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Throughfall Nitrogen Deposition Has Different Impacts on Soil Solution Nitrate Concentration in European Coniferous and Deciduous Forests

Hanne L. Kristensen,[1,2] Per Gundersen,[1*] Ingeborg Callesen,[1] and Gert Jan Reinds[3]

[1]Department of Forest Ecology, Forest and Landscape Research Institute, Hørsholm Kongevej 11, DK-2970 Hørsholm, Denmark; [2]Department of Horticulture, Danish Institute for Agricultural Sciences, Kirstinebjergvej 10, DK-5792, Denmark; [3]ALTERRA Green World Research, P.O. Box 47, 6700 AA Wageningen, The Netherlands

Abstract

Increases in the deposition of atmospheric nitrogen (N) influence N cycling in forest ecosystems and can result in negative consequences due to the leaching of nitrate into groundwaters. From December 1995 to February 1998, the Pan-European Programme for the Intensive and Continuous Monitoring of Forest Ecosystems measured forest conditions at a plot scale for conifer and broadleaf forests, including the performance of time series of soil solution chemistry. The influence of various ecosystem conditions on soil solution nitrate concentrations at these forest plots ($n = 104$) was then analyzed with a statistical model. Soil solution nitrate concentrations varied by season, and summer concentrations were approximately 25% higher than winter ones. Soil solution nitrate concentrations increased dramatically with throughfall (and bulk precipitation) N input for both broadleaf and conifer forests. However, at elevated levels of throughfall N input (more than 10 kg N ha^{-1} y^{-1}), nitrate concentrations were higher in broadleaf than coniferous stands. This tree-specific difference was not observed in response to increased bulk precipitation N input. In coniferous stands, throughfall N input, foliage N concentration, organic layer carbon–nitrogen (C:N) ratio, and nitrate concentrations covaried. Soil solution nitrate concentrations in conifer plots were best explained by a model with throughfall N and organic layer C:N as main factors, where C:N ratio could be replaced by foliage N. The organic layer C:N ratio classes of more than 30, 25–30, and less than 25, as well as the foliage N (mg N g^{-1}) classes of less than 13, 13–17, and more than 17, indicated low, intermediate, and high risks of nitrate leaching, respectively. In broadleaf forests, correlations between N characteristics were less pronounced, and soil solution nitrate concentrations were best explained by throughfall N and soil pH (0–10-cm depth). These results indicate that the responses of soil solution nitrate concentration to changes in N input are more pronounced in broadleaf than in coniferous forests, because in European forests broadleaf species grow on the more fertile soils.

Key words: carbon–nitrogen ratio; mixed linear model analysis; nitrate; nitrogen deposition; soil water; time series.

Introduction

Over the last half-century, anthropogenic emissions of nitrogen (N) compounds to the atmosphere have increased N deposition significantly in the industri-

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*Corresponding author; e-mail: pgu@kvl.dk

alized countries. High N deposition, especially in Western and Central Europe, has raised concern over the eutrophying and acidifying impact of N on forest soils and waters (for example, see Malanchuk and Nilsson 1989), as well as the potential negative impact on forest health (Nihlgård 1985; Schulze 1989). Increased N deposition to forests may result in a gradual buildup of N in plants and soil and lead to changes in N cycling processes. These conditions, in turn, may cause elevated nitrate leaching losses from forest ecosystems, a condition often referred to as "nitrogen saturation" (Aber and others 1989; Gundersen 1991).

In the mid-1990s, compilations drawing on more than 60 published input–output budgets for European forests showed that many sites were leaching more than 5 kg nitrate-N ha^{-1} y^{-1} (Dise and Wright 1995; Gundersen 1995). Nitrate leaching was found to occur mainly above a threshold of 10 kg N ha^{-1} y^{-1} in throughfall input. However, the direct correlation between input and output of N was rather weak. These preliminary reviews were later improved and updated with data compilations from studies conducted in plots and catchments (n = 139) over the period 1970–95 (Dise and others 1998a, 1998b) and in plots alone (n = 77) over the narrower time span of 1985–95 (Gundersen and others 1998a). Both data sets revealed correlations between N deposition, N concentrations in foliage, and the leaching of nitrate. The regression model that explained most of the variability in nitrate leaching included both N input and the C:N ratio of the organic layer; however, this model was based on only 30–40 sites, primarily from coniferous forests, and there was some overlap between the two data sets (Gundersen and others 1998a; Dise and others 1998b). An abundance of missing values in these compiled data sets prevented a thorough statistical analysis of all ecosystem parameters. Further, differences in methodology, as well as in temporal and spatial scales, may have introduced an unrecognized error in the detection of relationships in these data compilations.

In 1994, based on the EU Scheme for the Protection of Forests against Atmospheric Pollution and the International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP-Forest), the Pan-European Programme for the Intensive and Continuous Monitoring of Forest Ecosystems was established, with the aim of increasing our understanding of the impact of air pollution and other stress factors on forest ecosystems (De Vries and others 1998). For more than 800 selected forest plots, data on forest stands, biogeochemistry, and meteorological conditions are collected, following procedures set out by a common manual in the ICP-Forest Intensive Monitoring program (the so-called Level II) (UN-ECE 1998). However, the full program of monitoring and data collection is operated at only approximately 200 sites. The program includes intercalibration procedures and cross-evaluation of methods among the member countries, as well as quality and reliability checks on the database (De Vries and others 2001). Thus, the ICP-Forest overcomes some of the limitations of the literature compilations. Furthermore, it includes both conifer and broadleaf stands.

Soil water chemistry has been included in the Intensive Monitoring (Level II) since 1996, but because the program is based on plot-scale monitoring, data on leaching fluxes of nitrate and other ions below the root zone are not readily available without detailed modeling of the sites' water balances. This is time consuming, and the calculations add an unknown amount of error to the data set of estimated nitrate leaching fluxes.

In this study, we therefore used the measured time series of soil solution nitrate concentrations from the Intensive Monitoring plots in a regional analysis of nitrate leaching. Temporal variations in nitrate concentrations (for example, by season and with rainfall fluctuations) may be significant. However, an analysis of a comparable data set from a survey of soil solution nitrate concentrations in Denmark showed that despite the temporal variability, site factors such as forest size (in ha), management type, and soil texture significantly affected nitrate concentrations in soil solution (Callesen and others 1999).

