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Aluminum and iron chemistry in the O horizon changed by a shift in tree species composition

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Abstract. In the present study we characterized the buffering system including aluminum in the organic surface horizon (O) of field experiments with replicated plots of pure Norway spruce (*Picea abies* (L.) Karst) and replicated plots of spruce with a birch (*Betula pendula* Roth and *B. pubescens* Ehrh.) admixture. Our results show that a change in tree species composition may have a rather large, short-term (12 years) effect on the concentration of organically bound aluminum in the humus layer (H) of the O horizon. The pure spruce plots had a significantly higher concentration of exchangeable aluminum (Al_e) and organically bound (pyrophosphate extractable) aluminum (Al_P) in the H layer and a lower concentration of each base cation. Furthermore, our results confirm earlier findings that aluminum has base cation properties in acidic organic horizons. Thus, the change in tree species composition did not affect the pH in spite of a change in base saturation, because base cations were mainly compensated for by aluminum. The change in organically bound aluminum was accompanied by a similar change in organically bound pyrophosphate extractable iron (Fe_P). The observed differences between the mixed and pure spruce plots in the amounts of Al_P and Fe_P in the H layer could not be explained by estimated differences in biocycling of Al and Fe either by above-ground litterfall or by root turnover.

Introduction

In boreal regions, the O horizon is an important constituent of the soil system, because it often contains a large fraction of the fine-root biomass (Kimmins and Hawkes 1978; Brandtberg et al. 2000) and also contributes significantly to the cation exchange capacity of the soil. Furthermore, the O horizon is important in buffering acidity of anthropogenic origin (James and Riha 1986). Thus base cation and aluminum chemistry of such horizons may influence the quality of surface waters (cf. Cronan et al. (1986)).

An important effect of aluminum in O horizons with possible consequences for the growth and vitality of forests is its large ability to compete with base cations for exchange sites and thus to decrease the potential for storage of nutrients (Lawrence et al. 1995). Direct toxic effects of aluminum are seldom encountered in this layer, because dissolved aluminum in the O horizons is usually in an organically complexed, less toxic form (David and Driscoll 1984; Dahlgren et al. 1991) except possibly in heavily polluted (acidified) areas (cf. Kram et al. (1995)).

Lawrence et al. (1995) suggested that aluminum could be transferred from the mineral soil to the O horizon in three different ways: through litter cycling, through an upward movement of soil water from the mineral soil, where the concentration of dissolved Al is greater (cf. Mulder et al. (1991)), or through mixing of mineral particles into the O horizon. The above-ground input of aluminum mainly takes place via litterfall, whereas the cycling via canopy throughfall is of minor importance (Bergkvist 1987; Rustad and Cronan 1989). However, root turnover is in some cases considered to be much more important than above-ground litter turnover in the cycling of aluminum from the mineral soil (Vogt et al. 1987). Furthermore, van van Breemen et al. (2000) suggested that mycorrhizal fungi might be active in the transfer of aluminum from the mineral soil to the O horizon. Soil solution concentrations of aluminum have in several cases been found to be significant beneath the O horizon even before any contact with the E horizon has occurred (David and Driscoll 1984; Dahlgren et al. 1991; Giesler et al. 2000). Because of this, it has been suggested that the flux of biocycled aluminum may be significant in the process of podsolization, i.e. in the formation of a spodic B horizon (Driscoll et al. 1985; Giesler et al. 2000).

Forest stands dominated by conifers are often associated with a higher degree of cycling (biocycling) of aluminum than comparable hardwood stands (David and Driscoll 1984). For example, Bergkvist and Folkesson (1995) found significantly higher fluxes of aluminum via litterfall in pure Norway spruce (*Picea abies* (L.) Karst) stands compared to pure birch (*Betula pendula* Roth) stands in southern Sweden. Binkley and Valentine (1991) compared small, single species plots of green ash (*Fraxinus pennsylvanica* March), white pine (*Pinus strobus* L.) and Norway spruce in a replicated experiment. Norway spruce had a significantly lower concentration of Mg and a higher concentration of Al in the litterfall than had green ash. The upper mineral soil showed a higher concentration of Al and a lower concentration of Ca and Mg in the spruce plots than in the green ash plots.

In acidic organic horizons, the traditional view of aluminum as an acid cation is not valid (Skyllberg 1996; Ross et al. 1996; Skyllberg 1999). In such horizons, dissociated hydrogen ions mainly originate from acids stronger than the hydrated Al^{3+} ion; that is, organic acids and possibly acids of an anthropogenic origin. Consequently, aluminum remains mainly unhydrolysed, as do the base cations. This might be important to considered when evaluating the mechanisms behind tree species effects on forest floor pH.

In this study, we used field experiments with replicated and randomized plots of Norway spruce and Norway spruce with a birch admixture on acid forest soils. The objective was to test the hypothesis that an admixture of birch in spruce stands would cause a lower content of aluminum in the upper O horizon. We examined the potential rates of above- and below-ground biocycling of aluminum from data on aluminum in different biomass fractions. We also included iron in our study. Furthermore, we examined the relationships between pH and adsorbed cations.

Materials and methods

Site descriptions

The present study was based on four sites located in southern and central Sweden (Table 1). Three of the sites, Burhultsnäs (Bn), Huseby (Hb), and Södra skoga (Ss) had replicated and randomized plots containing either (i) 30 to 40-year-old birch (*Betula pendula* Roth and *B. pubescens* Ehrh.) growing as a shelter over similar-aged Norway spruce (*Picea abies* (L.) Karst), referred to as 'mixed', or (ii) spruce only, referred to as 'pure spruce'. The plots (0.075 ha) were established (1983–1985) from young stands of mixed birch and spruce that had developed from planted or naturally regenerated spruce and birch after clear cutting of previously forested sites. At the establishment of the plots the birch was (i) thinned to a shelter of approx. 500 stems ha^{-1}, to give mixed stands, or (ii) all birches were felled to give pure spruce stands. In addition (iii), at each of the Hb and Ss sites one plot was kept in the original state without any thinning, referred to as 'untreated plot'. In 1989, a thinning of the spruce was carried out in all plots except untreated plots. At each site the residues (slash) from the thinnings were left in one set of plots and removed from another set (Tham 1994; Mård 1996). The proportion of birch in terms of basal area in the mixed plots that were sampled for tree biomass (see below) at these sites was 23%, 41% and 58% at the Bn, Hb and Ss sites, respectively (cf. Table 1).

The trees at the fourth site, Siljansfors (Sf), were considerably older (approx. 90 years old) than those of the other stands. The mixed and pure spruce plots were established in 1933 from a mixed birch/spruce stand of 20–25 years of age. Thus, at the forest floor sampling (1995) there had been a difference in tree species composition for 52 years. In all subsequent thinnings, only stem wood was removed. The mixed plots consisted of birch and spruce in approximately equal proportions in terms of basal area. At this site, two plots were left in the original state (untreated plots).

