

How are N and S in deposition, in percolation water and in the upper soil layers reflected in the chemical composition of needles in Finland?

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Introduction

The impact of atmospheric deposition of nitrogen and sulphur on forest ecosystems is the main focus of the ICP Forests/Forest Focus monitoring programme. On the other hand, both of these elements are essential macronutrients the availability of which strongly regulates plant growth. The monitoring of foliar chemistry is one of the central activities of the programme because it has proved to be a useful and practical tool for diagnosing the nutrient status of the trees and to monitor the large-scale effects of atmospheric deposition on forest ecosystems. In principle, chemical analysis of the soil reflects the potential availability of nutrients, while plant analysis indicates the actual nutrient status of the plants (Marschner 1995). The aim of this study is to investigate how the concentrations of sulphur and nitrogen in the nutrient sources of plants, i.e. in deposition, in percolation water and in the upper soil layers, are reflected in the nutrient status of Scots pine and Norway spruce in Finland.

Material and methods

In Finland, the nutrient status of conifer needles has been monitored on both the Level I (extensive monitoring) and Level II (intensive monitoring) networks of the ICP Forests/Forest Focus programme. Needles have been sampled on a sub-set of the Level I plots almost every year since 1987. This has provided a useful time series for evaluating the extent to which elevated N and S deposition has affected the mineral nutrient composition of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* L. Karst.) needles during the period 1987–2000 (Luyssaert et al. 2004, 2005). Needle chemistry has been monitored biannually on 27 (on mineral soil sites) of the Level II plots since 1995, thus allowing us to explore the relationships between the elemental composition of needles and the concentrations of the respective elements in the soil and in percolation water.

The effect of N and S deposition on needle chemistry based on the Level I data

Needle samples were collected from 36 (16 spruce, 20 pine) of the Level I plots located on mineral soil sites in background areas in different parts of the country. The stands were sampled almost every year between 1987 and 2000, resulting in 367 needle samples (Luyssaert et al.

2005). Sampling and chemical analysis of the needles were carried out according to the ICP Forests Manual, and are presented and discussed in Luyssaert et al. (2004).

Tree nutrition was described by means of nutrient profiles (NPs) (Luyssaert et al. 2004, 2005). The NP of tree foliage is defined as the nutrient status that accounts for all the element concentrations, contents and interactions between two or more elements. Stands with similar NPs, and thus a similar elemental composition of the foliage, were characterized by a group nutrition profile (GNP). Current-year N, S and P concentrations and needle mass were used in calculating the GNPs. The values for Mg, Ca and Al were added when presenting the profiles. A neural network, in this case a self-organizing map (SOM) (Kohonen 2001) and an agglomerative clustering algorithm with pruning (Vesanto and Sulkava 2002), were used in calculating which NPs were members of a given GNP.

A two-step approach was applied in calculating the relationship between N deposition and the elemental composition of the needles. (1) The hypothesis was tested that the mean N deposition between already established GNPs could statistically not be considered equal. (2) The conditional probability was calculated that, given the GNP, the total N deposition was higher than $4.0 \text{ kg ha}^{-1} \text{ year}^{-1}$, which was considered to be an elevated deposition level (i.e. above the threshold level) in Finland. The same two-step approach was used to determine the relationships between the NPs and S deposition, using a threshold deposition of $5.0 \text{ kg ha}^{-1} \text{ year}^{-1}$.

A literature study of controlled experiments revealed that acidifying deposition mediates increasing N and S concentrations, and decreasing Mg:N and Ca:Al ratios in the needles. When this fingerprint for elevated N and S deposition in tree foliage was observed simultaneously with increased N and S inputs, it was considered sufficient evidence to assume that acidifying deposition had altered the elemental composition of the tree needles on that plot in the given year. Evidence for deposition-induced changes in the elemental composition of the tree foliage was calculated on the basis of a simple frequency model.

Relationships between soil and soil solution chemistry and needle chemistry

The organic and uppermost mineral soil layers were sampled once for chemical analyses at the beginning of the monitoring programme (1995–1997) on the 27 Level II plots located on mineral soil sites. Percolation water has been collected continuously at 4-week-intervals during the snow free period using zero tension lysimeters on 16 of the Level II plots. Sampling and chemical analysis of the needles, soil and soil percolation water were carried out according to the ICP Forests Manual (Manual on... 2006), and are presented and discussed in Merilä (2007) and in Derome et al. (2007).

Annual plot averages for S and N concentrations in current (c) needles, in the upper soil layers (organic and 0–5 cm mineral soil) and in percolation water (5 cm depth) were utilized in calculating Spearman rank correlation coefficients. Nitrogen and S in the needles were calculated per dry weight of needles (mg kg^{-1}), per needle and per needle biomass. Needle biomass was estimated using equation presented by Marklund (1987, 1988), and the N and S pools in needle biomass were then calculated by multiplying the biomass by the corresponding needle concentrations. Nitrogen and S in the organic and in the upper mineral soil (0–5 cm) layer were calculated per dry weight (mg kg^{-1}), and in case of the organic layer also on an areal basis (g m^{-2}).

