

# The effect of Scots pine, Norway spruce and silver birch on the chemical composition of stand throughfall and upper soil percolation water in northern Finland

Antti-Jussi Lindroos<sup>1)</sup>, John Derome<sup>2)†</sup>, Kirsti Derome<sup>2)</sup> and Aino Smolander<sup>1)</sup>

<sup>1)</sup> Finnish Forest Research Institute, P.O. Box 18, FI-01301 Vantaa, Finland

<sup>2)</sup> Finnish Forest Research Institute, P.O. Box 16, FI-96301 Rovaniemi, Finland

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The aim of this study was to determine the effect of pine (*Pinus sylvestris*), spruce (*Picea abies*) and birch (*Betula pendula*) on the chemical composition of stand throughfall (TF), percolation water (PW) and forest soil in northern Finland. The order of the tree species as regards the pH was approximately the same in both the soil and PW samples: birch > spruce > pine (O horizon), birch > spruce = pine (E horizon). Tree species did not have a notable effect on the DOC concentrations in PW. The base saturation and the Ca and Mg concentrations were the highest in the birch stand. The total Al concentration in PW was mainly related to the concentration of organic Al complexes in all the stands. The total and organically complexed Al concentration was its smallest at a depth of 10 cm in the spruce stand. Whether the properties of DOC present under spruce are the reason for the smaller formation of organic Al complexes in the spruce stand requires further research.

## Introduction

Tree species have an important effect on the chemical composition of stand throughfall (e.g. Hyvärinen 1990, Robertson *et al.* 2000). Due to differences in the canopy structure, for instance, spruce canopies have a higher potential to intercept dry deposition from the atmosphere than pine canopies (e.g. Bredemeier 1988). According to Mustajärvi *et al.* (2008), spruce has a larger and more layered canopy area than pine, and this affects the processes regulating nitrogen (N) fluxes as rainwater passes down through the canopy layer. Sulphate (SO<sub>4</sub>), dissolved organic carbon (DOC) and base cation fluxes in stand throughfall have been reported to be higher in

spruce than in pine stands in boreal coniferous forests in Finland (Lindroos *et al.* 2006, 2007, 2008). As compared with coniferous tree species, birch is generally considered to decrease deposition acidity and to increase the concentrations and fluxes of e.g. magnesium (Hyvärinen 1990).

Different tree species also have a variable effect on the chemical properties of the soil and soil solution. For example, Norway spruce has frequently been reported to have an increasing effect on soil acidity and a decreasing effect on the concentrations of exchangeable nutrients (Nihlgård 1971, Mikola 1985, Priha and Smolander 2000). In contrast, birch is generally considered to affect positively many soil properties related to site fertility (Gardiner 1968). An

increasing effect on soil pH and base saturation, as well as on nutrient concentrations, have been reported in many studies on the role of birch in forest ecosystems (e.g. Mikola 1985, Priha and Smolander 1999, Smolander *et al.* 2005). Microbial biomass and activities related to C and N cycling are often higher in soil under birch than under conifers (Priha and Smolander 1999, Smolander and Kitunen 2002, Smolander *et al.* 2005, Kanerva and Smolander 2007).

Although each tree species clearly has a different kind of effect on forest soil properties, it is often difficult to separate the tree species effect from the effect of natural soil factors prevailing in a specific area which, in turn, favour the establishment of a certain tree species. Forest management has had a considerable effect on the site-type distribution of tree species in our forests: up until recently, monoculture was the prevailing silvicultural practice, with specific tree species being restricted to the most favourable sites from the point of view of timber production. For example, pine stands are common on dry and dryish mineral soil sites where the nutrient availability is naturally relatively low, while spruce and birch are common on moist site types where the fertility is usually higher than on the dryer sites (Tamminen 2000). In order to be able to study the effect of tree species, the establishment of experiments in stands comprising only one tree species is absolutely essential. In Finland, the effect of birch, spruce and pine on soil properties has been studied, for example, in a tree species experiment located in northern Finland (e.g. Smolander and Kitunen 2002, Lindroos *et al.* 2003, Kanerva and Smolander 2007, Kanerva *et al.* 2008).

The aim of this study was to determine the effect of Scots pine, Norway spruce and silver birch on the chemical composition of stand throughfall (TF), percolation water (PW) and forest soil in a tree species experiment located in northern Finland. We hypothesised that tree species would have a significant effect on the acidity and DOC concentration of TF and PW, and possible different pH and DOC levels associated with the individual tree species would be related to the concentrations of Ca, Mg, Na, Si and Al in PW. Calcium and Mg are important plant nutrients and also play a decisive role in the buffering mechanisms of forest soils. Increased acidity can

be reflected as an increased weathering input of Na (and other base cations) and Si from the soil minerals. The Al concentration in soil solution is known to be controlled by acidity and DOC, and it is an important indicator of the forest soil acidity status and podzolisation processes.

