	$Na^{15}NO_3$ (75 kg N ha^{-1})	20%	-	11%	15%	50%	97%	"
Upland U3	$Na^{15}NO_3$ (40 kg N ha^{-1})	4%	6%	26%	6%	16%	58%	this study

(Li & Vitt 1997). However, over time, a larger proportion of the tracers should be found in trees as label tied to understory biomass will enter the litter pool. In the Uplands, the amount of N in understory biomass is underestimated because the S litter horizon is composed of both live and dead cells. In addition, the amount of label that could be stored in live mosses in U3 may have been underestimated because a part of the cover was lost during the experiment (Chapter 4).

Conclusion

Forest island and lichen patch communities in the upland boreal Shield forest are naturally at different stages of N saturation. Under natural condition, the low plant N content and low net N mineralization rates in forest islands indicate that plants and a portion of the soil microbial community are N-limited. In contrast, in lichen patches the larger net N mineralization rates and the occurrence of net nitrification suggest that soil microorganisms are N-saturated. Following the experimental addition of NO_3^- to this landscape, net N mineralization and net nitrification rates increased in lichen patches, further increasing the burden of N retention on plants and lichens. In contrast, forest islands soil microorganisms contributed at least indirectly to the retention of the elevated N input by mediating a net conversion of the added NO_3^- to NH_4^+ during internal cycling (Chapter 4).

The recovery of the ^{15}N label provided evidence that NO_3^- retention was through both plant uptake and microbial immobilization in forest islands, while retention appeared to be mainly driven by plant and lichen uptake in lichen patches (Fig. 5.8). Lichen patch soil microorganism did not immobilize the NO_3^- input because the litter supplied to them had a low C:N. In forest islands, the label recovery indicated that soil microorganisms directly contributed to NO_3^- retention by immobilizing N during the decomposition of sources of organic matter with a high C:N. The production of a litter depleted in N in forest islands favors a more efficient retention of N inputs by inducing N-limitation of soil microorganisms during early stages of litter decomposition.

Many aspects of N mineralization-immobilization dynamics in the upland boreal Shield forest must be determined to better characterize the response of this system to an

elevated N input. For the different sources of litter and CWD, the maximum potential for N immobilization and the critical C:N ratios must be determined (Aber & Melillo 1982; McClaugherty et al. 1985). Factors other than the C:N ratio could also influence the potential for N immobilization on fresh litter inputs, including the polyphenol content of litter (Northup et al. 1995a,b), environmental conditions (temperature and wetting-drying cycles), the supply of other nutrients, and the type of decomposers present (i.e., fungus vs. bacteria). Because they represent a large organic matter input to boreal soils, the potential for N incorporation during fine root growth and N immobilization during fine root decay should be assessed.

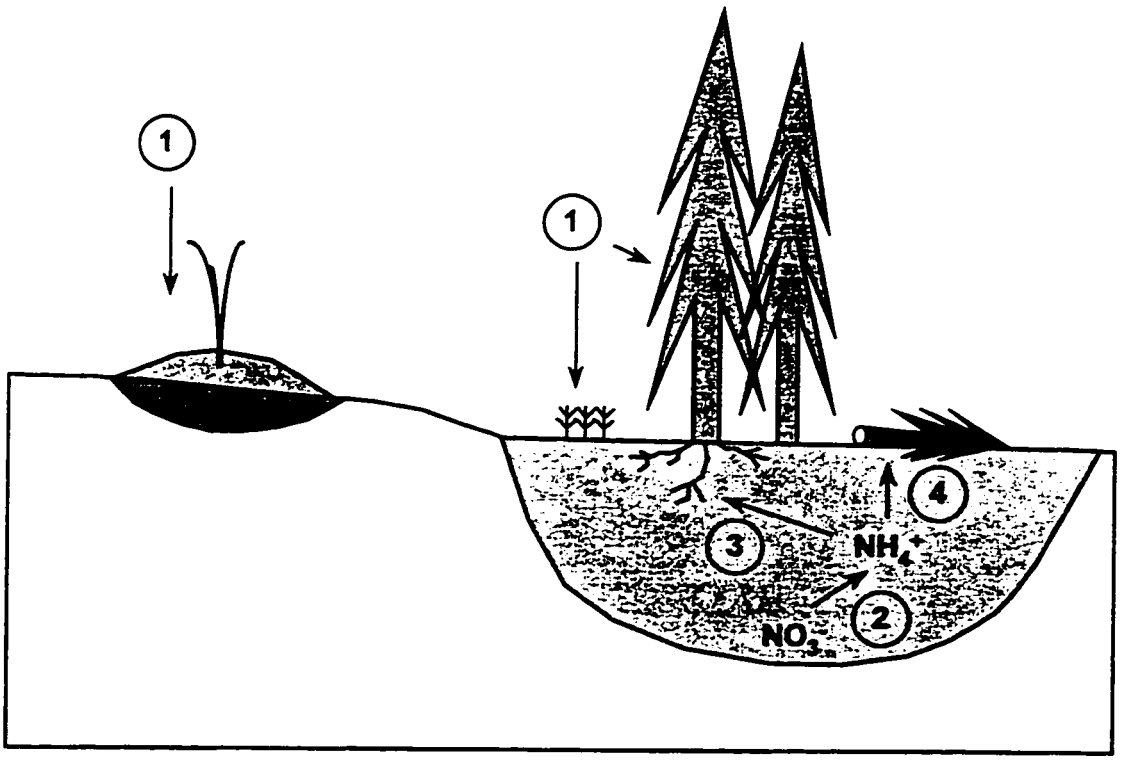

Fig. 5.9. Conceptual representation of the main retention mechanisms for NO_3^- inputs in the ELA Upland landscape. (1) Direct uptake of precipitation N by biomass. (2) Net conversion of NO_3^- to NH_4^+ by soil microorganisms followed by NH_4^+ retention in soils by ion-exchange and other abiotic immobilization processes. (3) Uptake of NH_4^+ or NO_3^- by roots. (4) Immobilization of N in decomposing organic matter with a high C:N.

Chapter 6. The Estimation of Error in Hydrochemical Fluxes from Upland Precambrian Shield Watersheds

Introduction

Mass-balances are powerful tools for the study of element cycles at the ecosystem scale. Although element export via stream runoff is often assumed to be the easiest component to measure, confidence in the estimates is seldom given (Winter 1981; LaBaugh and Winter 1984). In part, the lack of proper error analysis occurs because the emphasis is on the long-term temporal variability (i.e. decades) instead of the within-year variability of element export (Winter 1981). However, a proper error analysis can outline areas of weakness in a sampling program and lead to an improved and effective sampling design strategy. In addition, the complex interactions between measurement errors can yield biased estimates (i.e. under or overestimated), or confidence intervals that are unevenly distributed about the mean. Biased estimates with unknown error distribution may lead to erroneous conclusions being drawn from the analysis of hydrochemical budgets.

In this chapter, a method is developed to evaluate the error on hydrochemical budgets from small Precambrian Shield watersheds. Both the errors on the hydrological and chemical sampling components of the budgets were estimated. This analysis was developed in the context of a study of the response of a small 0-order catchment to an increased N load. The magnitude of the different sources of error was estimated from field data and from the literature. Different sampling procedures were utilized to determine runoff chemistry between catchments and between years, and therefore an error analysis specific to each sampling scheme was required. Three specific issues were addressed: 1) Were the different sampling schemes used to measure runoff N concentration unbiased estimates of the 'true' value? 2) Could the incorporation of measurement and sampling error modify the magnitude of export estimates? 3) Could the complex combination of different sources of error yield confidence intervals that are unevenly distributed about the mean?

Methods

Study site

This study was conducted at catchments U1, U2, and U3 at the Experimental Lakes Area, at the southern end of the boreal Shield forest in northwestern Ontario (Allan et al. 1993). The catchments are small (0.4 – 0.6 ha) and hydraulically responsive due to thin and patchy soil cover of 'forest islands' surrounded by areas of lichen and moss-covered bedrock outcrops. On an annual basis, snowmelt represents 22 to 50% of the hydrological budget. Runoff is intermittent, lasting for a few weeks during snowmelt and a few days following summer storms. The study period covered the summer of 1994, the post-snowmelt period for 1995, and the complete hydrograph for 1996. In 1995-96, catchment U3 received 40 kg N-NO_3^- ha^{-1} yr^{-1} as a part of an experiment on the effects of an elevated N load to an upland boreal forest (Chapter 4).

Mechanisms of runoff generation

To understand the potential for the variability in element concentration during storms in the Upland catchments, the diversity of runoff-generating mechanisms must be reviewed. Early in a precipitation event, once depression storage is satisfied (4-6 mm), runoff is generated as *Horton overland flow* on bedrock surfaces (Allan and Roulet 1994). Water from bedrock surfaces is enriched in elements such as NO_3^- and NH_4^+ because of lower retention of precipitation inputs and leaching of mineral-N from lichen patches (Allan 1993; Chapter 1). As the event proceeds, forest islands gradually become saturated with precipitation and runoff from upslope bedrock surfaces. Within a few hours from the beginning of the storm, additional runoff is produced by *sub-surface stormflow* from forest islands. This stormflow tends to be depleted in mineral N but enriched in dissolved organic matter. During intense storms, additional runoff is produced by *saturation overland flow* from forest islands. Runoff is highest when saturated overland flow occurs as at that time all three runoff-generating mechanisms are in operation. Because of greater energy available for erosion and transport, this period corresponds with the peak export of particulate N (PN) (Fig. 6.1). Once precipitation ceases, the remaining runoff occurs as subsurface stormflow from forest islands. The diverse flow paths and mechanisms of flow-generation of this system are reflected by

