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Aluminium chemistry in ploughed podzolic forest soils

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Academic dissertation

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ABSTRACT

Mechanical site preparation has been used to ensure efficient reforestation of clear-felled areas in Finland since the 1960s. About 18% (3.94 million ha) of the total forest land in Finland (21.9 million ha) has been site-prepared, of which one-third has been deeply tilled. In the present study, long-term effects of deep tilling on the chemical properties of soil and soil solution chemistry were evaluated at two forest sites that had been ploughed 17 and 31 years ago and planted with Norway spruce (*Picea abies* (L.) Karst.) seedlings. Particular interest was focused on the possible mobilisation of soil aluminium in the spodic B horizons exposed upon tilling. Mechanisms controlling Al solubility in the tilled soil profiles were also examined.

Decreased concentrations of soil extractable Al, mainly inorganic secondary Al, in the exposed Bs horizons of tilts and furrows and increased concentrations of organically complexed Al in the O horizons buried within the tilt indicate that some Al was mobilised at the ploughed forest sites. Accumulation of organic C on top of the tilts and furrows with the relatively high Norway spruce fine root biomass in the tilts indicated that the release of Al was mainly due to acidity produced by ecosystem internal processes such as organic acids excreted by roots or released during decomposition of above- and belowground litter.

Ploughing did not affect the processes controlling activity of Al^{3+} in soil solution. In the undisturbed and disturbed Bs horizons, Al solubility was controlled by secondary minerals while in the O and Ah/E horizons, solubility control by organically bound Al was observed. Although the soil exchangeable Al pool was small, the Al^{3+} - Ca^{2+} exchange based on the Gaines-Thomas equation succesfully described the relationship between these cations in soil solution and on exchange sites in the studied O and Bs horizons. In the O horizons, exchangeable Al had nonacidic properties similar to those of base cations, and the soil solution pH was explained by weak organic acid dissociation using the Henderson-Hasselbach equation.

The changes observed in soil chemical properties in the ploughed soil were consistent with the processes determining the Al chemistry in soil solution, and in accordance with the theory of podzolization. It may be expected that soil formation processes will in the course of time result in the development of a new spodic horizon in the tilts and furrows. Although the time elapsed since ploughing was only a few decades in this study, the occurrence of changes observed suggest that plant-derived organic matter and plant-soil interactions are already modifying the properties of ploughed podzols.

Keywords: fine roots, Norway spruce, podzolization, site preparation, soil organic matter, soil solution

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I came to work as a research assistant for PhD students Hannu Ilvesniemi and Ari Nissinen at the Department of Forest Ecology over 14 years ago. One of my first tasks was to sieve air-dried soil samples for further analysis in a dusty hot laboratory during sunny summer days. That work must have made a deep impression on me, because since those early days in lab, I have carried on working with the soil. Although later on, the scientific work has sometimes been quite tedious (with the numerous versions of the same stories repeated over and over again), from time to time, I have still had a feeling I'm a little child making sand cakes in a sandbox and experiencing new exciting world around me.

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LIST OF ORIGINAL ARTICLES

This thesis consists of the summary and the following substudies, which are referred to in the text by their Roman numerals. Papers are reproduced with the permission of the journals in question.

I **Tanskanen, N.** and Ilvesniemi, H. 2004. The amount of secondary Al in two ploughed podzolic forest soils. Geoderma 119: 249-260.

II **Tanskanen, N.**, Kareinen, T., Nissinen, A. and Ilvesniemi, H. 2004. Soil solution aluminium in disturbed and undisturbed podzolic profiles at two tilt-ploughed forest sites. Boreal Environment Research 9: 347-355.

III **Tanskanen, N.**, Nissinen, A. and Ilvesniemi, H. Aluminium solubility in disturbed and undisturbed podzolic profiles. Submitted manuscript.

IV **Tanskanen, N.** and Ilvesniemi, H. 2006. Cation-exchange reactions involving aluminium ions in podzols disturbed by deep tilling. Boreal Environment Research 11: In press.

