Fluxes of dissolved organic and inorganic nitrogen in relation to stand characteristics and latitude in Scots pine and Norway spruce stands in Finland

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We monitored the fluxes of nitrogen (N) compounds in throughfall (TF) and in percolation water (PW) in Scots pine and Norway spruce stands in Finland, and explored their dependence on N bulk deposition (BD) rates and general site and stand characteristics. During 1998–2004, N fluxes in BD, TF, and PW were low and remained relatively constant. Inorganic N was retained in the ecosystem (BD > TF > PW) more effectively in spruce stands, while the fluxes of dissolved organic nitrogen (DON) correspondingly increased. The canopy retention of inorganic N was correlated with the net increase in TF DON. BD DON was relatively constant, while the TF DON and BD deposition of inorganic N increased towards the south. DON accounted for 14% of the BD N, 48% of N in TF in spruce and 31% in pine stands, and 80% of the total N in PW. Stand characteristics (e.g. stand age) affected the TF fluxes of both inorganic N and DON, while only the NH_4-N flux in PW was related to deposition rates.

Introduction

Increased fossil fuel combustion and intensified agriculture have, since the latter half of the 20th century, resulted in a distinct increase in emissions of biologically active nitrogen (N) to the atmosphere (Schopp *et al.* 2003). When deposited on typically N-deficient boreal coniferous ecosystems, these inorganic N compounds have a growth increasing fertilization effect (Viro 1965, Högberg *et al.* 2006). This can, to some extent, mitigate the rise in atmospheric CO_2 concentra-

tions by stimulating the sequestration of carbon in biomass (Townsend *et al.* 1996, Magnani *et al.* 2007). However, excessive N deposition may lead to the detrimental situation of N saturation, in which the excess N is leached from forest ecosystems with serious consequences for surface and ground water quality (Aber *et al.* 1989, Matson *et al.* 2002). Furthermore, even low N inputs are known to result in changes in the composition of the vegetation (Nordin *et al.* 2005, 2006). Knowledge about the quantity and composition of deposited N compounds, and about transfor-

mations in these N compounds during passage through the canopy, understorey vegetation, and uppermost soil layers, is thus of utmost importance for understanding the potential impact of anthropogenic N deposition on the structure and functioning of boreal forest ecosystems.

Emission rates of inorganic N compounds are fairly well known, but there is limited information about the rate, sources and forms of organic N emissions (Holland *et al.* 2005). The main emission sources of NO_x are traffic and energy production, while most of the ammonia (NH_3) emissions originate from agriculture (Anon. 2006a). Internationally ratified protocols on the abatement of emissions of acidifying compounds have resulted in a dramatic reduction in sulphur emissions since their peak in the 1980s, but they have been less successful in the case of acidifying N compounds (Ruoho-Airola *et al.* 2004). During 1998–2004 the mean annual emissions of NO_x and NH_x compounds in Finland were 216 000 000 and 33 000 000 tonnes, respectively (Anon. 2006a). Nitrogen emission sources in Finland and in neighbouring countries are concentrated in the southern part of the country, leading to a clearly decreasing N load with increasing latitude.

Due to its reactivity and large surface area, the coniferous forest canopy effectively intercepts airborne N compounds in wet, dry and gaseous forms (Parker 1983, Ulrich 1983, Bredemeier 1988, Lindberg *et al.* 1989). Dry N deposition is normally assumed to be washed off as the rainwater passes down through the canopy. However, in boreal coniferous forests under low N deposition conditions, much of the N is taken up by the forest canopy through absorption into the needles or utilized by the microflora and mosses/lichens present on the surface of the foliage, leading to the typical reduction in N deposition in throughfall (Ferm and Hultberg 1998). The capture of airborne pollutants by the canopy is primarily a physical process that is influenced by the wind speed and turbulence, aerosol droplet size and canopy surface characteristics, which are related to tree size, density and species (Päivänen 1966, Cronan and Reiners 1983, Lovett and Lindberg 1984). Several studies have shown clear differences in foliar N uptake (Wilson 1992, Janson and Granat

1999) and in the quantity and composition of throughfall deposition between Norway spruce and Scots pine (Hyvärinen 1990, Robertson *et al.* 2000, Lindroos *et al.* 2006). In addition, the N retention capacity has been reported to decrease with increasing tree age (Parker 1983).

The topsoil in coniferous forests acts as a buffer between atmospheric inputs and the underlying ground water; especially the organic layer has been shown to be a long-term sink for N in undisturbed boreal forests (Berg and Dise 2004). However, several factors are involved in soil-water interactions and, together with the N input flux, influence the composition and amount of the output flux of N. While percolating down through the soil profile, the chemical composition of the water is modified by a number of soil processes, including nutrient uptake, weathering, ion exchange, adsorption/desorption, decomposition, mineralization and immobilisation. These biological and chemical soil processes are mainly driven by climatic factors (precipitation, temperature), the physical and chemical characteristics of the organic and inorganic soil horizons, and the type of vegetation cover. Earlier studies have shown that nitrate leaching in forest ecosystems is strongly related to the C/N ratio of the forest floor (e.g. Gundersen *et al.* 1998). Moreover, Seely *et al.* (1998) reported that the N retention capacity of the mineral soil was most likely related to changes in percolation rates and the surface area of soil particles (i.e. soil texture). Many soil processes are pH dependent and, therefore, there are strong grounds to assume that the characteristics of the N output flux would be related to the prevailing pH conditions. Earlier studies in field conditions have, however, generated relatively ambiguous results, making it difficult to draw general conclusions about this relationship (Michalzik & Matzner 1999, Solinger *et al.* 2001).

Most of the N in percolation water is incorporated in organic compounds (Piirainen *et al.* 1998). These compounds are also predominant in the input N fluxes in areas of low N deposition (Fahey *et al.* 1985, Stuanes *et al.* 1995, Currie *et al.* 1996, Campbell *et al.* 2000, Weathers *et al.* 2000). However, most studies on forest N cycling have focused on the fluxes of inorganic N (i.e. NH_4 and NO_3) only, despite the fact that dissolved organic nitrogen (DON) apparently plays

an important role in N cycling especially in background areas (Neff *et al.* 2002). In this study, we focused on the fluxes of both organic (DON) and inorganic nitrogen (NO_3-N and NH_4-N) in boreal forest ecosystems typically dominated by either Scots pine or Norway spruce. The first aim was to quantify the latitudinal and temporal variation in the input and output fluxes in these ecosystems and to compare the N fluxes between the two types of forest stand. Earlier studies indicated that there is a decreasing gradient in N deposition with increasing latitude, while temporal trends were expected to be non-significant. It was hypothesized that the N fluxes in Scots pine and Norway spruce stands differ due to differences in their canopy structure and the site conditions where the two tree species typically grow. Secondly, we also tested whether the flux of N compounds in throughfall and in percolation water could be modelled, using linear regression models, separately for the two types of stand using N deposition rates and general site and stand characteristics as predictors. The modelling exercise was based on the following hypotheses:

1. the throughfall N flux is related to the bulk deposition N flux and the surface area and age of the stand, and
2. the percolation water N flux is related to the pH, the characteristics of the input water flux, N uptake by the tree stand, the N concentration of the organic layer, and climate.

