

## Cation-exchange reactions involving aluminium ions in podzols disturbed by deep tilling

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The stratified structure of a podzolic soil is changed during deep tilling of forest soils. Here, we assessed whether (i) cation-exchange properties and (ii) cation-exchange reactions in podzolic soil were altered when the illuvial (B) horizon was subject to environmental conditions prevailing on the soil surface and the organic (O) horizon was buried within the mineral soil. The samples were taken from undisturbed and disturbed podzolic soil profiles at two forest sites that had been ploughed 17 and 31 years ago and planted with Norway spruce seedlings. An increase in soil organic C and effective cation-exchange capacity (CEC<sub>e</sub>) was observed in the Bs horizons exposed to the soil surface. The accumulation of soil C was mainly due to organic matter produced by the planted Norway spruce. The Al<sup>3+</sup>-Ca<sup>2+</sup> cation-exchange equilibria were similar in both the disturbed and undisturbed O and Bs horizons. This indicates that similar reactions between Al<sup>3+</sup> and Ca<sup>2+</sup> took place in different horizons of podzols irrespective of the disturbance. A positive correlation of CEC<sub>e</sub> in the Bs horizons with soil C indicated that soil organic matter played a major role in the cation-exchange reactions. The importance of exchangeable cations in determining pH variation in the O horizon was additionally supported by the success in describing the relationship between soil solution pH<sub>s</sub> and base saturation using the extended Henderson-Hasselbach equation in which exchangeable Al<sub>e</sub> had nonacidic properties similar to those of base cations. The results of this study suggest that organic matter, accumulated within the soil profile during soil formation and upon ploughing, had an important role in determining the cation-exchange properties and reactions in the studied podzols.

### Introduction

The state of the soil is usually determined by soil formation factors such as climate, parent material, topography and organisms which interact with each other over time (Birkeland 1984). The soil factors determine and control the rate of soil processes which result in soil properties and soil type.

Soils in Finland have been subject to soil formation since the retreat of the glacial ice, about 10 000 years ago (Eronen 1983). The most common soil-forming process in Finland is podzolization. Characteristic for podzolization is weathering of Al, Fe and base cations in an eluvial (E) horizon and subsequent migration and immobilisation of Al and Fe as well as organic matter in an illuvial (B) horizon.

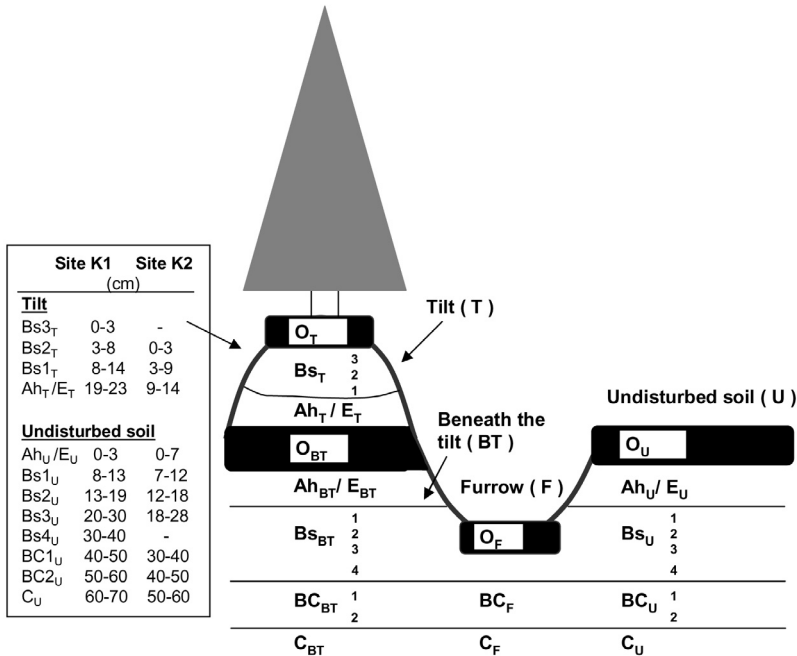


Fig. 1. A schematic representation of ploughed soil consisting of tilt (T), soil beneath the tilt (BT), furrow (F) and undisturbed soil (U). Sampling depths of the tilt and the undisturbed soil at both study sites K1 and K2 are shown.

Soil formation factors and processes may be altered by human activities such as cultivation, mining, pollution and forest management. In Finland, mechanical site preparation has been used to ensure efficient reforestation of clear-felled areas since the 1960s. It has been estimated that about 18% of the total forest land area in Finland (21.9 million ha) has been site-prepared (Finnish Forest Research Institute 2001), of which one-third has been deeply tilled (ploughed or mounded). As a result of site preparation, the stratified structure of the podzolic soil is altered to varying extents depending on the site preparation method used. In deep tilling, the soil profile down to and including the upper B horizon is inverted and placed on the soil surface, while the E and organic (O) horizons are buried within the tilt at the top of the original soil surface (Fig. 1).

As a result of exposure to the soil surface, Al in the inverted B horizon is subject to new environmental conditions, e.g. anthropogenically derived acidic deposition and accumulation of litter residues that slowly convert to an acid humus layer. Recently, Tanskanen and Ilvesniemi (2004) suggested that some Al was mobilized in the exposed Bs horizons upon ploughing. Concurrently, the amount of exchangeable Al ( $Al_e$ ) in the exposed Bs horizons increased.

The increase in exchangeable  $Al_e$  in the exposed Bs horizons indicates that part of the Al mobilized may be retained by soil exchange sites. If the amount of Al bound by exchange sites is substantially increased, the amount of base cations such as Ca, Mg and K may in turn decrease, leading to a lower base saturation (BS) in the exposed Bs horizons. The potential changes in soil cation-exchange properties are of particular interest in ploughed soil because the seedlings are planted in the tilt (Fig. 1). The consequences of intensive tilling on the chemical properties of podzolic forest soils have not been widely studied.

The significance of exchangeable cations in determining the cation concentrations in soil solutions of acid forest soils has recently been emphasized by Skyllberg (1994), Ross *et al.* (1996), Nissinen *et al.* (1998) and Johnson (2002). Nissinen *et al.* (1998) suggested that the Gaines-Thomas selectivity coefficient was apparently applicable to soil solutions obtained by centrifugation from podzolic forest soils. The work done by Skyllberg (1994), Ross *et al.* (1996) and Johnson (2002) showed a new insight into the concept of exchangeable acidity (EA) in acid forest soils. Traditionally, exchangeable  $H^+$  is often ignored in studies of exchangeable cation

ons due to difficulty in separating exchange and hydrolysis reactions of  $\text{Al}^{3+}$  (Thomas and Hargrove 1984). However, Ross *et al.* (1996) found that exchangeable hydrogen could be related to the pH of Spodosol Oa horizons. Skjellberg (1994) proposed that the relationship between BS and soil pH in the O horizon could effectively be modelled by the extended Henderson-Hasselbach equation, in which exchangeable Al had nonacidic properties similar to those of base cations. Johnson (2002) applied this model to acid forest soils in the northeastern USA and stated that the model could be incorporated into biogeochemical models to predict pH from measurements of exchangeable cations.