All sites were situated in plane or gently sloping terrain and were forested prior to the establishment of the present stands. The sites were moist to mesic and the humus form was a mor. The forest floor was already well developed at the establishment of the present vegetation. There was no evidence of previous soil preparation or other major site disturbance (e.g. windthrow) on the sites studied. The LF layer (see below) had an average thickness of 2–3 cm and the humus layer had on an earlier sampling occasion an average depth of approx. 10 cm (cf. Table 1). The amounts and dry bulk densities of organic matter (OM) of sampled parts of the O horizon are given in Table 2. For a classification of sampled organic horizons, see below. Typically on these sites, the O horizon was on top of an Eh or A horizon of 5–10 cm depth, under which was a Bh horizon of 10–20 cm depth. The parent material on all the sites was glacial till. The upper mineral soil horizons had a rather high percentage (50–90%) of coarse fragments (> 20 mm); i.e. gravel, cobbles and stones. Soil texture for the upper mineral soil horizons is given in Table 1. Furthermore, data on the number of plots in each treatment and site are given in Table 1,

Table 1. Description of the sites studied.

	Burhultsnäs (Bn)			Huseby (Hb)			Södra Skoga (Ss)			Siljansfors (Sf)		
Province	Västergötland			Småland			Värmland			Dalarna		
Latitude, longitude	57°54′ N, 12°15′ E			56°49′ N, 14°41′ E			60°03′ N, 13°23′ E			60°52′ N, 14°22′ E		
Altitude (m a.s.l.)	110			170			170			260		
Ann. mean temp (°C)[1]	+6.3			+6.4			+3.5			+3.6		
Prec. (mm/y)[1]	940			650			670			590		
Soil classification[2]	Typic Haplorthod			Aquic Haplorthod			Oxyaquic Dystrochrept			Oxyaquic Dystrochrept		
Soil texture[3]	Sandy loam			Loamy sand			Sandy loam			Sandy loam		
H layer (cm)[4]	5.4			13.9			10.1			9.7		
Site index (H100)[5]	23–29			30–35			30–31			26–28		
Stand age (1997)	32			37			39			87–97		
Stand type[6]	Mixed		Spruce	Mixed		Spruce	Mixed		Spruce	Mixed		Spruce
Slash left (n)[7]	1		1	1		1	2		2	2		2
Slash removed (n)[7]	1		1	1		1	1		2			
Species	Birch	Spruce	Spruce	Birch	Spruce	Spruce	Birch	Spruce	Spruce	Birch	Spruce	Spruce
Height (m)[8]	11	8	10	15	9	9	20	8	10	21	15	20
Diameter (cm)[8]	12	9	11	16	9	10	14	7	10	25	17	23
Basal area ($m^2 \cdot ha^{-1}$)[8]	6	19	26	12	17	25	28	20	27	28	20	39

[1] Average (1961–1990) annual mean temperature and precipitation are recorded at nearby climate stations (SMHI, SE-601 76, Norrköping).

[2] Soil classification according to USDA (1994).

[3] Soil texture of the upper 0–10 cm of the mineral soil.

[4] Average depth of the H layer as determined 1991 (Ss), 1992 (Hb and Bn) or 1994 (Sf).

[5] Height (m) of dominant spruce of 100 years of age.

[6] In addition to mixed and pure spruce plots there were untreated plots (Ref. plots) at the Hb, Ss and Sf sites (see text).

[7] Number of plots where slash was left or removed at the thinnings.

[8] Data based on trees in the 16 m × 16 m subplot (see text).

Table 2. Organic matter content of the LF layer per unit area of forest floor and bulk density of organic matter (root free) of the sampled upper 5 cm of the H layer in mixed (Mix) and pure spruce plots (Spr.) at the Bn, Hb, Ss and Sf sites. Standard errors are given within parentheses (n = 2).

		LF (OM kg m^{-2})		H (OM kg dm^{-3})	
Bn	Mix	0.51	(0.015)	0.21	(0.005)
Bn	Spr.	0.53	(0.011)	0.17	(0.025)
Hb	Mix	0.60	(0.037)	0.25	(0.010)
Hb	Spr.	0.38	(0.029)	0.26	(0.036)
Ss	Mix	0.74	(0.057)	0.21	(0.018)
Ss	Spr.	0.47	(0.087)	0.22	(0.010)
Sf	Mix	0.57	(0.10)	0.13	(0.028)
Sf	Spr.	0.49	(0.10)	0.13	(0.036)

as is also a brief description of the sites and stand structures. The sites have been described earlier by Saetre et al. (1997, 1999) and Brandtberg et al. (2000).

Forest floor sampling

The O horizon, including the litter and fermentation layer (LF layer) comprising freshly fallen litter as well as older material with recognizable structure, and the upper 5 cm of the humus layer (H layer), was sampled in October 1995 at Södra Skoga and Siljansfors and in October 1996 at Huseby and Burhultsnäs. A total of 36 points per plot were sampled as follows. The plot was subdivided into 36 equally sized squares. Within each square a tree was randomly selected with the constraint that its diameter should be > 5 cm. In the mixed plots, a birch was selected from every second square. One sampling point was randomly selected within a distance of 0.5–1.5 m from each tree. If the selected point was closer than 0.5 m from an adjacent tree a new point was selected. The LF layer was sampled with a cylinder corer (10 cm diam.). The upper 5 cm of the humus layer (H), which in this case is organic material with no recognizable structure and interwoven with roots, was sampled with a corer (4.5 cm diam.). Thus, in our study the LF layer is similar to the O_i+O_e horizon and the H layer is similar to the O_a horizon of Soil Taxonomy (Soil Survey Staff 1993). All 36 samples were bulked to form one composite sample per plot. On average, the H sample comprised the upper 93%, 36%, 50% and 51% of the entire H layer on the Bn, Hb, Ss and Sf site, respectively, according to an earlier measurement of H layer thickness (see Table 1).

Fresh LF and H samples were passed through a 4-mm mesh sieve. Twigs, cones, etc. were removed by hand from the LF samples and fresh leaves were cut to pass the sieve. Visible roots were removed from the H samples. Dry weights were determined at 105 °C and loss on ignition at 550 °C. The concentration of organic matter was determined by the loss on ignition. The mass of organic matter in the LF layer per unit soil area and the bulk density of organic matter in the sampled part of the H layer determined from sieved (root free) H material and known sampled volume are given in Table 2. The samples were stored at +4 °C prior to further analysis, which was done within 1 week. All chemical analyses were carried out in duplicate.

Soil pH, exchangeable cations, exchangeable acidity and total titratable acidity or base neutralizing capacity (BNC) were all determined using an organic matter to solution ratio of 5.0 g/100 mL. The pH was determined in deionized water (pH(H_2O)) and in 1 M KCl (pH(KCl)) after 4 h of extraction on a reciprocal shaker followed by sedimentation overnight. Exchangeable acidity and cations (including Al and Fe) were extracted (4 h) in 1 M KCl and 1 M NH_4Cl, respectively. The extracts were filtered through paper filters (Munktell 00K, Grycksbo, Sweden) and kept frozen until analysis. The NH_4Cl-extracts were analysed for K, Mg, Ca, Al, and Fe with an inductively coupled plasma atomic emission spectrophotometer, ICP-AES (JY-70 Plus, Longjumeau, France). The KCl-extracts were titrated to pH 6.5 with an autotitrator (ABU900, Radiometer, Copenhagen) to obtain the exchangeable acidity (EA).