The study was carried out using the empirical data collected on plots belonging to the intensive monitoring programme (EU/Forest Focus and UN-ECE/ICP Forests Level II) in Finland. The majority of the monitoring plots are located in background areas, where the dry deposition of N compounds can be assumed to be minor, and correlated with the N flux measured in bulk deposition.

Materials and methods

Monitoring plot network

The data were collected from eight Scots pine (*Pinus sylvestris*) and eight Norway spruce
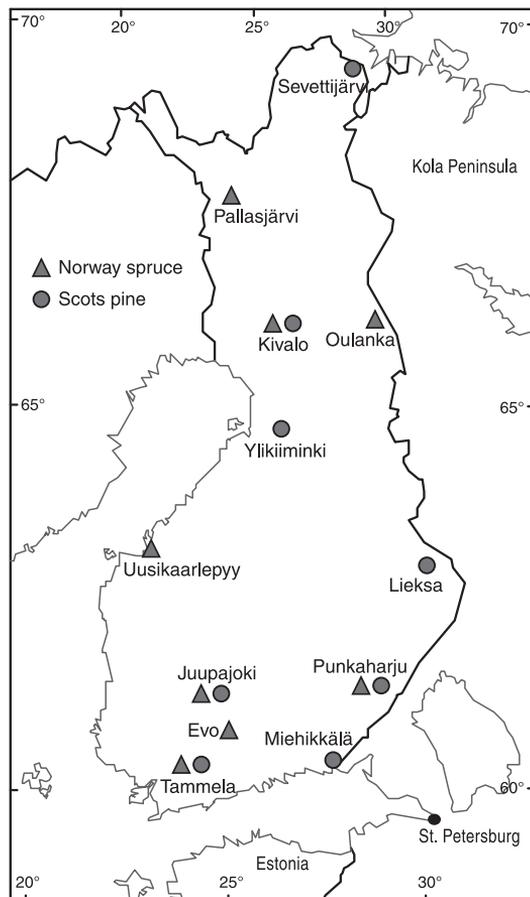
Fig. 1. Location of the Scots pine and Norway spruce plots.

(*Picea abies*) stands during 1998–2004 (Fig. 1 and Table 1). The sites belong to the Finnish network of intensively monitored forest plots (Level II), established as a part of the EU/Forest Focus and UN-ECE/ICP Forests forest condition monitoring programmes (Merilä *et al.* 2007). Of these plots, 13 are located in semi-natural, even-aged stands subjected to conventional forest management, and three (plots 19, 20 and 21, Table 1) in relatively natural, old-growth stands situated in nature conservation areas. The spruce stands are located on herb-rich and moist site types and the pine sites on less fertile dryish and dry sites (Derome *et al.* 2007). The soil texture on the spruce plots is till and on the pine plots sorted glaciofluvial material. The soil type on all the plots is podzol. The clay and silt content is typically higher on the spruce plots. Selected stand,

Table 1. Soil and stand characteristics of the monitoring plots (mean of 1999–2004). Mean diameter is weighted with the basal area. Stem volume is with bark.

Plot number and name	Lat. °N	Soil type[1]	Clay + silt (%)	Organic layer C/N ratio	Stem surface area (m² ha⁻¹)	Stem number (ha⁻¹)	Basal area (m² ha⁻¹)	Stand age (years)	Stem volume (m³ ha⁻¹)	Precipitation[2] (mm a⁻¹)	Growing season length[2] (days)	Effective temperature sum[2] (degree days)
Pine												
1 Sevettijärvi	69	Ferric Podzol	13	42	2437	356	13	200	69	432	106[3]	698[3]
6 Kivalo	66	Carbic Podzol	7	45	5019	1755	21	55	108	622	136	912
9 Ylikiiminki	64	Ferric Podzol	3	44	2425	564	13	90	80	569	156	1125
20 Lieksa	63	Haplic Podzol	13	53	4017	633	28	130	286	617	162[4]	1216[4]
10 Juupajoki	61	Ferric Podzol	3	36	3760	378	18	80	169	636	170	1333
16 Punkaharju	61	Ferric Podzol	3	42	7714	951	29	80	259	564	176	1454
13 Tammela	60	Haplic Podzol	2	33	4667	606	22	60	170	645	177	1367
18 Miehikkälä	60	Ferric Podzol	31	41	3500	422	17	120	149	637	174	1451
Spruce												
3 Pallasjärvi	67	Ferric Podzol	23	47	2273	973	12	140	56	572	133	764
5 Kivalo	66	Ferric Podzol	40	44	4290	1668	21	70	106	619	136	912
21 Oulanka	66	Haplic Podzol	38	47	3400	1515	24	170	142	438	141[4]	931[4]
23 Uusikaarlepyy	63	Cambic Podzol	43	27	7682	965	35	55	295	471	172	1254
11 Juupajoki	61	Dystric Cambisol	44	28	6791	864	33	80	300	636	169	1287
17 Punkaharju	61	Cambic Arenosol	32	28	5757	377	29	70	318	564	176	1454
19 Evo	61	Cambic Podzol	28	27	7036	1287	55	170	659	653	179[4]	1348[4]
12 Tammela	60	Haplic Podzol	42	31	5583	673	27	60	238	639	177	1367

[1] Nomenclature *see* World Reference Base for Soil Resources (1998). [2] mean 1998–2004 (*see* Lindroos *et al.* 2008). [3] year 2006. [4] data from the Finnish Meteorological Institute.

climatic and soil characteristics are presented in Table 1.

Sampling

We collected bulk deposition (BD) and throughfall (TF) deposition at 4-week intervals during winter and spring, and at 2-week intervals (combined in the laboratory to give one sample per 4-week interval) during summer and autumn. Bulk deposition was collected in an open area adjacent to the corresponding forest plot using three precipitation collectors ($\varnothing$ 0.2 m, h = 0.4 m) during the snow-free period, and two snow collectors ($\varnothing$ 0.36 m, h = 1.8 m) during winter. The throughfall samples were collected with 20 precipitation collectors and 6–10 snow collectors located systematically within the stand. The bulk and throughfall deposition samples from the individual samplers were combined and weighed in the field during the snowfree period, and weighed and combined (after first thawing) in the laboratory during the snow period. The design of the monitoring plot is described in detail in Merilä *et al*. (2007). The effect of the tree canopy on the fluxes of N was estimated as the net canopy throughfall (NTF), i.e. TF – BD. This gives only a minimum estimate of the N retained in the canopy because the dry deposition captured by the canopy is not included.

Soil percolation water (PW) was collected from 6 spruce and 8 pine plots (Fig. 1) at 4-week intervals during the snow-free period using five zero tension lysimeters located on each plot at a depth of 40 cm from the ground surface. The zero-tension lysimeters consisted of a plastic funnel ($\varnothing$ 20 cm) and a collection bottle attached to the bottom of the funnel. The lysimeters were installed on the plots in 1995/1996 by first removing an intact soil core ($\varnothing$ 30 cm) using a specially designed auger, and then inserting the lysimeter at a depth of 40 cm. The soil core was then carefully returned to its original position. The bottom of the funnel had a plastic sieve, and the upper part of the funnel was filled with washed quartz sand. The number of spruce plots from which percolation water was collected was six (and not eight as for deposition) because lysimeters could not be installed on plot 19 (Evo) owing to extreme

stoniness of the site. Furthermore, the results for plot 23 (Uusikaarlepyy) were not included in the study because it is located on an acid sulphate soil and therefore the sulphate budget method could not be used to calculate the water flux. The PW samples were weighed in the field, and each sample analysed separately.