In the present study, we assessed whether (i) cation-exchange properties in podzolic forest soil and (ii) cation-exchange reactions were altered when the B horizon was subject to environmental conditions prevailing on the soil surface and the O horizon was buried within the mineral soil. We applied the theories presented in current literature, the apparent cation-exchange equilibria and weak acid dissociation and examined these mechanisms in soil solutions obtained by centrifugation from undisturbed and disturbed podzolic soil profiles at two forest sites that had been ploughed 17 and 31 years ago and planted with Norway spruce (*Picea abies*) seedlings.

## Material and methods

### Sites

Soil samples were collected from two ploughed forest sites located in Karkkila (K1, 60°32'N, 24°16'E) and Kuorevesi (K2, 61°53'N, 24°35'E), in southern Finland. The mean temperatures in southern Finland are about -8 °C in January and 16 °C in July and yearly precipitation averages 600–700 mm (Finnish Meteorological Institute 1993).

The study sites were clear-cut and tilt-ploughed in 1979 (site K1) and 1966 (site K2) and planted with Norway spruce (*Picea abies*) seedlings. Site K1 was a fertile *Oxalis-Myrtillus* (OMT) type according to Finnish classification of forest types (Cajander 1925) whereas site K2 was a moderately fertile *Myrtillus* (MT)

type. Site K1 was classified as a Cambic Podzol (FAO-Unesco 1990) with an Ah horizon; the parent material was glacial till of a silt-loam texture. Site K2 was classified as a Haplic Podzol with an E horizon; the parent material was glacial till with a texture of sandy loam. The clay content expressed as a percentage of the fine-earth fraction (< 2 mm) was 4% at a depth of 50 cm at both study sites, whereas the coarse sand content (> 0.6 mm) was 5% at site K1 and 11% at site K2. In the Bs horizon, amounts of oxalate extractable Al and Fe were clearly higher than pyrophosphate extractable Al and Fe indicating that the Bs horizons were characterised by accumulation of sesquioxides at both sites (Tanskanen and Ilvesniemi 2004).

### Soil sampling

Soil samples were taken from four different positions: the undisturbed soil (U), the tilt (T), the soil beneath the tilt (BT) and the furrow (F) (Fig. 1). From each position, 8–11 core samples were taken with a steel auger (0.046 m diameter) and bulked by layer to give one composite sample of about 1 dm<sup>3</sup> per soil layer sampled. Sampling was carried out six times in early summer and autumn in 1996 at site K1 and four times in 1997 at site K2. During sampling, samples of the Bs and BC horizons were further divided into subhorizons based on depth (Fig. 1). Partitioning of the horizons in the ploughed soil was performed by visual examination of the horizons and by comparing the thicknesses of the horizons with that of the undisturbed soil. A new O horizon was formed in the disturbed soil profiles on top of the tilt ( $\text{O}_T$ ) and in the furrow ( $\text{O}_F$ ). The first three cm (0–3 cm) of the inverted Bs horizon (exposed Bs) beneath the  $\text{O}_T$  and  $\text{O}_F$  horizons were sampled separately at both study sites, since a darker soil colour compared with that of the soil beneath indicated the occurrence of changes in the soil. Consistent with the division into subhorizons in the undisturbed soil, these exposed Bs horizons were referred to as the  $\text{Bs}_{3T}$  horizon at site K1 and  $\text{Bs}_{2T}$  at site K2. The mineral soil beneath the tilt was similar to that of the undisturbed soil, and the buried O horizon ( $\text{O}_{BT}$ ) was located on top of it. When the division of

soil horizons was taken into account, the number of soil samples down to and including the Bs3 horizon was 176 representing a large range in temporal and spatial variation.

### Centrifugation and soil solution analyses

The soil solution was extracted from the soil samples using a centrifugation drainage technique (Giesler and Lundström 1993). A Sorvall RC5C centrifuge with a GSA rotor was used. The samples were centrifuged at 13 000 rpm for 30 min at a constant temperature of 5 °C; the relative centrifugal force was 15 500 g. Centrifugation was carried out within 48 h after sampling, and the samples were stored at 5 °C in between. Two subsamples, each containing approximately 120 cm<sup>3</sup> of soil, were centrifuged from each bulked soil sample. Soil solution volumes extracted from a subsample ranged between a few and 35 cm<sup>3</sup> depending on the moisture content of soil. The solutions obtained were combined for further analyses.

Immediately after centrifugation, the soil solution pH (pH<sub>s</sub>) was measured from a subsample with a combined pH glass electrode (6.0216.100, Metrohm 605; Herisau, Switzerland). The solution was filtered through a disposable syringe filter (Millex HV13) with a pore size of 0.45 μm (Millipore Corporation; Billerica, MA, USA). The concentrations of total monomeric Al and non-labile monomeric Al were measured by reaction with pyrocatechol violet using a flow-injection ion analyser (Lachat QuikChem 8000; Milwaukee, WI, USA). Non-labile monomeric Al was fractionated from total monomeric Al using the method described by Driscoll (1984). The concentrations of labile monomeric Al (assumed to be predominantly inorganic Al) were calculated as the difference in concentration between total monomeric Al and non-labile monomeric Al. Determination of the total concentrations of Al and other cations in the soil solution (Ca, Mg, Na, K) was carried out on acidified samples employing inductively coupled plasma-atomic emission spectrometry (ICP-AES). Ion chromatography (HPLC Waters; Milford, MA, USA) was used to determine the concentrations of SO<sub>4</sub>, Cl and NO<sub>3</sub>.

### Soil chemical analyses

Field moist soil samples were sieved (< 0.6 mm mineral soil and < 2 mm O horizons) and stored in a refrigerator prior to analyses. Effectively exchangeable cations were determined by shaking the samples (corresponding to 2 g of oven-dry humus and 10 g of mineral soil) in 100 ml of 0.1 M BaCl<sub>2</sub> for an hour (Hendershot and Duquette 1986). The suspensions were filtered through a 0.45-μm filter (Millipore HAWP 47 mm) with vacuum. After filtering, a 50-ml subsample was taken for immediate pH analysis to determine the exchangeable H (H<sub>e</sub>) and titration of exchangeable acidity (EA) with 0.01 M NaOH to pH 7. The Al, Ca, Mg, Na, K and Fe concentrations were determined with ICP-AES. The soil pH (pH<sub>Ca</sub>) was measured in 0.01 M CaCl<sub>2</sub> (soil:solution ratio 1:2.5). Total C and N were measured using a Leco CNS-1000 analyser (Leco Corporation; St. Joseph, MI, USA). Prior to analysis of the total C, the airdried and sieved samples were ground using a mill. The results of the mineral soil are given with reference to oven-dry soil (105 °C) in the < 0.6-mm fraction. The < 0.6-mm fraction in the mineral soil was preferred mainly to reduce sub-sampling bias since most of the soil chemical properties are related to soil particle sizes smaller than coarse sand.