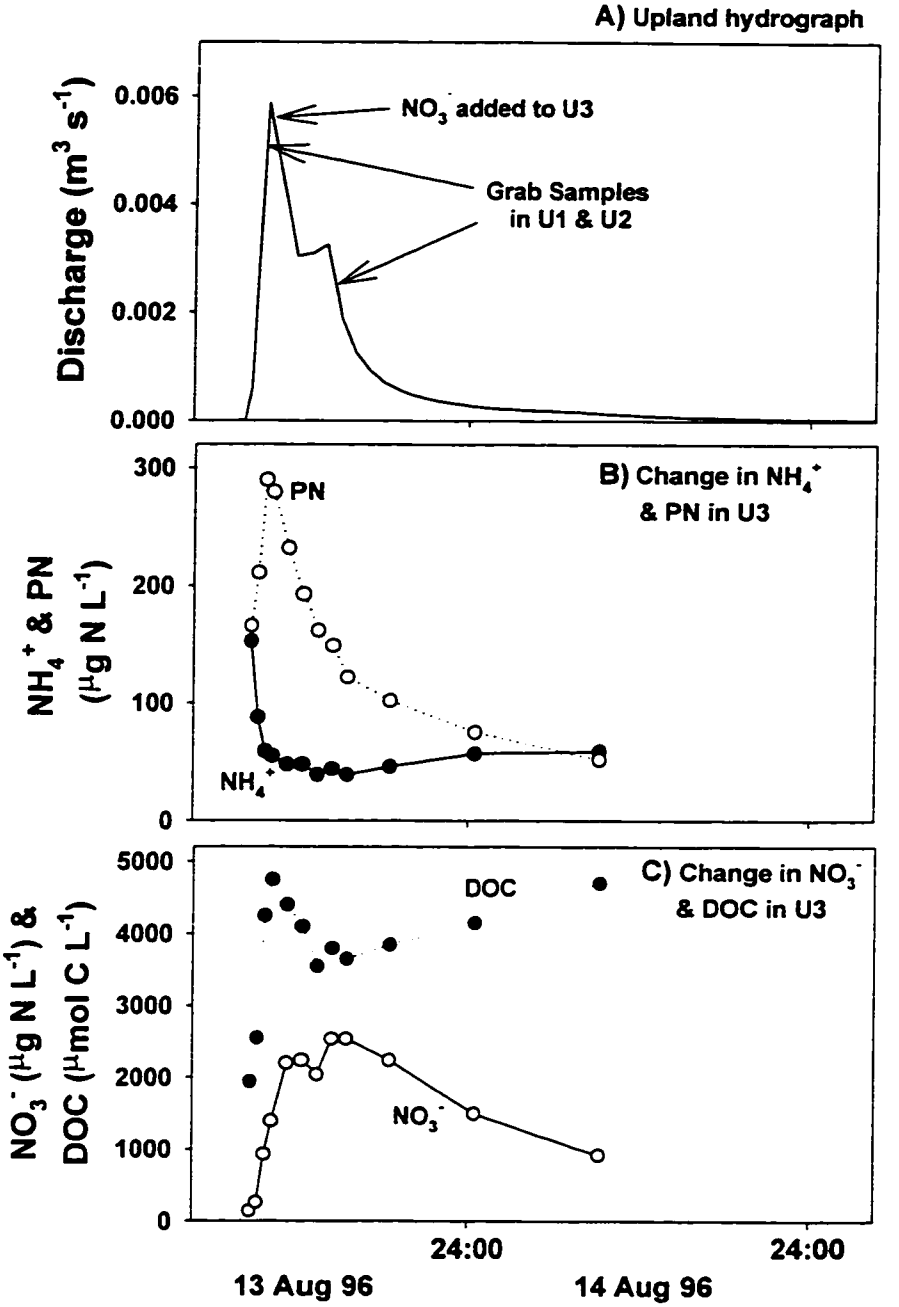

Fig. 6.1. Discharge and N concentration during the 13 August 1996 storm in catchment U3. Runoff chemistry was measured with a self-triggered autosampler which collected samples with decreasing frequency over a 1 day period. A $NaNO_3$ treatment was added to U3 mid-way through the storm (**A**) Discharge; (**B**) NH_4^+ and PN; (**C**) NO_3^- and DOC.

dynamic hydrographs with multiple peaks (Allan 1993; Allan and Roulet 1994). It is assumed that the crystalline bedrock is impervious and that no water exits the catchments as groundwater.

The main difference between the Upland and higher order catchments is the absence of groundwater baseflow or increased groundwater inputs during storms. In other systems, groundwater N may dampen the variability in N concentration which may be introduced by other stormflow-generating mechanisms. Due to the large variability in concentration between the rising and falling limbs of the hydrograph, the use of discharge-concentration relationships to estimate element flux in the Uplands is inappropriate.

Field measurements - Hydrology

Catchment outflows were gauged using 90° V-notch weirs. All runoff exits the catchments as overland flow, which was redirected towards the weirs using epoxy-covered concrete deflector walls. Stage height was recorded using Stevens F-recorders. The weirs were insulated and heated to prevent freezing during snowmelt. Considerable effort was given to the measurement of the stage-discharge relationship for each weir over the range of flow conditions encountered, *including an emphasis on higher flows.* One or two measurements of stage and discharge were made during most storms in 1994, with additional measurements made in 1995-96 (Table 6.1). Discharge was measured by filling a bucket from the V-notch three to five times. This method was precise at low to average discharge but less so at the highest flows because the biggest bucket (a 40 L garbage pail) filled up in a few seconds. Even though stage-discharge relationships were established, it is important to note that discharge is not necessarily constant at a given stage because of different slopes in the water table or the collection pond during the rising and falling limbs of the hydrograph (Winter 1981). In addition, water viscosity doubles over the range of temperature for Upland runoff (~25°C to ~0°C; Wetzel 1981). As stage-discharge measurements were made throughout the year, this type of storm-to-storm variability will be included in the stage-discharge relationships.

Table 6.1. Power function coefficients for the Upland catchments rating curves.

	a (intercept)	b (slope)	r^2	n	S_{yx}
U1	0.5070	2.240	0.992	19	0.0685
U2 (1994)	0.5032	2.282	0.982	17	0.115
U2 (1995-96)	0.7160	2.427	0.976	29	0.147
U3	0.2910	2.119	0.985	23	0.0947

The F-recorder charts were digitized and discharge data computerized using the program HCHART (K.G. Beaty, Freshwater Institute, 501 University Crescent, Winnipeg, MB, R3T 2N6). The stage-discharge relationship is incorporated in HCHART and the interpolation between digitized data points was made on discharge estimates. Because the stage-discharge relationship is a power function, discharge is underestimated when integration is made on stage values.

Runoff chemistry

Depending on the budget and sampling equipment available, three sampling schemes were used to monitor solute concentration. The underlying principle of all three schemes was to characterize water chemistry on a storm-by-storm basis (keeping in mind that there is no baseflow in these catchments). The first sampling scheme used automated samplers to integrate storm runoff chemistry over the entire event (all catchments in 1995, and U3 in 1996). The autosamplers were self-triggered and up to 24 samples were collected with decreasing frequency over time, *roughly* integrating runoff in a flow-proportional fashion. During summer months, ice was frequently added to the sample holder to keep them cool. Equal amounts of each sample were pooled to yield one sample per storm.

The other two schemes employed grab samples. In the first of these schemes (all catchments in 1994) two samples were collected per storm. One sample was taken during the rising limb of the hydrograph and the other during the falling limb (but close to peak flow, not the tailing end, see Fig. 6.1). The rationale for this procedure was that *in general* the rising and falling limbs include the extremes in N concentration and represent about half of total runoff. In the second grab sampling scheme (U1 and U2 in 1996), two samples were

collected one each during the rising and the falling limbs of the hydrograph, but these were subsequently combined in equal amounts to yield one sample per storm.

Chemistry samples were immediately stored at 4°C and analyzed within 1-2 days for NO_3^-, NH_4^+, PN, and total dissolved N (TDN) following Stainton et al. (1977). Dissolved organic N (DON) was estimated as TDN-NH_4^+-NO_3^- and Total N (TN) as TDN +PN.

Terminology

Throughout this discussion, the term *error* relates to the random variability about the mean (usually defined by the standard deviation, or SD). *Precision* (P) will strictly refer to the ratio of the standard deviation to the mean for a given distribution. This definition of precision was practical for the purpose of defining confidence intervals on the hydrochemical budgets and will be examined in the following discussion. *Bias* will refer to the systematic under- or overestimation of the 'true' mean due to a sampling artifact. The term *accuracy* will not be used here as it is often used synonymously with precision or bias. Sokal and Rohlf (1981) define accuracy as 'the closeness of a measurement or computed value to its true value' (i.e. an accurate measurement is unbiased) and precision as 'the closeness of repeated measurements of the same quantity'.

Estimation of error on hydrological measurements

Errors on stage readings and on the calculations made from stage-discharge relationships were the two sources of variability considered during the hydrological error analysis. Error associated with stage readings comprises error when setting the zero-head reference when charts are changed, error of the stage recording instrument, and digitizing errors (Herschy 1973; Winter 1981). Devito (1995) used stage errors ranging between ±2 mm to ±5 mm using comparable methodology. During this study, the sum of possible error in the calculation of stage error is assumed to have a standard deviation of ±3 mm (i.e. stage between ± 5.88 mm 95% of the time. Ideally, the stage error should have been measured by setting two chart recorders on the same weir and getting two different observers to collect and process the data.

The error on the stage-discharge relationship is probably the least appreciated source of both bias and variability in hydrological monitoring (Winter 1981). The stage-discharge relationship is usually a power function of the form:

$$Q = aH^b \tag{6.1}$$

where Q is discharge ($m^3 s^{-1}$) and H (m) the hydraulic head (or stage) over the weir notch in meters. The parameters a and b are estimated from a log-log transformation of field measurements of stage and discharge,

$$\log Q = \log a + b \log H + \varepsilon \tag{6.2}$$

Log a and b are the intercept and the slope of a least-square log-linear regression respectively. For each measurement of discharge, H was measured either at the weir notch or at a permanent reference and was assumed to have a negligible measurement error. Assuming that the residuals are normally distributed about the regression line, the error on log discharge estimated from the regression is approximated by the standard error of the residuals ($s_{y \cdot x}$). Unfortunately, once the log discharge estimates are backtransformed, the error term is no longer normally distributed about the mean (Sokal and Rohlf 1981; Bird and Prairie 1985). As illustrated in Figure 6.2, backtransformed log-normal distributions are found to be skewed towards high values.

One method to estimate the error on element export is first-order error propagation (ex. $s^2_{runoff} = s^2_{stage} + s^2_{stage\text{-}discharge}$; Winter 1981; Devito et al. 1989). However, this scheme is less practical when the sources of error have different distributions and is inapplicable when the sources of error are not independent of one another (it will be shown later that stage-discharge error is in part a function of stage error). In cases where linear error propagation does not apply, it may be possible to derive a more complex analytical solution to combine the different sources of error. However, in this study an equally suitable and straightforward method was designed using stochastic computer simulations.