Chemical analyses

The deposition and percolation water samples were pre-treated and analysed according to the sub-manuals of the ICP Forests Programme (Anon. 2002, 2006b). The pH was measured in unfiltered samples. Prior to the chemical analyses, the samples were filtered through membrane filters (0.45 μm, Whatman, ME 25, mixed cellulose ester) under positive pressure by means of a peristaltic pump. Total nitrogen (N_{tot}) was determined, after digestion of the samples in closed vessels in a mixture of $K_2(SO_4)_2$/NaOH in an autoclave, by flow injection analysis (FIA). NH_4^+, NO_3^- and SO_4^{2-} were determined by ion chromatography (IC). Dissolved organic nitrogen (DON), was calculated as N_{tot} – (NH_4-N + NO_3-N).

Flux calculations

The 4-week deposition fluxes of NH_4-N, NO_3-N, N_{tot} and DON were calculated by multiplying the amount of precipitation on each sampling occasion by the corresponding (volume weighted) concentration, and the annual deposition fluxes were determined as the sum of the 4-week deposition fluxes. As the calculation of DON includes three sources of analytical uncertainties (three different analyses) and N deposition in Finland is low, some negative values were obtained for the DON concentration. These values were substituted by zero when calculating the DON fluxes.

We calculated the water fluxes using the same technique as e.g. Nilsson *et al*. (1998) in a study on N retention in coniferous forest ecosystems in Sweden. In this approach, it is assumed that the annual amount of SO_4 deposited on the forest floor in stand throughfall is equal to the amount of SO_4 leached from the surface layers in perco-
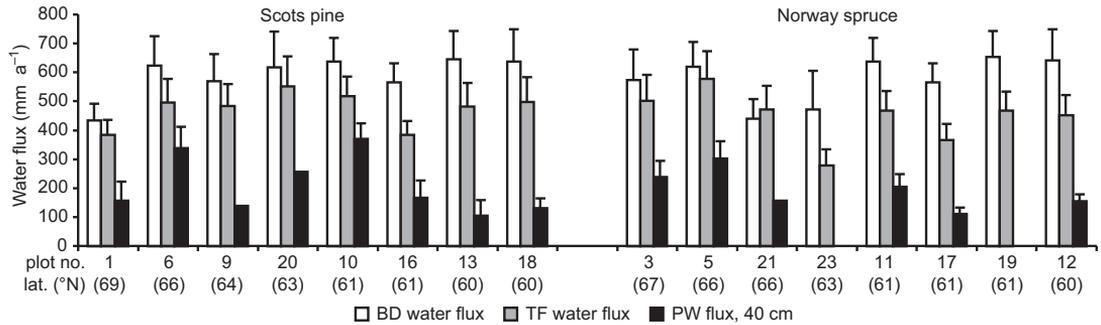
Fig. 2. Annual water fluxes (mean ± SD, 1998–2004) for the Scots pine and Norway spruce plots. The plots are arranged from left to right running from northern to southern Finland (latitude of the plot below the plot number). BD = bulk deposition, TF = stand throughfall, PW flux = estimated water flux at the depth of 40 cm.

lation water. It is possible, using this mass balance assumption, to calculate the annual water output flux (mm a^{-1}) in percolation water on the basis of the annual input of water (throughfall, mm a^{-1}), the mean annual SO_4 concentration (mg l^{-1}) in throughfall, and the mean annual SO_4 concentration (mg l^{-1}) in percolation water.

We used the SO_4 budget method to calculate the water fluxes in percolation water (mm a^{-1}) instead of the actual volume of water collected by the zero-tension lysimeters for two main reasons: (1) only 5 replicate lysimeters (total surface area 0.16 m^2) can, under no circumstances, be considered to give a reliable estimate of the water flux on a 30 × 30 m plot, and (2) during snowmelt in the spring the amount of percolation water is normally considerably greater than the amount of water that can be stored in the collection bottle located below the lysimeter. As a result, the water flux in the spring will clearly be underestimated.

The fluxes of NH_4-N, NO_3-N, total N and DON in PW were determined by multiplying the mean (arithmetical) annual concentration of these variables by the estimated annual PW flux (*see* Fig. 2 for measured BD and TF fluxes and estimated PW fluxes; *see* also Lindroos *et al.* 2008).

Stand characteristics

Tree species, diameter (at 1.3 m above ground level), tree height and the crown length were recorded on every tree with a breast height diameter of at least 4.5 cm. These data enabled accurate estimation of the individual tree vol-

umes and basal areas, as well as the respective stand level characteristics (Table 1). The KPL programme (Heinonen 1994) was used for calculating the characteristics of individual trees and for transforming them into stand level characteristics (Table 1). Taper curve functions by Laasasenaho (1982) were used for estimating the stem volumes of individual trees.

Needle biomass estimates for individual trees were calculated using the functions of Marklund (1987, 1988). These functions describe the biomass components (living and dead branches, stem wood, bark and needles) as a function of tree species, diameter, tree height and crown length. The needle mass function for Scots pine also includes the latitudinal coordinate. Stem surface area was defined as the surface area of the above-ground tree stem. The taper curve of each stem was determined using functions by Laasasenaho (1982), and then dividing each stem into 10-cm-long sections. The surface area for each section was then calculated using cylindrical approximation.

Fine root biomass

Twelve root cores were taken from each stand with a cylindrical soil auger (diameter 40 mm). The cores were divided into sections consisting of the organic layer, and the 0–5, 5–10, 10–20 and 20–30 cm mineral soil layers. Both understorey and tree roots were separated from the soil by washing and sorted into living and dead roots (Persson 1983). Roots smaller than 2 mm were regarded as fine roots (Persson 1983, Vogt *et al.*

1983) including mycorrhizal root tips, and roots with a diameter of 2–5 mm were classified as small roots. The samples were dried at 70 °C for 48 h and weighed. The sampling and analysis of the fine roots is described in detail in Helmisaari *et al.* (2007).

Statistical analysis

Trends in N deposition were tested for each plot separately by calculating linear regressions between the years and deposition fluxes.

To explore the relationship between N deposition and site characteristics and to study whether we could construct the regression models to predict N fluxes in TF, we calculated Spearman rank correlation coefficients (r_s) between the N fluxes in TF, N fluxes in BD and the stand characteristics given in Table 1. As the temperature and precipitation, as well as the length of the growing season, all decrease towards the north, the effects of climatic variables were studied using latitude as the predictor. The same method was used to identify relationships and to construct the multiple regression models for predicting the fluxes of NO_3-N, NH_4-N and DON in PW using the BD and TF N rates of N_{tot}, DON, NH_4-N and NO_3-N, together with the C/N ratio of the organic layer, fine root biomass, pH of PW and TF and latitude as predictors.

In order to model N in throughfall and to study the relationships between BD and TF and stand characteristics, as well as N in PW and soil properties, pH and latitude, we computed multiple linear regression models using SAS (ver. 9.1.3) procedure PROG REG with the "best possible subsets" method to find the best fitting model with one, two or three of the best predictive variables. The highest R^2_{adj} value was used as the selection criterion. These models also had the lowest Akaikes Information Criteria (AIC), which tests the difference between a given model and the "true" underlying model (Akaike 1973). In addition to sample size, this information criterion estimates the effects of the number of variables added to the model. Models with more than three predictors were not reported as they were not feasible owing to the small number of data points.