### Calculations

#### Apparent cation-exchange equilibria

A number of equations have been used to describe the cation-exchange equilibria in soil. In the present study, the Gaines-Thomas selectivity coefficient was used to express the cation-exchange equilibria since it is commonly used in soil acidification models (e.g. Tiktak and van Grinsven 1995). Moreover, earlier work showed that Gaines-Thomas selectivity coefficient was less variant than Gapon selectivity coefficient in podzolic forest soils (Tanskanen 1995). If the cation-exchange reaction between cations on negatively charged exchange sites (CaX and AlX) and cations in soil solution (Ca<sup>2+</sup> and Al<sup>3+</sup>) is assumed to be



the Gaines-Thomas selectivity coefficient  $K_{Al-Ca}$  (Gaines and Thomas 1953) is defined by the equation

$$K_{Al-Ca} = \frac{E_{Al}^2 (Ca^{2+})^3}{E_{Ca}^3 (Al^{3+})^2}, \quad (2)$$

where the terms in parentheses represent the activity in the soil solution and  $E$  the charge fraction of exchangeable cations (e.g. Nissinen *et al.* 1998). The right-hand side of Eq. 2 can be divided into two parts: relating to ions in the soil solution ( $S$ ) and ions on the exchange sites ( $Q$ ), respectively:

$$S_{Al-Ca} = \frac{(Ca^{2+})^3}{(Al^{3+})^2} \quad (3)$$

and

$$Q_{Al-Ca} = \frac{E_{Ca}^3}{E_{Al}^2}. \quad (4)$$

Now  $\log_{10} K$  may be written as:

$$\log K_{Al-Ca} = \log S_{Al-Ca} - \log Q_{Al-Ca}, \quad (5)$$

and, a linear regression model, based on Eq. 5

$$\log S_{Al-Ca} = a + b \log Q_{Al-Ca} \quad (6)$$

may be used to determine  $\log K$  as the intercept ( $a$ ). Two criteria were used: (i) the coefficient of determination ( $R^2$ ) should be high, so that much of the variation in  $\log S$  is explained by the variation in  $\log Q$ , and (ii) the regression coefficient ( $b$ ) should be near unity. When  $b$  equals 1, the intercept  $a$  is an estimate of  $\log K$  (Coulter and Talibudeen 1968). If  $b$  is significantly different from 1, the selectivity coefficient is dependent on the composition of exchangeable cations, and an invariant selectivity coefficient cannot be applied.

The selectivity coefficients were estimated for the  $Al^{3+}-Ca^{2+}$ ,  $Al^{3+}-Mg^{2+}$ ,  $Al^{3+}-K^+$ ,  $Al^{3+}-Na^+$  and  $Al^{3+}-H^+$  reactions. Aluminium was selected as a reference cation because Al is one of the major cations present on exchange sites in podzolized forest soils (e.g. Tamminen and Starr 1990). The charge fraction of each exchangeable cation was calculated as  $Al_e/CEC_e$ , where the effective cation-exchange capacity ( $CEC_e$ ) is the sum of charges of the exchangeable cations  $H_e$ ,  $Al_e$ ,  $Ca_e$ ,  $Mg_e$ ,  $K_e$  and  $Na_e$ . Exchangeable  $Fe_e$  was also determined but considered insignificant

in calculation of  $CEC_e$  because the Fe content was less than 1% of EA in the majority of the soil samples ( $0.4\% \pm 0.6\%$ , mean and S.D.). The ion activities in the soil solution were calculated using the extended Debye-Hückel formula (Lindsay 1979). Labile monomeric Al was assumed to consist of  $Al^{3+}$ , different Al-hydroxy species and Al sulphate complexes. The equilibrium constants and heats of reaction for inorganic Al species given by Nordstrom and May (1989) were used to calculate the speciation of Al.

The horizons studied were the O, Ah, E and Bs, i.e. those horizons that were inverted as a result of ploughing. The lowest Bs3 subhorizon in the undisturbed soil was omitted from the calculation of the selectivity coefficients, since the variation in the estimated selectivity coefficients was large. This may partly have been due to the analytical methods used, e.g. difficulty in measuring low soil solution concentrations, such as inorganic Al and K in subhorizons deeper in the soil.

## Weak acid dissociation

In acid forest soils, the negative charge on soil organic matter (SOM) is predominantly derived from carboxylic functional groups (R-COOH). Assuming that the dissociation of a weak acid explains the  $pH_s$  in centrifuged soil solutions, the modified Henderson-Hasselbach equation (Thomas and Hargrove 1984) can be used:

$$pH = pK_{app} + n \log \left( \frac{\alpha}{1-\alpha} \right), \quad (7)$$

where the  $pK_{app}$  is an apparent dissociation constant for the functional groups providing charge,  $\alpha$  is the fraction of dissociated functional groups, and  $n$  is an empirical constant. Bloom and Grigal (1985) proposed that the pH of soil solutions could be explained by using the base saturation (BS) as a surrogate for  $\alpha$ :

$$pH = pK_{app} + n \log \left( \frac{BS}{1-BS} \right) \quad (8)$$

which in a linear form is expressed as

$$pH = a + b \log \left( \frac{BS}{1-BS} \right). \quad (9)$$

Recently, a nonacidic behaviour of Al was

ascribed to acid forest soils (Skylberg 1994, Ross *et al.* 1996, Johnson 2002), and a revised form of Eq. 8 was proposed:

$$\text{pH} = \text{pK}_{\text{app}} + n \log \left( \frac{\text{BS}_e^*}{1 - \text{BS}_e^*} \right) \quad (10)$$

and consequently,

$$\text{pH} = a + b \log \left( \frac{\text{BS}_e^*}{1 - \text{BS}_e^*} \right) \quad (11)$$

where  $\text{BS}_e^*$  is the effective base saturation com-

puted with  $\text{Al}_e$  (Skylberg 1994, Johnson 2002). In this study, we examined the relationship between  $\text{pH}_s$  in centrifuged soil solutions and both  $\text{BS}_e$  (Eq. 9) and  $\text{BS}_e^*$  (Eq. 11).

## Statistics

A one-way analysis of variance, a Kruskal-Wallis test and a Wilcoxon rank-sum test were used to compare the amounts of elements and

**Table 1.** Selected soil properties expressed as mean values (and standard error in parentheses) for each horizon in the undisturbed soil (U), tilt (T), in the O horizon beneath the tilt (BT) and furrow (F) at site K1 and site K2. Amounts in individual horizons in various soil profiles differing from the corresponding undisturbed horizon ( $P < 0.05$ ) are marked with an asterisk (\*).