The aim of this study was to explore the Intensive Monitoring data set for the influence of atmospheric N deposition and site-specific factors on soil solution nitrate concentrations and to compare the response of conifer and broadleaf stands. We used a statistical model (mixed linear model) in the analysis that takes into account the repeated sampling of soil solution. To further illustrate some of the main results, we present traditional linear regressions on average soil solution nitrate concentrations. Both sets of models were estimated for all plots as well as for conifer and broadleaf plots separately.

Methods

Sites and Parameters

The Intensive Monitoring program is carried out on forest plots at sites selected by each participating

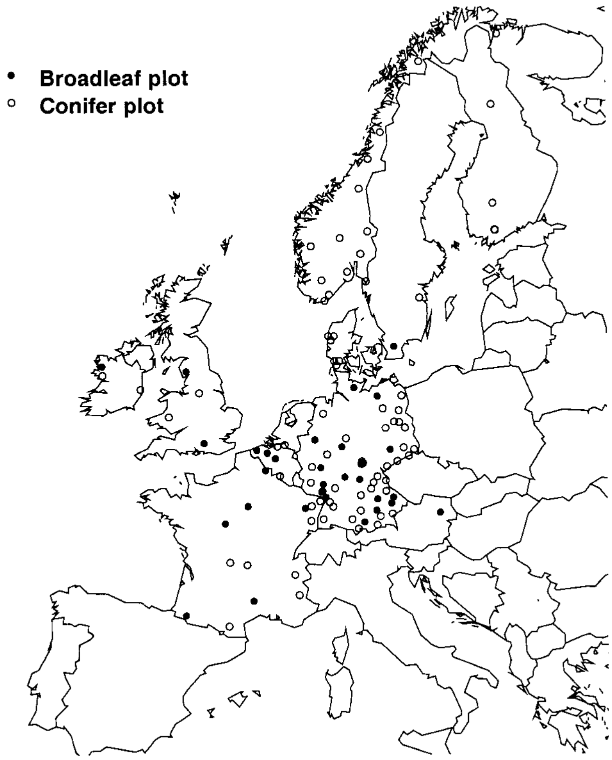

Figure 1. Location of sites from the ICP-Forest Intensive Monitoring program in Europe where soil solution chemistry was measured between December 1995 and February 1998, ●, broadleaf plot; ○, conifer plot.

country in Europe. It comprises mandatory surveys of crown condition, foliar chemistry, soil chemistry, and forest growth, as well as optional surveys of atmospheric deposition, meteorology, ground vegetation, and soil solution chemistry. The number of sites in the soil solution chemistry survey has been increasing steadily since the program's inception in 1996. Currently, measurements are performed at 250 sites (De Vries and others 2001).

For this analysis, quality-assured soil solution chemistry data were available from 160 sites for the period December 1995 to February 1998. Data from some sites/countries were excluded from the analyses due to low sampling frequency (for example, 14 sites from the Netherlands where only one sampling was done per year) or due to the short duration of the measurements (sites with less than 1 year of data). Remaining were 111 sites from 10 countries: Germany (55 sites), France (15 sites), Norway (15 sites), Belgium (six sites), Denmark (six sites), Finland (four sites), the UK (four sites), Ireland (three sites), Sweden (two sites), and Austria (one site) (Figure 1). The sites were mainly located in managed forests dominated by one tree species or plantation monocultures. Three broadleaf species (*Quercus robur* L., *Quercus petraea* L. ex Liebl., *Fagus sylvatica* L.) and six conifer species (*Picea abies* (L.) Karsten, *Picea sitchensis* (Bong.) Carrière, *Abies alba* Mill., *Pinus sylvestris* L., *Pinus nigra* Arnold, *Pseudotsuga menziesii* (Mirbel) Franco) were represented. Averages and ranges of selected site characteristics are given in Table 1 for the broadleaf and conifer groups. Details on sampling and chemical analyses can be found in De Vries and others (1998, 1999, 2000).

At most sites, soil solution nitrate concentrations were measured at several depths. The concentration measured in the depth closest to 100 cm was chosen to represent nitrate concentration in soil water leaching from the rhizosphere. The chosen depths ranged from 40 to 250 cm. Solutions were collected continuously in tension lysimeters (suction cups) using five to 25 samples per site (De Vries and others 1999).

For throughfall and bulk precipitation N input, we calculated averages at each site for as long a period as possible (2–5 years), ending in 1997. Because the lifetime of N in the ecosystem may be several years, we used this longer average as a measure of "pollution load" instead of only the N input in the actual 2 year period with soil solution data. In the statistical analyses, we preferred to use throughfall N input as a measure of N input to the sites rather than bulk precipitation N input. Throughfall N input includes a large amount of dry deposition and therefore more closely reflects the actual N input to the system than does bulk precipitation N input (Ivens 1990). Data on N input were missing at seven sites, thus leaving 104 sites for most of the statistical analyses.

In the analysis, we considered 45 variables (including those listed in Table 1) covering site, stand, and soil characteristics; N input; N and P contents in soil and foliage; and climate.

Statistical Models

Correlation analysis and analysis of variance (ANOVA) were used in a first step to identify significant correlations between average soil solution nitrate concentration and biogeochemical characteristics and to limit the number of variables tested in more complex statistical models. Average soil solution nitrate concentration (December 1995 to February 1998) correlated with throughfall N input, bulk precipitation N, foliage N content, C:N ratio and total N in the organic layer, soil pH, and temperature and was influenced by climate zone (boreal/north, Atlantic north, sub-Atlantic, Mediterranean/south) and humus type (mull, moder, mor, raw humus) (Table 2).

Table 1. Simple Averages and Ranges of Selected Ecosystem Characteristics for Conifer and Broadleaf Sites

	Conifers			Broadleaves		
	Sites (*n*)	Average	Range	Sites (*n*)	Average	Range
Latitude (°N)	80	53	43–69	31	50	43–56
Altitude (m)	80	375	25–1375	31	325	25–1375
Average annual air temperature (°C)	80	7	–3–13	31	9	6–14
Throughfall N input (kg N ha^{-1} y^{-1})	73	14.2	0.3–41.8	31	14.2	2.3–22.8
Soil pH_{CaCl2} 0–10 cm	77	3.4	2.8–5.6	30	3.8	2.8–7.3
Soil pH_{CaCl2} 20–40 cm	61	4.3	3.2–6.3	26	4.2	2.9–7.6
Soil base saturation 0–10 cm (%)[a]	75	20	3–92	27	35	5–97
Soil base saturation 20–40 cm (%)[a]	57	14	1–95	22	32	3–96
Organic layer C:N	72	28.3	17.3–46.4	31	25.5	14.2–45.1
Soil C:N 0–10 cm	80	23.9	12.8–45.0	31	18.8	12.3–42.5
Organic layer (kg m^{-2})	52	6.0	0.5–15.0	29	4.5	0.7–31.0
Stand age (y)	80	70	30–150	31	90	50–150
Current year foliage N (mg g^{-1})	74	14.8	9.9–22.5	28	25.3	20.3–30.9
Soil solution nitrate concentration (mg^N L^{-1})	80	1.54	0.00–15.1	31	2.62	0.00–18.1