## Material and methods

### Study site

The study site was located in Kivalo, northern Finland (66°N, 26°E). In this tree species experiment, silver birch (*Betula pendula*), Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) stands had been established close to each other on the same geomorphological formation. According to the Finnish forest site type classification, the site type was *Hylocomium–Myrtillus* (Cajander 1949). This means that these two species are characteristic of the understorey vegetation cover. This forest site type is of the “mesic” type, and is of medium fertility. The moss coverage was the most evenly distributed in the pine stand, and the birch stand had more grasses and herbs than the pine and spruce stands (Smolander and Kitunen 2002). According to Nieminen and Smolander (2006), the average coverage (%) of the main understorey species in the birch, pine and spruce stands were: *Vaccinium myrtillus* (42%, 41%, 25%), *Deschampsia flexuosa* and other grasses and herbs (23%, 2%, 0.5%). The coverage of *Pleurozium schreberi* was > 50% in the pine stand, and it was almost absent in the birch stand.

The soil type was podzol, and the soil material consisted of unsorted till. The soil material (C horizon, < 0.063 mm fraction) was composed of the following minerals in the decreasing order of abundance: quartz, amphibole, albite, magnetite and mica (XRD analysis) (Lindroos *et al.* 2003). The original soil properties in all three stands, as well as the prevailing climatic conditions, were similar. The study area had originally been a homogenous spruce stand, and the birch, spruce and pine stands were established about 70 years ago after clear-cutting of the spruce stand and subsequent prescribed burning. The birch stand was naturally regenerated and, at the

time of the experiment, a pure, single-species stand. The spruce-dominated stand was planted in 1930, and gradually developed an admixture of birch. The pine-dominated stand, which also contained an admixture of birch, was established at a time when pine was favoured in stand cleaning, and the pines were naturally regenerated after the unsuccessful sowing of spruce (Smolander and Kitunen 2002). A detailed description of the stand characteristics is given in Smolander and Kitunen (2002). The basal area ( $\text{m}^2 \text{ha}^{-1}$ ) of the birch stand was 21.3, of the spruce stand 28.4 (spruce 20.0, birch 5.4, pine 3.0), and of the pine stand 22.0 (pine 20.8, birch 1.3). The number of stems per ha were: 1003, 1243 and 875, respectively, and mean height (m): 15.5, 14.6 and 14.9 (Smolander and Kitunen 2002). The mean annual precipitation in the Kivalo area was 622 mm, the mean length of the growing season 136 days, and the mean effective temperature sum (threshold  $+5^\circ\text{C}$ ) 912 d.d. during 1998–2004 (Lindroos *et al.* 2008).

### Sampling of stand throughfall and percolation water

Three sub-plots,  $25 \times 25$  m in size, were established in each stand. Stand throughfall (TF) was collected during the snow-free period in 2000–2003 on one of the sub-plots in each stand using 20 bulk deposition collectors located systematically on the sub-plot. The 20 sub-samples were combined in the field, and a sample was taken for the determination of chemical parameters in the laboratory. Percolation water (PW) was collected during the snow-free period using 15 zero-tension lysimeters located immediately below the organic layer (depth 0 cm), and 15 lysimeters at a depth of 10 cm in the mineral soil for each tree species. The thickness of the E horizon was about 10 cm in all the stands, which means that the percolation water studied in our experiment represented the O (depth 0 cm) and E (depth 10 cm) horizons. The construction and installation of the lysimeters are described in detail in Derome *et al.* (1991). The 15 lysimeters/depth/tree species were divided among the 3 sub-plots/tree species so that there were 5 lysimeters at both depths on each of the 3 sub-

plots for each tree species. The five PW samples from the same depth on the same sub-plot were combined in the field at each sampling occasion, i.e. there were potentially 3 combined PW samples for each tree species per sampling occasion for the depths 0 cm and 10 cm. There was a total of 22 sampling occasions during 2000–2003. The number of TF samples was 20 for each tree species, i.e. on two sampling occasions there was no rainfall. The 3 PW samples at a depth of 0 cm from the 3 sub-plots were obtained for almost every sampling occasion and for each tree species, i.e. the number of samples varied between 61–66. However, it was not possible to obtain samples from the depth of 10 cm on every sampling occasion, and the number of samples was therefore lower than at a depth of 0 cm. The number of samples was also lower for the Al fractionation results owing to the fact that only the samples containing a sufficient volume of water could be used for this analysis.