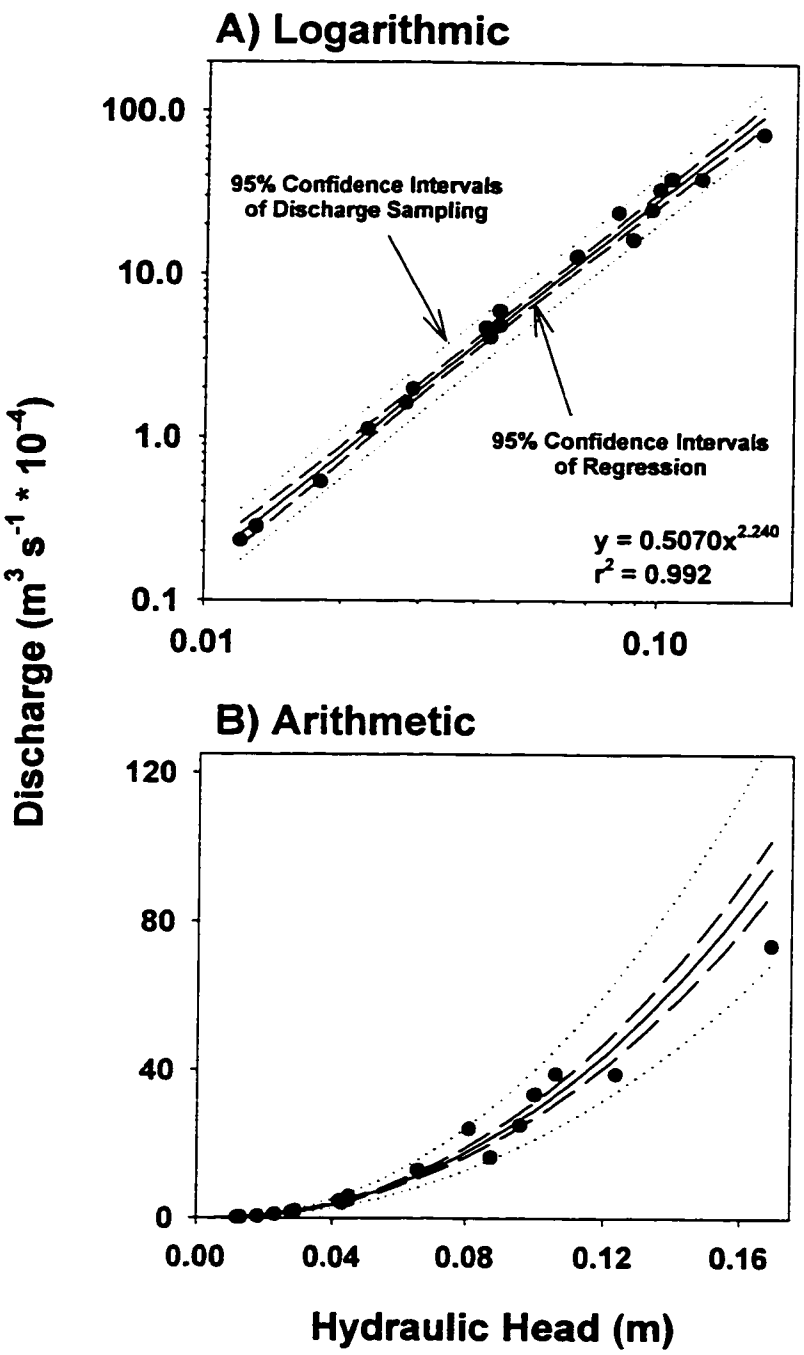

Fig. 6.2. Relationship between stage and discharge on **(A)** the logarithmic and **(B)** the arithmetic scales. The confidence intervals of linear regressions have the property of becoming larger when moving away from the mean X value. Stage-discharge parameters are usually determined on a logarithmic scale, where the error in the estimated Y values varies normally on each side of the regression line. However, on the arithmetic scale the error will be larger on the upper side of the regression line and much larger at higher Y values.

Yearly runoff simulations

Daily volumetric discharge rates (m^3 s^{-1}) obtained from HCHART were converted back to a 'volume-weighed' average stage for each day. Error was added to daily stage using:

$$H'_{i,j} = H_i + Z'_{i,j} \quad (6.3)$$

where,

$H'_{i,j}$ = the new stage for the i^{th} day and j^{th} simulation,

H_i = the original stage for each day,

$Z'_{i,j}$ = the stage error for each time interval and simulation.

where $Z'_{i,j}$ was defined as:

$$Z'_{i,j} = \Delta'_{i,j} \sigma_S \quad (6.4)$$

where,

$\Delta'_{i,j}$ = values picked at random from a normal distribution with $\mu = 0$ and $\sigma = 1$ for each i and j, and

σ_S = the standard deviation of the stage error (0.003 m).

Daily water flux including the error on the predictions from the stage-discharge relationship was then estimated using:

$$Q_{i,j} = 10^{\log a + b \log(H'_{i,j}) + Z'_{i,j}} \bullet \frac{t}{A} \quad (6.5)$$

where,

$Q_{i,j}$ = discharge for the i^{th} day and j^{th} simulation (mm),

a = intercept of the stage-discharge relationship,

b = slope of the stage-discharge relationship,

t = number of seconds in a day,

A = a conversion factor from volumetric to areal discharge (i.e m^3 day^{-1} ha $catchment^{-1}$ to mm day^{-1}), and

$Z''_{i,j}$ = stage-discharge error for the i^{th} day and j^{th} simulation.

$Z''_{i,j}$ was estimated using:

$$Z''_{i,j} = \Delta''_{i,j} \; S_{\hat{Y}} \tag{6.6}$$

where,

$\Delta''_{i,j}$ = a number picked at random from a normal distribution with $\mu = 0$ and $\sigma = 1$ for each i and j, and

$S_{\hat{Y}}$ = the standard error of the estimates for a given stage-discharge relationship (log m^3 s^{-1}).

For each i and j, $S_{\hat{Y}}$ was estimated from:

$$S_{\hat{Y}} = \sqrt{S^2_{Y \cdot X}\left[\frac{1}{n} + \frac{(X_i - \bar{X})^2}{\sum x^2}\right]} \qquad \text{(Sokal and Rohlf 1981; 6.7),}$$

where,

$X_i = H'_{i,j}$ (the stage at a given i^{th} time interval and j^{th} simulation),

$\bar{X}$ = the mean stage for the stage-discharge data set used to estimate a and b

Σx^2 = the sum of the squared stages used to estimate a and b, and

n = the number of measurements of stage and discharge.

Thus, $S_{\hat{Y}}$ has the interesting property of increasing in size at very low and very high stage values (Sokal and Rohlf 1981). One thousand yearly hydrographs were generated for each catchment and for each of the study years. The comparison of the mean flux from the 1000

simulated hydrographs relative to the flux obtained from HCHART (i.e. with no error component) provides an estimate of bias (i.e. was yearly runoff over- or underestimated when error was not taken into account?). Both the standard deviation of the 1000 means and the 2.5^{th} and 97.5^{th} percentiles were used as estimates of the confidence intervals. The percentile estimates are the most robust as they do not need to satisfy the assumption of normality (Efron and Tibshirani 1993). One restriction on the simulations was that when daily flow was nil it stayed nil (i.e. there is no baseflow in this system). As indicated in Eq. 6.6, a normal distribution was used to estimate stage-discharge error because a *t*-distribution generator was not available on the computer software used for the simulations. Because of the relatively large sample size used to calculate the stage-discharge relationships (n = 17 – 29), the discrepancy between the distributions is small (Sokal and Rohlf 1981).

Error on N chemistry

Sampling and analytical error were the sources of variability considered for N concentration measurements. As an approximation, analytical error was obtained from replicated measurements of precipitation samples at the ELA. It is likely that analytical error varies along the large range in N concentration found in the Upland catchments, but this will need to be addressed in future studies. Overall, the analytical error is probably much smaller than sampling error in Upland runoff. Thus, the potential to underestimate the flux confidence intervals by underestimating analytical error is small.

The error associated with the different sampling strategies for storm chemistry is the most difficult to estimate. Sampling error for different N species was estimated using the data from two storms where detailed chemical sampling was conducted. As will be explained in the next section, either some measure of the variance in N concentration during those storms or computer simulations were used to estimate sampling error. The first storm (14 June 1988, 53 mm; Allan 1993) was representative of dry antecedent conditions as it occurred following a 6 week drought period. Allan (1993) collected 12-14 grab samples at various stages of the 14 June 88 storm in catchments U1, U2, and U3. The second event (13 August 1996; 39 mm) had wetter antecedent conditions and was only sampled intensively in catchment U3. Samples were collected using an automated sampler (12 samples analyzed separately; Fig.

6.1). Catchment U3 was undergoing a NO_3^- addition experiment in 1995-96 (Chapter 3) and one application of the NO_3^- treatment was made mid-way through the storm. The volume of water discharged between samples was known for both storms, which allowed an estimation of sampling bias relative to the 'true' volume-weighed mean concentration.

Estimating bias and P for the different sampling schemes

The error on the mean storm chemistry for the automated sampler was estimated by 'bootstrapping' the 13 August 96 data set (Fig. 6.3). In bootstrapping, numerous pseudostorms are generated by randomly picking with replacement elements from the original data set (Efron and Tibshirani 1993). The standard deviation of the bootstrapped means is a robust estimator of the 'true' standard error of the mean (Efron and Tibshirani 1993). The number of elements picked to create each pseudostorm was the same as in the original data set (12). Ideally, the sampling error for the autosampler should have been estimated by sampling the storm with even more frequency than the autosampler was capable of itself. This would have allowed the generator to pick randomly *between* adjacent samples instead of from the whole data set during sampling simulations. As storm chemistry was not random through time (Fig. 6.1), the 'bootstrapped' sampling error for the autosampler probably overestimated the 'true' sampling error. Nevertheless, as this sampling error was still relatively small compared to the other sampling schemes, it was retained as a first approximation.