Results

A number of plots in southern Finland had significant ($p < 0.05$) decreasing trends in the nitrogen deposition fluxes (BD and TF) (Fig. 3): No. 11 (NO_3-N_{BD}), No. 12 (NO_3-N_{TF}), No. 13 (NO_3-N_{TF}), and No. 18 (NO_3-N_{BD}, N_{totBD}, NH_4-N_{TF} and N_{totTF}) (data not shown).

The bulk (BD) and throughfall (TF) mean annual depositions of ammonium (NH_4-N) and total nitrogen (N_{tot}) increased southwards for both tree species (Fig. 3), but of nitrate (NO_3-N) only on the pine plots. DON in TF increased with decreasing latitude on both the spruce and pine plots, while DON in BD was not related to latitude (Fig. 3). The DON:N_{tot} ratio in TF decreased towards the south only on the spruce plots ($n = 8$, $r_s = 0.84$, $p < 0.01$).

The inorganic N TF fluxes were generally lower than those of BD, and on the spruce plots they were 55% lower than on the pine plots (Table 2 and Fig. 3). Plot No. 23 on the western coast was an exception: the deposition rates of N on this plot were relatively high — as compared with those on the other plots — due to ammonia emissions from local fur farms. TF deposition of inorganic N exceeded the BD deposition on this plot (Fig. 3a and b), and it was therefore excluded when calculating the mean annual deposition values and correlations on the spruce plots. In contrast to the situation for inorganic N, the DON flux increased by 116%, on the average, as precipitation passed down through the canopy (Table 2 and Fig. 3c).

The effect of the tree canopy on the fluxes of N was estimated by calculating net canopy throughfall: NTF = TF – BD. This gives only a minimum estimate of the N retained in the canopy because it does not include all of the dry deposition retained in the canopy. The spruce canopies retained 25% more NH_4-N and 45% more NO_3-N than the pine canopies, when plot No. 23 was excluded (Table 2). The canopy uptake of N when calculated as the relative net throughfall (NTF_r = (TF – BD)/BD × 100%) of both NH_4-N and NO_3-N was higher on the spruce plots than on the pine plots (spruce: 61% ± 3% and 42% ± 4%, pine: 43% ± 4% and 23% ± 4% for NH_4-N and NO_3-N, respectively).

There was a significant negative correlation between net canopy throughfall of inorganic
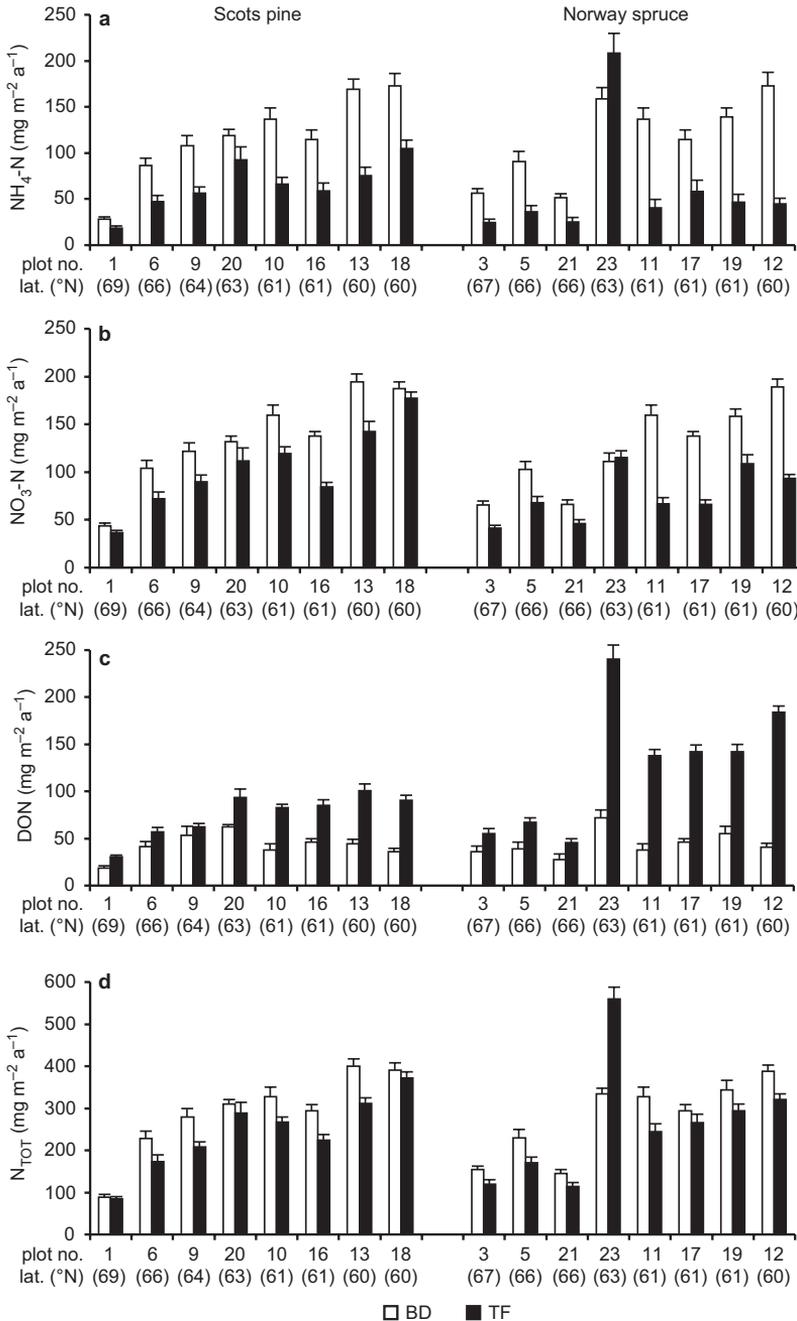
Fig. 3. Stand mean (+ SD) (**a**) ammonium, (**b**) nitrate, (**c**) dissolved organic nitrogen, (**d**) and total nitrogen deposition in bulk deposition (BD) and in stand throughfall (TF) during 1998–2004 on eight Scots pine and eight Norway spruce plots.

N (NH_4-N_{NTF} + NO_3-N_{NTF}) and the net canopy throughfall of DON (Fig. 4). However, some of the N was retained in the canopy because the N_{tot} in precipitation decreased on passing down through the forest canopy (Fig. 3d and Table 2). The proportion of DON in the total TF N flux was higher on the spruce plots (48% ± 3%) than on the pine plots (32% ± 1%).

In general, the net canopy throughfall of inorganic N decreased and of NTF DON increased towards the south with increasing inorganic N deposition (Table 3). An exception to this was NO_3-N_{NTF}, which was not related to inorganic N in BD on the pine plots. DON in NTF on the spruce plots and the canopy uptake of NH_4-N increased with increasing stem surface area

(Table 3). Needle biomass, stem number or stem volume were not correlated with canopy N uptake or DON_{NTF} on either the spruce or pine plots. On the pine plots, NO_3-N_{NTF} (Table 3) and N_{totNTF} ($n = 8, r_s = -0.861, p < 0.01$) showed a significant negative correlation with stand age. The NTF_r of NH_4-N or NO_3-N were not related to latitude or the N deposition rate, but on the pine plots they decreased with increasing stand age (NO_3-N_{NTFr}, $n = 8, r_s = -0.766, p < 0.01$; NH_4-N_{NTFr}, $n = 8, r_s = -0.766, p < 0.01$).