The pH was measured on the TF and PW samples, and the samples were filtered through a  $0.45 \mu\text{m}$  membrane filter. The calcium (Ca), magnesium (Mg) and sodium (Na) concentrations were determined using ion chromatography (IC), the aluminium (Al) and silicon (Si) concentrations (PW only) using inductively coupled plasma atomic emission spectrophotometry (ICP/AES), and the dissolved organic carbon (DOC) concentration on a TOC analyser. Aluminium fractionation of the PW samples was carried out according to the procedure described by Derome *et al.* (1998). In addition to the total Al measured by the ICP/AES, total reactive Al was determined by flow injection analysis (FIA) both before and after the passage of the sample through a cation exchange column. The monomeric  $\text{Al}^{3+}$  fraction was calculated by subtracting non-exchangeable reactive Al fraction from total reactive Al.

Significance of differences among the mean values for the birch, spruce and pine stands were tested using ANOVA followed by Tukey's test. Correlations between the chemical parameters were evaluated by calculating Pearson's correlation coefficients. Differences and correlations were considered significant at  $p < 0.05$ . No statistical tests were performed on the soil results due to the small number of observations ( $n = 3$ ).

## Soil chemical analysis

Soil samples were taken from 4 soil profiles (C horizon sample from 2 profiles) on each sub-plot (three sub-plots per tree species), and a composite sample was prepared by combining 4 (2) sub-samples per soil layer (organic layer: Of, Oh, mineral soil horizons: E, B, C) from the same sub-plot. This gave three soil samples per layer for each tree species. The pH was determined in a soil/water slurry (15:25 v:v). Exchangeable base cations (Ca, Mg, K, Na) and Al, Fe and Mn were determined by extraction with  $\text{BaCl}_2$  and the extract analysed by ICP/AES (Hendershot and Duquette 1986, Hendershot *et al.* 1993). Exchangeable acidity was determined by titration with NaOH to pH 7 (Halonen *et al.* 1983). Effective cation exchange capacity (CEC) was calculated as the sum of the equivalent values of the base cations and exchangeable acidity, and base saturation (BS, %) as the proportion of base cations out of CEC. The C and N concentrations of the soil samples were determined on a total CHN analyser (Leco).

## Results

### Soil properties

In the organic layer (Of and Oh) and E horizon, the soil pH was the highest in the birch stand and the lowest in the pine stand (Table 1). In the B and C horizons, the soil pH was the lowest in the spruce stand, with similar values for soil pH in the birch and pine stands. The C concentration (%) in the organic layer was the lowest in the birch stand, but similar in the mineral soil in the three stands. The C/N ratio in the Of horizon followed the order birch < spruce < pine and in the Oh horizon birch = spruce < pine, but the values were relatively similar in all the other soil horizons in all three stands (Table 1).

The exchangeable Ca and Mg concentrations in the organic and E horizons were the highest in the birch stand, and the exchangeable Al concentrations correspondingly the lowest in the same horizons in the birch stand. The exchangeable Al concentration was the highest in all the soil horizons (except the upper part of the B horizon) in

the spruce stand (Table 1). There were no clear consistent differences between the tree species in the cation exchange capacity (CEC) of the individual soil horizons (Table 1). On the other hand, the base saturation (BS, %) was the highest in all the soil horizons in the birch stand (Table 1).

### Stand throughfall and percolation water

#### Acidity and DOC

The mean pH of the TF and PW (depth 0 and 10 cm) were significantly ( $p < 0.05$ ) higher in the birch than in the spruce and pine stands. Furthermore, the mean pH of the TF and PW (0 cm) was also significantly higher in the spruce stand than in the pine stand. At a depth of 10 cm in the mineral soil, the pH values were at a similar level in both the spruce and pine stands (Fig. 1).

The DOC concentration in TF was higher in the spruce and pine stands than in the birch stand (Fig. 1). At a depth of 0 cm the highest mean DOC concentration occurred in the pine stand, and the value was significantly higher than for birch; there was no significant difference found between the pine and spruce stands. The DOC values were at a similar level at a depth of 10 cm in all three stands.