	C (%)	C/N	$\text{pH}_{\text{Ca}}^b$	$\text{Al}_e^c$ (mmol <sub>c</sub> kg <sup>-1</sup> )	$\text{Ca}_e^c$ (mmol <sub>c</sub> kg <sup>-1</sup> )	$\text{CEC}_e^c$ (mmol <sub>c</sub> kg <sup>-1</sup> )	$\text{BS}_e$	$\text{CEC}_e/\text{C}$ (mmol <sub>c</sub> g <sup>-1</sup> )
Site K1								
Undisturbed								
O <sub>U</sub>	24 (3.3)	21 (1.0)	3.54 (0.07)	27 (5.0)	112 (14)	194 (15)	74 (3)	0.90 (0.15)
Ah <sub>U</sub>	7.4 (1.0)	22 (0.5)	3.60 (0.09)	44 (3.8)	21 (40)	80 (6.9)	38 (4)	1.03 (0.08)
Bs1 <sub>U</sub>	2.7 (0.2)	23 (1.7)	4.24 (0.06)	17 (1.9)	5 (1.0)	23 (4.0)	29 (2)	0.79 (0.12)
Bs2 <sub>U</sub>	2.2 (0.1)	23 (1.6)	4.51 (0.02)	8 (0.5)	5 (0.4)	14 (0.8)	48 (3)	0.63 (0.04)
Bs3 <sub>U</sub>	1.6 (0.1)	25 (1.6)	4.68 (0.02)	4 (0.5)	5 (0.9)	10 (1.0)	51 (5)	0.64 (0.04)
Tilt								
O <sub>T</sub>	27 (3.6)	23 (2.0)	3.97 (0.20)	24 (8.0)	176 (48)	249 (62)	82 (7)	0.92 (0.18)
Bs3 <sub>T</sub>	2.9 (0.2)*	21 (0.9)	4.22 (0.05)*	12 (1.8)*	6 (1.7)	20 (1.8)*	40 (8)	0.72 (0.05)
Bs2 <sub>T</sub>	2.3 (0.2)	23 (0.8)	4.39 (0.08)	12 (2.2)	4 (0.3)*	17 (2.3)	28 (4)*	0.76 (0.05)
Bs1 <sub>T</sub>	2.3 (0.1)	22 (1.1)	4.29 (0.09)	14 (2.5)	3 (0.4)	19 (3.8)	22 (5)	0.66 (0.13)
Ah <sub>T</sub>	5.9 (0.6)	23 (1.1)	3.70 (0.10)	44 (3.9)	18 (4.2)	75 (9.9)	33 (5)	1.18 (0.09)
O <sub>BT</sub>	19 (2.6)	40 (16)	3.21 (0.06)*	55 (3.0)*	118 (13)	228 (18)	61 (3)*	1.17 (0.09)
Furrow								
O <sub>F</sub>	23 (5.2)	33 (12)	4.02 (0.20)	24 (3.0)	104 (18)	173 (30)	80 (3)	0.85 (0.11)
Bs3 <sub>(0-3)F</sub> <sup>a</sup>	2.7 (0.3)	32 (7.7)	4.27 (0.10)*	15 (4.3)	5 (0.9)	23 (4.5)	33 (5)	0.74 (0.08)
Bs3 <sub>(3-8)F</sub> <sup>a</sup>	2.1 (0.1)	27 (1.3)	4.24 (0.20)	11 (1.1)	5 (0.6)	17 (0.4)	36 (8)	0.85 (0.04)
Site K2								
Undisturbed								
O <sub>U</sub>	39 (3.3)	28 (0.5)	3.09 (0.06)	140 (29)	65 (22)	264 (18)	32 (8)	0.68 (0.02)
E <sub>U</sub>	1.6 (0.4)	29 (1.4)	3.88 (0.04)	19 (2.0)	2 (0.7)	24 (2.8)	12 (3)	1.63 (0.21)
Bs1 <sub>U</sub>	3.4 (0.3)	25 (1.2)	4.39 (0.08)	17 (3.6)	2 (0.5)	21 (4.3)	16 (1)	0.61 (0.09)
Bs2 <sub>U</sub>	2.5 (0.6)	26 (1.8)	4.60 (0.03)	9 (4.5)	2 (0.7)	12 (5.4)	20 (2)	0.43 (0.08)
Bs3 <sub>U</sub>	1.8 (0.7)	28 (1.8)	4.67 (0.09)	5 (2.8)	1 (0.5)	6 (3.4)	29 (5)	0.32 (0.05)
Tilt								
O <sub>T</sub>	38 (5.8)	30 (0.5)	3.79 (0.40)	16 (5.0)	197 (39)	273 (41)	86 (4)	0.64 (0.07)
Bs2 <sub>T</sub>	4.6 (0.5)	24 (1.6)	4.24 (0.02)	21 (0.9)	5 (1.6)	29 (2.7)	22 (5)	0.65 (0.10)
Bs1 <sub>T</sub>	4.2 (0.3)	25 (1.3)	4.30 (0.01)	20 (1.8)	1 (0.3)	23 (2.4)	10 (1)	0.58 (0.08)
E <sub>T</sub>	2.5 (0.2)	31 (0.5)	3.85 (0.10)	24 (3.0)	2 (0.4)	30 (2.4)	11 (2)	1.22 (0.10)
O <sub>BT</sub>	32 (2.3)	34 (2)*	3.29 (0.09)	86 (20)	135 (35)	301 (30)	50 (10)	0.93 (0.06)*
Furrow								
O <sub>F</sub>	44 (0.2)	28 (1.0)	3.49 (0.10)	152 (22)	34 (7.0)	216 (34)	20 (1)	0.48 (0.11)
Bs2 <sub>F</sub>	2.8 (0.3)	24 (0.4)	4.30 (0.05)	15 (2.8)	2 (0.7)	19 (3.5)	14 (1)	0.56 (0.05)
Bs3 <sub>F</sub>	2.3 (0.6)	25 (0.4)	4.48 (0.07)	11 (4.1)	1 (0.5)	14 (5.3)	17 (1)	0.53 (0.10)

<sup>a</sup> Two subhorizons in the furrow were referred to as the Bs3 horizon at site K1.

<sup>b</sup> Soil pH in 0.01 M  $\text{CaCl}_2$ . <sup>c</sup> Extracted with 0.1 M  $\text{BaCl}_2$ .

logarithms of selectivity coefficients ( $\log K$ ) in different sites, horizons and positions (T, F, BT and U). The nonparametric tests, Kruskal-Wallis test and Wilcoxon rank-sum test, were often preferred because variances often differed from each other and the data distribution in many cases was not normal. A linear regression model was used to analyse the logarithmic relationships in Eqs. 6, 9 and 11. Statistics were analysed using SAS version 6.12. Differences were considered to be significant at the 0.05 level.

## Results

### Cation-exchange properties in disturbed and undisturbed soil

Similar depth gradients were found in the undisturbed soil for  $\text{pH}_{\text{Ca}}$ ,  $\text{CEC}_e$  and  $\text{BS}_e$  at both study sites (Table 1) although the sites in most cases differed significantly in their chemical properties such as C/N,  $\text{Ca}_e$  and  $\text{BS}_e$ .

The  $\text{pH}_{\text{Ca}}$  and cation-exchange properties in the disturbed mineral horizons were in general not significantly different from those in the undisturbed soil (Table 1). The only exception was the exposed Bs subhorizon at site K1 ( $\text{Bs}_{3r}$ ) where the amount of  $\text{Al}_e$ ,  $\text{CEC}_e$  and soil organic C were significantly greater and the soil  $\text{pH}_{\text{Ca}}$  significantly lower than in the corresponding undisturbed subhorizon (Table 1). The chemical properties in the exposed Bs horizon of the furrow were similar to those observed in the tilt (Table 1). At site K2, only a few statistically significant differences were observed, partly because the number of samples in each individual subhorizon was low ( $N = 4$  at site K2 and  $N = 6$  at site K1).