[a]*Measured at soil pH (0.1 M $BaCl_2$) at 95% of the sites (De Vries and others 1998)*

In the second step, these factors were examined in the construction of a mixed linear model (SAS Proc Mixed) (Littell and others 1996, 1998). A mixed linear model including random and fixed effects is a suitable method to analyze data from repeated samplings such as soil solution concentrations where the samplings are dependent (autocorrelated). The monitoring data fit a split-plot type design (Christensen 1996), with sites as "main plots" where site, stand, and biogeochemical characteristics are measured once and with the repeated samplings (time) as "subplots."

Sampling frequencies varied from biweekly to seasonal at the sites. To simplify the analysis, we used seasonal averages—spring (March–May), summer (June–August), autumn (September–November), and winter (December–February)—calculated on the data available for December 1995 to February 1998. Thus, there were three to nine repeated measurements per site. Soil solution nitrate concentrations were transformed prior to analysis by the function y = log (x + 0.05) to obtain homogeneity of variance. The value 0.05 (mg NO_3-N L^{-1}) was added to avoid observations equal to zero, which cannot be log-transformed. The resulting estimates and confidence intervals were calculated by retransformation to the original scale and therefore correspond to median (midpoint) nitrate concentrations (Parkin and Robinson 1994).

Because throughfall N correlated strongly with soil solution nitrate and several other factors (Table 2), each other factor was subsequently tested for significant effects on soil solution nitrate concentration in a model including throughfall N. The following factors were found to be significant: tree type, the C:N ratio of the organic layer, humus type, and foliage N content. The model was further used to test for interactions (covariance). The model that best explained soil solution nitrate was found in an iterative process for reducing insignificant factors and interactions. The resulting model for log-transformed soil solution nitrate observations at site (s) and season (t) was:

$$\text{Soil } NO_3^-(s,t) = \text{season}(t) + \text{throughfall N}(s) + \text{tree type}(s) + \text{throughfall N} * \text{tree type}(s) + \text{C:N organic layer}(s) + \text{site}(s) + \text{error}(s,t) \quad (1)$$

The estimates of intercept and coefficients for the model are given in Table 3. The terms "site" and "error" are random gaussian variables. By taking "site" as a random effect with expected mean zero and variance σ^2, degrees of freedom (*df*) were liberated for the analysis of biogeochemical site characteristics. These general features were the focus of the analysis, rather than attempts to predict concentrations at specific sites. This represents the main difference from a multiple regression approach.

In Figure 2, the "site" term is illustrated for a specific site as the difference between model pre-

Table 2. Results of Correlation Analysis and Analysis of Variance (ANOVA) of Relationships between Simple Averages of Soil Solution Nitrate Concentrations, Throughfall N Input, and Biogeochemical Characteristics for All Sites

	Average Soil Solution Nitrate Concentration			**Throughfall N Input**		
	n	*R*	*P*	*n*	*R*	*P*
Correlation analyses						
Throughfall N input	104	0.54	0.0001	104	1	
Bulk precipitation N	104	0.35	0.0003	104	0.76	0.0001
Average annual air temperature	111	0.23	0.02	104	0.42	0.0001
Current year foliage N	102	0.33	0.0008	95	0.23	0.02
Total N in organic layer	81	0.34	0.002	74	0.16	NS
Organic layer C:N	103	−0.26	0.01	96	−0.41	0.0001
Soil pH_{CaCl2} 0–10 cm	107	−0.12	NS	100	−0.38	0.0001
Soil pH_{CaCl2} 10–20 cm	93	−0.37	0.0004	88	−0.55	0.0001
	n	**Mean (mg N L^{-1})**	*P*	*n*	**Mean (kg N ha^{-1} y^{-1})**	*P*
ANOVA						
Climate zone	111		0.0001	104		0.0001
Boreal/north	17	0.1 a		17	2.2 a	
Atlantic north	29	3.5 b		25	14 b	
Sub-Atlantic	50	1.8 b		48	17 b	
Mediterranean/south	15	1.1 b		14	11 b	
Humus type	111		0.0001	104		0.0002
Raw humus	26	0.7 a		24	6.4 a	
Mor	24	3.3 b		20	12 ab	
Moder	39	2.0 b		39	18 b	
Mull	22	1.6 b		21	11 ab	

In ANOVA, different letters indicate significant differences between estimated means for each climate and humus category.

dictions including and excluding the random site effect. This particular site from Belgium has a large site effect and thus deviates strongly from the predictions by the main factors in the model. The deviation between observations and the solid line is the "error". An $r^2 = 0.92$ for the model was calculated by use of sum of squares of observed values of soil solution nitrate concentrations and residuals from predicted values. This r^2 cannot be interpreted as in a traditional regression model, because as shown in Figure 2, part of the variability is captured in the "site" term. When r^2 was calculated by use of the residuals from model predictions excluding the random site effect, it was reduced to 0.58. Thus, approximately 34% of the variation was captured in the random "site" term.

The model (Eq. 1) was used to estimate medians for each level of main factors. Medians were calculated as weighted values based on the distribution of sites at different levels of main factors. Differences between weighted medians were tested by Student *t*-tests with Bonferroni correction for multiple comparisons (Christensen 1996).