The PW fluxes of all forms of N, except of NO_3-N, were higher on the pine plots than on the spruce plots (Table 2 and Fig. 5a). The main form of N in percolation water was DON, representing, on the average, 82% ± 5% of the N_{tot} flux on the pine plots and 80% ± 7% on the spruce plots. The mean annual fluxes of inorganic N in PW were very small (Table 2 and Fig. 5b).

Thus the fluxes of inorganic N decreased (BD > TF > PW), while those of DON increased (BD < TF < PW), as water passed down through the forest ecosystem. Overall, the N budget (BD – PW at 40 cm depth) was positive and increased towards the south (Fig. 6). However, the mean annual N budget was negative on the northern pine plots, Nos. 1 and 6.

Predicting nitrogen fluxes in throughfall and in percolation water

On the pine plots, the most predictive single variable for both $NH4$-N_{TF} and DON_{TF} was N_{totBD}
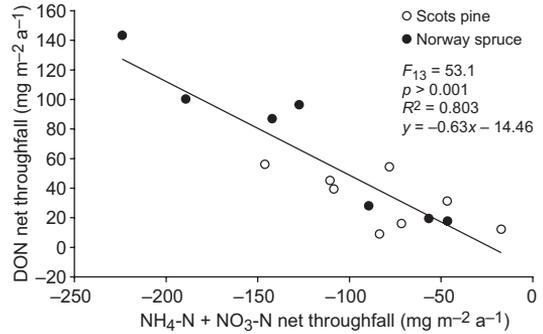
Fig. 4. Correlation between the net inorganic N (NH_4-N and NO_3-N) and dissolved organic N (DON) fluxes in throughfall.

(Table 4, model 1_{NH4-N} and model 4_{DON}). NH_4-N_{BD} and needle biomass resulted in an even higher R^2_{adj} for NH_4-N_{TF} (Table 4, model 2_{NH4-N}) The second model for the DON_{TF} deposition flux included stem volume and N_{totBD} (Table 4, model 5_{DON}), and the third, which included diameter and basal area of the stands, had an even higher coefficient of determination (R^2_{adj}) (Table 4, model 6_{DON}). Linear regression model 3_{NO3-N}, which included NO_3-N_{BD} and stand age, best predicted NO_3-N in TF.

On the spruce plots N_{totBD} predicted NO_3-N relatively well (Table 4, model 7_{NO3-N}), and adding stem number to the model further increased its fit (Table 4, model 8_{NO3-N}). The best single predictor for DON_{TF} on the spruce plots was latitude (Table 4, model 9_{DON}), but the best model included NH_4-N_{BD} with tree diameter (Table 4, model 10_{DON}).

Table 2. Means (± SD) of ammonium (NH_4-N), nitrate (NO_3-N), dissolved organic nitrogen (DON), and total nitrogen (N_{tot}) fluxes in bulk deposition (BD), canopy throughfall (TF), net canopy throughfall (TF – BD) and percolation water (PW) (mg m⁻² a⁻¹) in Scots pine ($n = 8$) and Norway spruce ($n = 7$ [plot no. 23 excluded] except in PW $n = 6$) stands for the period of 1998–2004.

	NH_4-N (mg m⁻² a⁻¹)	NO_3-N (mg m⁻² a⁻¹)	DON (mg m⁻² a⁻¹)	N_{tot} (mg m⁻² a⁻¹)
Pine				
BD	116 ± 50	134 ± 48	42 ± 13	288 ± 99
TF	64 ± 27	104 ± 43	75 ± 23	239 ± 89
TF – BD	–52 ± 27	–31 ± 17	32 ± 18	–49 ± 30
PW	22 ± 9	4 ± 2	114 ± 52	140 ± 53
Spruce				
BD	114 ± 45	123 ± 4	44 ± 14	275 ± 91
TF	39 ± 12	69 ± 24	110 ± 53	217 ± 84
TF – BD	–69 ± 37	–56 ± 31	70 ± 30	–50 ± 20
PW	10 ± 2	3 ± 2	57 ± 37	70 ± 38

Table 3. Spearman rank correlation coefficients between site and stand characteristics, bulk nitrogen (N) deposition, throughfall N, uptake of inorganic N and release of organic N on the Scots pine ($n = 8$) and Norway spruce ($n = 7$, plot No. 23 excluded) plots. $* p < 0.05$, $** p < 0.01$.

	NH$_4$-N$_{TF}$ (mg m^{-2} a^{-1})	NO$_3$-N$_{TF}$ (mg m^{-2} a^{-1})	N$_{totTF}$ (mg m^{-2} a^{-1})	DON$_{TF}$ (mg m^{-2} a^{-1})	NH$_4$-N$_{NTF}$ (mg m^{-2} a^{-1})	NO$_3$-N$_{NTF}$ (mg m^{-2} a^{-1})	DON$_{NTF}$ (mg m^{-2} a^{-1})	Lat. (°N)	Precipitation (mm a^{-1})
Pine									
Lat. (°N)	–0.831*	–0.892**	–0.916**	–0.831*	0.868**		–0.916**		
Precipitation (mm a^{-1})		0.833**	0.762*		–0.762*		0.786*	–0.735*	
Needle biomass (kg ha^{-1})	–0.786*	–0.714*							
Stem area (m^2 ha^{-1})				0.762*		–0.714*			
Stand age (years)						–0.802*			
NH$_4$-N$_{BD}$ (mg m^2 a^{-1})	0.928**	0.976**	0.976**	0.833**	–0.786*		0.881**	–0.952**	0.810*
NO$_3$-N$_{BD}$ (mg m^2 a^{-1})	0.810*	0.905**	0.905**	0.833**	–0.905**		0.929**	–0.988**	0.786*
N$_{totBD}$ (mg m^2 a^{-1})	0.881**	0.976**	0.952**	0.881**	–0.833**		0.905**	–0.952**	0.833**
Spruce									
Lat. (°N)	–0.805*		–0.898**	–0.898**	0.786*	0.786*			
Precipitation (mm a^{-1})	0.786*				–0.786*				
Stem area (m^2 ha^{-1})		0.857*							
Stem volume (m^3 ha^{-1})	0.893**								
Stem number (ha^{-1})				–0.786*					
Basal area (m^2 ha^{-1})							0.786*		
Diameter (cm)	0.893**								
NH$_4$-N$_{BD}$ (mg m^2 a^{-1})		0.833**	0.976**	0.881**	–0.964**	–0.893**	0.893**	–0.898**	0.857**
NO$_3$-N$_{BD}$ (mg m^2 a^{-1})		0.905**	0.952**		–0.964**	–0.929**	0.929**	–0.954**	
DON$_{BD}$ (mg m^2 a^{-1})	0.893**								
N$_{totBD}$ (mg m^2 a^{-1})					–0.964**	–0.893**	0.893*	–0.898**	0.857**