#### Ca, Mg, Na, Al and Si

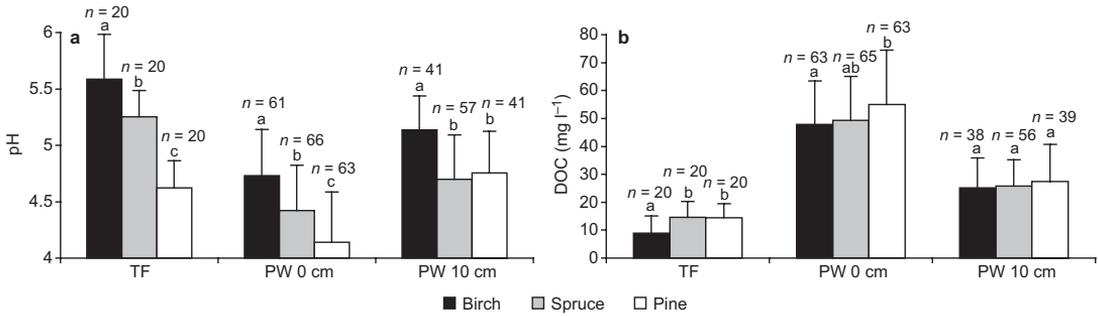
The mean Ca concentrations in TF were at a similar level in the birch, spruce and pine stands. The mean Ca concentration in PW (0 and 10 cm) was the highest for birch; the value was significantly higher than that for pine at a depth of 0 cm, and also as compared with that for spruce at a depth of 10 cm (Fig. 2).

There were no statistically significant differences in the mean Mg concentrations in TF and PW (10 cm) among the tree species. However, there were clear significant differences in PW at a depth of 0 cm. The mean values decreased in the following order: birch, spruce, pine (Fig. 2).

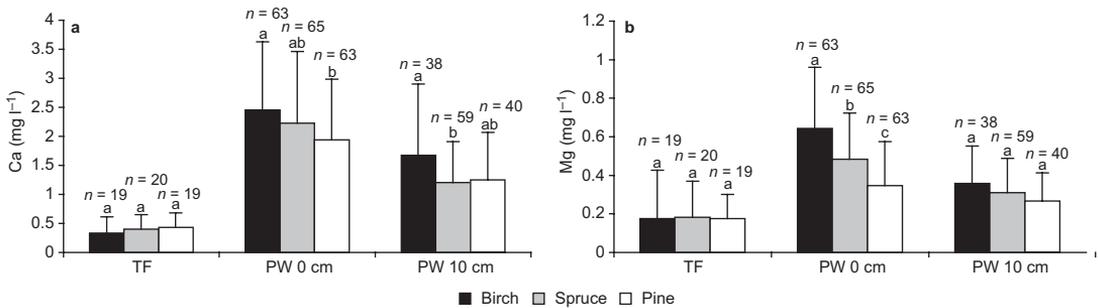
There were no significant differences in the mean Na concentration in TF and PW (depth 10 cm) between the tree species. However, the mean Na concentration was the lowest at a depth

**Table 1.** Thickness of the soil horizons, pH(H<sub>2</sub>O), C concentrations, C/N ratios, the concentrations of exchangeable Ca, Mg, Al, the cation exchange capacity (CEC) and the base saturation (BS). Given are means ± SDs (n = 3).