In the grab sampling schemes samples were collected so that storm chemistry was divided roughly into 'rising' and 'falling' limbs of the hydrograph. In the 'unpooled' scheme (where one sample per limb was analyzed separately), the standard deviation of the 'rising' and 'falling' data was the only possible measure of error. However, bootstrapped 'rising' and 'falling' means were generated to infer the underlying distribution in N concentration (i.e., normal or log normal). For the 'pooled' sampling scheme, a distribution of possible mean values was obtained by randomly picking and averaging one sample from each limb of the storm (Fig. 6.4). As for the autosampling scheme, the standard deviation of these simulated means was used as the measurement of error.

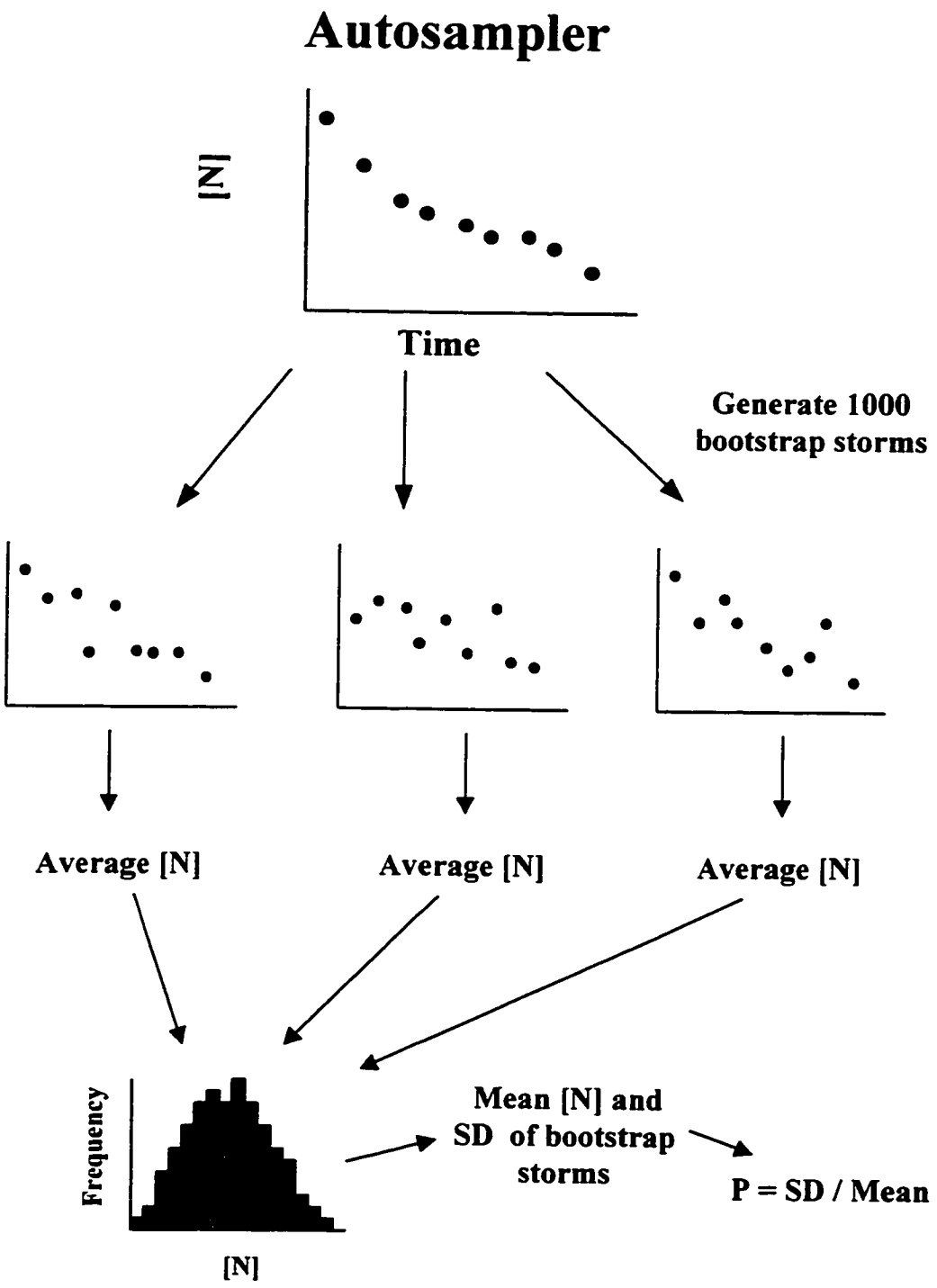

Fig. 6.3. Summary of the procedure used to estimate sampling precision when using an autosampler.

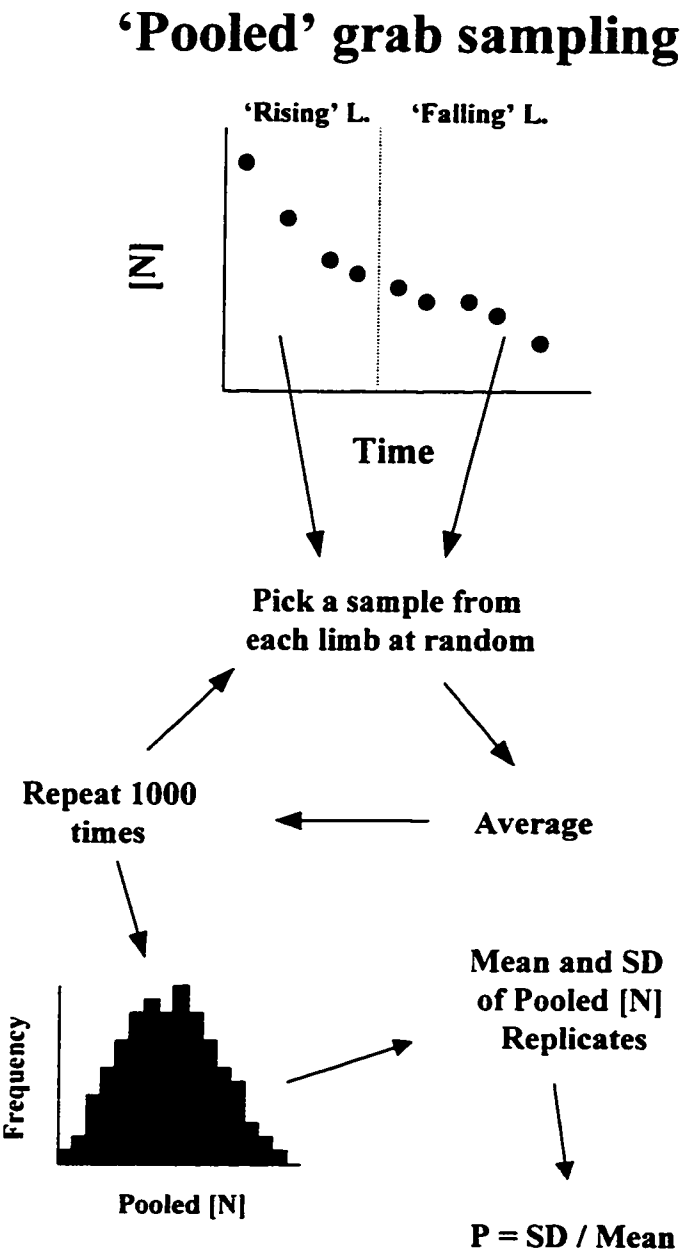

Fig. 6.4. Summary of the procedure used to estimate sampling precision with the 'pooled' grab sampling scheme.

The assumption of normality

For the standard deviation to be an appropriate measure of the error about the mean, the distribution of simulated mean chemistry values must be either normally distributed (i.e. bell-shaped) or distributed normally following a mathematical transformation. A distribution's departure from normality can be tested using a χ^2 or a Kolmogorov-Smirnov test for goodness of fit (Sokal and Rohlf 1981). Unfortunately, because of the large number of simulations used (1000) it would have been easy to obtain statistically significant differences from normality from minute differences in distribution (Efron and Tibshirani 1993). In other words, statistically significant departure from normality could be irrelevant from a biogeochemical point of view. All simulations were performed with the N concentration data on the arithmetic and logarithmic scales. For a given N species and sampling scheme, 'the assumption of normality' was assessed using frequency distributions obtained from the transformed and untransformed data sets. Whichever distribution was most appropriate was used to estimate P. Usually, the choice was straightforward as one distribution would depart strongly from normality (i.e. was multimodal or strongly skewed).

Error on yearly N flux estimates

Simulations incorporating random error on both the hydrological fluxes and runoff N concentration were used to estimate the yearly N flux and confidence intervals. Using Eq. 6.5, 1000 yearly hydrographs were simulated and yearly fluxes estimated using:

$$\sum F_{i.j.k} = Q_{i.j} \bullet N_{i.j.k} \bullet A \qquad (6.8)$$

where,

$F_{i,j,k}$ = Flux of the k^{th} N species (kg N ha^{-1}) for the time interval covered by the i^{th} sample and j^{th} simulation,

$Q_{i,j}$ = runoff (m^3) during the i^{th} time interval and j^{th} simulation,

$N_{i,j,k}$ = N concentration (μg N L^{-1}) during the i^{th} time interval for the j^{th} simulation, and

A = a conversion factor from ($m^3 \cdot$ catchment $area^{-1} \cdot \mu g$ N L^{-1}) to kg N ha^{-1}.

The matrix N_{ijk} was defined by first estimating:

$$C^{S}_{i,j,k} = C_{i,k} + C_{i,k}\ \Delta'_{i,j}\ P^{S}_{k} \qquad (6.9)$$

where,

$C^{S}_{i,j,k}$ = the concentration including sampling error for the k^{th} N species at the i^{th} time interval and j^{th} simulation.

$C_{i,k}$ = the measured concentration of the k^{th} N species during the i^{th} time interval,

$\Delta'_{i,j}$ = values picked at random from a normal distributions with $\mu = 0$ and $\sigma = 1$, and

P^{S}_{k} = the sampling P for the k^{th} N species for a given sampling scheme.

Thus, P was used to define the sampling standard deviation as a fixed proportion of N concentration. For sampling schemes and N species for which P was better represented by a log-normal distribution, $C^{s}_{i,j,k}$ was estimated using:

$$C^{S}_{i,j,k} = C_{i,j,k} + 10^{(\log C_{i,k}\ \Delta'_{i,j}\ P^{S}_{k})} \qquad (6.10)$$

Finally, $N_{i,j,k}$ was estimated by adding analytical error to $C^{S}_{i,j,k}$:

$$N_{i,j,k} = C^{S}_{i,j,k} + C^{S}_{i,j,k}\ \Delta''_{i,j}\ P^{A}_{k} \qquad (6.11)$$

The bias in flux estimates was obtained by comparing the mean annual flux of an element with and without error terms. The confidence intervals were estimated using the standard deviation of the simulated mean fluxes and (preferably) the 2.5^{th} and 97.5^{th} percentiles of the simulated means.