BD = bulk deposition, TF = throughfall, NTF = TF – BD, DON = dissolved organic nitrogen, N$_{tot}$ = total nitrogen.
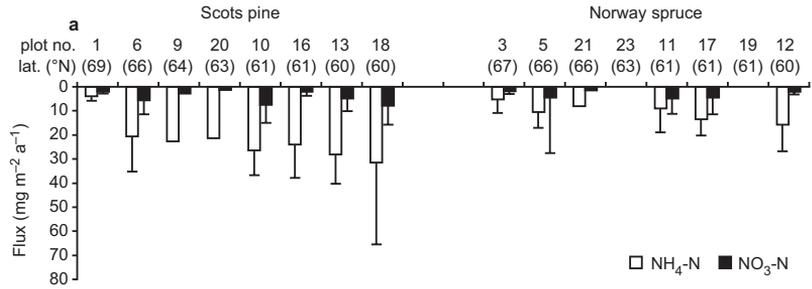
Fig. 5. The mean (+ SD) annual inorganic nitrogen (NH_4-N and NO_3-N) fluxes (**a**) and total (N_{tot}) and dissolved organic (DON) nitrogen fluxes (**b**) in percolation water during 1998–2004 on eight Scots pine and six Norway spruce plots.
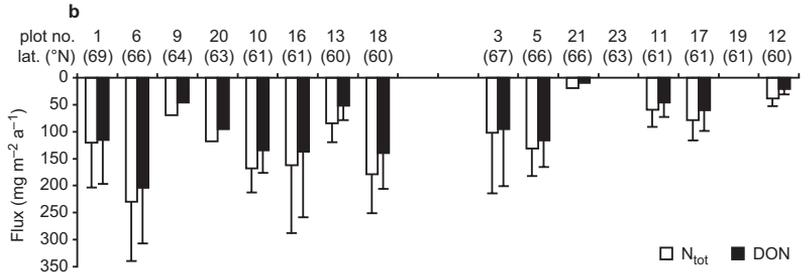
Fig. 6. The mean (± SD) annual net output flux of nitrogen (bulk deposition flux – percolation water flux at depth of 40 cm) on eight Scots pine and six Norway spruce plots during 1998–2004.
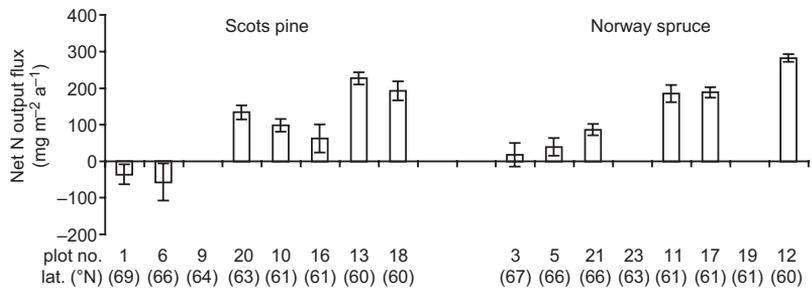
The fluxes of DON in percolation water were not correlated with any of the variables tested (NO_3-N in BD and TF, amount of precipitation, NH_4-N, N_{tot} or DON, pH in TF and PW, C/N ratio in the organic layer, latitude and fine root biomass). Because the NO_3-N fluxes were only correlated with the amount of BD precipitation ($n = 8$, $r_s = 0.714$, $p < 0.05$), we could not construct a regression model to predict the leaching of DON or NO_3-N.

The inorganic N fluxes in PW on the pine plots were more strongly related to NH_4-N and NO_3-N in BD than the corresponding values in TF (Table 5), and on the spruce plots the NH_4-N in PW correlated only with the pH of TF ($n = 8$, $r_s = –0.893$, $p < 0.01$). The best predictor on the pine plots for the NH_4-N flux in PW was N_{tot} in BD (Table 6, model $1_{NH4-N PW}$), but adding the water flux at 40 cm depth (Table 6, model $2_{NH4-N PW}$) improved the model. A good model for

predicting the output of NH_4-N at 40 cm depth was also obtained using only latitude and precipitation as predictors (Table 6, model $3_{NH4-N PW}$) or alternatively fine root biomass with latitude (Table 6, model $4_{NH4-N PW}$).

On the spruce plots the best model for predicting NH_4-N flux in PW included latitude and fine root biomass as predictors (Table 6, model $5_{NH4-N PW}$), and the other significant model the pH of TF and the C/N ratio (Table 6, model $6_{NH4-N PW}$).

Discussion

The mean total N deposition in bulk deposition on the 16 plots was 280 mg m^{-2} a^{-1}, which is very low compared to mean deposition values in Central Europe. The fluxes were within the range reported in earlier studies in Finland (Ukonmaanaho and Starr 2002). Decreasing trends in

Table 4. Selected multiple regression models for estimating throughfall nitrogen fluxes (mg m⁻² a⁻¹) as ammonium (NH_4-N), nitrate (NO_3-N) and dissolved organic nitrogen (DON) on the Norway spruce ($n = 7$) and Scots pine ($n = 8$) plots.

Model	Constant	N_{totBD} (mg m² a⁻¹)	NH_4-N_{BD} (mg m² a⁻¹)	NO_3-N_{BD} (mg m² a⁻¹)	Volume (m³ ha⁻¹)	Age (years)	Lat. (°N)	Stems (ha⁻¹)	dbh (cm)	b_a (m² ha⁻¹)	Needle biomass (kg ha⁻¹)	SE_{est}	R^2_{adj}	p
Pine														
1 $_{NH4-N}$	–4.321	0.238										14.2	0.724	0.005
2 $_{NH4-N}$	60.50		0.340								–0.011	13.0	0.767	0.011
3 $_{NO3-N}$	65.05			1.021		0.307						12.3	0.921	0.001
4 $_{DON}$	10.43	0.233										8.7	0.864	0.001
5 $_{DON}$	8.59	0.189			0.102							5.0	0.954	< 0.001
6 $_{DON}$	–22.44	0.940							0.185	0.922		1.0	0.998	< 0.001
Spruce														
7 $_{NO3-N}$	11.51	0.217										13.6	0.678	0.001
8 $_{NO3-N}$	0.587	0.399										17.3	0.843	0.004
9 $_{DON}$	1200.18						–17.27	–0.017				13.6	0.936	< 0.001
10 $_{DON}$	–47.156		1.003						0.997			10.8	0.973	0.001

N_{tot} = total N, BD = bulk deposition, Volume = stem volume, Age = stand age, Stems = number of stems, dbh = diameter at breast height, b_a = basal area.

N deposition were found on a number of plots during 1998–2007, probably due to the slight decreasing trend in nitrogen emissions during the study period (Ruoho-Airola *et al*. 2004). These trends occurred on the plots in the south, where the reductions in emission rates have also been more pronounced than in the north. We also found a clear increasing gradient in inorganic N in bulk deposition on all the plots, as well as in throughfall N on the pine plots towards the south, where the emissions and concentrations of anthropogenic N in deposition are also higher (Ruoho-Airola *et al*. 2004). However, the DON rates in bulk deposition were relatively constant throughout the country.