The same iterative procedure was used to construct separate mixed models for conifers and broadleaves. The significance of all factors and interactions were tested followed by reduction of the resulting model by removal of nonsignificant factors and interactions. The resulting models were:

Conifers ($r^2 = 0.93$; excluding the random site effect $r^2 = 0.59$):

$$\text{Soil } No_3^-(s,t) = \text{season}(t) + \text{throughfall N}(s) + \text{C:N organic layer}(s) + \text{site}(s) + \text{error}(s,t) \quad (2)$$

Broadleaves ($r^2 = 0.87$; excluding the random site effect $r^2 = 0.58$):

$$\text{Soil } NO_3^-(s,t) = \text{season}(t) + \text{throughfall N}(s) + \text{soil pH } (0\text{–}10 \text{ cm})(s) + \text{site}(s) + \text{error}(s,t) \quad (3)$$

Table 3. Estimates of Intercept and Coefficients in the Overall Model (Eq. 1), Conifer Model (Eq. 2), and Broadleaf Model (Eq. 3) Predicting log (NO_3 (mg N L^{-1}) + 0.05)

Effect	Level	All Data (n = 104)	Conifers (n = 73)	Broadleaves (n = 31)
Intercept		−0.93	−0.51	−2.84
Season	Autumn	0.02	0.03	−0.006
	Spring	0.06	0.08	0.03
	Summer	0.07	0.06	0.09
	Winter	0	0	0
Throughfall N		0.09	0.05	0.11
Tree Type	Conifers	0.30	NA	NA
	Broadleaves	0	NA	NA
Tree type × Throughfall N	Conifers	−0.04	NA	NA
	Broadleaves	0	NA	NA
C:N Organic Layer		−0.02	−0.02	NS
Soil pH 0–10 cm		NS	NS	0.29

NA, not analyzed

For a categorical factor (tree type), the coefficient is added in the equation; for continuous factors, the coefficient is multiplied to the factor and added. As an example, in the overall model (Eq. 1), conifer in spring with a throughfall of 30 kg N ha^{-1} y^{-1} at C:N 25 will yield: log (NO_3 + 0.05) = −0.93 + 0.06 + 0.09 × 30 + 0.3–0.04 × 30–0.02 × 25 = 0.43; back-transformed 1.5 mg NO_3-N L^{-1}.

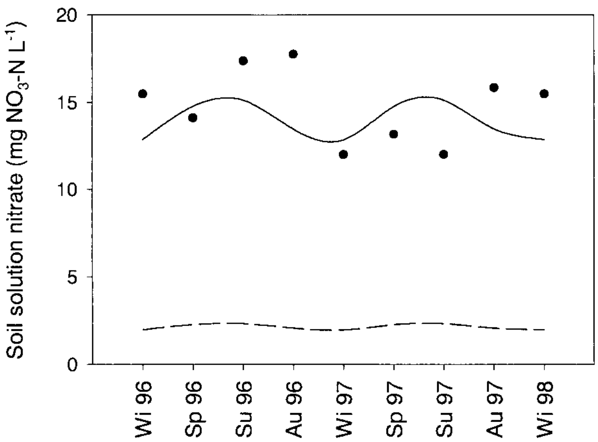

Figure 2. Observed nitrate concentration time series for plot 15 (Belgium, *Pinus sylvestris*, organic layer carbon–nitrogen (C:N) ratio 34.9, and throughfall input 32.1 kg N ha^{-1} y^{-1}) and predicted concentrations found by use of the model (Eq. 1), including the random site effect (*solid line*) and excluding the random site effect (*dashed line*). Note that the predicted values are back-transformed (log) values, which explains why the random site effect (the difference between the solid and the dashed lines) does not seem constant over time.

The estimates of intercept and coefficients in the equations for the models (Eqs. 2 and 3) are given in Table 3.

In addition, to further illustrate the main effects found in the models and to focus on the differences between conifer and broadleaf forests, we present scatterplots and results from regression analyses. Linear (and multiple) regressions between average soil solution nitrate concentrations and site properties were performed by the use of SAS Proc GLM, as well as tests for homogeneity of slopes (SAS Institute 1990).

Results and Discussion

In this section, we present and discuss the results obtained with mixed linear models for all sites (Eq. 1) as well as for conifers (Eq. 2) and broadleaf sites (Eq. 3) separately, based on the time series of soil solution nitrate concentration from the ICP-Forest Intensive Monitoring sites. The differences in soil solution nitrate concentrations are discussed in relation to other ecosystem characteristics, including the covariance of different N variables (throughfall N input, bulk N precipitation, C:N ratio of organic layer, foliage N) and temperature.

Overall Results

The Intensive Monitoring data set available for this analysis covers the gradient found in N deposition from Northern to Central Europe (less than 1–40 kg N ha^{-1} y^{-1}) and broad ranges in climate and soil conditions (Table 1). The sites represent Northern, Western, and part of Central Europe with the main cluster of sites is in Germany (Figure 1).

The overall median of soil solution nitrate concentration in the analyzed data set was low, at 0.53 mg N L^{-1} (Table 4), despite the 0–18 mg N L^{-1} range in the data (Table 1). The distribution was

Table 4. Estimated Medians of Nitrate Concentration in Soil Solution and Test of Significant Differences between Estimates at the Average Throughfall of 14.2 kg N ha^{-1} y^{-1} in the Common Mixed Model for Broadleaves and Conifers

Variable	Sites (n)	Observations (n)	Median Nitrate Concentration (mg N L^{-1})	Confidence Interval (95%)
Overall Median	104	777	0.53	0.38–0.74
Season (P = 0.011)				
Winter	103	225	0.47 a	0.33–0.67
Spring	104	183	0.55 ab	0.39–0.77
Summer	104	185	0.59 b	0.41–0.82
Autumn	103	184	0.52 ab	0.37–0.74
Throughfall N ($P < 0.0001$)	104	777		
Tree Type ($P = 0.276$)				
Tree Type × Throughfall N ($P = 0.045$)	104	777		
Conifers	73	545	0.32 a	0.24–0.43
Broadleaves	31	232	0.64 b	0.42–0.95
C:N Organic-Layer ($P = 0.025$)				
> 30	30	228	0.13 a	0.07–0.22
25–30	25	188	0.47 b	0.24–0.88
< 25	49	361	1.23 c	0.84–1.78

Different letters indicate significant differences between estimated medians for each main factor.

skewed toward zero, with 60% of the sites having concentrations below 1 mg N L^{-1} and only 2.8% (three sites) exceeding the European standard for nitrate in drinking water (11.3 mg N L^{-1}). However, in this analysis, 14 sites in the Netherlands with high N deposition (more than 25 kg N ha^{-1} y^{-1}) had been excluded due to low sampling frequency. When these sites were included, the median was 0.7 mg N L^{-1} (De Vries and others 2000) and the drinking water standard was exceeded at 10% of the sites (that is half of the Netherlands sites).