Niina Tanskanen participated in planning the research, was responsible for conducting the laboratory and data analysis and was the main author in all papers.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrophotometry
BS_e	Effective base saturation
CEC_e	Effective cation-exchange capacity
DOC	Dissolved organic carbon
EA	Exchangeable acidity
FIA	Flow-injection ion analyzer
HPLC	High pressure liquid cromatography
IAP	Ion activity product
ICP-AES	Inductively coupled plasma-atomic emission spectrometry
ITM	Imogolite-type materials
LMW	Low molecular weight organic acids
TA	Total acidity
SOM	Soil organic matter

1. INTRODUCTION

1.1. Background

The most common soil-forming process in Finland is podzolization. This process is characterised by the translocation of aluminium (Al) and iron (Fe) from the upper soil and accumulation deeper in the soil. Besides its important role in soil formation, Al in the soil and its mobilisation has been widely studied in relation to acidic deposition (Cronan et al. 1986, Dahlgren et al. 1989, Mulder et al. 1989, Mulder and Stein 1994) because acidification of soils through the atmospheric deposition such as nitrogen-oxides and sulphur-oxides enhances the liberation of Al. High concentrations of Al in soil solution, especially of inorganic Al^{3+} ions, are potentially toxic to plant roots and soil organisms (e.g. Ulrich et al. 1980, Cronan and Grigal 1995), and, upon leaching, to aquatic life (Driscoll et al. 1980) since Al concentrations in freshwaters are clearly influenced by Al discharge from the surrounding soils. Because Al is a common element in soils, and it is strongly complexed in many soils, Al exerts a strong influence on the sorption of heavy metals in soils through competition effects. Thus, behaviour of Al in soils is also important when heavy metal binding and leaching in contaminated soils are evaluated.

Despite numerous studies about Al solubility in acid forest soils, the processes controlling release and retention of Al are still not thorougly understood (Gustafsson et al. 2001). A better understanding of these processes needs to be known if the impacts of air pollution or soil disturbance are to be predicted. The development and changes in soil properties are generally slow. The time needed for the development of a podzolic morphology in the Nordic countries range between a few hundred and thousand year (Starr 1991, Mokma et al. 2004). Manipulation and disturbance of soil through cultivation, forest management, air pollution and climate change may, however, result in immediate or relatively fast changes in soil properties. The stratified structure of a podzolic forest soil is dramatically changed by site preparation. Site preparation has been widely carried out in Finland since the 1960s to ensure efficient reforestation of clear-felled areas. In deep tilling the illuvial B horizon, enriched in Al, is exposed on the soil surface. How Al in the soil responds to deep tilling has, however, received little attention.

1.2. Aluminium in soil

Aluminium is the most common metal in the Earth's crust (Sposito 1989) where it occurs in a range of primary silicate minerals. As these minerals weather, the Al released is transported downwards through leaching and subject to precipitation within the soil profile as secondary minerals, largely as aluminosilicates. During subsequent weathering of the secondary minerals, silicon is lost more rapidly than Al, leaving the latter to precipitate as oxides and hydroxides. Soils that are in an advanced stage of weathering, such as Ferralsols in the tropics, are characteristically rich in such Al oxides. Some of the Al released during weathering and dissolution processes may also become complexed with soil organic matter or become electrostatically bound to negative charge sites on soil particles (clays and organic colloids).

Due to its small ionic radius and high charge, Al^{3+} exerts a strong electrostatic attraction towards any ligand that carriers a negative charge. In aqueous solution, the most common ligand is the water molecule but complexes with fluoride, sulphate, silica and organic acids are also important in natural waters (Driscoll and Schecher 1988).

The Al^{3+} ion and water molecules are tightly bound and together behave like a single large $Al(H_2O)_6^{3+}$ ion in solution. As the pH is raised from 4 to 5 the coordinated water molecules lose some of their protons. This reaction is called hydrolysis or alternatively, deprotonation. With the coordinated waters explicitly written, the first hydrolysis step of Al is:

$$Al(H_2O)_6^{3+} + H_2O \leftrightarrow AlOH(H_2O)_5^{2+} + H^+ \; . \tag{1}$$

The sequence of hydrolysis steps of Al (ignoring the water ligands) with equilibrium constants (log *K)* and heats of reaction ($\Delta H°$) is presented in Table 1. The $Al(H_2O)_6^{3+}$ ion is thus a weak acid with a hydrolysis constant value of log *K* –5.00, i.e. half of the Al^{3+} ions at a pH value 5 are present as $AlOH(H_2O)_5^{2+}$ ions. At higher pH values, the hydrolysis of Al progressively continues, ultimately resulting in the precipitation of $Al(OH)_3$ (Table 2). Temperature affects the hydrolysis of Al, as also the dissolution and precipitation reactions of $Al(OH)_3$. The log *K* value for any desired temperature can be calculated by using the van't Hoff equation (Atkins 1990):