Base neutralizing capacity (BNC) was determined by titrating an amount of fresh H material, corresponding to 2.5 g of dry organic matter, in 50 mL 1 M KCl. Increments of 0.75 mL of 1 M NaOH were added until pH 6.5 was obtained. After each addition, the slurry was stirred thoroughly and allowed to equilibrate for 24–36 h with an additional stirring at half way. Then pH was measured in the supernatant with a glass electrode (cf. Binkley et al. (1989)).

To obtain an estimate of organically bound aluminum and iron, pyrophosphate extractable aluminum (Al_P) and iron (Fe_P) were determined in LF and H material that had been stored frozen at –4 °C. LF or H material corresponding to 2 g organic matter (OM) was extracted with 100 mL 0.2 M sodium pyrophosphate for 16 h on a reciprocal shaker, whereafter the extracts were centrifuged at 2000 r.p.m. and filtered through a 0.2 μm membrane filter (Schleicher & Schuell, NC20). Al_P and Fe_P were determined by ICP-AES. Sodium pyrophosphate is frequently used to extract Al^{3+} and Fe^{3+} associated with organic matter (McKeague et al. 1971) for example forest O horizons (Lawrence et al. 1995). Sodium pyrophosphate may also extract $Al(OH)_3$ (Kaiser and Zech 1996) which, however, is seldom present in Spodosol O horizons (cf. Lawrence et al. (1995)).

HNO_3 digestible aluminum (Al_H) and iron (Fe_H) were determined by dry combustion of 2 g air-dried LF or H material at 550 °C for 6 h followed by digestion of the ash in 10 mL of boiling concentrated HNO_3 for 20 min. The digests were diluted 1:2 with distilled water and then filtered through paper filters (Munktell 00H, Grycksbo, Sweden) into 100-mL volumetric flasks. The volume was then adjusted to 100 mL with distilled water. Al_H and Fe_H were determined by ICP-AES. The nitric acid digestion includes aluminum and iron associated with the organic matter. In samples from the H layer it may also include aluminum and iron from mineral grains (cf. Lawrence et al. (1995)).

Exchangeable base cations (K^+, Ca^{2+} and Mg^{2+}) are denoted BC_e. We define CEC_e as the sum of BC_e and EA. The sum of BC_e and BNC is an estimate of the amount of dissociable acidic groups to pH 6.5, i.e. cation exchange capacity at pH 6.5, denoted $CEC_{pH6.5}$. Concentrations of aluminum (Al_e, Al_P and Al_H) and iron

(Fe_e, Fe_P and Fe_H) are expressed as $mmol_c$ per unit weight of organic matter, assuming that these elements are present as Al^{3+} and Fe^{3+}.

Tree and root sampling

Trees were sampled in September 1997 from mixed and pure spruce plots from which slash had been removed at the Bn and Hb sites, whereas at the Ss site the untreated plot with birch and spruce was used instead of the mixed one because of damage to the latter. The sampling was carried out within a 16 m × 16 m subplot (34% of total plot) which was randomly located within the main plot. All trees within this subplot were measured for diameter at 1.3 m above ground level. At the Sf site, sampling was carried out in September 1998 in one mixed and two pure spruce plots. One of the mixed plots was excluded because of recent waterlogging due to clearcutting of an adjacent stand. In each of the 16 m × 16 m subplots, 4 trees per species were randomly selected within strata made by sorting all trees of a species by size of stem basal area and creating four strata with equal numbers of trees. The trees were felled and subsamples taken. Stem and bark were sampled from 5-cm thick discs that were taken at 5 evenly distributed locations along the stem. For spruce, one branch per whorl was taken in a spiral manner along the stem whereas for birch, approximately one quarter of the branches (< 3 cm diam) including foliage was taken as a subsample. For birch, parts with a diameter less than 3 cm were considered to be branches and larger fragments were considered to be furcations of the stem and were treated accordingly. Trees and subsamples were weighed and subsamples were taken to the laboratory for further treatment.

Leaves were manually separated from branches of birch, as were shoots with current-year needles from branches of spruce. These fractions were dried at 70 °C. Defoliated branches from birch and branches from spruce with associated > 1-year old needles were air-dried at 40 °C. After drying of spruce branches, associated needles could easily be separated from the branches. Dry weights were determined of all samples after drying at 70 °C. On stem discs the bark was separated from the wood and samples were weighed fresh and after drying at 70 °C.

Roots were sampled in September 1997 from the humus layer at the Bn, Hb and Ss sites and in September 1998 at the Sf site. The sampling was done with a corer (4.5 cm diam.) in 16 evenly distributed sampling points within the same 16 × 16 m subplots as the tree sampling. Root samples from every odd sampling point were pooled to give one subsample and the rest to give another subsample; i.e. two subsamples per plot. Roots from the H-layer samples were picked out manually, cleaned in running water and kept in a 0.9 % NaCl solution when investigated using a dissecting microscope. Morphological characters such as surface structure and color were used to separate fine roots (< 2 mm) of birch and spruce. Obviously decayed roots were excluded. Total root dry weights (65 °C) were determined for each species and subsample. The two subsamples from each plot were pooled before grinding and subsequent chemical analyses. All biomass fractions (needles, leaves, stemwood, branches, bark, fine roots) were ground after drying and subsamples of 0.4 g (dryweight) were digested in 10 mL of boiling concentrated perchloric and nitric acid (1:10). Fe and Al were determined by ICP-AES. For each tree species, element, fraction and plot, we calculated a weighted average of the amount per unit stem basal area. The weights were proportional to the stem basal area of the trees.

The average amount of above-ground tree (including foliage) Al and Fe obtained from the four trees (kg m^{-2} basal area) in each 16 × 16 m plot was multiplied by the total basal area in the same plot, to give the standing crop content of the element ($mmol_c$ m^{-2}) in 1997 (Sf: 1998). The basal area removed in thinnings was relatively small compared to the basal area of the standing crop in 1997 and was not considered.

Statistical analysis

We performed a factorial analysis of variance with the following independent factors: (i) location (LOC) with three levels (Bn, Hb and Ss), and (ii) tree species composition (TSC) with two levels (mixed and pure spruce). In the analysis of data on forest floor chemistry, we also used a block factor (BLOCK) nested within site (LOC), which was the slash or non-slash treatment at Bn, Hb and Ss. In the model we used LOC, TSC and BLOCK and the interaction LOC × TSC. In the analysis of tree and fine root data we used LOC and TSC in the model. At the Ss site there were duplicates of the treatments mixed/slash left, spruce/slash left and spruce/slash removed (cf. Table 1). These were averaged before the factorial analyses to get a balanced design. The untreated (self thinned) plots at the Hb, Ss and Sf sites were not included in the analysis. The site at Sf was analysed separately. Interactions with an F-value smaller than 1 were excluded from the model. We considered $p < 0.05$ to be significant, $0.05 < p < 0.10$ to be a tendency and $p > 0.10$ to be non significant (n.s.).

We also performed regression analyses on pH and characteristics of the cation exchange complex of the H layer from all plots including untreated ones. The program SuperAnova (Abacus Concepts, Inc.) was used for analysis of variance and the program Statview (Abacus Concepts, Inc.) for the regression analyses.