Seasonal Effects

Winter concentrations were significantly (P = 0.011) lower than summer concentrations (Table 4). This finding can be explained by the diluting effect of increased water infiltration during winter due to higher rainfall and decreased evapotranspiration, in addition to decreased nitrifying activity during the cold season. In a similar study of dormant season soil solution nitrate concentrations in Danish forests, Callesen and others (1999) observed the lowest concentrations in January and concluded that absolute water content explained part of the variation in nitrate concentrations (lower concentration at higher water content). The seasonal pattern in soil solution (Table 4) is opposite to the concentration pattern usually observed in streamwater, where very low concentrations occur in the summer when plant uptake is high and higher concentrations occur in the winter (for example, see Stoddard 1994). Apart from the possible effect of dilution in winter, the reason for this difference in concentration pattern between soil solution and streamwater data sets may be that the sampling generally occurred below the main rooting zone, limiting the influence of plant uptake from this layer. Thus, nitrate that has leached down the profile in the dormant season may remain in the subsoil in the summer where water movement is limited by evapotranspiration.

Although significant, the differences between seasons were relatively small (0.12 mg N L^{-1}, or 25% at the median concentration) (Table 4). The effect of years (1996, 1997) on soil solution nitrate concentrations was tested in the mixed model as well, but it was not significant and therefore not included in the model (Eq. 1).

Throughfall and Bulk Precipitation N Input

Throughfall N input was the strongest predictor of soil solution nitrate concentrations ($P < 0.0001$). Nitrate concentrations above the limit of detection occurred (with a few exceptions) above a threshold of 7 kg N ha^{-1} y^{-1} in throughfall (Figure 3a). Nitrate concentrations above 1 mg N L^{-1} occurred when throughfall was higher than 10 kg N ha^{-1}

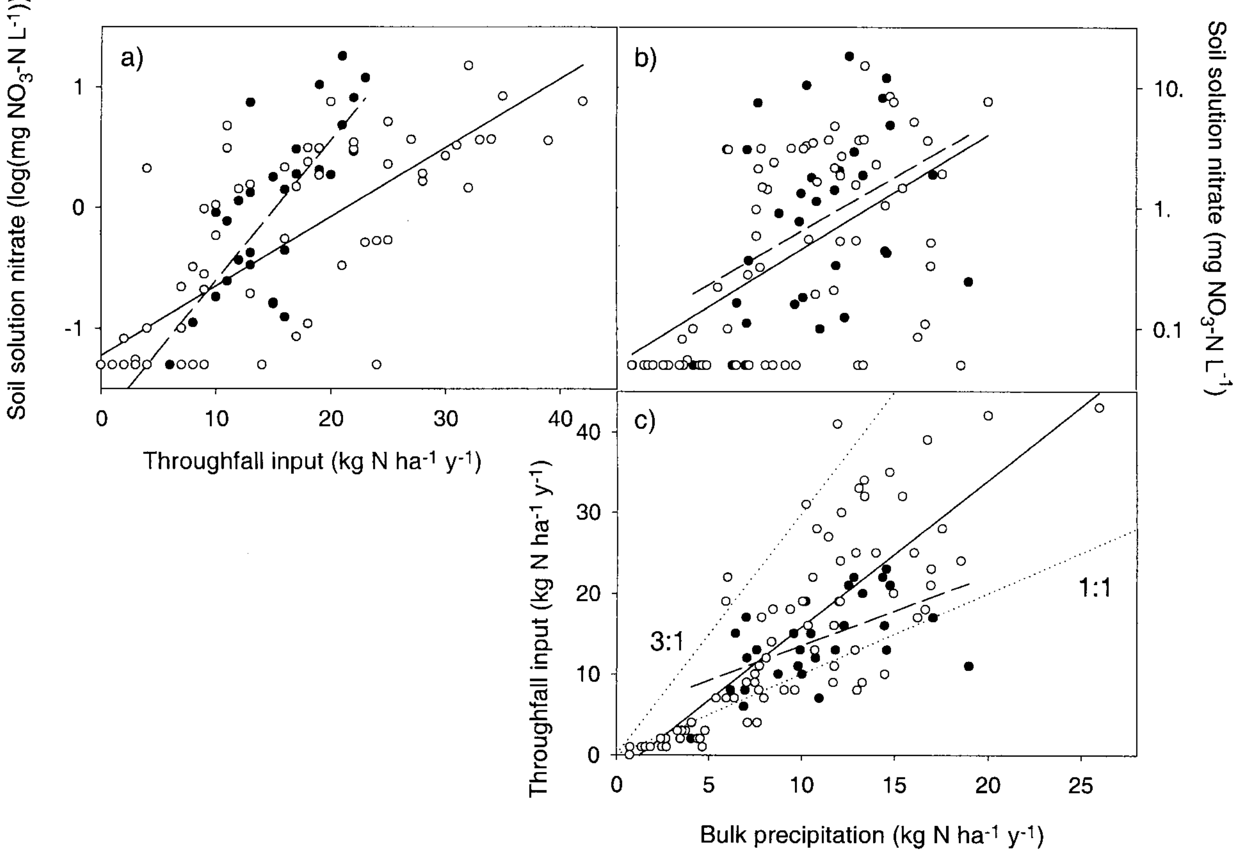

Figure 3. Nitrate concentrations in soil solution (log-transformed averages for December 1995 to February 1998) versus (**a**) throughfall nitrogen–(N) input and (**b**) bulk precipitation N (both calculated averages for 1993– 97 from the Intensive Monitoring sites. (**c**) Throughfall N input versus bulk precipitation N. The dashed lines show the 1:1 and 1:3 relationships. Conifers, ○; broadleaves; ●. The regressions are for **a** conifers: log(y) = 0.06x–1.2 (r^2 = 0.59, P = 0.0001); broadleaves: log(y) = 0.12x–1.8 (r^2 = 0.65, P = 0.0001); **b** conifers: log(y) = 0.09x–1.3 (r^2 = 0.32, $P < 0.0001$); broadleaves: log(y) = 0.09x–1.18 (r^2 = 0.16, P = 0.02); **c** conifers: y = 1.8x–2.3 (r^2 = 0.65, P = 0.0001); broadleaves; y = 0.86x–4.9 (r^2 = 0.32, P = 0.0008).

y^{-1}. This threshold corresponds to the one observed in earlier studies of input–output budgets (Dise and Wright 1995; Gundersen 1995; Dise and others 1998b; Gundersen and others 1998a).