Inorganic N fluxes in throughfall were generally 41% lower (range 19%–64%) than the fluxes in bulk deposition. The amount of N in throughfall represents a balance between leaching, canopy uptake and the entrapment of dry deposition (Parker 1983). In low N deposition areas the tree canopies retain more N from the total (wet + dry) deposition than they capture as dry deposition, due to uptake by epiphytic lichens, microbial immobilisation within the canopy, and N sorption into the foliage and assimilation by the tree leaves and stems (Garten *et al*. 1998). The only plot where N deposition exceeded N uptake by the trees (i.e. N in TF > N in BD) was No. 23, which had N deposition levels corresponding to those in central Europe

Table 5. Significant Spearman correlation coefficients between annual ammonium (NH_4-N) flux in percolation water (PW) and various soil characteristics, precipitation and nitrogen deposition on eight Scots pine plots. TF = throughfall, C/N = C/N ratio in the organic layer, BD = bulk deposition, N_{tot} = total nitrogen; * $p < 0.05$, ** $p < 0.01$.

	NH_4-N_{PW} (mg m² a⁻¹)
Latitude (°)	−0.964**
Bulk precipitation (mm a⁻¹)	0.738*
pH_{TF}	−1.000**
C/N	−0.762*
NH_4-N_{BD} (mg m² a⁻¹)	0.929**
NO_3-N_{BD} (mg m² a⁻¹)	0.952**
N_{totBD} (mg m² a⁻¹)	0.905**
NH_4-N_{TF} (mg m² a⁻¹)	0.762*
NO_3-N_{TF} (mg m² a⁻¹)	0.905**
N_{totTF} (mg m² a⁻¹)	0.857**

Table 6. Selected regression models for estimating ammonium (NH_4-N) fluxes (mg m² a⁻¹) in percolation water (PW) on Scots pine (n = 8) and Norway spruce (n = 6) plots.

Model	Constant	N_{totBD} (mg m² a⁻¹)	Water flux (mm a⁻¹)	Lat. (°N)	pH_{TF}	Precipitation (mm a⁻¹)	C/N	Fine root biomass (kg ha⁻¹)	$SE_{est.}$	R^2_{adj}	p
Pine											
1 NH_4-N PW	−1.107	0.081							2.5	0.908	< 0.001
2 NH_4-N PW	−5.953	0.085	0.23						2.3	0.925	0.001
3 NH_4-N PW	80.26			−1.446		0.056			2.3	0.947	0.001
4 NH_4-N PW	205.25			−3.064				0.041	1.6	0.964	< 0.001
Spruce											
5 NH_4-N PW	74.47			−1.178				0.039	1.6	0.971	0.026
6 NH_4-N PW	175.39				−32.537		−0.184		1.5	0.838	0.030

N_{tot} = total N, BD = bulk deposition, Water flux = Soil water flux at 40 cm depth, TF = throughfall, C/N = C/N ratio in the organic layer.

(Lorentz *et al.* 2006). As we did not estimate the dry deposition captured by the canopy, the real canopy N uptake on these plots (dry deposition + wet deposition – TF) is therefore higher than the difference between bulk deposition and throughfall. According to Tuovinen *et al.* (1990), about 35% of inorganic N is deposited as dry deposition in the open area in Finland, but the deposition rates are probably very different under tree canopies (Hyvärinen 1990).

DON represented 15% ± 1% of total N bulk deposition and 39% ± 1% of N in throughfall. The mean annual DON fluxes in throughfall were, on the average, 150% ± 36% higher than in bulk deposition and increased towards the south, although no latitudinal trends were found for bulk deposition DON. This is probably due to the higher temperatures and longer growing season (Starr and Ukonmaanaho 2004), as well as to the higher inorganic N deposition in the southern parts of the country. The increase in DON in throughfall could be caused by either wash off of dry deposited DON or the transformation of inorganic N into DON by microbiological processes in the tree canopy. The net DON flux from the canopy was highly correlated with the retention of inorganic N by the canopy. Ferm and Hultberg (1999) also found strong correlation between the dry deposition of NH_3 + particle NH_4^+ and organic N in net canopy throughfall, indicating that inorganic N, consumed by processes in the canopy, will sooner or later appear as organic N in throughfall. This emphasises the importance of determining N_{tot} when assessing the N input to the forest floor.

The values obtained for the N output fluxes in percolation water are strongly affected by the method used in calculating the water fluxes. In this study we used the sulphate budget method for estimating the water flux. Chloride, being a conservative anion, is normally used (instead of SO_4) in this kind of mass balance, but this was not possible on our plots because the Cl concentrations were extremely low and there was no logical increase in Cl concentrations with increasing depth. Nilsson *et al.* (1998) calculated water fluxes using both the Cl and SO_4 mass balance methods, and found that both methods gave comparable results and were strongly inter-correlated. The water fluxes on the plots are reported

and discussed in more detail in Lindroos *et al.* (2008) in this volume.

The N fluxes in percolation water on the plots were very low as compared with mean values for the whole of Europe (Lorentz *et al.* 2006), and there was no clearly increasing or decreasing trend in N fluxes in percolation water during 1998–2004. This indicates that the N retention capacity of the soil was not exceeded. The dominant form of N in the percolation water flux was DON, ranging from 8.85 to 203.2 mg m^{-2} a^{-1} and accounting for 49% to 95% of the N_{tot} in percolation water. The percolation water N flux consisted of 77% ± 4% of DON at 40 cm depth, which is very close to the value of 74% reported earlier by Piirainen *et al.* (2002) for a mature spruce forest in eastern Finland. Thus, the amount of N leaving the ecosystem in the percolation water will be greatly underestimated if the output flux of organic N is not measured.

The N fluxes decreased as precipitation passed down through the canopy and soil to a depth of 40 cm. The composition of total N also changed as inorganic N was retained as it passed through the ecosystem (BD > TF > PW), and the amount of DON correspondingly increased (BD < TF < PW). The minimum retention of N (BD – PW, dry deposition not included) indicated that, on the average, 170 mg m^{-2} a^{-1} was retained in the forest ecosystems. Although soil acidification and nitrate leaching into the ground water are not a major concern in Finland, N is slowly accumulating in the forest ecosystems in southern Finland. The anthropogenic N input has been suggested as one of the reasons for the increased forest growth observed in recent decades (Spiecker *et al.* 1996), and chronic N accumulation in previously N-deficient forest ecosystems may lead to changes in the composition of the field layer communities (Nordin *et al.* 2005), where the *Vaccinium*-dominated understorey vegetation is gradually replaced by *Deschampsia*.

Interestingly, the net output (BD – PW) of N on some of the northern plots was negative, indicating that N is being lost from the ecosystems. This is partly due to the fact that BD only provides a minimum estimate of the N input to forest ecosystem because dry deposition captured by the canopy is not included. Also more

than half of the annual precipitation in the north occurs as snowfall, and the peaks in the water flux are more pronounced during snowmelt. This may lead to a situation where the N cycle in the north is open and a high proportion of the N is lost during outflow peaks before the plants are able to assimilate it (Sah *et al*. 2006). Furthermore, our N input did not include mineralization or the assimilation of N by symbiosis between cyanobacteria and bryophytes, of which a *Pleurozium schreberi* carpet alone can supply as much as 210 mg N m^{-2} a^{-1} in boreal forest ecosystems (DeLuca *et al*. 2002). The major part of the annual N requirement of forest ecosystems is supplied by recycling. Litterfall, which is a part of the N recycling flux in forest ecosystems, is the major supply of N to the forest floor; on these plots it ranged from 640 to 2370 mg N m^{-2} a^{-1} on the pine plots, and from 490 to 5850 mg N m^{-2} a^{-1} on the spruce plots (Ukonmaanaho *et al*. 2008). The N requirement of conifers has been proposed to be 3000–7000 mg m^{-2} a^{-1}. Our results suggests that bulk deposition alone, including DON, supplies about 3%–10% of the total N requirements of coniferous forests, which is relatively well supported by the studies of Helmisaari (1995) (10%) and Piirainen *et al*. (1998) (3%–8%).