Results

LF layer

The main proportions of aluminum and iron in the LF layer were not exchangeable with NH_4Cl. The concentration of exchangeable aluminum (Al_e) was only 4% of HNO_3 digestible aluminum (Al_H) whereas the concentration of pyrophosphate extractable aluminum (Al_P) was 38% of HNO_3 digestible aluminum (Al_H). The corresponding figures for iron were 0.9% and 20%, respectively (cf. Table 3).

At the Bn, Hb and Ss sites, concentrations of exchangeable aluminum (Al_e) were significantly lower in the LF in mixed plots compared to that in pure spruce plots.

Table 3. Concentration of exchangeable aluminum (Al_e) and iron (Fe_e), pyrophosphate extractable aluminum (Al_P) and iron (Fe_P) and HNO_3 digestible aluminum (Al_H) and iron (Fe_H). TSC and LOC are effect of tree species composition (mixed or pure spruce) and location (Bn, Hb, Ss and Sf), respectively. TSC*LOC is interaction. Duplicate plots at the Ss site were averaged before analysis (see text). Standard error within parentheses (n = 2, except Hb and Ss Ref; n = 1). Effects having p > 0.1 are denoted p = n.s.

		Al_e		Al_p		Al_H		Fe_e		Fe_p		Fe_H	
								(mmol$_c$ kg^{-1} OM)					
LF-layer													
Bn	Mix[1]	1.5	(0.09)	16	(5.4)	76	(23)	0.31	(0.03)	5.4	(1.3)	47	(17)
Bn	Spr.[2]	3.5	(1.6)	44	(22)	111	(16)	0.39	(0.10)	12.2	(4.4)	47	(11)
Hb	Mix	1.3	(0.29)	17	(12)	45	(15)	0.22	(0.00)	5.5	(4.2)	33	(18)
Hb	Spr.	3.3	(0.04)	18	(0.60)	48	(0.42)	0.35	(0.02)	4.9	(0.3)	20	(1)
Ss	Mix	1.0	(0.02)	25	(1.8)	60	(5.0)	0.11	(0.03)	2.6	(0.7)	27	(4)
Ss	Spr.	8.6	(0.98)	77	(14)	123	(16)	0.24	(0.02)	18.9	(6.5)	49	(11)
TSC:		p = 0.0098		p = n.s.		p = n.s.		p = 0.030		p = 0.089		p = n.s.	
TSC*LOC:		p = 0.065		p = n.s.		p = n.s.		p = n.s.		p = n.s.		p = n.s.	
Sf	Mix	1.1	(0.06)	15	(5.1)	45	(1.1)	0.20	(0.01)	8.8	(6.6)	33	(17)
Sf	Spr.	1.1	(0.09)	9.6	(2.1)	34	(4.2)	0.19	(0.01)	4.4	(3.3)	15	(5)
TSC:		p = n.s.		p = n.s.		p = n.s.		p = n.s.		p = n.s.		p = n.s.	
Hb	Ref.[3]	1.4		15		48		0.25		2.9		25	
Ss	Ref.	0.81		14		37		0.11		2.1		19	
Sf	Ref.	1.1	(0.65)	19	(15)	47	(28)	0.10	(0.00)	1.3	(0.2)	10	(2)
H-layer													
Bn	Mix	66	(4.5)	223	(53)	364	(74)	1.7	(0.17)	158	(52)	315	(89)
Bn	Spr.	96	(17)	346	(23)	641	(118)	2.0	(0.71)	280	(86)	506	(149)
Hb	Mix	37	(7.3)	130	(21)	184	(14)	1.3	(0.81)	107	(67)	175	(73)
Hb	Spr.	113	(1.1)	284	(5.6)	340	(2.8)	2.1	(0.01)	180	(6)	258	(2)
Ss	Mix	119	(4.1)	502	(42)	634	(59)	2.1	(0.14)	332	(16)	453	(12)
Ss	Spr.	147	(0.92)	646	(112)	839	(139)	2.7	(0.06)	468	(112)	650	(140)
TSC:		p = 0.0030		p = 0.0011		p = 0.0062		p = 0.083		p = 0.044		p = 0.030	
TSC*LOC:		p = 0.049		p = n.s.		p = n.s.		p = n.s.		p = n.s.		p = n.s.	
Sf	Mix	61	(15)	383	(128)	680	(232)	2.4	(1.95)	588	(140)	943	(164)
Sf	Spr.	93	(37)	463	(218)	689	(242)	1.1	(0.11)	843	(503)	1412	(815)
TSC:		p = n.s.		p = n.s.		p = n.s.		p = n.s.		p = n.s.		p = n.s.	
Hb	Ref.	109		276		363		2.8		230		323	
Ss	Ref.	83.4		425		581		1.6		329		458	
Sf	Ref.	72	(43)	498	(305)	705	(336)	1.8	(0.55)	419	(47)	670	(125)

[1] Mixed plots.

[2] Pure spruce plots.

[3] Untreated reference plot.

The same was true for the concentrations of exchangeable iron (Fe_e). The concentration of pyrophosphate extractable iron (Fe_P) tended to be lower in mixed plots whereas the concentrations of Al_P, Al_H and Fe_H did not differ significantly between stand types (Table 3).

At the Sf site there were no significant differences between stand types in the concentration of aluminum (Al_e, Al_P and Al_H) and iron (Fe_e, Fe_P and Fe_H) in the LF layer (Table 3).

The total amount of HNO_3 digestible aluminum per unit area in the LF, 37 $mmol_c\ m^{-2}$ in mixed and 45 $mmol_c\ m^{-2}$ in pure spruce plots at the Bn, Hb and Ss sites, did not differ significantly between the two stand types (Figure 1a). The same was true for the total amount of HNO_3 digestible iron in the LF layer, which was 21 $mmol_c\ m^{-2}$ and 18 $mmol_c\ m^{-2}$ in mixed and pure spruce plots, respectively (Figure 1b).

At the Sf site the total amount of HNO_3 digestible aluminum per unit area in the LF layer was 25 $mmol_c\ m^{-2}$ and 17 $mmol_c\ m^{-2}$ in mixed and pure spruce plots, respectively, whereas the total amount of HNO_3 digestible iron was 19 $mmol_c\ m^{-2}$ and 7 $mmol_c\ m^{-2}$ in mixed and pure spruce plots, respectively. Neither of these differed significantly between stand types.

H layer

The H layer had considerably higher concentrations of aluminum and iron than the LF layer. However, similarly to the LF layer, a rather small fraction of aluminum and iron was exchangeable in the H layer; Al_e was on average 27% of Al_P and 18% of Al_H (Table 3) whereas Fe_e was on average only 0.7% of Fe_P and 0.5% of Fe_H.

At the Bn, Hb and Ss sites, the concentrations of Al_e, Al_P, Al_H, Fe_P and Fe_H were significantly lower in the humus of mixed plots compared to that of pure spruce plots. The concentration of Fe_e tended to be lower in the humus of mixed plots compared to that of pure spruce plots but the difference was not significant (Table 3). Neither $pH(H_2O)$ nor pH(KCl) differed significantly between treatments whereas the concentrations of exchangeable base cations (BC_e) were significantly higher in the humus of mixed plots (Table 4). The concentration of exhangeable acidity was significantly lower in the H layer of mixed plots. The BNC did not differ significantly between stand types (Table 4). If exchangeable base cations (BC_e) were expressed as a percentage of CEC_e, the resulting effective base saturation was significantly higher ($p = 0.0022$) in mixed plots (71%) compared to pure spruce plots (58%). The same was true when BC_e was expressed as a percentage of $CEC_{pH6.5}$. In this case the base saturation was 16% in the H layer of mixed plots and 13% in that of pure spruce plots ($p = 0.046$).