$$\ln K_2 - \ln K_1 = \frac{-\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{2}$$

in which K_1 and K_2 are equilibrium constants, R is the gas constant (8.314 J K^{-1} mol^{-1}), $\Delta H°$ is heat of reaction and T is temperature (in Kelvin degrees). When the temperature decreases from 25° to 5°C, the hydrolysis constant for the first hydrolysis step of Al decreases from –5.00 to –5.73, resulting in half of the Al^{3+} being present as $AlOH(H_2O)_5^{2+}$ ions in a solutions having a pH value of 5.73. In the case of gibbsite ($Al(OH)_3$) solubility (Table 2), the log *K* increases from 7.74 to 9.06 as the temperature decreases from 25° to 5°C, indicating that gibbsite is more soluble at lower temperatures.

Table 1. Equilibrium constants and heats of reaction at 298 K and 1 atm for inorganic Al species.

Reaction	log *K*	ΔH_r^0 (kJ mol^{-1})	Reference
$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+$	-5.00	57.7	Nordstrom and May (1989)
$Al^{3+} + 2\ H_2O \leftrightarrow Al(OH)_2^+ + 2\ H^+$	-10.10	122.5	Nordstrom and May (1989)
$Al^{3+} + 3\ H_2O \leftrightarrow Al(OH)_3^0 + 3\ H^+$	-16.80	176.3	Nordstrom and May (1989)
$Al^{3+} + 4\ H_2O \leftrightarrow Al(OH)_4^- + 4\ H^+$	-22.70	206.1	Nordstrom and May (1989)
$Al^{3+} + SO_4^{2-} \leftrightarrow AlSO_4^+$	3.02	9.0	Ball et al. (1980)
$Al^{3+} + H_4SiO_4 \leftrightarrow AlH_3SiO_4^{2+} + H^+$	-2.38	66.6	Pokrovski et al. (1996)

Table 2. Equilibrium constants and heats of reaction at 298 K and 1 atm for solid Al-phases.

Reaction	$\log K_s^0$	ΔH_r^0 (kJ mol^{-1})	Reference
$Al(OH)_3$ (s) + 3 $H^+ \leftrightarrow Al^{3+}$ + 3 H_2O / gibbsite	7.74	-105.0	Palmer and Wesolowski (1992)
$Al(OH)_3$ (s) + 3 $H^+ \leftrightarrow Al^{3+}$ + 3 H_2O / Al hydroxide (soil)	8.29	-105.0	Gustafsson et al. (1998)
$0.5(HO)_3Al_2O_3SiOH$ (s) + 3 $H^+ \leftrightarrow Al^{3+}$ + 0.5 H_4SiO_4 + 1.5 H_2O / imogolite	6.00	-96.8	Farmer and Fraser (1982)
$0.5(HO)_3Al_2O_3SiOH$ (s) + 3 $H^+ \leftrightarrow Al^{3+}$ + 0.5 H_4SiO_4 + 1.5 H_2O / proto-imogolite sol	7.02	-96.8	Lumsdon and Farmer (1995)
$0.5(HO)_3Al_2O_3SiOH$ (s) + 3 $H^+ \leftrightarrow Al^{3+}$ + 0.5 H_4SiO_4 + 1.5 H_2O / imogolite (soil)	6.64	-96.8	Gustafsson et al. (1998)
$0.5Al_2O_5Si_2(OH)_4$ (s) + 3 $H^+ \leftrightarrow Al^{3+}$ + H_4SiO_4 + 0.5 H_2O / kaolinite	2.87	-147.5	Manley et al. (1987)

1.3. Aluminium in podzolized soils

Soils in Finland have been subject to soil formation since the retreat of the glacial ice that started about 11 000 - 10 000 years ago (Eronen 1983). The type of soil present can be related to soil formation factors, including climatic, parent material, topographical and biological, all of which have interacted with each other over time (Jenny 1941). The soil factors determine and control the rate of soil processes, which result in the soil properties that define the soil type.