Because the samples were collected at 2- to 4-week periods, there is a possibility of N transformations (e.g. microbial conversion of NH_4^+ to NO_3^-) in the rainwater and percolation water samples during storage in the field prior to sampling. However, these transformations were minimised by the special design of the collectors. The rainwater in the precipitation collectors was stored in the dark in the base of the collectors, located at a depth of 50 cm below the ground surface, and the percolation water in the zero-tension lysimeters was stored in the bottom of the lysimeters in the dark at a depth of 100 cm. The integrity of the NO_3-N and NH_4-N concentrations in the rainwater samples was checked by comparing the annual bulk deposition (open field) values with those reported by the Finnish Meteorological Institute (FMI), based on the daily collection of samples. The annual deposition values were in good agreement, and the ratio between NH_4-N and NO_3-N deposition in our data and the FMI's reported data was approximately the same (comparison not presented here).

The effects of stand and site characteristics on nitrogen in throughfall and percolation water

Differences in N fluxes between the pine and spruce plots

The differences in throughfall fluxes between the spruce and pine plots supported our hypothesis that the higher retention of inorganic N, leading to smaller fluxes of inorganic N and N_{tot} under spruce as compared with those under pine, is most probably due to differences in the canopy structure. Spruce has a larger, more layered canopy surface area to support biological interaction processes with the rainwater passing down through the canopy, and thus for the conversion of inorganic N to organic compounds, as well as to retain precipitation.

The DON fluxes as well as the N_{tot} fluxes in percolation water collected at a depth of 40 cm were higher on the pine plots than on the spruce plots. The pine stands are located on soil consisting of relatively coarse, stratified sandy material, which is readily permeable to water and therefore also to soluble compounds, while the spruce stands are growing on till soil with a higher proportion of fine material and a greater absorbing surface for DON molecules. The clay content especially can affect soil solution chemistry by increasing the soil water-retention capacity, cation exchange and DOM adsorption (Fahey and Yavitt 1988). Also, due to the differences in canopy structure, less precipitation and N reaches the forest floor in spruce stands. Differences in the root distribution and, consequently, in the efficiency of N uptake between pine and spruce may also influence the N fluxes in percolation water.

Site characteristics in predicting TF and PW

Our hypothesis that throughfall N is related to the stand surface area was supported by the fact that the DON in throughfall on the pine plots increased with increasing stem volume, basal area and diameter, indicating that the DON flux in throughfall from large trees may be especially high. The N flux in throughfall on the pine plots

also decreased with increasing needle biomass. In stands with a large stem volume and basal area, as well as high needle biomass, the interaction between the canopy and rainfall may be greater than that in less dense stands (Starr and Ukonmaanaho 2004), leading to higher DON fluxes. However, because tree growth is faster in southern Finland the relationships between these factors may also be influenced by climatic factors and the south–north gradient in N deposition. Tree age also had an effect on the N fluxes, as hypothesized: the younger pine stands were more effective in retaining NO_3-N than the older ones. More efficient N retention in younger stands has also been reported by Lemeé (1974), as reviewed in Parker (1983).

As the throughfall fluxes were related to the bulk deposition fluxes and stand characteristics, we were able to produce regression models for all the forms of N, except for NH_4-N in spruce stands. This is probably due to the strong retention of deposited NH_4-N in spruce stands. Although the inclusion of stand characteristics improved the models, the throughfall flux was relatively well predicted by the bulk deposition fluxes alone. The use of needle biomass, which is very laborious and time-consuming to measure, may not be necessary to estimate the NH_4-N flux in pine stands.

Especially on the pine plots, the NH_4-N output flux in percolation water correlated with the N deposition rates and throughfall acidity and, consequently, using them as input variables to predict the NH_4-N output flux in percolation water resulted in regression models with high coefficients of determination. When interpreting this relationship it is important to take into account the fact that, in Finland, N deposition rates and throughfall acidity are correlated with precipitation and the C/N ratio in the organic layer, i.e. with soil fertility, because all these variables show a decreasing trend from south to north. Precipitation and the N concentration in the organic layer, as indicated by the C/N ratio, most probably at least partly account for the NH_4-N output flux in percolation water. These underlying relationships make our finding of a high correlation between input and output rates of N in N-limited forest ecosystems under relatively low N deposition rates more plausible.

However, the fact that the NH_4-N output flux in percolation water was closely related to precipitation in the pine stands suggests a low water and nutrient retention capacity in these ecosystems.

Fine root biomass is difficult to measure and its inclusion in determining the NH_4-N flux may therefore not be necessary when estimating the NH_4-N flux in percolation water. However, it is interesting that the fine root biomass exhibited some relationship with NH_4-N flux at a soil depth of 40 cm. This may be due to mineralization of N from decomposing fine roots rather than to the N uptake by roots. A higher fine root biomass may be related to higher fine root litter production and more substrate for N mineralization, if the turnover rates are at similar levels.

In Finnish conditions where the ground is frozen during winter, most of the N leaching has been reported to occur when the roots are inactive, e.g. during late autumn or early spring during snow melt (Helmisaari and Mälkönen 1989, Piirainen *et al*. 1998). Thus the leaching of N compounds, especially of NO_3-N, is probably a relatively random effect that is dependent on fine-scale weather conditions (time of snow melt, temperature changes and timing, and variation in precipitation) and is therefore difficult to model. A low C/N ratio (< 25) in the organic layer has been reported to be associated with nitrate leaching (input – output) (Nohrstedt *et al*. 1996, Gundersen *et al*. 1998). In our pine stands, the C/N ratio in the organic layer varied from 33 to 53 and we found a negative correlation between NH_4-N in percolation water and the C/N ratio of the organic layer.

The hypothesis that the N flux in percolation water was related to the throughfall N input, and could be modelled using the soil properties in these stands, was not supported by our data. The DON flux in percolation water was not related to latitude, N deposition or to soil properties. Similar findings have been reported by Michalzik *et al*. (2001). The behaviour of DON in soil water is most probably related to the composition and relative importance of the individual chemical groups in DON, which may react differently to changes in environmental factors. The relationship between the DON flux from the soil and soil properties may also be dependent on the temporal and spatial scale. The relationships found

in short-term laboratory experiments or at the plot scale may not be the same as those taking place over extended periods at the regional scale (Michalzik *et al*. 2001).

Relatively few studies have been carried out on the fluxes of DON in forest ecosystems, despite the fact that dissolved forms of organic nitrogen should to be taken into account before we can fully understand N cycling in forest ecosystems. Our study shows that a relatively high proportion of the N in boreal, low N-deposition areas passes through forest ecosystems in an organic form, emphasizing the importance of measuring total nitrogen when studying nitrogen fluxes. Our study also provides valuable new information about the variation in DON fluxes in low N-deposition areas in relation to climate, deposition rates and the dominant tree species in the stand. However, more studies are needed to understand the factors controlling the fluxes of DON in forest ecosystems, and especially to understand the factors related to the release of DON in forest soils.

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