The  $\text{CEC}_e$  in the disturbed and undisturbed Bs horizons was positively correlated to soil organic C at both sites (Fig. 2), and the intercept of the modeled regression did not significantly differ from zero ( $P = 0.87$ ) indicating that SOM was the predominant source of exchange sites in the Bs horizons and that inorganic surfaces made an insignificant contribution. When the exchangeable cations were expressed in relation to soil C (e.g.  $\text{Al}_e/\text{C}$ ,  $\text{CEC}_e/\text{C}$ ), no significant differences were observed between correspond-

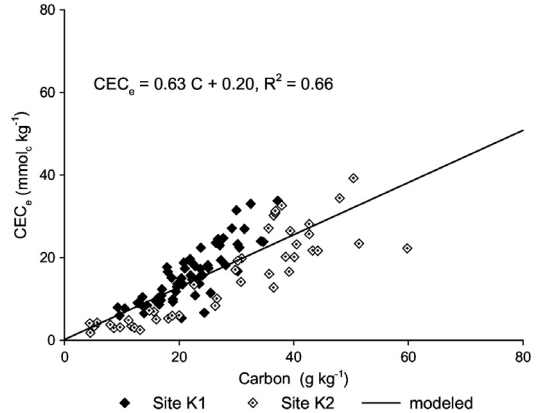


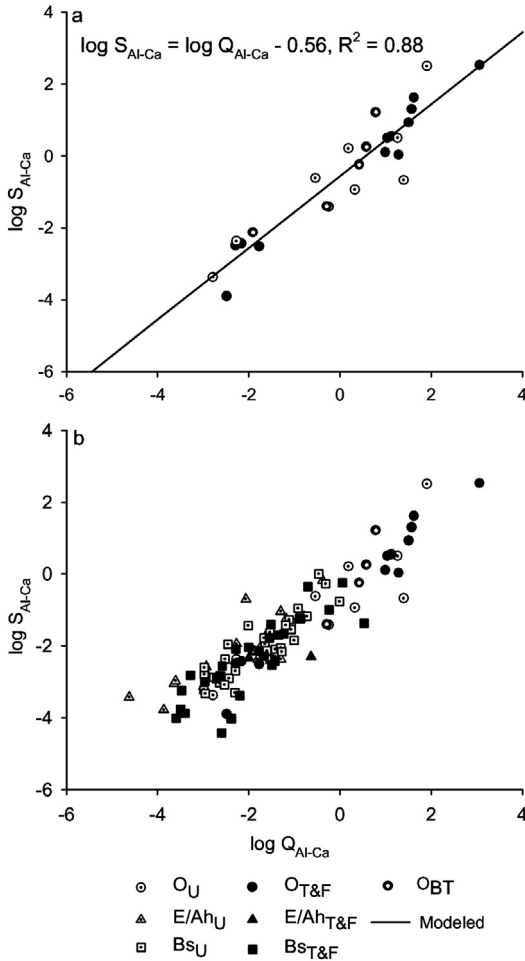
Fig. 2. Relationship between effective cation-exchange capacity ( $\text{CEC}_e$ ) and soil organic carbon in the Bs horizons at both study sites K1 and K2.

ing subhorizons in disturbed and undisturbed soils. The only exception was that  $\text{Na}_e/\text{C}$  in the exposed Bs horizons was lower ( $0.010 \pm 0.003 \text{ mmol}_c \text{ g}^{-1}$ , mean and S.D.) than in the corresponding undisturbed Bs horizons ( $0.021 \pm 0.008$ ) at both sites.

The amounts of  $\text{Al}_e$  in the buried  $\text{O}_{\text{BT}}$  horizons at both study sites were greater than in the undisturbed  $\text{O}_{\text{U}}$  horizon at site K1 (Table 1). The amounts of  $\text{Al}_e$  in the  $\text{O}_{\text{U}}$  and  $\text{O}_{\text{F}}$  horizons at site K2 were also greater and over sevenfold greater than that found in O horizons of southern Finland in general ( $18.9 \text{ mmol}_c \text{ Al}_e \text{ kg}^{-1}$ ; Tamminen and Starr 1990). Concurrently,  $\text{BS}_e$  was relatively low in these horizons (Table 1). The elevated amounts of  $\text{Al}_e$  in these surface horizons may indicate that some mixing of the mineral soil and humus has occurred, and subsequent dissolution and retention on exchange sites might explain the high Al amounts observed. The organic C content in these  $\text{O}_{\text{U}}$  and  $\text{O}_{\text{F}}$  horizons, however, suggests that the mixing with mineral soil was small (Table 1).

### Apparent cation-exchange equilibria

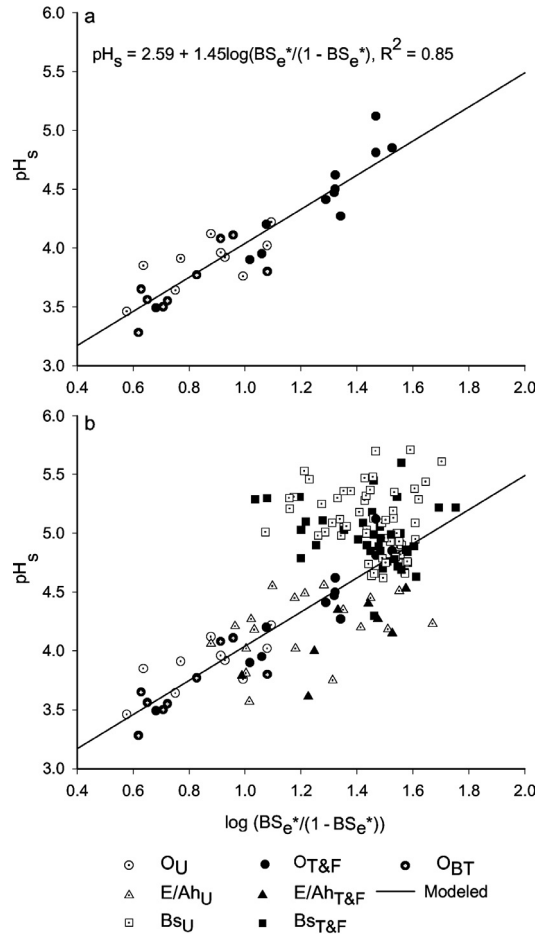
The fit of Eq. 6 for cation exchange between  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$  is illustrated in Fig. 3. The slope of the modeled regression ( $b$ ) for the O horizons was not significantly different from unity and, thus, the intercept could be taken as an estimate of  $\log K_{\text{Al-Ca}}$  (Table 2 and Fig. 3a). The



**Fig. 3.** Relationships between  $\log S$  and  $\log Q$  in  $\text{Al}^{3+}$ - $\text{Ca}^{2+}$  exchange in the undisturbed and disturbed (a) O horizons and (b) in the O, E/Ah and Bs horizons.

exchange equation was similar in all disturbed and undisturbed O horizons (Fig. 3a). The  $\text{Al}^{3+}$ - $\text{Ca}^{2+}$  exchange in both disturbed and undisturbed Bs horizons was not significantly different from that in the O horizons (Table 2 and Fig. 3b). Also in the disturbed and undisturbed E and Ah horizons, results from fitting Eq. 6 were similar to those of the O and Bs horizons (Fig. 3b), but the estimated slope was lower than unity (Table 2).

In the exchange reactions between  $\text{Al}^{3+}$  and other cations ( $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{H}^+$ ),  $R^2$  values were high and the slope was near unity in various O horizons (Table 2). The  $R^2$  values in the mineral horizons were, however, clearly lower than in the O horizons, and the model did not



**Fig. 4.** Henderson-Hasselbalch relationships between  $\text{pH}_s$  and effective base saturation calculated by including  $\text{Al}_e$  as a base cation ( $\text{BS}_e^*$ ) in the undisturbed and disturbed (a) O horizons, (b) O and E/Ah and Bs horizons. The line shown is the linear regression fitted in the O horizon.

succeed in describing the  $\text{Al}^{3+}$  and  $\text{H}^+$  exchange in the Bs horizons (Table 2).