Results & Discussion

Are hydrological fluxes underestimated when error is not taken into account?

Hydrological fluxes were underestimated by 2% to 4% when stage and stage-discharge error were not taken into account (Table 6.2). The confidence intervals and standard deviations in yearly runoff were variable between catchments and from year-to -year (Table 6.2). In general, fluxes were more precise during the year with numerous storms (1996) than during the driest year (1995). Thus, runoff error was additive between storms (i.e. during wet years, a randomly 'high' storm was more likely to be compensated by a 'low' storm during the simulations). Both sources of error contributed to define the size of runoff confidence intervals (Table 6.3). The sources of error were partially additive because when one was removed the size of confidence intervals only diminished slightly (Table 6.3). The 95% confidence intervals obtained with the percentiles were similar to the ones obtained with the standard deviation (as $\pm 1.96 \cdot SD$; Fig. 6.5). However, the 97.5^{th} percentile tended to be slightly larger than the upper confidence interval derived from the standard deviation (Table 6.3).

Were the different sampling schemes used to measure runoff N concentration unbiased estimates of the 'true' value?

All sampling schemes tended to slightly underrepresent peak flow chemistry. The average storm concentration tends to be underestimated for forms of N with a peak in concentration at peak flow, such as PN and NO_3^- (Table 6.4). On the other hand, average storm concentration was overestimated for N forms with an elevated concentration during the recession phase of the storms (NH_4^+ in the 13 Aug 96 storm; Table 6.4). Overall, the magnitude and direction of the bias was not always consistent from storm to storm (Table 6.4). Thus, as a first approximation, it will be assumed that sampling bias can be neglected. This assumption likely would not hold for all storms. For example, in catchment U1 for the June 1988 storm, simulated grab sampling underestimated NO_3^- concentration several-fold (Table 6.4).

Table 6.2. Annual runoff (mm) calculated with and without error for three Upland catchments, 1994-96. Error on simulated runoff was obtained by adding random error on a daily basis on stage reading and on the predictions from stage-discharge relationships.

	Runoff without Error	Average Simulated Runoff	Simulated SD	SD 95% Confidence Interval	Percentile 95% Confidence Interval
U1 – '94	124	127	7.1	113 – 141	113 – 142
U1 – '95	125	130	7.5	115 – 145	117 – 146
U1 – '96	404	414	11.5	391 – 437	391 – 438
U2 – '94	144	148	10.1	128 – 168	130 – 169
U2 – '95	133	138	10.2	118 – 158	118 – 159
U2 – '96	395	403	13.5	377 – 429	378 – 431
U3 – '94	163	167	9.6	148 – 186	148 – 186
U3 – '95	153	157	9.6	138 – 176	139 – 176
U3 – '96	419	431	13.1	405 – 457	405 – 458

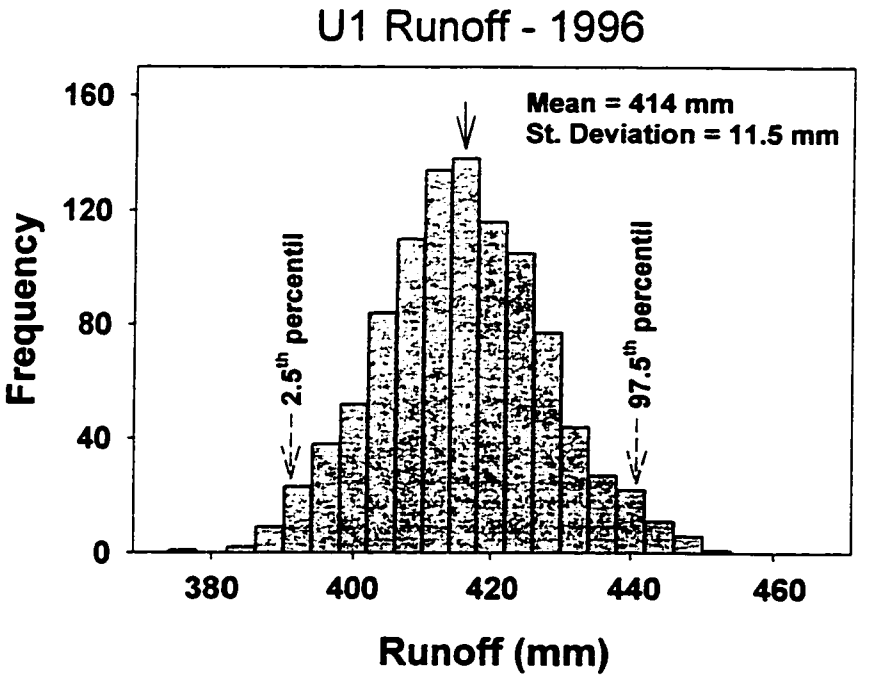

Fig. 6.5. Frequency distribution for 1000 simulations of the U1 – 1996 runoff generated by daily random variability on the stage and on predictions from the stage-discharge relationship.

Table 6.3. Effect of the variation in stage reading and stage-discharge errors on the hydrological budget of catchment U1 in 1996. In bold are the parameters used for budget calculation in Chapter 4.

Stage SD (mm)	Stage-Discharge SD	Mean Runoff (mm)	SD Runoff (mm)	95% Confidence Interval (mm)
0	0	404		-
0.1	0.0685	408	8.3	392 – 425
1	0.0685	409	8.9	392 – 427
3	**0.0685**	**414**	**11.5**	**391 – 438**
5	0.0685	421	16.4	390 – 456
3	0.0001	409	8.2	393 – 425
3	0.0343	412	10.0	392 – 431
3	0.1028	415	12.6	392 – 440

Table 6.4. Bias in average N concentration obtained with different sampling schemes relative to the volume-corrected average concentration for the 13 August 1996 storm in U3 and the 14 June 1988 storm in U1, U2, and U3. Concentrations for the automated and the grab sampling scheme are the mean and the 95% confidence intervals (in brackets) obtained from 1000 simulations of storm sampling.

	NO_3^- ($\mu g\ N\ L^{-1}$)	NH_4^+ ($\mu g\ N\ L^{-1}$)	PN ($\mu g\ N\ L^{-1}$)	TDN or DOC ($\mu g\ N\ L^{-1}$ or $\mu mol\ C\ L^{-1}$)
U3 – 13 Aug 1996				
Flow proportional	1660	56	181	3940*
Automated sampler	1580 (1110-2040)	61 (44 – 78)	168 (128 – 208)	3810 (3360-4270)
Grab	1490 (610-2370)	59 (39 – 90)	162 (131 – 200)	3630 (2520-8200)
U1 – 14 Jun 1988				
Flow proportional	92	49	45	553
Grab	68 (30 – 152)	42 (14 - 125)	54 (25 – 114)	661 (460 – 948)
U2 – 14 Jun 1988				
Flow proportional	70	30	80	658
Grab	68 (24 – 187)	32 (20 – 50)	91 (41 - 201)	631 (458 – 869)
U3 – 14 Jun 1988				
Flow proportional	191	50	67	743
Grab	72 (30 – 178)	50 (20 – 129)	66 (40 – 110)	741 (455 – 1207)

* DOC was used as an approximation for TDN for this storm

Normal vs log-normal P values

In general, the error terms on runoff chemistry were normally distributed when using an autosampler (Fig. 6.6) and log-normally distributed with grab sampling (Fig. 6.7). The P values from storm-to-storm varied considerably for all forms of N (Table 6.5). The P values selected for the simulations were the averages between the 1988 and the 1996 storms. Evidently, a fixed P value from storm-to-storm is a coarse approximation, but it was the most practical option to integrate sampling error in the element flux simulations. For the purpose of the simulations, the most important finding was that error was normally distributed with the autosampler and log-normally distributed with grab sampling. Thus, grab sampling concentration estimates have much larger upper than lower confidence intervals. It is common for means to have a skewed distribution when they are obtained by averaging few samples (Sokal and Rohlf 1981).

Are N fluxes underestimated when hydrological and runoff concentration errors are not taken into account?

The flux of N was always underestimated when error was not taken into account (Table 6.6). On average, fluxes were underestimated by 10% for NO_3^-, 5% for NH_4^+, PN, and DON, and 4% for TN (Table 6.6). The use of autosamplers appears to only slightly reduce the bias in flux measurement. However, this assessment was biased because autosamplers were used in all catchments in 1995 (i.e. the most difficult year to sample). The potential for error in U3 in 1995-96 was much larger for DON exports because the difference between TDN and NO_3^- + NH_4^+ concentrations was much smaller than in the other catchments.

The use of grab sampling schemes results in a bias in the calculation of NO_3^- export. As previously demonstrated, the average storm NO_3^- concentration can be strongly underestimated by grab sampling. In addition, if sampling error is not incorporated, another bias is introduced by failing to account for the log-normal distribution of the NO_3^- sampling error. Unlike other dissolved N forms (NH_4^+ and DON), NO_3^- has little interaction with soils and can rapidly be flushed out of catchments. The major limitation of grab sampling schemes

is that a large fraction of NO_3^- export can occur in a short period of time, leading to greater uncertainty in NO_3^- fluxes estimated from few samples per storm.

The sensitivity of the bias and the uncertainty in the flux estimates to the four types of error was tested by changing the magnitude of each error terms by ±50% in separate simulations. In general, changing the magnitude of a given error term did not change the outcome of the simulations greatly (Table 6.7), consistent with the additivity of random error (Meyer 1975).