At the Sf site, none of the above variables differed significantly between mixed and pure spruce plots. However, the $pH(H_2O)$ tended ($p = 0.073$) to be higher in the H layer in mixed plots than in the H layer in pure spruce plots (Table 4).

At the Bn, Hb and Ss sites, loss on ignition of the H layer did not differ significantly between mixed and pure spruce plots and was on average 84% in mixed and 73% in pure spruce plots or 80% if one pure spruce plot with an exceptionally low (40%) loss on ignition was excluded. Furthermore, the bulk density of root free

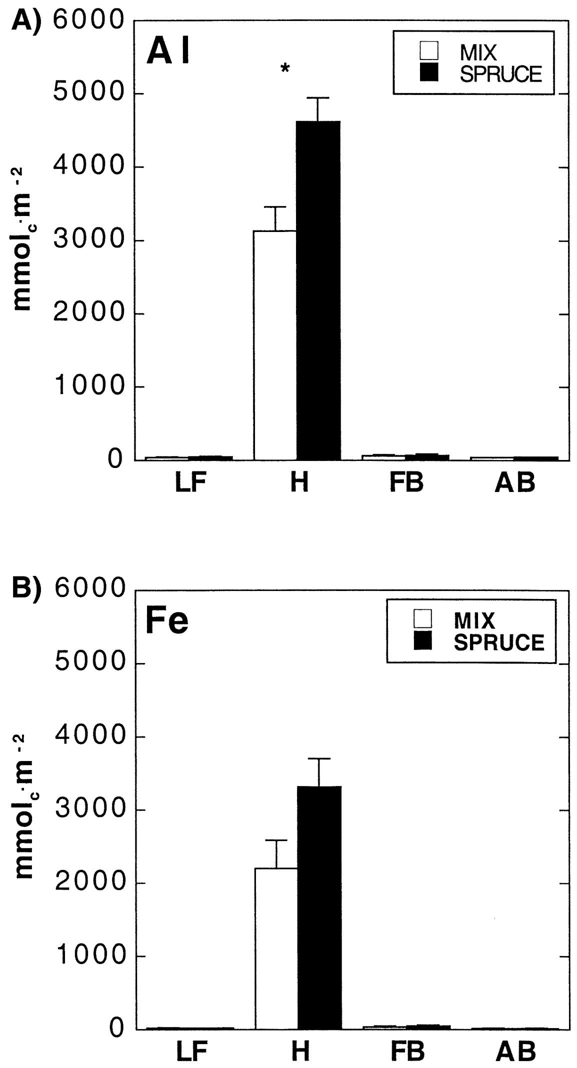

Figure 1. Average amounts (Bn, Hb and Ss sites) of aluminum (a) and iron (b) in the LF layer (HNO_3 digestible), in the H layer (pyrophosphate extractable), in fine root biomass of the H layer (FB) and in the above-ground biomass including foliage (AB). White bars: mixed birch/spruce plots; black bars: pure spruce plots. Least square means and standard errors are given (LF and H; n = 6, FB and AB; n = 3).

organic matter (OM) of the sampled upper 5 cm of the H layer did not differ significantly between mixed and pure spruce plots at the Bn, Hb and Ss sites and was on average 230 kg m^{-3} in mixed and 220 kg m^{-3} in pure spruce plots, respectively. At the Sf site the loss on ignition was 78% in both mixed and pure spruce plots, whereas the bulk density of root free organic matter was 130 kg m^{-3} in both stand types (Table 2).

Table 4. pH in water and 1M KCl, exchangeable base cations (K^+, Ca^{2+} and Mg^{2+}), exchangeable acidity, and base neutralizing capacity to pH 6.5 (BNC). TSC and LOC are effect of tree species composition (mixed or pure spruce) and location (Bn, Hb, Ss and Sf), respectively. TSC*LOC is interaction. Duplicate plots at the Ss site were averaged before analysis (see text). Standard error within parentheses (n = 2, except Hb and Ss Ref; n = 1). Effects having p > 0.1 are denoted p = n.s.

		pH(H_2O)		pH(KCl)		B_e		EA		BNC	
						(mmol$_c$kg^{-1} OM)					
H-layer											
Bn	Mix[1]	4.04	(0.11)	2.87	(0.13)	243	(6.1)	84.1	(2.0)	1158	(77)
Bn	Spr.[2]	4.13	(0.04)	3.05	(0.06)	228	(9.8)	99.6	(2.5)	1121	(38)
Hb	Mix	3.85	(0.08)	2.76	(0.12)	259	(55)	74.0	(6.7)	1225	(57)
Hb	Spr.	3.78	(0.03)	2.78	(0.03)	168	(8.9)	137	(4.3)	1359	(19)
Ss	Mix	4.05	(0.03)	3.10	(0.02)	205	(0.5)	123	(6.0)	1213	(13)
Ss	Spr.	4.10	(0.15)	3.13	(0.14)	157	(6.9)	152	(1.3)	1283	(29)
TSC:		p = n.s.		p = n.s.		p = 0.047		p = 0.0006		p = n.s.	
TSC*LOC:		p = n.s.		p = n.s.		p = n.s.		p = 0.0076		p = n.s.	
Sf	Mix	4.39	(0.11)	3.50	(0.14)	218	(43)	65.0	(15)	917	(50)
Sf	Spr.	4.00	(0.03)	3.23	(0.03)	165	(23)	103	(35)	1138	(125)
TSC:		p = 0.073		p = n.s.		p = n.s.		p = n.s.		p = n.s.	
Hb	Ref.[3]	3.73		2.80		235		120		1329	
Ss	Ref.	3.98		3.06		232		94.3		1210	
Sf	Ref.	4.19	(0.17)	3.44	(0.16)	185	(35)	76.1	(33)	938	(51)

[1] Mixed plots.

[2] Pure spruce plots.

[3] Untreated reference plot.

When (Al_P) in the H layer was expressed as total amounts per unit area of forest floor in the sampled upper 5 cm of the H layer, the total amount of pyrophosphate extractable aluminum (Al_P) was significantly (p = 0.025) lower in the mixed plots (3100 mmol$_c$ m^{-2}) compared to the pure spruce plots (4600 mmol$_c$ m^{-2}) at the Bn, Hb and Ss sites. That is, there was a difference of 1500 mmol$_c$ m^{-2} between the stand types (Figure 1a). The total amount of pyrophosphate extractable iron (Fe_P) in the H layer at these sites was 2200 mmol$_c$ m^{-2} in mixed plots and 3300 mmol$_c$ m^{-2} in pure spruce plots, i.e. a difference of 1100 mmol$_c$ m^{-2} between stand types (p = n.s.) (Figure 1b).

At the Sf site the total amount of pyrophosphate extractable aluminum (Al_P) in the H layer was calculated to be 2500 mmol$_c$ m^{-2} in mixed and 3000 mmol$_c$ m^{-2} in pure spruce plots, whereas the total amount of pyrophosphate extractable iron (Fe_P) was calculated to be 4000 mmol$_c$ m^{-2} in mixed and 5500 mmol$_c$ m^{-2} in pure spruce plots. However, none of these figures differed significantly between treatments.