The most common soil forming process in the northern boreal zone with a cool, humid climate is podzolization. Podzols are typically found on coarsely textured, nutrient-poor parent materials under coniferous forest or heath vegetation. Characteristic of podzolization is the weathering of mineral-forming elements in the upper soil and the subsequent migration, immobilisation and accumulation of Al and Fe and organic matter at depth. This process results in the formation of an eluvial (E) horizon underlying by an illuvial (B) horizon enriched in Al and Fe. Below the B horizon is C horizon which consists of relatively unaltered parent material. The moist and cool climatic conditions of the boreal zone favour the development of an organic horizon (O) on the soil surface.

The exact mechanisms involved in mobilization, transportation and immobilization of Al, Fe and organic matter in podzols are not thorougly understood although podzols have been studied for a long time (see review by Lundström et al. 2000a). Two major groups of processes have been proposed to explain podzolization: 1) formation and translocation of Al and Fe as organic metal complexes within the soil profile; and 2) silicate weathering followed by downward tranport of Al and Si as inorganic colloidal sols and subsequent immobilization as imogolite-type materials (ITM) in the B horizon (Farmer et al. 1980, Anderson et al. 1982). Imogolite is a short-range ordered aluminosilicate with an Al:Si ratio of 2:1, and a less ordered material with the same chemical composition is referred to as proto-imogolite allophane (Farmer et al. 1980). Together imogolite and proto-imogolite allophane are referred to as imogolite-type materials. In the case of the organic metal complexes, the immobilisation of the organically bound Al and Fe in the illuvial horizon is ascribed to precipitation/adsorption of organic complexes as a critical C/metal ratio is reached (Schnitzer and Skinner 1963, Petersen 1976). De Coninck (1980) concluded that immobilization of organic metal complexes in the B horizon occurs through supplementary fixation of cations, desiccation or on arrival at a level with different ionic concentrations. Recent findings suggest that the organic matter, in particular, low molecular weight (LMW) organic acids exuded by roots and mycorrhizal fungi play a crucial role in weathering and translocation of Al in podzolic forest soils (Lundström et al. 2000b). The organic complex formers may be microbially decomposed during migration through the soil profile, leaving the inorganic Al and Fe to precipitate as inorganic phase like ITM and ferrihydrite (Lundström et al. 2000b).

As a result of illuviation, spodic B horizons contain a wide range of Al and Fe complexes, secondary oxides and oxyhydroxides that form coatings on the primary particles and peds. Due to the heterogeneity and low crystallinity of the accumulated material in the B horizons it is often loosely referred to as sesquioxide-organic matter complexes or spodic material. An operationally defined fractionation scheme suggested by McKeague and coworkers (1971), which is based on selective extractions by dithionite-citrate, acid ammonium oxalate and sodium pyrophosphate, made it possible to broadly divide secondary Fe and Al into crystalline, amorphous and organically bound fractions. The combination of quantative data from selective extractions with qualitative spectroscopic evidence from infrared (IR) and Mössbauer spectroscopy has shown the existence of imogolite and imogolite-type minerals (Farmer et al. 1980, Gustafsson et al. 1995, Karltun et al. 2000) and ferrihydrite (Parfitt and Childs 1988, Karltun et al. 2000) in the spodic B horizon. Small amounts of gibbsite have also been identified in the B horizons (Gustafsson et al. 1995, 1999).

As a result of illuviation, the cation-exchange capacity (CEC) of a spodic B horizon is greater than that of the parent material due to accumulation of organic matter. The soil's capacity for adsorption of weak acid anions, such as SO_4^{2-} and organic acids is also increased due to the surface reactivity of the poorly-ordered oxides (Karltun et al. 2000). Soil water retention properties are also affected by spodic horizon formation. Spodic horizons have an increased capacity to hold water compared to their coarsely textured parent materials (Mecke et al. 2002).