Due to a significant interaction between throughfall N and tree type (P = 0.045), broadleaves had significantly higher nitrate concentrations than conifers at average throughfall (14.2 kg N ha^{-1} y^{-1}) (Table 4). This interaction indicates that the difference in soil solution nitrate concentrations between broadleaves and conifers depended on the level of throughfall N input, which is further illustrated by the linear regression between throughfall N and the log-transformed average nitrate concentration in soil solution (Figure 3a). Broadleaves (at throughfall greater than 10 kg N ha^{-1} y^{-1}) had higher soil solution nitrate concentrations than conifers at the same throughfall N input level. The slopes of the regression lines were significantly different for conifers and broadleaves (P = 0.0069), suggesting that nitrate concentration in soil solution will respond more strongly to throughfall N input changes under broadleaves than under conifers. Earlier compliations of data from the literature have shown that nitrate leaching increases with increasing throughfall N input (Dise and others 1998b; Gundersen and others 1998a). No differences between tree types were found, but this could be due to the small sample size for broadleaves in these data compilations.

Bulk precipitation N input correlates with throughfall N input (Figure 3c) and can usually replace throughfall N in the relationships found in this type of regional analysis (Dise and Wright 1995; Gundersen 1995; Tietema and Beier 1995). When throughfall N was replaced by bulk precipitation N in the statistical model (Eq. 1), there was, however, no interaction between tree type and bulk precipitation N input ($P = 0.73$). Nor was there any effect for tree type alone ($P = 0.64$), as also shown in Figure 3b by simple regression analysis on site average nitrate values ($P = 0.32$). The other factors stayed significant in the mixed linear model (results not shown). However, much less variation was explained by bulk precipitation N ($r^2 = 0.33$) in the statistical model than by throughfall N ($r^2 = 0.58$), as indicated in the difference in r^2 for regressions in Figure 3a and b. The fact that the tree type effect in Eq. 1 disappears if throughfall N is replaced by bulk precipitation N suggests that the differences in soil solution nitrate between broadleaves and conifers at increasing throughfall N input (Figure 3a) may be a result of complex interactions between N input, cycling, and retention.

Conifers are generally found to have higher throughfall N input than broadleaves at high levels of bulk precipitation N input (Rothe and others 2002). This was confirmed in the present data set (Figure 3c), although the slopes of the regression lines for conifers and broadleaves were not significantly different ($P = 0.11$). At some conifer sites, throughfall N was more than three times bulk precipitation N (Figure 3c). This result can be attributed in part to the filtering effect afforded by the conifer canopy, which is larger in surface area and rougher than the broadleaf canopy, and in part to the evergreen nature of conifers (for example, see Rothe and others 2002). This difference is not observed at low levels of N deposition (less than 5 kg N ha^{-1} y^{-1}), where direct assimilation of N in the canopy may decrease throughfall N relative to bulk precipitation N input (Figure 3c). With higher N input to conifers, one might expect higher nitrate concentration underneath conifers than underneath broadleaves. Accordingly, a compilation of data from adjacent pairs of Norway spruce and beech stands grown on the same soil (and receiving the same bulk precipitation N input) at 16 European sites showed that the spruce stands had higher throughfall N input and higher nitrate concentration in the subsoil than the beech stands (Rothe and others 2002). This is contrary to the results presented here from the monitoring program (Figure 3a), where broadleaves had a higher nitrate concentration than conifers under conditions of intermediate to high throughfall N input. We suspect that this finding reflects a difference in soil conditions between the two tree types rather than an effect of the tree types alone, because broadleaves had a higher base saturation and lower C:N ratio in the mineral soil than conifers (Table 1). In European plantation forestry, broadleaves are more abundant on fertile and N-rich soils, whereas conifers dominate on less fertile, N-poor soils, which was also the case in the two groups of sites in our analysis. It was not possible to determine whether fertile soil conditions increase nitrate concentrations irrespective of tree type, because all of the fertile conifer sites in our data set received low throughfall N input. In a similar analysis of soil solution nitrate concentrations at 111 sites in Danish forests, Callesen and others (1999) observed low concentrations at sites with sandy, infertile soils and higher concentrations at sites with fertile, loamy soils and could not detect an effect of tree species.

The C:N Ratio of the Organic Layer

The C:N ratio of the organic layer was the only biogeochemical property other than throughfall N input that significantly explained nitrate concentrations in the common model (Eq. 1) for broadleaves and conifers (Table 4). When the same factors (throughfall N, tree type, and C:N organic layer) were tested in the equivalent regression analysis on average nitrate concentrations, the C:N ratio was not a significant factor ($P = 0.19$) in the linear model. This indicates that use of the information in the time series of seasonal fluctuations in nitrate concentrations increased the analytical power of the statistical models. It may also be due in part to the higher number of *df* that the use of time series in the Proc Mixed procedure provides.

The result that the C:N ratio of the organic layer is a significant factor in the model (Eq. 1) is in line with previous work by Gundersen and others (1998a), who, based on analysis of three independent data sets, found that nitrate leaching in forests was increasing with decreasing C:N ratio in the organic layer. They suggested that the C:N ratio in the organic layer could be used as an indicator of the N status of the ecosystem and therefore as a predictor of the risk for nitrate leaching from the system. They also proposed that three C:N classes greater than 30, 25–30, and less than 25—could be used to characterize forests with low, intermediate, and high risks for nitrate leaching, respectively. When we tested these C:N classes in the mixed model (Eq. 1), we found that the weighted medians of nitrate-N concentration in the three C:N classes were significantly different, increasing from 0.13 mg L^{-1} in the greater than 30 class, to over 0.49 mg L^{-1} in the 25–30 class, and to 1.24 mg L^{-1} in the less than 25 class (Table 4).

In the separate model analyses of the two tree types (Eqs. 2 and 3), the C:N ratio of the organic layer entered the model for conifers ($P = 0.029$) but

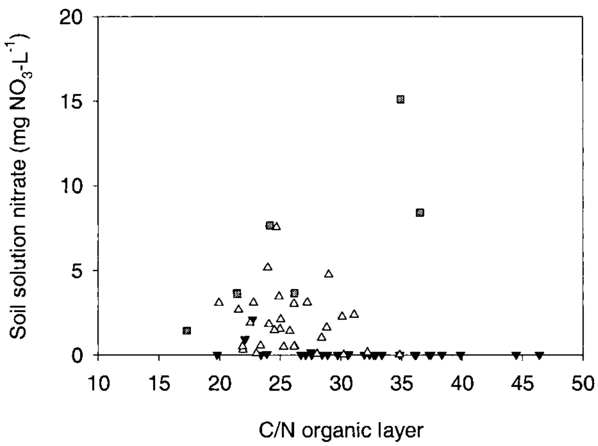

Figure 4. Nitrate concentrations in soil solution (averages for December 1995 to February 1998) versus organic layer carbon–nitrogen (C:N) ratio in conifers at low (▼, less than 10 kg N ha^{-1} y^{-1}), intermediate (Δ, 10–30 kg N ha^{-1} y^{-1}), and high (▤, more than 30 kg N ha^{-1} y^{-1}) throughfall nitrogen (N) inputs at the Intensive Monitoring sites.

not for broadleaves. Thus, only the results from conifers support the hypothesis that the organic layer C:N ratio is a predictor of the risk for nitrate leaching from the system. Also the data in the study by Gundersen and others (1998a) were mainly from coniferous forests.