Trees and fine roots

The concentration of aluminum was lower in birch foliage compared to spruce foliage but the difference was not significant. In contrast the concentration of iron tended (Bn, Hb and Ss sites; $p = 0.054$) to be higher in birch foliage compared to spruce foliage. In branches of birch the concentration of both aluminum and iron was lower than in branches of spruce (p = n.s.). As regards bark, there was a tendency (Bn, Hb and Ss sites; $p = 0.094$) for a lower concentration of aluminum in bark of birch than in that of spruce. The concentration of aluminum and iron in wood was considerably lower than in any other tree fraction but no clear trends regarding tree species were obvious (Table 5). The concentrations of aluminum and iron in birch and spruce fine roots were almost an order of magnitude higher than in any of the above-ground tree fractions but no species related trends were obvious (Table 6).

The total amount of aluminum (HNO_3+$HClO_4$ digestible) in total above-ground biomass including foliage (1997) expressed per unit soil area was 36 $mmol_c$ m^{-2} in mixed plots and 42 $mmol_c$ m^{-2} in pure spruce plots at the Bn, Hb and Ss sites. The corresponding figures for iron were 16 $mmol_c$ m^{-2} in mixed plots and 15 $mmol_c$ m^{-2} in pure spruce plots (Figures 1a, 1b). At the Sf sites the corresponding figures (1998) for aluminum were 40 $mmol_c$ m^{-2} and 48 $mmol_c$ m^{-2} and for iron 13 $mmol_c$ m^{-2} and 17 $mmol_c$ m^{-2} in mixed and pure spruce plots, respectively. None of the above data differed significantly between treatments.

In total above-ground biomass of spruce at the Bn, Hb and Ss sites, 80% of the aluminum and iron present was in branches and foliage. The corresponding figures were somewhat lower for the Sf site; 50% of the aluminum and 60% of the iron present was in branches and foliage. The distribution of aluminum in birch above-ground biomass contrasted to that of spruce, since only a small fraction of the aluminum present in birch above-ground biomass was in foliage and branches, 17% on average for all sites. Iron in birch total above-ground biomass at the Bn, Hb and Ss sites was mainly in branches (47%) whereas at the Sf site iron in birch above-ground biomass was mainly in wood (71%) (data recalculated from Table 5).

The total amounts of aluminum and iron (HNO_3+$HClO_4$ digestible) in fine roots expressed per unit soil area were of the same order of magnitude as the amounts in total above-ground biomass. In fine roots, the total amount of aluminum was less than 70 $mmol_c$ m^{-2} and the total amount of iron was less than 50 $mmol_c$ m^{-2} in both mixed and pure spruce plots at the Bn, Hb and Ss sites (Figures 1a, 1b). This was also true at the Sf site.

pH and metal saturation

At the Bn, Hb, and Ss sites, the effective base saturation (BC_e/CEC_e) was unrelated to pH (H_2O) in the H layer (p = n.s., $R^2 = 0.012$, $n = 17$). The same was true if the base saturation was expressed as a percentage of $CEC_{pH6.5}$ (p = n.s., $R^2 = 0.019$, $n = 17$). However, pH (H_2O) in the H layer was positively correlated with $BC_e + Al_p$ saturation of the exchange complex, $(BC_e+Al_P)/(CEC_{pH6.5})$, $p = 0.0001$,

Table 5. Concentration of aluminum and iron in foliage, branch, bark and wood from birch and spruce at the different sites. The average amount of each tree fraction is given per unit of stem basal area. N is number of plots upon which means are based. Duplicate plots at the Ss site were averaged before analysis (see text). Standard error is shown within parentheses. Effects having $p > 0.1$ are denoted p = n.s.

	PLOT	TREE	N	Fract. ($kg \cdot m^{-2}$)	Al ($mg \cdot kg^{-1}$)		Fe ($mg \cdot kg^{-1}$)	
Foliage								
Bn Hb Ss	Mix[1]	Birch	3	119	33	(10)	72	(10)
Bn Hb Ss	Mix	Spruce	3	459	124	(54)	44	(15)
Bn Hb Ss	Spr.[2]	Spruce	3	544	111	(18)	38	(2.7)
					p = n.s.		p = 0.0537	
Sf	Mix	Birch	1	112	23		41	
Sf	Mix	Spruce	1	358	81		22	
Sf	Spr.	Spruce	2	278	94	(33)	22	(3.3)
Branch								
Bn Hb Ss	Mix	Birch	3	366	15	(3.2)	82	(28)
Bn Hb Ss	Mix	Spruce	3	431	119	(50)	157	(75)
Bn Hb Ss	Spr.	Spruce	3	574	89	(15)	114	(35)
					p = n.s.		p = n.s.	
Sf	Mix	Birch	1	186	19		33	
Sf	Mix	Spruce	1	495	55		58	
Sf	Spr.	Spruce	2	466	53	(1.7)	111	(44)
Bark								
Bn Hb Ss	Mix	Birch	3	702	19	(3.7)	17	(3.7)
Bn Hb Ss	Mix	Spruce	3	224	76	(22)	46	(19)
Bn Hb Ss	Spr.	Spruce	3	266	78	(18)	26	(4.6)
					p = 0.094		p = n.s.	
Sf	Mix	Birch	1	694	17		12	
Sf	Mix	Spruce	1	370	49		24	
Sf	Spr.	Spruce	2	429	77	(7.9)	18	(5.8)
Wood								
Bn Hb Ss	Mix	Birch	3	3412	3.9	(0.9)	3.9	(0.6)
Bn Hb Ss	Mix	Spruce	3	1867	9.2	(4.4)	5.0	(1.1)
Bn Hb Ss	Spr.	Spruce	3	2290	5.4	(1.0)	4.8	(0.7)
					p = n.s.		p = n.s.	
Sf	Mix	Birch	1	5045	9.0		4.6	
Sf	Mix	Spruce	1	3316	4.7		5.9	
Sf	Spr.	Spruce	2	3832	7.0	(1.5)	4.1	(0.6)

[1] Mixed plots.

[2] Pure spruce plots.

$R^2 = 0.72$. When the variation in $CEC_{pH6.5}$ was accounted for in a multiple regression with $(BC_e+Al_P)/(CEC_{pH6.5})$ and $CEC_{pH6.5}$ as independent variables, the model fit improved substantially ($p = 0.0001$, $R^2 = 0.93$). If pH(KCl) was used instead of pH(H_2O), nearly all of the variation was explained ($p = 0.0001$, $R^2 = 0.98$) by $(BC_e+Al_P)/(CEC_{pH6.5})$ and $(CEC_{pH6.5})$. At the Sf site ($n = 6$), regressions of

Table 6. Total amounts of fine roots in the H layer per unit area of forest floor and concentration of aluminum and iron in fine roots of birch and spruce in mixed (Mix) and pure spruce (Spr.) plots at the sites studied. N is number of plots upon which means are based. Duplicate plots at the Ss site were averaged before analysis (see text). Standard error is shown within parentheses.