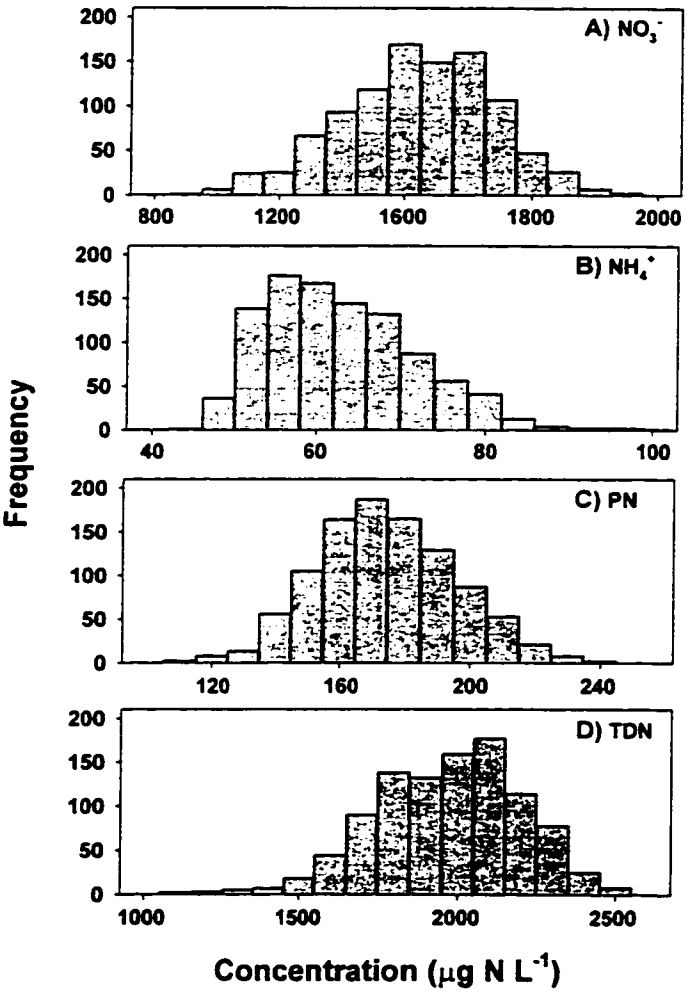

Fig. 6.6. Frequency distribution of mean storm N chemistry obtained be 're-sampling' the U3 – 13 August 1996 dataset using bootstrapping.

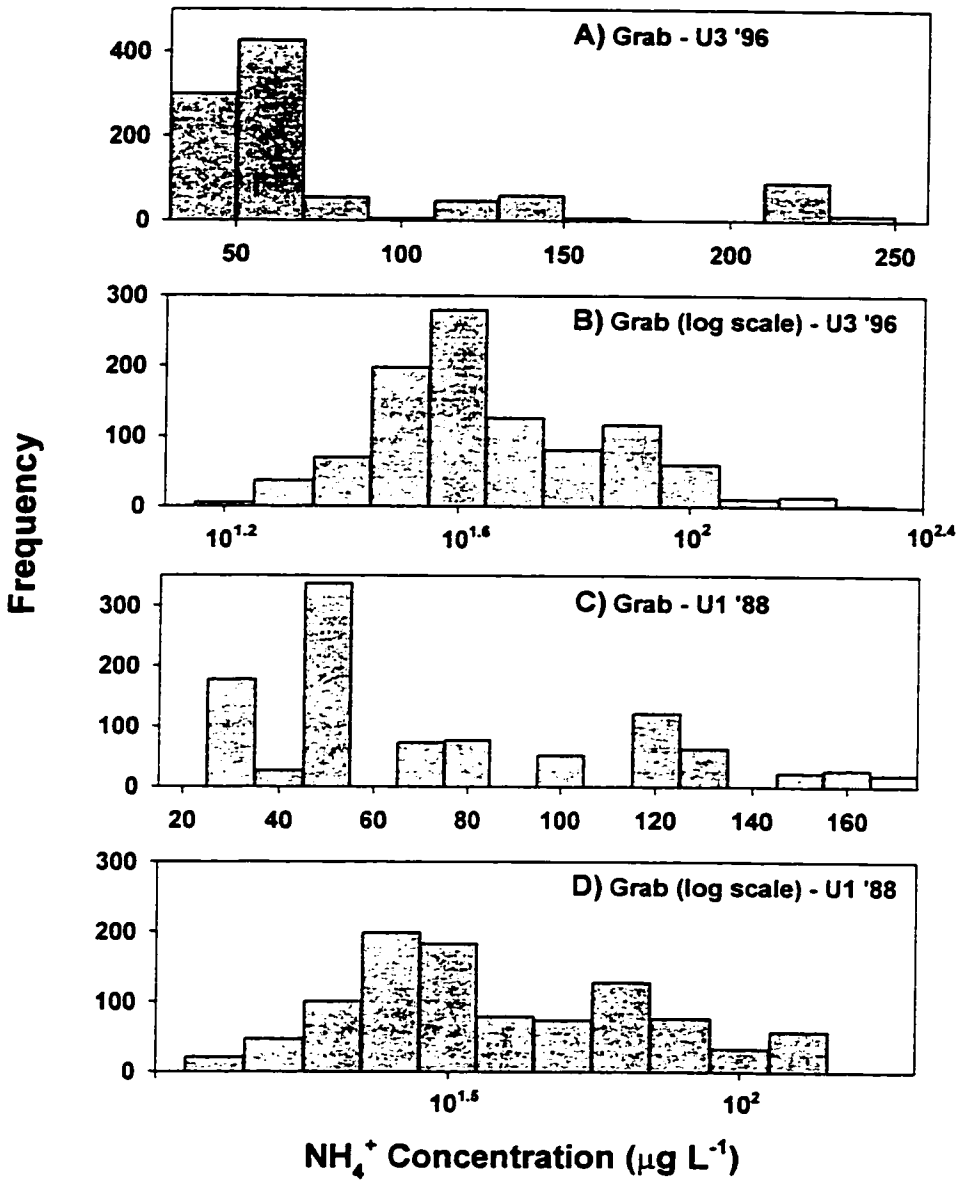

Fig. 6.7. Frequency distribution of simulated mean NH_4^+ concentrations for the (A) the U1 – 1988 datset at the arithmetic scale and (B) the logarithmic scale; (C) the U3 – 1996 data set at the arithmetic scale and (D) the logarithmic scale.

Table 6.5. P values for different sampling schemes derived from the detailed sampling of two storms. The 14 June 1988 storm occurred following a prolonged drought period (data from Allan 1993). The 13 August 1996 event had wetter antecedent conditions and received a NO_3^- addition mid-way through the storm. Whether P should be estimated on the arithmetic (A) or logarthimic scale (L) was determined from frequency distributions.

		NO_3^-	NH_4^+	PN	TDN	DOC
Automated sampler	13 Aug 96	0.150 (A)	0.144 (A)	0.121 (A)	-	0.0609 (A)
Grab (single)	Rise – U1 '88	0.0996 (L)	0.164 (L)	0.166 (L)	0.0533 (L)	-
	Rise – U2 '88	0.180 (L)	0.0780 (L)	0.130 (L)	0.0544 (L)	-
	Rise – U3 '88	0.174 (L)	0.179 (L)	0.117 (L)	0.0798 (L)	-
	Avg. Rise	**0.151 (L)**	**0.140 (L)**	**0.138 (L)**	**0.0625 (L)**	-
	Fall – U1 '88	0.269 (L)	0.329 (L)	0.124 (L)	0.0371 (L)	-
	Fall – U2 '88	0.204 (L)	0.137 (L)	0.144 (L)	0.131 (L)	-
	Fall – U3 '88	0.104 (L)	0.204 (L)	0.0485 (L)	0.0306 (L)	-
	Avg. Fall	**0.192 (L)**	**0.223 (L)**	**0.106 (L)**	**0.0662 (L)**	-
	Rise – U3 '96	0.191 (N)	0.108 (L)	0.0435 (L)	-	0.0507 (L)
	Fall – U3 '96	0.297 (N)	0.0494 (L)	0.106 (L)	-	0.0115 (L)
	Average P	**0.172 (L)[a]**	**0.130 (L)**	**0.0984 (L)**	**0.0477(L)[b]**	
Grab (pooled)	U1 '88	0.0978 (L)	0.150 (L)	0.0965 (L)	0.0284 (L)	-
	U2 '88	0.123 (L)	0.0673 (L)	0.0893 (L)	0.0254 (L)	-
	U3 '88	0.107 (L)	0.123 (L)	0.0615 (L)	0.0376 (L)	-
	Avg. '88	**0.109 (L)**	**0.113 (L)**	**0.0824 (L)**	**0.0305 (L)**	-
	U3 '96	0.302 (N)	0.0529 (L)	0.0466 (L)	-	0.0227 (L)
	Average P	**0.109 (L)[a]**	**0.0830 (L)**	**0.0645 (L)**	**0.0266(L)[b]**	

[a] Excluding Aug 96 values
[b] DOC values used for missing TDNs

Are the flux confidence intervals evenly distributed about the mean?

In general, N flux confidence intervals ranged between 6% to 35% of the mean (Table 6.8). Flux confidence intervals estimated from percentiles were similar to the ones obtained from the standard deviation (Table 6.8). However, percentile confidence intervals tended to be slightly larger on the upper side of the mean (Fig. 6.8).

Limitations of the randomization exercise

The N flux confidence intervals obtained with the randomization exercise are a reasonable, but probably conservative, estimate of the 'true' magnitude of the error. Only 'measurable' forms of error were included in the analysis and some were only coarsely

approximated. Other sources of error, such as debris temporarily obstructing weirs or tree frogs sunning themselves on stage-recording floats, are less tractable but undoubtedly significant. Regardless of the limitations, the major contribution of this analysis is the demonstration that N flux from the Upland catchments is underestimated when error is not taken into account.

The weakness in the randomization exercise was in the characterization of the sampling error for runoff concentration. Sampling error was designed as a fixed proportion of concentration during the simulations, which may be an oversimplification. Because of the large variability in N concentration during storms in the Upland catchments, it is preferable to collect several samples per storm for the mean to be precise (and unbiased). Ideally, runoff chemistry should be measured using a flow-proportional automated sampler. However, this requires expensive equipment that is not always fool-proof particularly during extreme and highly variable field conditions. To properly estimate sampling error, it is necessary to sample several storms with much more intensity than the 'baseline' sampling scheme.

Covariance of error terms was not included in this study and would probably affect the mean fluxes and the size of confidence intervals (Winter 1981). Covariance will be of concern for species like Total N and DON, which are combinations of several analyses. For example, if NO_3^- and NH_4^+ concentration positively covary during a storm, the error on DON measurement will be larger. In general, the correlation between N species during storms was not strong ($r < \pm 0.5$), and covariance can be neglected as a first approximation (Winter 1981).