Parameter	Horizon	Birch	Spruce	Pine
Thickness (cm)	Of	2.0 (0.6)	2.0 (1.0)	3.0 (0.0)
	Oh	2.0 (1.0)	2.0 (0.6)	2.0 (0.0)
	E	11.0 (0.6)	10.0 (1.0)	11.0 (2.1)
	B1	11.0 (3.6)	14.0 (1.2)	14.0 (4.2)
	B2	23.0 (7.8)	21.0 (3.8)	30.0 (6.6)
	C			
pH	Of	4.2 (0.3)	4.0 (0.1)	3.6 (0.1)
	Oh	3.9 (0.2)	3.8 (0.2)	3.4 (0.0)
	E	4.6 (0.3)	4.4 (0.2)	4.3 (0.1)
	B1	5.4 (0.5)	5.1 (0.1)	5.4 (0.3)
	B2	5.5 (0.2)	5.1 (0.1)	5.5 (0.1)
	C	5.7 (0.1)	5.2 (0.2)	5.5 (0.0)
C (%)	Of	48.0 (7.6)	51.0 (2.1)	51.0 (4.6)
	Oh	35.0 (14.0)	40.0 (6.2)	48.0 (3.0)
	E	0.4 (0.2)	0.4 (0.1)	0.4 (0.1)
	B1	3.3 (3.1)	3.9 (2.8)	4.2 (3.4)
	B2	0.5 (0.0)	0.6 (0.3)	0.3 (0.1)
	C	0.1 (0.0)	0.3 (0.2)	0.1 (0.0)
C/N	Of	26.8 (2.0)	30.9 (2.0)	37.5 (2.3)
	Oh	32.7 (1.1)	32.4 (0.5)	40.2 (1.5)
	E	12.9 (6.6)	12.3 (2.2)	13.1 (0.8)
	B1	25.7 (4.9)	25.0 (4.6)	25.2 (5.0)
	B2	19.9 (4.8)	15.1 (2.9)	13.3 (5.5)
	C	8.8 (2.8)	11.5 (4.1)	10.9 (4.7)
Ca (mmol <sub>c</sub> kg <sup>-1</sup> )	Of	212.0 (22.55)	142.0 (37.85)	143.0 (10.19)
	Oh	148.0 (77.32)	81.0 (32.28)	124.0 (15.75)
	E	1.47 (0.17)	0.66 (0.39)	0.95 (0.29)
	B1	5.20 (4.47)	5.22 (3.60)	6.80 (7.74)
	B2	0.69 (0.27)	0.56 (0.14)	0.60 (0.26)
	C	0.36 (0.15)	0.42 (0.15)	0.36 (0.06)
Mg (mmol <sub>c</sub> kg <sup>-1</sup> )	Of	58.0 (6.72)	43.0 (16.66)	36.0 (3.40)
	Oh	40.0 (22.18)	26.0 (13.42)	30.0 (13.07)
	E	0.51 (0.02)	0.37 (0.19)	0.29 (0.02)
	B1	0.56 (0.30)	0.55 (0.30)	0.60 (0.44)
	B2	0.17 (0.02)	0.13 (0.03)	0.11 (0.02)
	C	0.17 (0.05)	0.13 (0.02)	0.08 (0.01)
Al (mmol <sub>c</sub> kg <sup>-1</sup> )	Of	4.10 (2.58)	34.77 (37.91)	20.73 (9.79)
	Oh	21.97 (12.71)	77.20 (72.42)	39.63 (33.10)
	E	4.83 (0.77)	7.60 (2.36)	6.14 (2.35)
	B1	29.03 (47.41)	25.55 (25.04)	15.57 (18.02)
	B2	1.57 (1.42)	3.55 (2.10)	0.66 (0.22)
	C	1.21 (0.51)	2.59 (1.07)	0.85 (0.12)
CEC (mmol <sub>c</sub> kg <sup>-1</sup> )	Of	381.0 (8.29)	337.0 (9.70)	320.0 (20.39)
	Oh	287.0 (130.31)	265.0 (25.34)	316.0 (23.06)
	E	8.89 (1.83)	10.75 (1.37)	9.51 (2.01)
	B1	32.39 (47.97)	30.82 (26.69)	22.76 (25.04)
	B2	1.99 (0.98)	5.06 (1.49)	2.21 (0.89)
	C	1.47 (0.23)	3.04 (1.77)	2.68 (0.68)
BS (%)	Of	81.7 (6.4)	68.3 (10.0)	64.7 (3.5)
	Oh	70.3 (6.4)	48.7 (18.5)	54.3 (3.8)
	E	26.7 (2.5)	13.7 (5.0)	17.3 (5.5)
	B1	58.7 (43.1)	23.7 (7.8)	54.3 (39.7)
	B2	65.0 (35.5)	18.3 (6.7)	40.0 (8.7)
	C	55.0 (6.2)	28.3 (10.0)	24.0 (7.9)



**Fig. 1.** (a) pH and (b) DOC concentration (mean + SD, 2000–2003) in stand throughfall (TF) and percolation water (PW) (0 and 10 cm depths in the mineral soil) in the birch, spruce and pine stands. Statistically significant ( $p < 0.05$ ) differences between the tree species are indicated using different letters (ANOVA followed by Tukey's test).



**Fig. 2.** (a) Ca and (b) Mg concentrations (mean + SD, 2000–2003) in stand throughfall (TF) and percolation water (PW) (0 and 10 cm depths in the mineral soil) in the birch, spruce and pine stands. Statistically significant ( $p < 0.05$ ) differences between the tree species are indicated using different letters (ANOVA followed by Tukey's test).

of 0 cm in PW in the birch stand (Fig. 3).