	PLOT	TREE	N	Tot ($kg{\cdot}m^{-2}$)	Al ($g{\cdot}kg^{-1}$)		Fe ($g{\cdot}kg^{-1}$)	
Bn Hb Ss	Mix	Birch	3	0.28	0.77	(0.17)	0.88	(0.27)
Bn Hb Ss	Mix	Spruce	3	0.44	0.71	(0.13)	0.86	(0.18)
Bn Hb Ss	Spr.	Spruce	3	0.69	0.89	(0.13)	1.26	(0.17)
					p = n.s.		p = n.s.	
Sf	Mix	Birch	1	0.11	0.37		0.63	
Sf	Mix	Spruce	1	0.17	0.38		0.89	
Sf	Spr.	Spruce	2	0.46	1.17	(0.98)	1.49	(1.32)

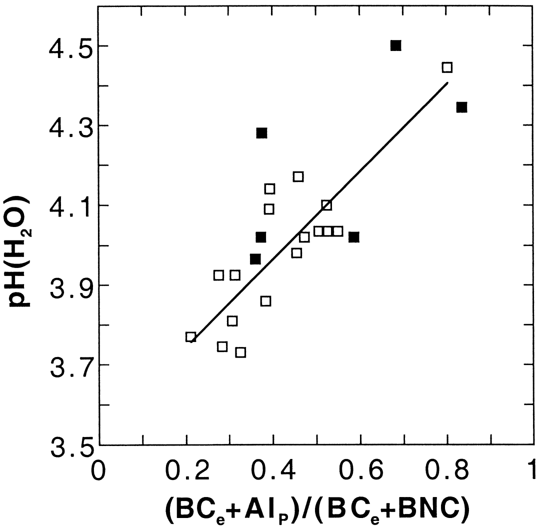

Figure 2. Variation in pH(H2O) of H layer for all plots at the Bn, Hb and Ss sites (unfilled squares) and at the Sf site (filled squares). The x axis (1.00 = 100%) represents saturation with exchangeable base cations and phyrophosphate extractable aluminum (BC_e+Al_p) as a percentage of $CEC_{pH6.5}$. Regression line refers to the Bn, Hb and Ss sites (p = 0.0001, R^2 = 0.72, n = 17). Sf site (p = n.s., R^2 = 0.40, n = 6).

aluminum+base saturation vs pH yielded R^2 = 0.40 (p = n.s.). The analogous multiple and pH(KCl) regressions yielded R^2 = 0.65 (p = n.s.) and R^2 = 0.89 (p = 0.036), respectively. The regression of pH(H_2O) on saturation ($CEC_{pH6.5}$) with aluminum and base cations for all sites and stand types is shown in Figure 2.

Discussion

Our results show that a change in tree species composition from mixed birch/spruce to pure spruce stands can have a rather large short-term effect on the aluminum and iron that is exchangeable and complex-bound by organic matter in the forest floor. In the following, we discuss whether any of the mechanisms mentioned in the introduction could be responsible for the observed effects.

Litter and root turnover

Our data indicate that the rates of litter and root turnover most likely are an order of magnitude too small to be relevant for the differences in complex bound aluminum in the H layer. This was suggested by estimating the recycling of elements through litterfall based on the total amounts of elements in the foliage per unit ground area, and estimates of the yearly turnover of foliage. For both birch and spruce, the resorption of aluminum and iron before the abscission of leaves and needles can probably be neglected. The yearly turnover of foliage is 100% for birch and approx. 20% for spruce. Thus, we considered a yearly spruce foliage turnover of 20% and assumed that no aluminum is resorbed before abscission. The data of Table 5 and stand basal areas of Table 1 indicate that Al on average is added at a rate of 3.0 mmol$_c$ m^{-2} y^{-1} in mixed and 3.5 mmol$_c$ m^{-2} y^{-1} in pure spruce plots at the Bn, Hb, and Ss sites. This is slightly less than that reported by Rustad and Cronan (1989) who obtained a yearly Al deposition of 5.56 mmol$_c$ m^{-2} through litterfall of red spruce in the northeastern USA. Bergkvist and Folkesson (1995), who investigated pure spruce and birch stands in southern Sweden, reported litterfall additions of Al in birch stands of 2–4 mmol$_c$ m^{-2} y^{-1} and in spruce stands of 9–11 mmol$_c$ m^{-2} y^{-1} which indicates that pure stands of the two species differ in this respect. However, the difference obtained between the stands in the present study (0.5 mmol$_c$ m^{-2}) is far from sufficient to explain the difference between mixed and pure spruce plots in pyrophosphate extractable aluminum in the H layer (1500 mmol$_c$ m^{-2}) that has developed during the 12 years that have passed since the establishment of the plots. This conclusion is validated by the average total amount of aluminum in the LF layer, which did not differ between mixed and pure spruce plots and which was very small (41 mmol$_c$ m^{-2}) compared to Al in the H layer (> 3000 mmol$_c$ m^{-2}) (Figure 1a). Litterfall consisting of small branches and twigs might be of the same order of magnitude as that of needle and leaf litterfall. The concentrations of aluminum and iron found in branches of birch and spruce were similar to those in foliage (Table 5), suggesting that the contribution of small branches and twigs can at the most double the input rate of aluminum and iron to the forest floor. Other tree fractions such as cones and catkins comprise a modest input of litter (cf Alriksson and Eriksson (1998)) and most likely of aluminum and iron to the forest floor.

The addition of aluminum to organic horizons via decomposing root litter has been considered important (Vogt et al. 1987). The amount of aluminum in roots (62 mmol$_c$ m^{-2}) was of the same order of magnitude as the amount in the LF layer and in the above-ground biomass but far less than the amount in the H layer (Figure 2). Because the amount of aluminum per unit area in fine roots did not differ between mixed and pure spruce plots (Figure 2), root turnover is an unlikely explanation of the differences. One could argue that the turnover of root biomass could have differed between birch and spruce. Majdi and Kangas (1997) estimated the mean life span of spruce fine roots in a Norway spruce stand in Southwestern Sweden to be 280 days. However, even if the turnover of spruce fine roots were set to 280 days and that of birch to 12 years, differences in fine root turnover would not be sufficient to explain the differences. Furthermore, Rustad and Cronan (1995) pointed out that the aluminum in roots in the H layer may not neccessarily originate from the mineral soil.

Weathering of mineral particles in the O horizon

The composition of tree species may affect the soil fauna, which may enhance the mixing of mineral particles into the O horizon and thereby increase the transport of Al and Fe to the O horizon (cf Rustad and Cronan (1995)). However, the population of earthworms was very small at the sites studied (Saetre et al. 1999) and the amount of mineral particles did not differ significantly between the two stand types (see Results). Furthermore, the difference in Al and Fe concentrations between mixed and pure spruce plots was not an effect of these elements being diluted in a larger quantity of organic matter in the H layer of mixed plots because the total amount of organic matter per unit area in the H layer has been shown to be similar in these mixed birch/spruce and pure spruce plots (Brandtberg et al. 2000).