1.3.1. Aluminium solubility in podzolized soils

The primary source of reactive Al in the podzolized soils is from silicate minerals. However, in the short-term secondary Al minerals may control dissolved Al concentrations through chemical equilibria reactions. Batch experiments and field measurements have shown that Al hydroxides (e.g. gibbsite) control Al solubility in spodic B horizons (Dahlgren et al. 1989, Berggren and Mulder 1995, Gustafsson et al. 1998, 2001). If the activity of Al^{3+} in the soil solution is in equilibrium with an $Al(OH)_3$ phase, the following equilibrium reaction can be applied:

$$AlOH_3(s) + 3H^+ \leftrightarrow Al^{3+} + 3H_2O\,. \qquad (3)$$

In logarithmic form, Eq. 3 is written as:

$$\log(Al^{3+}) = \log K - 3pH \qquad (4)$$

where log K is the logarithm of the equilibrium constant to base-10. A log K_s^0 value for crystalline gibbsite of 7.74 at 25 °C was reported by Palmer and Wesolowski (1992). For less crystalline $Al(OH)_3$ this value is larger. Gustafsson and co-workers (1998) reported a log K_s^0 value of 8.29 for $Al(OH)_3$ in spodic B horizons (Table 2). However, gibbsite and other $Al(OH)_3$ phases have rarely been identified in podzolic forest soils. It has therefore been suggested that hydroxy-Al polymers, which may be present in clay mineral interlayers and have a solubility similar to that of $Al(OH)_3$, control Al solubility in spodic B horizons (Dahlgren and Ugolini 1989). Alternatively, it has been suggested that only a small amount of noncrystalline $Al(OH)_3$ is present (Berggren and Mulder 1995, Gustafsson et al. 1998) due to redissolution of reactive $Al(OH)_3$ to form less soluble ITM (Gustafsson et al. 1998, Zysset et al. 1999).

It has also been proposed that Al solubility in spodic B horizons is controlled by imogolite (Dahlgen et al. 1989, Zysset et al. 1999), a short-range ordered aluminosilicate with an Al:Si ratio of 2:1, or by a less ordered material with the same chemical composition referred to as proto-imogolite allophane (Farmer et al. 1980). However, results from other studies examining soil solutions from podzolized forest soils have not found equilibria with respect to any secondary Al solids (Matzner et al. 1998, Nissinen et al. 2000, van Hees et al. 2000, 2001).

The soil solutions from O horizons and upper mineral soil rich in organic matter are undersaturated with respect to inorganic secondary Al phases and Al solubility appears to be controlled by organic complexation (Cronan et al. 1986, Walker et al. 1990). Organic Al-complexes may also control dissolved Al concentrations in acid mineral horizons even when the amount of soil organic matter (SOM) is relatively low (Bloom et al. 1979, Mulder and Stein 1994, Wesselink et al. 1996). When the activity of Al^{3+} in the soil solution is controlled by complexation reactions with SOM, the following equilibrium reaction can be applied:

$$AlR^{(3-n)} + n\,H^{+} \leftrightarrow H_nR + Al^{3+}\,, \qquad (5)$$

where R denotes the organic ligand of SOM and n represents the number of H^+ ions that are exchanged for each Al^{3+}. In logarithmic form, Eq. 5 is written as:

$$\log(Al^{3+}) = -n\,pH + \log(K\left[AlR^{(3-n)}\right]/\left[H_nR\right])\,, \qquad (6)$$

where K denotes the equilibrium constant and the brackets denote the activities of the solid phases. Thus, Al^{3+} activity is a function not only of H^+ activity but also of degree of saturation of the organic complexation sites with Al. Wesselink et al. (1996) proposed that the degree of saturation of complexation sites could be described by the molar ratio of pyrophosphate-extractable Al to soil C (Al_p/C) in acid mineral soils. Simonsson and Berggren (1998) found that Al solubility, defined as $\log(Al^{3+}) + 1.65$ pH, in upper B horizon of podzols was closely related to the molar Al to C ratio in pyrophosphate extracts, at least when the ratio was low (< 0.1).