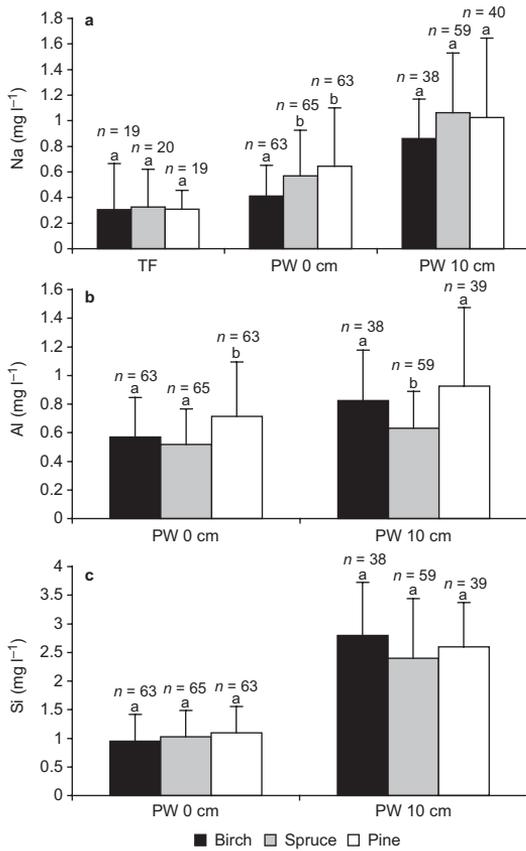
The Al and Si concentrations were determined only on the percolation water (Fig. 3). The mean Al concentration was the highest at a depth of 0 cm in the pine stand. At a depth of 10 cm, the mean Al concentration was the lowest in the spruce stand. No significant differences were found in the Si concentration between the tree species (Fig. 3).

### Relationships between the chemical parameters, and Al fractionation

The pH correlated negatively with the Al and DOC concentrations in PW at both depths (0 and 10 cm) for all three tree species, and the correlations were, in general, stronger at a depth of 10 cm in the mineral soil (Table 2). However, the relationships between the pH values and Al concentrations were somewhat different between the tree species at a depth of 10 cm. The Al concen-

trations increased with decreasing pH values for all the tree species, but higher Al concentrations occurred already at higher pH values for birch compared with the distributions for the spruce and pine stands. The Al concentrations were also clearly lower in the spruce stand at lower pH values than in the pine stand.

In general, the DOC concentration correlated positively with the Ca and Mg concentrations in TF and PW. The only clear exception to this was the lack of correlations with Ca for pine and spruce at a depth of 10 cm (Table 2). The DOC concentration correlated positively with the Al concentration at both depths for all three tree species (Table 2). The distribution of the DOC concentrations in PW (depth 10 cm) was very similar for all the tree species, as was also the case for the mean values at this depth (Fig. 1). The Al concentrations increased linearly in the pine and birch stands with increasing DOC concentrations (Fig. 4). In the spruce stand, however, the Al concentration increased with



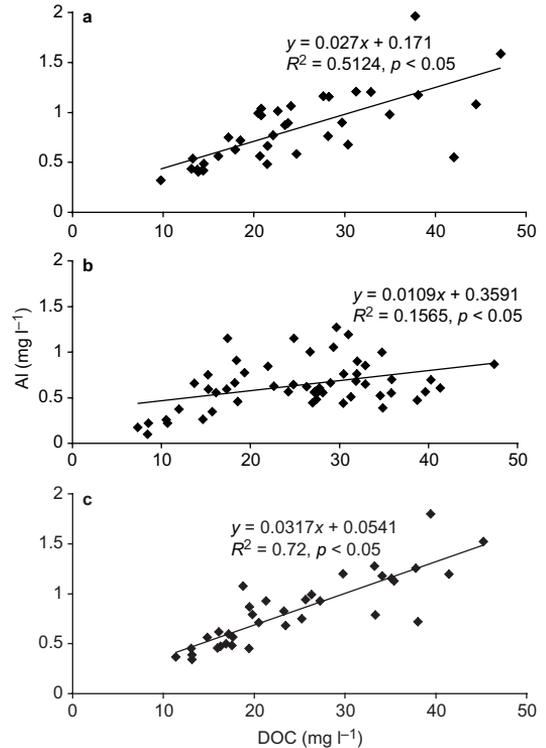
**Fig. 3.** (a) Na, (b) Al<sub>tot</sub> and (c) Si concentrations (mean + SD, 2000–2003) in stand throughfall (TF) and percolation water (PW) (0 and 10 cm depths in the mineral soil) in the birch, spruce and pine stands. Statistically significant ( $p < 0.05$ ) differences between the tree species are indicated using different letters (ANOVA followed by Tukey's test).

increasing DOC concentrations only at low DOC concentrations. In contrast, there was no clear increase in the Al concentration when the DOC values increased above ca. 20 mg l<sup>-1</sup> (Fig. 4).

The concentration of the Al<sup>3+</sup> fraction (monomeric Al) in PW was very low at depths of 0 and 10 cm (Fig. 5). At the 10 cm depth, the total Al concentration, as well as the non-exchangeable Al fraction (Al<sub>tot</sub> - Al<sup>3+</sup>, primarily organically complexed Al), were the lowest in the spruce stand (Fig. 5).

## Discussion

The fact that the pine stand represented the



**Fig. 4.** The relationship between the DOC and total Al concentration in percolation water collected at a depth of 10 cm in the mineral soil in (a) birch, (b) spruce and (c) pine stands.