Forest stands of Norway spruce often generate considerably larger quantities of acidity than comparable hardwood stands. This is mainly an effect of higher average concentrations of base cations in spruce above-ground biomass and a higher yield of Norway spruce than hardwoods on comparable sites and, consequently, a larger accumulation of base cations in spruce than in hardwood above-ground biomass (cf. Alriksson and Eriksson (1998)). The larger accumulation of base cations in pure spruce stands is balanced by a larger export of H^+ acidity to the soil (Binkley and Richter 1987), especially to the O horizon where both birch and spruce have their highest concentration of fine roots (Brandtberg et al. 2000). An estimate of the accumulation of base cations in the above-ground biomass indicated that approximately half the difference in concentration of base cations in the humus layer between mixed and pure spruce could be explained by this mechanism.

Furthermore, the capture of dry deposition, although probably moderate at most of the sites, is also larger in spruce than in birch stands (Bergkvist and Folkesson 1995). However, Lawrence et al. (1995) pointed out that unless the pH of the throughfall water is less than that of the humus layer, the input of H^+ acidity through this mechanism cannot increase weathering of admixed mineral particles within the humus layer. Mycorrhizal fungi associated with tree roots may produce low molecular weight organic acids such as oxalic acid. However, we do not know of any investigation that has yet shown that the mycorrhizae of birch and spruce differ in this respect. Raulund-Rasmussen et al. (1998) found that spruce stands were associated with a higher concentration of DOC in the O horizon compared to stands of several broadleaved tree species. This may contribute to the weathering of admixed mineral particles.

Thus, the higher amount of H^+ acidity and organic complexants that is probably generated in the humus layer in pure stands of Norway spruce compared to mixed stands of birch and spruce may have increased the weathering of the mineral soil particles and produced more Al in secondary forms, e.g. exchangeable and complex-bound Al, under pure spruce than in mixed stands (cf Lawrence and David (1997)). This hypothesis can be tested in field or laboratory experiments.

Upward transport of aluminum from the mineral soil

An upward transport of water from the mineral soil, where the concentration of dissolved Al is generally greater, may increase the amount of organically bound aluminum in the H layer if the groundwater level reaches the soil surface (cf. Mulder et al. (1991)) which is most likely to occur in discharge areas (cf. Giesler et al. (1998)). Observations in the present stands, which are neither typical recharge nor discharge areas, suggest that the groundwater level could occasionally be close to the soil surface during wet conditions but we have no indications of any difference between stand types in this respect. Lawrence et al. (1995) suggested that there might be an upward capillary transport of water from the mineral soil through rapid drying of the forest floor. Capillary rise could be promoted if a large proportion of the water that was taken up came from the uppermost part of the profile, and tree species have been shown to differ in this respect (Bishop and Dambrine 1995). We estimated a maximum contribution from this mechanism in explaining our results as follows:

A typical concentration of dissolved aluminum in soil water from the upper mineral soil may be around 0.12 $\text{mmol}_c\ L^{-1}$. This is an average of several investigations on acidic forest soils in stands of Norway spruce and mixed Norway spruce/Scots pine (Pinus sylvestris) in France, northern Sweden and southern Finland (Giesler et al. (1998, 2000); Augusto and Ranger 2001). The actual evapotranspiration in the region of the sites is approx. 300–500 mm y^{-1} (Brandt et al. 1994). Assuming that the pure spruce stands evapotranspirate 500 mm y^{-1} and that the whole flux is used to transport water with an Al concentration of 0.12 $\text{mmol}_c\ L^{-1}$ from the upper mineral soil to the O horizon, a maximum of 720 $\text{mmol}_c\ m^{-2}$ of Al could have been transported to the H layer during the 12 years in pure spruce stands. This corresponds to half the difference in O horizon Al content, 1500 $\text{mmol}_c\ m^{-2}$, between spruce and mixed stands of the present study. However, we have not taken into account any similar transport in the mixed stands, or the fact that only a fraction of the total evapotranspiration is used to transport soil water upwards from the mineral soil (cf. Giesler et al. (2000)). Furthermore, the concentration of iron in soil water in upper mineral soil horizons is typically 1/5 of the concentration of aluminum (Giesler et al. 2000; Augusto and Ranger 2001). We found that the difference between mixed and pure spruce stands in the concentration of complex bound iron (Fe_P) in the H layer was 1100 $\text{mmol}_c\ m^{-2}$, which is close to the difference in complex bound aluminum (Figure 2). This indicates that capillary rise can only explain part of the observed difference between mixed and pure spruce stands in complex bound aluminum and iron content of the forest floor.

We have no data that could support or reject the hypothesis that differences between stand types in associations of mycorrhizal fungi and their activity in the transfer of aluminum from the mineral soil to the O horizon were responsible for the effect found. This hypothesis could be tested in controlled field or laboratory experiments, however.

Base saturation and pH

Our data on pH and aluminum and base saturation of the exchange complex confirm the idea presented by Skyllberg (1996) that aluminum in acidic organic horizons could be considered as a base cation due to a weak hydrolysis at low pH. We found that the pH measured in water was unrelated to base saturation expressed as a percentage of the effective cation exchange capacity (CEC_e) and as a percentage of cation exchange capacity at pH 6.5 ($CEC_{pH6.5}$). Instead, the pH in water was positively correlated with the saturation of the exchange complex ($CEC_{pH6.5}$) with exchangeable base cations (BC_e) and pyrophosphate extractable aluminum (Al_P) (Figure 2). The higher base saturation in the mixed birch/spruce stands compared to the pure spruce stands did not result in a higher pH. The explanation is that the higher base saturation in mixed stands was compensated for by a lower aluminum saturation, whereas the hydrogen ion saturation, which controlled the pH (cf. Ross et al. (1996)) remained more or less unchanged. It is noteworthy that the positive relationship between pH and $Bc_e + Al_P$ saturation of $CEC_{pH6.5}$ held over a wide range of saturation (0.21–0.84). However, a positive relationship between aluminum saturation and pH is expected as long as the soil acids that are neutralised by aluminum are stronger than the adsorbed or complexed hydrated aluminum ion (cf. Bloom et al. (1979) and Skyllberg (1999)).

At the older Sf site, there was a tendency ($p = 0.073$) for a higher pH in the H layer in mixed stands than in pure spruce stands (Table 4) which confirms earlier observations of a higher pH under birch (Hesselman 1926). It is noteworthy that the aluminum plus base saturation did not differ significantly between stand types at this site whereas the concentration of acidic groups ($CEC_{pH6.5}$; Table 4) and the acid strength of soil acids as revealed from titration curves (Brandtberg 2001) tended to be higher in the organic material that had developed under pure spruce. Thus, the common observation of pH being lower in spruce stands than in stands of broadleaf species or mixed stands may be related to the quality of accumulated organic matter rather than the base saturation (cf Binkley and Valentine (1991)).

Conclusions

A change in tree species composition from mixed birch/spruce to pure spruce stands can have a rather large short-term effect on the aluminum and iron that is complex-bound by organic matter in the forest floor. Estimates of the above- and below-ground litter cycling of aluminum and iron in mixed and pure spruce stands indicated that these did not differ between the two stand types and were an order of magnitude too small to be able to explain the differences in aluminum and iron concentration of the forest floor. Other mechanisms related to tree species must be responsible for the effect.

A shift in tree species composition that increases the base saturation of acid forest floors will not increase the pH of these horizons if the increased base saturation is mainly compensated for by a decreased aluminum saturation and not by a decreased hydrogen saturation.

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