Table 6.6. Difference in flux measurements when hydrochemical budgets are estimated with and without error for the Upland catchments. Bias (%) is defined as ((flux+error) – flux)/flux * 100. The average bias for grab sampling and for the autosampler are not quite comparable as 1995 (autosampler only) was the driest year with the most variation in runoff chemistry. A negative bias indicates that fluxes were larger when error was taken into account.

	NO_3^-	NH_4^+	PN	DON	TN
Grab Sampling					
U1 – '94	-31%	-4%	-9%	-1%	-2%
U2 – '94	-6%	-7%	-5%	-3%	-4%
U3 – '94	-12%	-7%	-4%	-3%	-3%
U1 – '96	-11%	-7%	-6%	-1%	-3%
U2 – '96	-6%	-6%	-3%	-2%	-3%
Autosampler					
U1 – '95	-10%	-11%	-11%	-12%	-12%
U2 – '95	-5%	-3%	-3%	-4%	-4%
U3 – '95	-3%	-2%	-2%	-7%	-3%
U3 – '96	-2%	-2%	-5%	-15%	-6%
Average bias	-10%	-5%	-5%	-5%	-4%

Table 6.7. Mean NO_3^- flux and 95% confidence intervals for U1 – 1996 as a function of error parameters in hydrological and runoff concentration measurements. Values in bold are the ones modified (± 50%) relative to the standard run.

Stage Error (mm)	Stage-Discharge Error ($S_{y.x}$)	Analytical Error	Sampling Error (log normal)	NO_3^- flux (kg N ha^{-1} yr^{-1})	NO_3^- Flux SD	NO_3^- flux C.I.
0	**0**	**0**	**0**	0.230		-
3	0.0685	0.0513	0.109	0.251	0.0132	0.227 – 0.279
1.5	0.0685	0.0513	0.109	0.249	0.0106	0.229 – 0.271
4.5	0.0685	0.0513	0.109	0.255	0.0175	0.223 – 0.291
3	**0.1030**	0.0513	0.109	0.253	0.0151	0.225 – 0.283
3	**0.0343**	0.0513	0.109	0.250	0.0121	0.227 – 0.273
3	0.0685	**0.0770**	0.109	0.252	0.0152	0.224 – 0.284
3	0.0685	**0.0257**	0.109	0.251	0.0136	0.226 – 0.279
3	0.0685	0.0513	**0.164**	0.252	0.0143	0.226 – 0.282
3	0.0685	0.0513	**0.055**	0.251	0.0141	0.225 – 0.280

Table 6.8. Comparison of SD and percentile based confidence intervals for the export of NO_3^- and DON from catchments U1 and U3 between 1994-96. 40 kg N ha^{-1} yr^{-1} was applied to U3 in 1995-96. All fluxes are in kg N ha^{-1} yr^{-1}.

	Mean NO_3^- Flux	NO_3^- SD - C.I.	NO_3^- Percentil – C.I.	Mean DON Flux	DON SD – C.I.	DON Percentil –C.I.
U1						
1994	0.0162	0.0131 – 0.0193	0.0135 – 0.0196	0.555	0.491 – 0.619	0.495 – 0.623
1995	0.103	0.0761 – 0.130	0.0785 – 0.131	0.478	0.406 – 0.550	0.412 – 0.554
1996	0.251	0.224 – 0.278	0.226 – 0.278	1.2	1.13 – 1.27	1.13 – 1.28
U3						
1994	0.0224	0.0186 – 0.0262	0.0190 – 0.0261	0.860	0.757 – 0.963	0.758 – 0.968
1995	3.53	2.94 – 4.12	2.94 – 4.16	1.36	0.890 – 1.83	0.930 – 1.85
1996	13.3	11.7 – 14.9	11.8 – 14.9	4.86	4.10 – 5.62	4.16 – 5.67

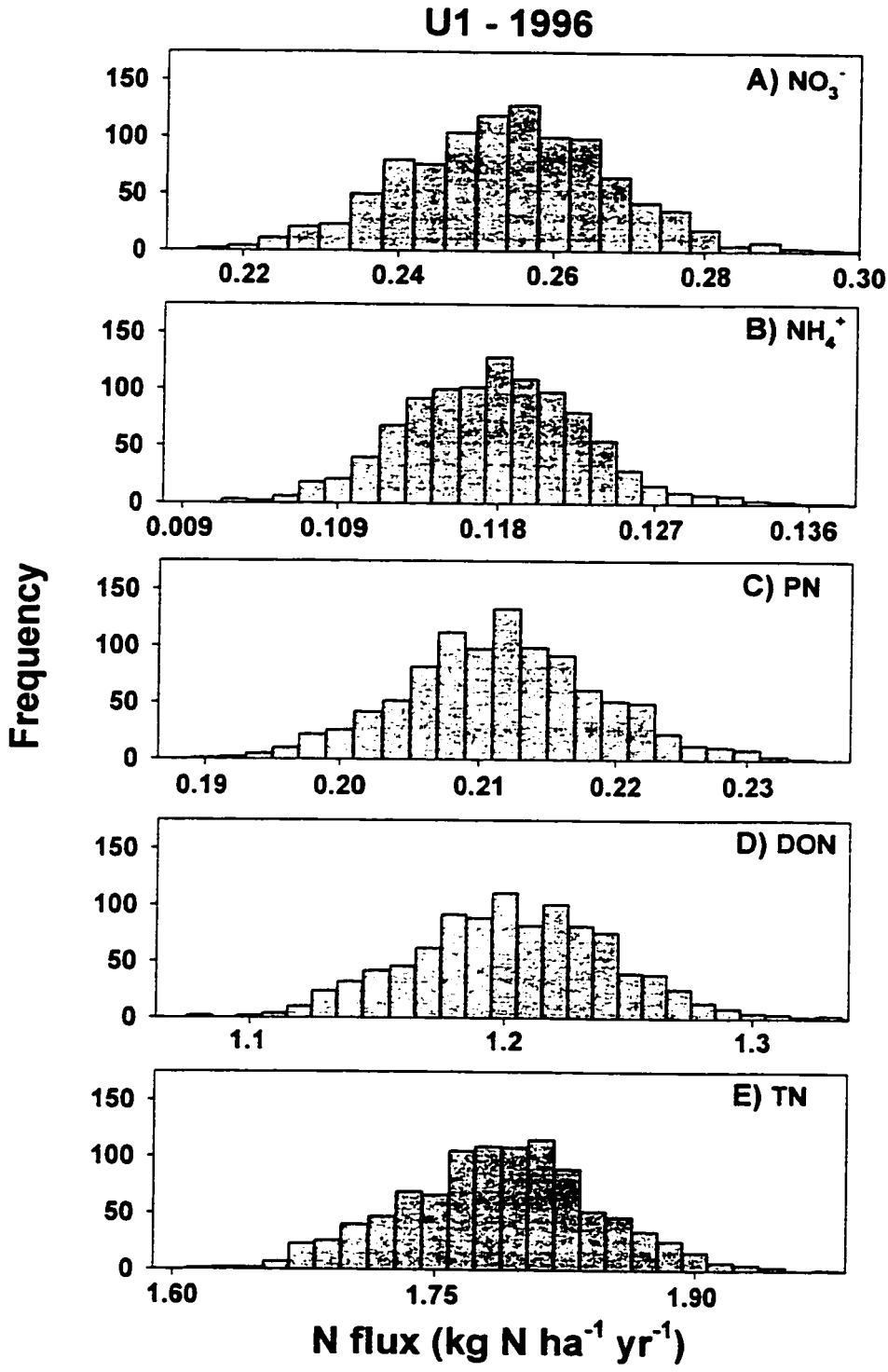

Fig. 6.8. Frequency distribution of 1000 simulated N exports for U1 in 1996. **(A)** NO_3^-; **(B)** NH_4^+; **(C)** PN; **(D)** DON; **(E)** TN.

Conclusion

This analysis demonstrates that an estimation of the error associated with sampling schemes and hydrological measurements must be incorporated in the assessment of the mean and confidence intervals of hydrochemical fluxes from small Shield watersheds. Sampling schemes other than flow-proportional sampling are biased because they tend to underrepresent chemistry at peak flow (Hinton et al. 1997). In addition, when the non-normality of error for runoff and runoff chemistry is not recognized fluxes will be underestimated. The failure to properly assess the error associated with the estimation of hydrochemical budgets can lead to erroneous conclusions about the exports. For example the load of a given element to a lake through runoff may appear not to overlap a certain guideline, when in fact it does. This may have serious implications when studying perturbations within watersheds, where the increased output of nutrients is often used as a measurement of environmental impact.

The nitrogen fluxes and their uncertainty obtained with this analysis were used in a study of the N cycle in small upland boreal Shield catchments. Determining the error associated with the fluxes was used to determine whether differences from year-to-year could be attributed to sampling error or to climatic conditions (Chapter 1). Retention coefficients of N inputs (R_{TN} = {input – output} / input) were used as a response variable during an experimental addition of NO_3^- to one small catchment. One problem with the use of R_{TN} is that when the difference between inputs and outputs is small, it is difficult to determine if the catchment is a net sink or a net source. Knowing the error on runoff fluxes enabled to calculate the error on the R_{TN}s. For example, a R_{TN} of –0.06 was obtained for a small bedrock surface sub-catchment following two years of N addition (Chapter 4), suggesting that the catchment became a net source for N (instead of a sink previously). However, the error on this estimate (±0.13) indicates that it cannot be determined whether the catchment was a net sink or a net source. It could be said, however, that it was either a weak sink or a weak source.

It must be emphasized that the catchments used in this study are 0-order, with dynamic hydrographs, no baseflow, and with a significant variability in N concentration during storms.

High runoff events can occur throughout the year instead of mostly during snowmelt and fall. Thus, using similar methods, it may be possible to obtain more precise flux estimates in higher order systems because groundwater inputs may buffer some of the variability in N concentration associated with surface runoff flowpaths.

Conclusion

The objectives of this thesis were 1) to describe the N cycle in small upland boreal Shield catchments, and 2) to study the processes involved in N retention in this system using an experimental addition of NO_3^- to one small catchment.