### Weak acid dissociation

The  $\text{pH}_s$  in both the disturbed and undisturbed O horizons was positively correlated to  $\log(\text{BS}_e^*/(1-\text{BS}_e^*))$ , where  $\text{BS}_e^*$  included  $\text{Al}_e$  (Fig. 4a). The range in the x-axis in Fig. 4a varied between 0.6 and 1.6 corresponding to a range in  $\text{BS}_e^*$  from 0.80 to 0.98. The  $\text{BS}_e^*$  in most of  $O_T$  and  $O_F$  horizons was greater than in  $O_U$  horizon, but all O horizons followed a common relationship



(Fig. 4a). When the linear regression was fitted (Eq. 11),  $R^2$  was 0.85 and the estimated  $pK_{app}$  as determined by  $a$  was 2.59 (Table 3 and Fig. 4a).

The  $pH_s$  in the undisturbed and disturbed E and Ah horizons was positively correlated with  $\log(BS_e^*/(1 - BS_e^*))$  but the relationship was weaker than that in the O horizons (Fig. 4b and Table 3). The  $pH_s$  values in undisturbed and disturbed Bs horizons were positively correlated with  $BS_e$  (Eq. 9), whereas a weak negative correlation was found when  $Al_e$  was included as a "base cation" in  $BS_e^*$  (Table 3 and Fig. 4b).

## Discussion

### Changes in cation-exchange properties caused by ploughing

The studied Bs horizons were characterised by accumulation of inorganic secondary Al and relatively low amount of organic C and  $CEC_e$ , and were consistent with properties found commonly in boreal podzols (Tamminen and Starr 1990, Gustafsson *et al.* 1995, Karlton *et al.* 2000). Thus, similar depth gradients for cation-

**Table 2.** Fit of the Gaines-Thomas model to  $Al^{3+}$  exchange with different cations using Eq. 6. Model parameters, their coefficients of determination ( $R^2$ ) and number of observations for the linear regression of  $\log S$  on  $\log Q$  are presented. Regression coefficients ( $b$ ) differing significantly from unity ( $P < 0.05$ ) are marked with an asterisk (\*). The mean values of  $\log K$  and standard deviation (S.D.) are also shown. Horizon-specific values of  $\log K$  which differ from each other are marked with different letters.

Exchange	Horizon	$\log S = a + b \log Q$				$\log K$		N
		$a$	$b$	SE of $b$	$R^2$	Mean	S.D.	
Al-Ca	O	-0.56	1.00	0.07	0.88	-0.56 <sup>c</sup>	0.59	26
	E/Ah	-0.73	0.66*	0.11	0.66	-0.03 <sup>d</sup>	0.68	20
	Bs	-0.58	0.89	0.07	0.73	-0.39 <sup>cd</sup>	0.54	63
Al-Mg	O	0.56	0.93	0.08	0.84	0.71 <sup>c</sup>	0.60	26
	E/Ah	-0.03	0.69	0.15	0.51	1.28 <sup>d</sup>	0.68	20
	Bs	0.15	0.70*	0.09	0.5	1.42 <sup>d</sup>	0.57	63
Al-K	O	-1.07	0.97	0.1	0.8	-0.93 <sup>c</sup>	0.62	26
	E/Ah	-3.47	0.72	0.29	0.26	-1.89 <sup>d</sup>	0.74	19
	Bs	-3.13	0.79	0.24	0.23	-2.17 <sup>d</sup>	0.90	38
Al-Na	O	0.34	1.06	0.13	0.75	-0.04 <sup>c</sup>	0.40	26
	E/Ah	-0.09	1.03	0.32	0.37	-0.28 <sup>c</sup>	0.58	20
	Bs	-4.97	0.30*	0.12	0.09	-1.13 <sup>d</sup>	0.66	63
Al-H	O	-3.98	1.28*	0.13	0.8	-4.68 <sup>c</sup>	0.61	27
	E/Ah	-5.84	0.56	0.23	0.24	-4.20 <sup>c</sup>	0.68	21
	Bs	0	-0.06*	0	0	-5.23 <sup>d</sup>	0.56	64

**Table 3.** Model parameters, their coefficients of determination ( $R^2$ ) and number of observations for extended Henderson-Hasselbach equation using  $\log(BS_e/(1 - BS_e))$  (Eq. 9) and  $\log(BS_e^*/(1 - BS_e^*))$  where  $BS_e^*$  included exchangeable  $Al_e$  (Eq. 11). Regression coefficients ( $b$ ) differing significantly from zero ( $P < 0.05$ ) are marked with an asterisk (\*).

Horizon	$pH = a + b \log(BS_e/(1 - BS_e))$				$pH = a + b \log(BS_e^*/(1 - BS_e^*))$				N
	$a$	$b$	SE of $b$	$R^2$	$a$	$b$	SE of $b$	$R^2$	
O	3.99	0.19	0.17	0.04	2.59	1.45*	0.11	0.85	31
E/Ah	4.13	-0.12	0.17	0.02	3.55	0.51*	0.24	0.15	28
Bs	5.26	0.54*	0.07	0.37	5.59	-0.38	0.19	0.04	97

exchange properties were found at both study sites although amounts of base cations, soil C and C/N ratio indicated site-specific differences in site fertility and organic matter quality.

The horizons of the disturbed soil retained their cation-exchange properties as compared with corresponding undisturbed horizons (Table 1). This indicates that irrespective of soil relocation by ploughing, no major changes have occurred due to changes in environmental conditions such as soil temperature and moisture in the tilt (e.g. Ritari and Lähde 1981). Accumulation of organic matter in the exposed Bs horizons of the tilt and furrow (0–3 cm) was, however, observed at both sites indicating that the disturbed soil was subject to soil development after ploughing. Since the canopy at both sites was already closed, the ground vegetation in the tilts was scarce, and the main above-ground litter source was spruce needles. The trees produce C also to the mineral soil through root excretions and root litter. This was also supported by the finding that Norway spruce fine roots were unevenly distributed at ploughed forest sites, the biomass was highest in the tilt, 624 and 452 g m<sup>-2</sup> at sites K1 and K2, respectively (N. Tanskanen unpubl. data).

Although the time scale studied — 17 and 31 years after ploughing — was a relatively short period, accumulation of organic matter in the exposed Bs horizons was consistent with studies where soil development after disturbance has been assessed. Scalenghe *et al.* (2002) studied pedogenesis in disturbed alpine soils and suggested that vegetation plays a key role in development of soils: soil formation under a coniferous forest leads to the appearance of podzol-like features. Bormann *et al.* (1995) found that after windthrow disturbance, well-developed spodic and albic horizons were found in soil surfaces less than 150 years old. The first 50 years after windthrow were characterised by rapid accumulation of organic matter into the top of the mineral soil and active rooting into the profile (Bormann *et al.* 1995). Thus, it may be assumed that in the present study, the exposed Bs horizons beneath the newly formed O horizons are subject to soil formation i.e. podzolization, and as a result, new spodic horizons will develop in the disturbed soil in the course of time. Recently, Buurman and

Jongmans (2005) suggested an amended podzolization theory in which root-derived organic matter has a predominant role in the accumulation of C in the B horizon and consequently, in the formation of the B horizon of boreal podzols. The changes observed in the exposed Bs horizons indicate that further development of the ploughed Bs horizons in the course of time offers a unique opportunity to study the importance of the environment and plant-soil interactions in modifying the properties of boreal podzols.