Other reactions at the soil solution-soil interface, such as cation exchange, may also have an effect on the Al^{3+} activity in the soil solution. The significance of exchangeable cations in determining the cation concentrations in acid forest soil solutions has been emphasized in several studies (Skyllberg 1994, Ross et al. 1996, Nissinen et al. 1998, 2000, van Hees et al. 2000 and Johnson 2002). Nissinen et al. (1998) used Gaines-Thomas selectivity coefficients to describe cation exchange and cation concentrations in centrifuged soil solutions from podzolic forest soils. If the exchange reaction between cations held on the negatively charged exchange sites (e.g. CaX and AlX) and those in soil solution (Ca^{2+} and Al^{3+}) is assumed to be

$$3\,CaX + 2\,Al^{3+} \leftrightarrow 2\,AlX + 3\,Ca^{2+}\,, \qquad (7)$$

the Gaines-Thomas selectivity coefficient, $K_{Al\text{-}Ca}$, for this reaction (Gaines and Thomas 1953), is defined by the equation

$$K_{Al-Ca} = \frac{E_{Al}^{2}\,(Ca^{2+})^{3}}{E_{Ca}^{3}\,(Al^{3+})^{2}}\,, \qquad (8)$$

where the terms in parentheses ( ) represent the ion activities in soil solution and E the charge fraction of soil exchangeable cations (Nissinen et al. 1998). The right-hand side of Eq. 8 can be divided into two parts, one relating to the ions in the soil solution (S) and the other to the ions on the exchange sites (Q), respectively:

$$S_{Al-Ca} = \frac{(Ca^{2+})^3}{(Al^{3+})^2} \tag{9}$$

and

$$Q_{Al-Ca} = \frac{E_{Ca}^3}{E_{Al}^2} \; . \tag{10}$$

Now log K may be written as:

$$\log K_{Al-Ca} = \log S_{Al-Ca} - \log Q_{Al-Ca} \; , \tag{11}$$

and, a linear regression model, based on Eq. 11

$$\log S_{Al-Ca} = a + b \log Q_{Al-Ca} \; , \tag{12}$$

may be used to determine log $K_{Al\text{-}Ca}$ as the intercept (a).

The work by Skyllberg (1994), Ross et al. (1996) and Johnson (2002) highlighted the importance of exchangeable H^+ in exchange reactions in acid forest soils. Exchangeable H^+ has traditionally been ignored due to difficulty in separating exchangeable H^+ from hydrolysis reactions of Al^{3+} (Thomas and Hargrove 1984). However, Ross and co-workers (1996) found that exchangeable H^+ explained the pH of Spodosol O horizons and exchangeable Al did not appear to behave as a weak acid due to the low pH. Skyllberg (1994) proposed that soil pH in O horizons is explained by the dissociation of weak organic acid groups. In acid forest soils, the negative charge on SOM is predominantly derived from carboxylic functional groups (R-COOH). When the dissociation of weak organic acids in soil explains soil solution pH, the modified Henderson-Hasselbach equation (Thomas and Hargrove 1984) can be used:

$$pH = pK_{app} + n \log\left(\frac{\alpha}{1-\alpha} \right), \tag{13}$$

where the pK_{app} is an apparent dissociation constant for the carboxylic functional groups providing the charge, α is the fraction of dissociated R-COO$^-$ functional groups, and n is a parameter that accounts for solution conditions. Bloom and Grigal (1985) proposed that potential base saturation (BS) could be used as a surrogate for α:

$$pH = pK_{app} + n \log\left(\frac{BS}{1-BS} \right). \tag{14}$$

Skyllberg (1994) applied this model to O horizons of podzols and proposed that the relationship between effective base saturation (BS_e) and soil pH in the O horizon could be effectively modelled by the extended Henderson-Hasselbach equation,

$$pH = pK_{app} + n \log\left(\frac{BS_e^*}{1 - BS_e^*}\right) \tag{15}$$

in which BS_e^* is the effective base saturation computed with Al_e (Skyllberg 1994, Johnson 2002). In a linear form, Eq. 15 is written as

$$pH = a + b \log\left(\frac{BS_e^*}{1 - BS_e^*}\right). \tag{16}$$

Johnson (2002) applied this model to acid forest soils in northeastern USA and found that the model could be incorporated into biogeochemical models to predict pH from measurements of soil exchangeable cations.

1.4. Aluminium in site prepared forest soils

Mechanical site preparation is done to ensure efficient reforestation at clear-felled areas and has been carried out in Finland since the late 1960s (Figure 1). Depending on the site preparation method used, the stratified structure of the podzolic soil is altered to varying extent. With 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 O horizons are buried within the tilt at top of the original soil surface (Figure 2). About 18% (3.94 million ha) of the total forest land 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).