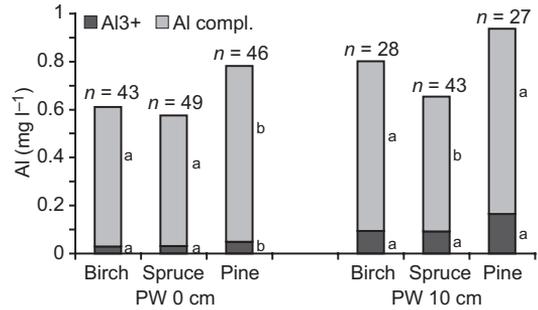
most acidic conditions in stand throughfall as well as in the uppermost layers of the podzolic soil (both soil and percolation water, PW) was somewhat surprising, because earlier studies in boreal forests in Finland reported lower soil pH values in spruce than in pine stands (e.g. Priha and Smolander 1999). However, the situation became reversed in our stands on moving deeper down the soil profile; the soil pH in the B and C horizons was clearly the lowest in the spruce stand.

Birch had a less acidifying effect on the uppermost layers of the soil compared to the situation in the spruce or pine stands, which is in good agreement with several other studies (e.g. Mikola 1985, Priha and Smolander 1999). This was reflected as a higher soil pH in the organic layer and in the E horizon, as well as a higher percolation water pH in the birch than in the spruce and pine stands. Hyvärinen (1990) reported that TF in southern and central Finland is less acidic

in birch-dominated stands than in spruce and pine stands, and concluded that this phenomenon was at least partly due to the decreasing effect of birch leaf litter on acidity. The mean pH of the stand throughfall in our study in northern Finland was also significantly higher in the birch stand than in the spruce and pine stands.

The acidity status of the soil was in good agreement with the buffering properties of the soil in our study. The base saturation (BS), exchangeable Ca and Mg concentrations, and the Ca and Mg concentrations in PW, were the highest in the birch stand. Priha and Smolander (1999) also reported that birch was associated with the highest BS values in their tree species experiment, which comprised the same species as in our study.

In our study, the starting point when studying the effect of tree species on percolation water chemistry by relating the pH values and DOC concentrations to the other chemical parameters, was the fact that the acidity status varied between the tree species in the uppermost part of the soil, but there were no major differences in the DOC concentrations. The lower pH in PW below the



**Fig. 5.** The concentrations of total Al, organically complexed Al and monomeric Al<sup>3+</sup> (mean 2000–2003) in percolation water (depths 0 and 10 cm in the mineral soil) in the birch, spruce and pine stands. Statistically significant ( $p < 0.05$ ) differences between the tree species are indicated for the complexed Al and monomeric Al<sup>3+</sup> using different letters (ANOVA followed by Tukey's test).

organic layer (depth 0 cm) in the spruce and pine stands was reflected as a higher Na concentration in PW at the same depth. Na is released in the weathering of soil minerals, and this process also consumes H<sup>+</sup> ions (van Breemen *et al.* 1984, Schwertman *et al.* 1987). According to Giesler *et al.* (2000) and Johnson *et al.* (2000), there can be

**Table 2.** Significant Pearson's correlation coefficients ( $p < 0.05$ ) for correlations between the chemical parameters in stand throughfall (TF) and percolation water (PW).

		pH			DOC		
		Birch	Spruce	Pine	Birch	Spruce	Pine
TF	Al	–	–	–	–	–	–
	Ca	–	–	–	0.78	0.57	–
	Mg	–	–	–	0.86	0.61	0.52
	Na	–	–	–	0.54	–	0.85
	Si	–	–	–	–	–	–
	DOC	–	0.67	–	–	–	–
	n	19	20	19	19	20	19
PW (0 cm)	Al	–0.35	–0.55	–0.34	0.47	0.63	0.51
	Ca	–	–	–0.45	0.70	0.67	0.72
	Mg	–	–0.28	–0.33	0.69	0.75	0.67
	Na	–	–	–0.25	–	–	–
	Si	–0.27	–0.25	–	–	0.60	0.54
	DOC	–0.27	–0.39	–0.27	–	–	–
	n	61	65	63	61	65	63
PW (10 cm)	Al	–0.60	–0.40	–0.43	0.72	0.40	0.85
	Ca	–0.40	–	–0.46	0.65	–	–
	Mg	–0.42	–	–0.59	0.61	0.31	0.37
	Na	–	–	–	–	–	–
	Si	–	–	–	–	–	–
	DOC	–0.76	–0.63	–0.77	–	–	–
	n	37	55	39	37	55	35

a significant amount of weathering of the mineral soil particles in the organic layer. Sodium is released into the solution, for example, in the weathering of albite (Na plagioclase feldspar), and this process is favoured by increasing acidity (Crabtree 1986). According to Lindroos *et al.* (2003), albite is a relatively common mineral in the < 0.063 mm soil particle fraction on our sample plots. The location of our sample plots in a low-pollution, non-marine environment means that an important source of the acidity is organic acids produced in the organic layer under a cool and moist climate, and the main source of Na is soil minerals since the Na input from deposition is very low.