Results and discussion

The effect of N and S deposition on needle chemistry based on Level I data

The chemical composition of the tree needles (NPs) was classified into six distinct GNPs (Luyssaert et al. 2004, 2005). The relationship between the N and S deposition and the established GNPs showed that high N deposition coincided more often within two groups (1 and 5) than within the other GNPs for spruce. For pine, on the other hand, there was no evidence to show that the mean N deposition values were different for different GNPs. However, there was a significant relationship between the exceedance of the threshold for N or S deposition and the occurrence of GNPs 1 or 5 for both tree species. In addition, GNPs 1 and 5 were best described as profiles that are consistent with the expectations of the needle composition for simultaneously elevated N and S deposition. On the average, the elemental composition of <13% of the spruce samples and 6% of the pine samples was associated with elevated N and S deposition during 1987–2000. The extent to which elevated deposition affected the elemental status of spruce needles decreased during 1987–2000. The same trend was not apparent in pine. When fitted using Logit models, the relationships between the NPs and selected stand, site and climatic variables were found to be non significant.

Relationships between soil and soil solution chemistry and needle chemistry

The N concentrations in the organic and 0–5 cm mineral soil layers correlated strongly with the respective concentration in the c needles on the spruce plots. On the pine plots, however, the correlations were non-significant (Table 1). On the spruce plots, the correlation between the N status of the organic layer and N in the needles was also significant when the needle N status was expressed as the N content per needle. There were no significant correlations between the N pool in the needle biomass and the N concentrations in the uppermost soil layers.

On the spruce plots, the concentration of total N and dissolved organic N (DON) in percolation water consistently showed positive correlation ($0.047 < p < 0.10$) with the N concentration in the c needles in every year of needle sampling (1999, 2001, 2003 and 2005, $n = 6-8$). In contrast, there were only sporadic significant correlations between the inorganic forms of N in percolation water and the needle N concentrations. On the pine plots, only DON in percolation water correlated positively with the N concentration in the c needles; this occurred in 2003 ($p = 0.071$, $n = 8$) and in 2005 ($p = 0.094$, $n = 7$).

The S concentration in the c needles correlated significantly only with the amount of S in the organic layer, calculated on an areal basis (combined dataset of pine and spruce; Table 1). On the spruce plots, the total S and $\text{SO}_4\text{-S}$ concentrations in percolation water were consistently positively correlated with the S concentration in the needles in every sampling year (1999, 2001, 2003 and 2005). On the pine plots, positive correlation between the total S and $\text{SO}_4\text{-S}$ concentrations in percolation water and needle S was found only in 1999 ($p < 0.076$).

In conclusion, the needle S and N concentrations showed significant correlations with the concentrations of N and S in the organic layer, in the upper mineral soil layer, and in percolation water, more consistently on the spruce than on the pine plots. One reason behind this difference might be that in pine plots water availability limits nutrient uptake. The consistent significant

Table 1. Spearman rank correlation coefficients between a) nitrogen (N) and b) sulphur (S) concentrations in the organic layer, in the uppermost mineral soil layer (0-5 cm) and in current (c) needles sampled in 1997 (n = 13, 13 and 26 in pine, in spruce and on all plots, respectively; p < 0.001 ***, p < 0.01**, p < 0.05*).

a)	N, mg kg ⁻¹ in organic layer			N, mg kg ⁻¹ in mineral soil			N, g m ⁻² in organic layer		
	Pine	Spruce	Total	Pine	Spruce	Total	Pine ¹	Spruce ²	Total ³
N, mg kg ⁻¹ dwt. needles	0.391	0.802 **	0.494 *	0.352	0.749 *	0.299	0.433	0.786 *	0.772 **
N, needle ⁻¹	0.360	0.773 *	-0.047	0.108	0.351	-0.316	0.082	0.357	-0.174
N, needle biomass ⁻¹	0.074	0.470	0.363	-0.230	0.225	0.362	-0.209	0.500	0.146

b)	S, mg kg ⁻¹ in organic layer			S, g m ⁻² in organic layer		
	Pine	Spruce	Total	Pine ¹	Spruce ²	Total ³
S, mg kg ⁻¹ dwt. needles	0.434	0.295	0.351	0.414	0.679	0.538 *
S, needle ⁻¹	0.148	0.192	-0.151	0.009	0.071	-0.203
S, needle biomass ⁻¹	-0.011	0.302	0.210	-0.182	0.107	0.075

¹n = 11, ²n = 7, ³n = 18

relationship between the DON concentration in percolation water and the N status of the trees suggests that DON may serve as an important indicator of N availability in boreal forest ecosystems.

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