It was determined that the upland boreal Shield landscape at the ELA is composed of two distinct communities having contrasting N cycles. The large net N mineralization and net nitrification rates in lichen patches and the export of mineral-N in bedrock surface runoff during dry years indicated that lichen patches are intrinsically N-saturated. In contrast, low plant tissue N content, low net N mineralization rates, the absence of net nitrification, and the efficient retention of mineral-N inputs showed that forest islands were N-limited.

Forest islands and lichen patches reacted oppositely to an increased NO_3^- load. After two years of NO_3^- addition, N was no longer retained on bedrock surfaces. In contrast, during the growing forest islands N retention remained as efficient as in the reference catchments. The different response of soil microorganisms to the NO_3^- addition was a determinant factor in generating the patterns of N retention in each community. In lichen patches net nitrification doubled, further increasing the burden of N retention on plants and lichens. In contrast, forest islands soil microorganisms directly and indirectly contributed to NO_3^- retention. Direct retention occurred when soil microorganisms immobilized NO_3^- during the decomposition of litter inputs with a high C:N. Retention was also mediated indirectly by the net tendency to convert NO_3^- inputs into NH_4^+ during internal cycling. This indirect retention occurred because assimilatory NO_3^- reduction decreased the demand on the recycled NH_4^+ pool, allowing for NH_4^+ to accumulate in the soil instead of NO_3^-. Unlike NO_3^-, NH_4^+ can be retained in catchments by a variety of abiotic immobilization mechanisms and is less likely to be lost in runoff.

Although plants and lichen directly contributed to N retention by taking up some of the added N, plants also indirectly contributed to N retention in forest islands by producing a litter with a high C:N. During early stages of decomposition, microorganisms consuming

conifer litter and coarse woody debris will tend to be N-limited because of the very high C:N of this substrate. In contrast, in lichen patches the litter produced by mosses and lichens has a low C:N (<30) that should not induce N-limitation of decomposers at any stage of decomposition. The maximum potential for N immobilization and the critical C:N ratios (i.e., the ratio at which the balance between N immobilization and mineralization is nil) still need to be determined for the litter and coarse woody debris produced in forest islands.

The results of this study have important implications for the fate of elevated N inputs to acid-sensitive areas of the boreal Shield forest. Bedrock surfaces are intrinsically N-saturated and will not retain an elevated N input even on the short-term. It must be emphasized that under natural conditions bedrock surfaces contain as much N as forest islands and retain N inputs as efficiently during wet years. In addition, the export of NH_4^+ and NO_3^- from bedrock surfaces was more closely related to mineralization and nitrification rates underneath lichen patches than to precipitation inputs. Thus, the mineral-N leaving bedrock surfaces is not simply precipitation inputs quickly flushing through the system – it is derived in part from internal recycling. Although forest islands did not become N-saturated during a short-term NO_3^- addition, the increased load from surrounding bedrock surfaces may accelerate the onset of N saturation on the longer term. This process may repeat itself at larger scales, resulting in N saturation occurring as a cascading effect in the upland boreal Shield landscape.

Although some agricultural influence can be detected in precipitation inputs at the ELA, N deposition is presently relatively low in the central boreal forest in North America. However, the potential for ongoing changes in agricultural practices in the Prairies to increase N deposition to the boreal forest in the future should not be neglected. The European example shows that the long-term development of intensive agriculture can increase N deposition to remote, acid-sensitive areas (UKRGIAN 1994). Because of a strong 'edge effect' in dry N deposition, the transition between the Prairie and boreal ecosystem may be most susceptible to an increased N input in the future.

More could be learned about the boreal N cycle by further understanding the processes leading to the contrasting N cycles in the Upland catchment forest islands and lichen patches. Most of the organisms occurring in this landscape, such as black spruce, the *Cladina* lichens, and the mosses *Polytrichum* and *Pleurozium scheberi*, are widespread throughout the boreal biome. Thus, learning detailed information about their nutrient use and response to perturbation in the Upland catchment environment may also be applicable at the larger scale. The preferred source of N for these organisms (NH_4^+, NO_3^- and DON) and how it is obtained (precipitation vs. recycling) should be determined. When comparing forest islands to lichen patches, the effect on the internal N cycle of the source of organic matter provided to soil microorganisms deserves further attention. Hobbie (1996) suggested that following an eventual climate warming, the internal N cycle in the tundra environment would be more strongly affected by a change in plant composition (and the type of litter produced) than a change in soil temperature per se. Through a similar effect, intensification of forestry practices in the boreal forest may bring strong changes in its internal N cycle. On the long-term, the net effect of wood removal from the boreal forest could be to decrease the supply of coarse woody litter to the forest floor. Coarse woody litter has by far the largest C:N and is the most likely to induce N-limitation of soil microorganisms during decomposition. The effect of forestry practices on the soil internal N cycle may be further amplified if faster-growing tree species are selected for the second growth forest. Faster-growing boreal trees tend to produce a faster decomposing litter with a lower C:N (Flanagan & Van Cleve 1983; Van Cleve et al. 1983; Van Cleve & Yarie 1986), possibly leading to a soil microbial community that would be less N-limited during early stages of litter decomposition. On the other hand, regular biomass removal may slow-down the rate of N accumulation in the ecosystem. In addition, the potential for increased N retention by plant uptake is favored by maintaining the forest in an aggrading state (Aber et al. 1989). In the central boreal forest where forest fires are frequent and N losses during fires important (MacLean et al. 1983), a state of N limitation could be maintained under elevated N deposition because large N pools would be less likely to accumulate.

There will be complex feedback mechanisms in the boreal C and N cycles should increased N deposition, climate change, and the intensification of forestry practices occur

simultaneously (Houghton et al. 1998). Thus, making long-term predictions on the impact of elevated N inputs to the boreal forest is difficult. Although the information derived from the rocky ridge component does not necessarily apply to the whole boreal biome, the study of the N cycle in the ELA Upland catchments has showed a diversity and dynamism hitherto unrecognized for the boreal forest.

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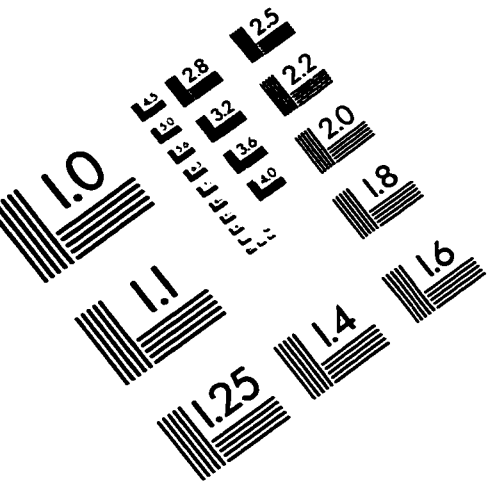
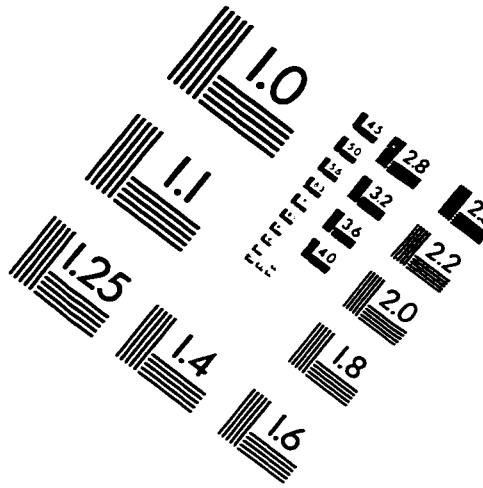
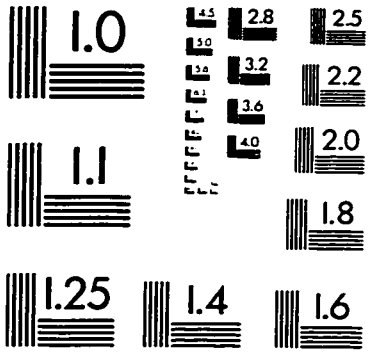
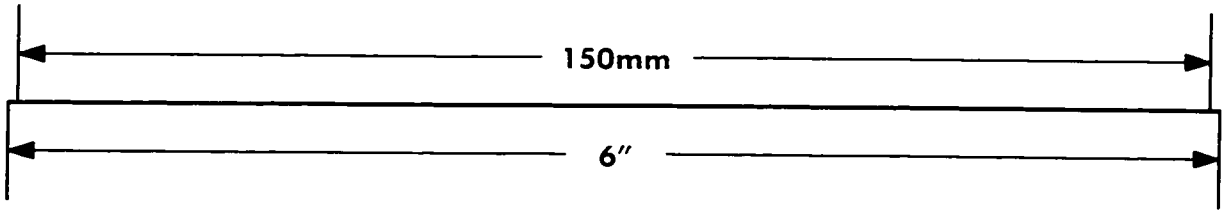
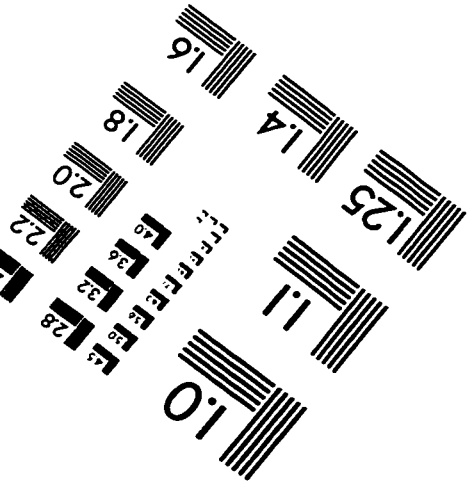
IMAGE EVALUATION TEST TARGET (QA-3)

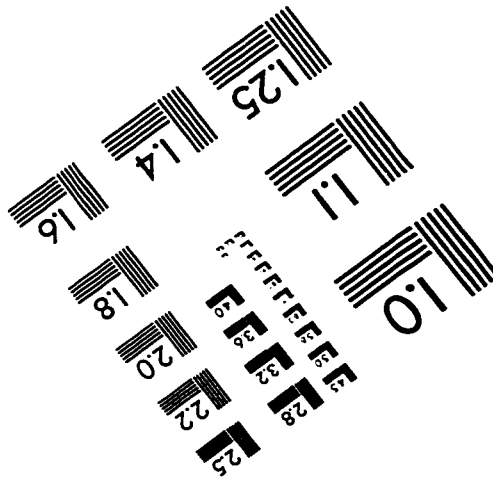












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