There were no differences in the Si concentrations in PW between the tree species. The correlation between pH and the Na and Si concentrations was weak or absent within each stand. The Na and Si concentrations are most probably related to the release of Na and Si through weathering. Another possible source of Si in the soil solution in podzolic soils is phytoliths (Farmer *et al.* 2005).

The total Al concentration in PW was the highest at a depth of 0 cm in the pine stand, where the pH was also the lowest and the DOC concentration slightly higher than in the other stands. Both the lower pH and higher DOC could have contributed to the higher total Al concentration, but the role of organic complexes is the most important factor controlling the total Al concentration immediately below the O horizon. The proportion of complexed Al (i.e.  $Al_{tot} - Al^{3+}$ ) out of total Al was more than 95% at this depth, and the concentration of complexed Al was the highest in the pine stand. Many studies have demonstrated that most of the total Al in soil solution is associated with organic complexes in the upper layers of podzolic soils (e.g. Nilsson and Berqkvist 1983, Berggren 1992, Lundström 1993). The source of Al in the soil solution can be both cation exchange processes and weathering, and the latter process can also be considerable in the O horizon or boundary layer between the O and E horizons, as already discussed (Giesler *et al.* 2000, Johnson *et al.* 2000).

The total Al concentration increased with decreasing pH in all the stands and, for example, at a depth of 10 cm the total Al concentration

increased already at higher pH values in the birch stand compared to the situation in the pine stand. A logical explanation for this is that the total Al concentration is, in actual fact, controlled by the concentration of organic complexes (DOC) and not pH, and the relationship we found in this study is a product of the dependence between DOC and pH. The regulating role of organic complexes on the Al concentrations was also evident at a depth of 10 cm, because about 85% of the total Al was in the complexed form of Al. The total Al concentration also increased with increasing DOC concentration.

The total Al concentration was its smallest at a depth of 10 cm in the spruce stand. However, the total Al concentration increased with increasing DOC concentration only at DOC values of below 20 mg l<sup>-1</sup> in the spruce stand, which was a completely different pattern to that in the pine and birch stands, where the total Al concentrations increased more clearly with increasing DOC. The results of Al fractionation also indicated that the proportion of complexed Al was clearly lower in the spruce stand than in either the pine or birch stands. This also accounted for the lower total Al concentration in PW at 10 cm depth in the spruce stand. The question arises of why less organic Al complexes are formed in the spruce stand, even though the mean DOC concentration was similar to those in the pine and birch stands. The results presented by Lindroos *et al.* (2003) for DOC fractionation of PW collected below the organic layer in this experiment indicated that the proportion of hydrophobic acids and neutrals, as well as hydrophilic acids, were relatively similar in both the pine and birch stands, and that the situation in these two stands clearly differed from that in the spruce stand. However, whether the properties of DOC produced under spruce are the reason for the smaller formation of Al complexes requires further research in the future. For example, expressed per unit organic matter, the concentration of water-extractable DOC was the highest in the organic layer under birch but no major tree-species-specific differences were found in the percentage distribution of DOC into different chemical or molecular size fractions (Smolander and Kitunen 2002). Kiikkilä *et al.* (2006) showed that the degradability of DOC,

collected by centrifugation, was the highest in the litter layer under birch and the highest in the organic layer under spruce. Lindroos *et al.* (2003) found no clear differences in the weathering potential of the soil solution between the tree species, even though there were some differences in the DOC concentrations and fractions of the soil solution collected immediately below the organic layer.

Bulked soil and percolation water samples were used in our study for each tree species, which means that this reduced the possibility to study the variation within each tree species. Only one mean value was calculated for each tree species for PW parameters, because it was not possible to obtain samples from all or the same lysimeters per subplot on each sampling occasion. Therefore the results presented here give an overall picture of the differences between the tree species, but there can be considerable variation in the soil and soil solution composition within each stand (Giesler and Lundström 1993).

In our experiment, the tree species effect on many of the parameters was relatively small. Nitrogen, which is one of the key elements in the nutrient cycling in forest ecosystems, was not investigated in this study. However, an earlier study (Kanerva and Smolander 2007) showed tree-species-specific differences in soil N transformations. This could be reflected to the percolation water characteristics as well.

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