In an European data set compiled from the literature, Dise and others (1998a) found that sites with throughfall N input below 10 kg N ha^{-1} y^{-1} had low nitrate leaching regardless of the C:N ratio. At sites with deposition levels of 10–30 kg N ha^{-1} y^{-1}, nitrate leaching increased with decreasing C:N ratio. With deposition levels above 30 kg N ha^{-1} y^{-1} the results were more variable and nitrate leaching was observed at all sites, including those with C:N ratios above 30. We observed similar results for the Intensive Monitoring data for conifers (Figure 4). In general, sites with deposition levels below 10 kg N ha^{-1} y^{-1} had soil solution nitrate concentrations close to zero, irrespective of C:N ratio. Two sites had high nitrate concentrations at C:N ratios above 30, and both of them had deposition levels well above 30 kg N ha^{-1} y^{-1}. Neither the general model (Eq. 1) nor the conifer model (Eq. 2) predicted high soil solution nitrate at these sites, as illustrated for one of the sites in Figure 2 by the high random site effect of 0.8. De Schrijver and others (2000) suggested that nitrate leaching at the other site could be due to transport of throughfall ammonium down through the upper soil layers to deeper layers with lower C:N ratios and higher nitrifying activity.

Intercorrelations between C:N, Throughfall N, Foliage N, Temperature, and Soil Solution Nitrate Concentrations

The C:N ratio of the organic layer is related to other ecosystem N fluxes and concentrations; as such, it may be an indicator of ecosystem N status (Gundersen and others 1998b) and nitrate leaching (Gundersen and others 1998a). With time, elevated N input may increase N concentrations in plants and soils and decrease the C:N ratio of the organic layer. The decades of elevated deposition seem to have influenced the C:N ratio of this layer in European forests, because the organic layer C:N ratio decreased with throughfall N input for both tree types (Figure 5c), although the slopes of the regression lines differed significantly by tree type (P = 0.015). The organic layer C:N ratio decreased two units for conifers and five units for broadleaves per 10 kg N ha^{-1} y^{-1} increase in throughfall N (Figure 5c). However, throughfall N input increased with average annual temperature due to similar north–south gradients in deposition and temperature for conifers in the data set (r^2 = 0.30, $P < 0.0001$) (results not shown). This correlation was not found for broadleaves (r^2 = 0.05, P = 0.22). Thus, the trend of decreasing C:N with N input may have a climatic component, at least for conifers. In multiple regression analysis of the conifer data set, C:N ratio of the organic layer was predicted (r^2 = 0.36, $P < 0.0001$) by throughfall N ($P < 0.0001$), temperature (P = 0.02), and interaction between the two (P = 0.0002). The relative importance of temperature and throughfall input in relation to C:N ratio could not be explored further with the current data set due to the distribution of average temperatures and the strong covariation between temperature and throughfall N input.

Another factor of importance for the C:N ratio is the N status of the litter input. Litterfall N was not measured at the Intensive Monitoring sites; however, foliage N concentration was measured, and it has been shown to correlate with litter N concentration (Tietema and Beier 1995). Foliage N content was not included in the overall mixed model due to strong covariance with throughfall N and to species differences. Foliage N concentration decreased as the C:N ratio of the organic layer increased for conifers (Figure 5b) but not for broadleafs (P = 0.52), and foliage N concentration was different for broadleafs (25.3 mg g^{-1}) and conifers (14.8 mg g^{-1}) (Figure 5b and Table 1). In addition, foliage N content increased with throughfall N input for conifers (Figure 5a) but not for broadleaves (P = 0.71). One possible explanation for these differences is that