### Apparent cation-exchange equilibria and weak acid dissociation

Aluminium and Ca<sup>2+</sup> are the most abundant cations on exchange sites in podzolized forest soils (e.g. Tamminen and Starr 1990), and their exchange reactions in the O horizon could be adequately represented using the Gaines-Thomas selectivity coefficient. The Al<sup>3+</sup>-Ca<sup>2+</sup> exchange reactions, as estimated by Eq. 6, were similar in the undisturbed and disturbed O and Bs horizons. This indicates that quite similar reactions between Al<sup>3+</sup> and Ca<sup>2+</sup> took place in different horizons of the podzols and that disturbance did not affect the apparent cation-exchange equilibria in soil. Since the clay content (< 4%) in the mineral horizons was low, SOM played a major role in the cation-exchange reactions. The importance of organically complexed Al in controlling Al<sup>3+</sup> activity in a salt extract of exchangeable cations in podzolic soils was previously shown by Skyllberg (1999) and Nissinen *et al.* (1999).

Selectivity coefficients for Al<sup>3+</sup>-Ca<sup>2+</sup> exchange were less than one ( $\log K_{\text{Al-Ca}} < 0$ ) in all horizons indicating that Ca<sup>2+</sup> was preferred over Al<sup>3+</sup>. This is opposite to many earlier works where a preference of Al<sup>3+</sup> over Ca<sup>2+</sup>, mainly in clay minerals, is found (e.g. Coulter and Talibudeen 1968, Foscolos 1968). However, a preference of Ca<sup>2+</sup> over Al<sup>3+</sup> was also found by Chung *et al.* (1994) and for podzolic forest soils by Nissinen *et al.* (1998). Nissinen *et al.* (1998) reported that the  $\log K_{\text{Al-Ca}}$  values in the O horizon (–2.08) were smaller than in the B horizon (–0.32) indicating a decreasing preference for Ca<sup>2+</sup> over Al<sup>3+</sup> with increasing depth. In the present study, the  $\log K_{\text{Al-Ca}}$  values in the O and Bs horizons (–0.56

and  $-0.39$ , respectively) did not, however, significantly differ from each other and were consistent with those presented for the B horizons by Nissinen *et al.* (1998). The smaller  $\log K_{\text{Al-Ca}}$  values in the O horizon found by Nissinen *et al.* (1998) may be partly due to different analytical methods used to analyse monomeric Al (Bartlett *et al.* 1987), and, thus, may to a greater extent include organic monomeric Al, especially, in the O horizon where concentrations of organic ligands are naturally high.

For the other cation-exchange pairs ( $\text{Al}^{3+}\text{-Mg}^{2+}$ ,  $\text{Al}^{3+}\text{-K}^+$ ,  $\text{Al}^{3+}\text{-Na}^+$  and  $\text{Al}^{3+}\text{-H}^+$ ), the Gaines-Thomas equation succeeded in describing the exchange reactions in the O horizon, but in the mineral horizons, the fit of the model was poor for many cation pairs. The poorer fit in the mineral horizons may partly be due to low cation concentrations in the soil solution and on the exchange sites, and thus, to our inability to measure and represent the exchange reactions in these horizons by the analysis methods used.

The relationship between base saturation and  $\text{pH}_s$  in various O horizons could effectively be modelled by the extended Henderson-Hasselbach equation, in which exchangeable  $\text{Al}_e$  is included as a base cation (Skjallberg 1994). Thus, in these horizons,  $\text{Al}_e$  did not appear to behave as an acid due to the low pH (Ross *et al.* 1996). Similar results have been reported for O and E horizons of podzols (Skjallberg 1999).

The higher  $\text{pH}_s$  in the neo-formed O horizons suggests that the quality of organic matter may have been less humified thereby producing higher  $\text{pH}_s$  in the soil solution. However, the estimated  $\text{pK}_{\text{app}}$  value was 2.59 in different O horizons indicating that organic matter behaved similarly. Consequently, weak acid dissociation explained the  $\text{pH}_s$  in the O horizons indicating that exchangeable cations, displaced by a neutral salt extract, adequately described the pools of these dissociated and undissociated functional groups. Equilibria of weak acids has been shown to determine the  $\text{H}^+$  activity in salt extractions of soils in laboratory experiments (e.g. Nissinen *et al.* 1999, Johnson 2002). In the present study, weak acid dissociation explained the  $\text{H}^+$  activity in *in situ* soil solutions of the O horizons representing a large range in temporal and spatial variation in the field conditions.

The relationship between  $\text{BS}_e^*$  and  $\text{pH}_s$  was clearly weaker in the mineral horizons than in the O horizons. This suggests that soil solution  $\text{pH}_s$  in mineral soil was determined by other processes than weak acid dissociation. Skjallberg and co-workers (2001) showed that by taking the complexation of Al, Ca and Mg to SOM into consideration, a modification of Eq. 9 could be used to describe the pH variation also in mineral soil horizons of acid soils. Consequently, the poorer fit of the extended Henderson-Hasselbach equation in the mineral horizons in the present study does not necessarily mean that dissociation of weak acid was absent. Instead, it is likely that processes characteristic for the organic matter took place also in the mineral soil as shown in the case of the  $\text{Al}^{3+}\text{-Ca}^{2+}$  exchange model, but in the Bs horizons were masked by analytical constraints (to extract and express adsorbed cations). Weak acid dissociation in the Bs horizons may, however, also be overridden by other processes such as Al solubility control by a  $\text{Al}(\text{OH})_3$  phase (Gustafsson *et al.* 2001). Other reactions such as hydrolysis of exchangeable and nonexchangeable Al were also likely to occur in the  $\text{pH}_s$  values observed in the Bs horizons. Additionally, soluble organic acids may contribute to the control of the  $\text{Al}^{3+}$  activity in the soil solutions of the E and B1 horizons (van Hees *et al.* 2000). The importance of organic complexation reactions of Al in controlling the Al solubility in the upper B horizons of podzols was shown by Simonsson and Berggren (1998).

## Conclusions

We studied the cation-exchange properties and reactions in the undisturbed and disturbed podzolic soil profiles at two forest sites that had been ploughed 17 and 31 years ago and planted with Norway spruce seedlings. The increase observed in soil organic C and in the  $\text{CEC}_e$  in the exposed Bs horizons (0–3 cm) in the few decades after ploughing suggest that the inverted Bs horizons were subject to soil development since ploughing, and that the development was mainly due to organic matter produced by the planted Norway spruce. The Gaines-Thomas selectivity coefficient for  $\text{Al}^{3+}\text{-Ca}^{2+}$  exchange was similar

in both the disturbed and undisturbed O and Bs horizons. This indicates that quite similar reactions between  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$  took place in different horizons of the podzols and that the disturbance did not affect the apparent cation-exchange equilibria in soil. The  $\text{pH}_s$  variation in different O horizons was explained by weak acid dissociation — the modified Henderson-Hasselbach equation in which exchangeable Al<sub>e</sub> had nonacidic properties similar to those of base cations. The results of this study suggest that organic matter, accumulated within the soil profile during soil formation and after ploughing, had an important role in determining the cation-exchange properties and reactions in the studied podzols disturbed by deep tilling.