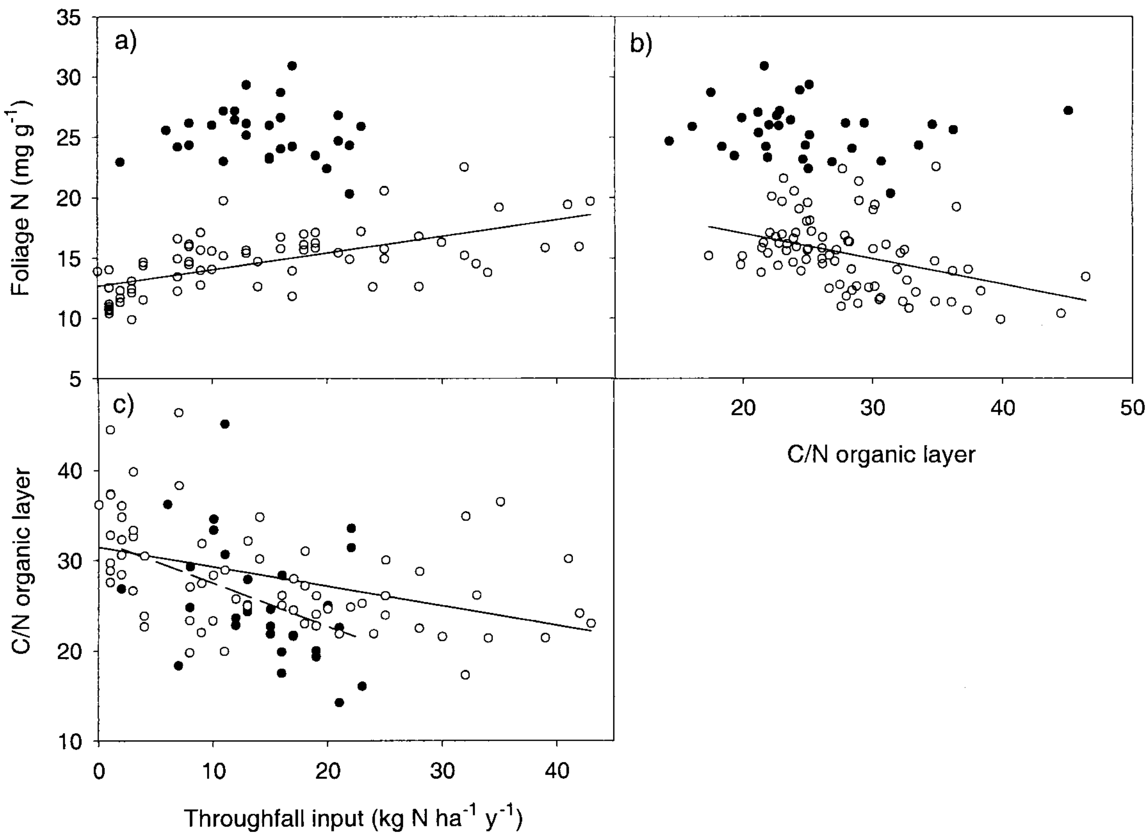

Figure 5. Foliage nitrogen (N) concentration versus **a** throughfall N input and carbon–nitrogen (C:N) **b** ratio of the organic layer, **c** C:N ratio of the organic layer versus throughfall N input (averages for 1993–97). Conifers, ○; broadleaves, ●. The regressions are for **a** conifers: y = 12.7 + 0.14x (r^2 = 0.40, $P < 0.0001$); **b** conifers: y = 21.2–0.21x (r^2 = 0.16, P = 0.0003); and **c** conifers: y = 31.5–0.21x (r^2 = 0.19, P = 0.0002); broadleaves: y = 32.3–0.48x (r^2 = 0.14, P = 0.036).

retranslocation of N prior to senescence may be a more important process in broadleaves, making broadleaf foliage more independent of N input. Another possibility, as discussed above, is that broadleaf species are generally found on more fertile soils.

Along with the significant covariation between throughfall N, C:N ratio, and foliage N concentration for conifers, a correlation between soil solution nitrate concentration and foliage N content could be expected in conifers (Figure 6). Two thresholds can be set for conifer foliage N content: one at 12.6 mg g^{-1}, below which no nitrate was found in soil solution, and one at 17.0, above which the nitrate concentration was always above detection limits. Thus, the foliage N (mg N g^{-1}) classes of less than 13, 13–17, and greater than 17 may indicate low, intermediate, and high risks of nitrate leaching, respectively. A threshold of 13 mg N g^{-1}, where nitrate starts to occur in soil solutions, corresponds surprisingly well with the threshold of 13–14 mg N

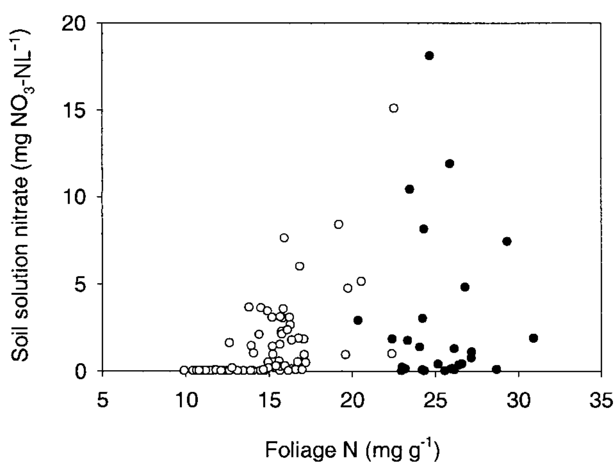

Figure 6. Nitrate concentrations in soil solution (averages for December 1995 to February 1998) versus foliage nitrogen (N) concentration at the Intensive Monitoring sites. Conifers; ○; broadleaves, ●. The regression is for conifers: y = 0.54x–6.5 (r^2 = 0.34, $P < 0.0001$).

g^{-1}, where several conifers no longer show a significant growth response to fertilizer additions (Brockley 2000 and refs. therein; Sikström and others 1998).

When the C:N ratio in Eq. 2 was replaced with foliage N content in the mixed model analysis of conifers, a significant relationship to nitrate concentration was also found ($P < 0.0001$). For broadleaves, neither the C:N ratio ($P = 0.54$) nor the foliage N content ($P = 0.89$) had a significant relationship to nitrate concentration in soil solution in the mixed model analysis.

Relationships to Soil pH

In previous studies, a negative correlation was found between the pH of the B-horizon of European forests and nitrate leaching; this relationship may be explained by the acidifying effect from deposition and nitrification when nitrate is leached from the soil (Dise and others 1998b). A negative correlation was also found in the present study (Table 2), but it was not significant in the overall model (Eq. 1). In addition, for conifers alone, pH was only significant when throughfall N input was not included in the model (results not shown). In contrast, for broadleaves, both throughfall N and soil pH entered the final model (Eq. 3). Thus, it is possible that soil type and characteristics are more important for the response to N deposition in broadleaf than in coniferous forests. A nonlinear effect of pH on nitrate concentration may be expected with high nitrate at both low pH (due to the acidifying effect of nitrate leaching) and high pH (due to complete nitrification of N inputs). There was an indication of such an effect in the data for broadleaves, but there were not enough sites with high pH to substantiate such a relationship.

CONCLUSION

Soil solution nitrate concentrations are low (less than 1 mg N l^{-1}) at 60% of the Intensive Monitoring plots where soil solution measurements were taken. Concentrations are generally lower in winter than in summer, but seasonal differences are small. Elevated nitrate concentrations occurred above a threshold of 7 kg N ha^{-1} y^{-1} in throughfall input. Coniferous and broadleaf forests respond differently to N deposition in throughfall; therefore, these two tree types need to be analyzed separately.

In coniferous forests ($n = 73$), N input with throughfall, foliage N concentration, organic layer C:N ratio, and nitrate leaching covary. Soil solution nitrate concentrations are best explained by a model with throughfall N and organic layer C:N as main factors, although the C:N ratio can be replaced by foliage N. The results confirm conclusions from previous literature reviews (Gundersen and others 1998a; Dise and others 1998a) that the organic layer C:N ratio classes of greater than 30, 25–30, and less than 25 indicate low, intermediate, and high risks of nitrate leaching, as do the foliage N (mg N g^{-1}) classes of less than 13, 13–17, and greater than 17, respectively.

In broadleaf forests ($n = 31$), correlations among N characteristics are less pronounced than in conifers, but our sample size of broadleaves was less than half that for conifers. A model that includes throughfall N and soil pH (0–10 cm) as main factors best explains soil solution nitrate concentrations. The results suggest that the responses of soil solution nitrate concentration to changes in throughfall N deposition (if throughfall N is higher than 10 kg N ha^{-1} y^{-1}) will be more pronounced in broadleaf than in coniferous forests in Europe, mainly because broadleaf forests grow on more fertile soils than coniferous forests.

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