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## References

- Bartlett R.J., Ross D.S. & Magdoff F.R. 1987. Simple kinetic fractionation of reactive aluminum in soil 'solutions'. *Soil Sci. Soc. Am. J.* 51: 1479–1482.
- Birkeland P.W. 1984. *Soils and geomorphology*. Oxford University Press, New York.
- Bloom P.R. & Grigal D.F. 1985. Modeling soil response to acidic deposition in nonsulfate adsorbing soils. *J. Environ. Qual.* 14: 489–495.
- Bormann B.T., Spaltenstein H., McClellan M.H., Ugolini F.C., Cromack K.Jr. & Nay M.S. 1995. Rapid soil development after windthrow disturbance in pristine forests. *J. Ecol.* 83: 747–757.
- Buurman P. & Jongmans A.G. 2005. Podsolisation and soil organic matter dynamics. *Geoderma* 125: 71–83.
- Cajander A.K. 1925. The theory of forest types. *Acta For. Fenn.* 29: 1–108.
- Chung J.-B., Zasoski R.J. & Burau R.G. 1994. Aluminum-potassium and aluminum-calcium exchange equilibria in bulk and rhizosphere soil. *Soil Sci. Soc. Am. J.* 58: 1376–1382.
- Coulter B.S. & Talibudeen O. 1968. Calcium:aluminium exchange equilibria in clay minerals and acid soils. *J. Soil Sci.* 19: 237–250.
- Driscoll C.T. 1984. A procedure for the fractionation of aqueous aluminum in dilute acidic waters. *Intern. J. Environ. Anal. Chem.* 16: 267–283.
- Eronen M. 1983. Late Weichselian and Holocene shore displacement in Finland. In: Smith D.E. & Dawson A.G. (eds.), *Shorelines and isostasy*, Institute of British Geographers, Special Publication 16, Academic Press, pp. 183–207.
- FAO-Unesco 1990. *Soil map of the world*. Revised legend, FAO, Rome, World Soil Resources Report No. 60.
- Finnish Forest Research Institute 2001. *Finnish statistical yearbook of forestry 2001*. Agriculture, Forestry and Fishery, 2001: 52, Helsinki.
- Finnish Meteorological Institute 1993. *Meteorological yearbook of Finland 1991*. Finnish Meteorological Institute, Helsinki.
- Foscolos A.E. 1968. Cation-exchange equilibrium constants of aluminum saturated montmorillonite and vermiculite clays. *Soil Sci. Soc. Am. Proc.* 32: 350–354.
- Gaines G.L. & Thomas H.C. 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. *J. Chem. Phys.* 21: 714–718.
- Giesler R. & Lundström U. 1993. Soil solution chemistry: effects of bulking soil samples. *Soil Sci. Soc. Am. J.* 57: 1283–1288.
- Gustafsson J.P., Berggren D., Simonsson M., Zysset M. & Mulder J. 2001. Aluminium solubility mechanisms in moderately acid Bs horizons of podzolized soils. *Eur. J. Soil Sci.* 52: 655–665.
- Gustafsson J.P., Bhattacharya P., Bain D.C., Fraser A.R. & McHardy W.J. 1995. Podzolisation mechanisms and the synthesis of imogolite in northern Scandinavia. *Geoderma* 66: 167–184.
- Hendershot W.H. & Duquette M. 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Am. J.* 50: 605–608.
- Johnson C.E. 2002. Cation exchange properties of acid forest soils of the northeastern USA. *Eur. J. Soil Sci.* 53: 271–282.
- Karlton E., Bain D.C., Gustafsson J.P., Mannerkoski H., Murad E., Wagner U., Fraser A.R., McHardy W.J. & Starr M. 2000. Surface reactivity of poorly-ordered minerals in podzol B horizons. *Geoderma* 94: 265–288.
- Lindsay W.L. 1979. *Chemical equilibria in soils*. Wiley-Interscience, New York.
- Nissinen A., Ilvesniemi H. & Tanskanen N. 1998. Apparent cation exchange equilibria in podzolic forest soils. *Eur. J. Soil Sci.* 49: 121–132.
- Nissinen A., Ilvesniemi H. & Tanskanen N. 1999. Equilibria of weak acids and organic Al complexes explain activity of  $\text{H}^+$  and  $\text{Al}^{3+}$  in a salt extract of exchangeable cations. *Eur. J. Soil Sci.* 50: 675–686.
- Nordstrom D.K. & May H.M. 1989. Aqueous equilibrium data for mononuclear aluminum species. In: Sposito G. (ed.), *The environmental chemistry of aluminum*, CRC Press, Boca Raton, FL, pp. 29–53.
- Ritari A. & Lähde E. 1978. Effect of site preparation on physical properties of the soil in a thick-humus spruce stand. *Commun. Inst. For. Fenn.* 92: 1–37.
- Ross D.S., David M.B., Lawrence G.B. & Bartlett R.J. 1996. Exchangeable hydrogen explains the pH of spodosol Oa horizons. *Soil Sci. Soc. Am. J.* 60: 1926–1932.
- Scalenghe R., Bonifacio E., Celi L., Ugolini F.C. & Zanini E. 2002. Pedogenesis in disturbed alpine soils (NW Italy). *Geoderma* 109: 207–224.

- Simonsson M. & Berggren D. 1998. Aluminium solubility related to secondary solid phases in upper B horizons with spodic characteristics. *Eur. J. Soil Sci.* 49: 317–326.
- Skyllberg U. 1994. Aluminum associated with a pH-increase in the humus layer of a boreal Haplic Podzol. *Interciencia* 19: 356–365.
- Skyllberg U. 1999. pH and solubility of aluminium in acidic forest soils: a consequence of reactions between organic acidity and aluminium alkalinity. *Eur. J. Soil Sci.* 50: 95–106.
- Skyllberg U., Raulund-Rasmussen K. & Borggaard O.K. 2001. pH buffering in acidic soils developed under *Picea abies* and *Quercus robur* — effects of soil organic matter, adsorbed cations and soil solution ionic strength. *Biogeochemistry* 56: 51–74.
- Tamminen P. & Starr M.R. 1990. A survey of forest soil properties related to soil acidification in southern Finland. In: Kauppi P., Anttila P. & Kenttämies K. (eds.), *Acidification in Finland*, Springer-Verlag, Berlin, pp. 235–251.
- Tanskanen N. 1995. *Kationinvaihdon tasapainokertoimet metsämaassa*. M.Sc. thesis, University of Helsinki, Department of Limnology and Environmental Protection.
- Tanskanen N. & Ilvesniemi H. 2004. The amount of secondary Al in two ploughed podzolic forest soils. *Geoderma* 119: 249–260.
- Thomas G.W. & Hargrove W.L. 1984. The chemistry of soil acidity. In: Adams F. (ed.), *Soil acidity and liming*, 2nd ed. Agronomy No. 12, American Society of Agronomy, Madison, WI, pp. 4–56.
- Tiktak A. & van Grinsven H.J.M. 1995. Review of sixteen forest-soil-atmosphere models. *Ecol. Model.* 83: 35–53.
- van Hees P.A.W., Lundström U.S., Starr M. & Giesler R. 2000. Factors influencing aluminium concentrations in soil solution from podzols. *Geoderma* 94: 289–310.