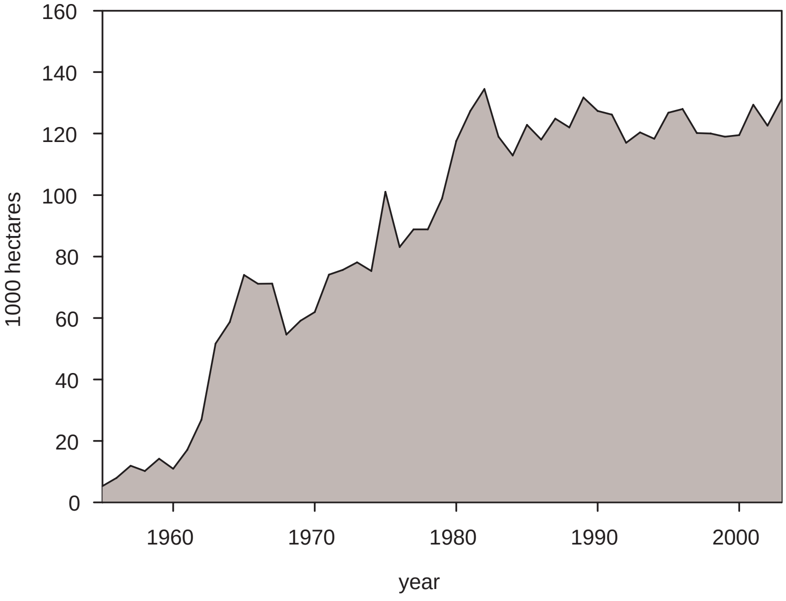
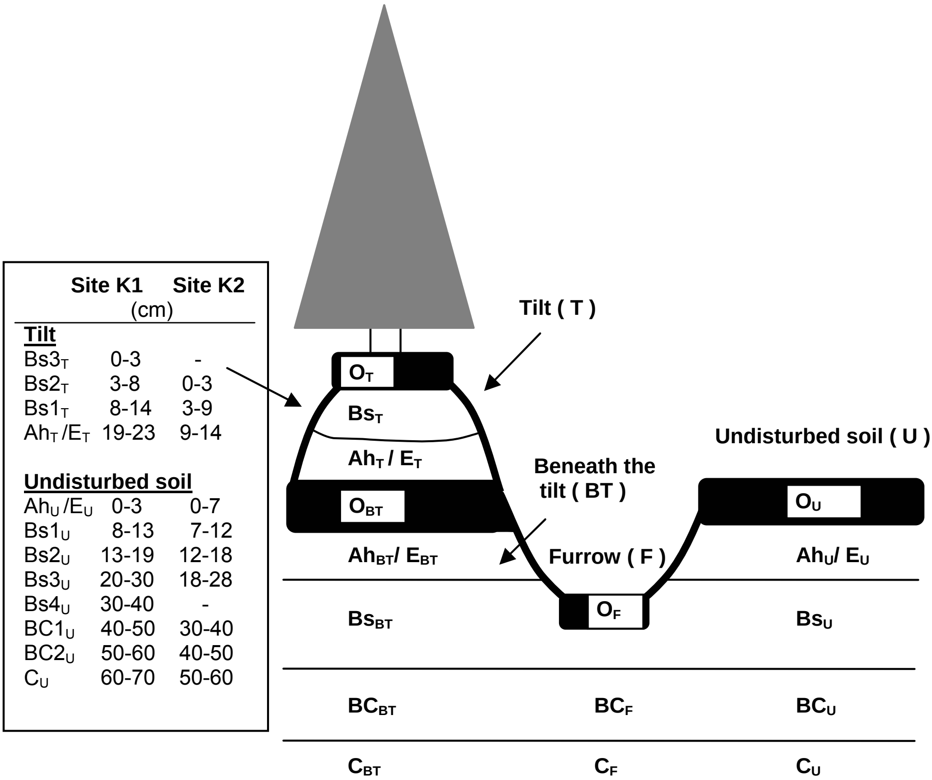


Figure 1. Areas prepared for regeneration annually between the period from 1955 to 2002 (Finnish Forest Research Institute 2004).



	Site K1	Site K2
	(cm)	
Tilt		
$Bs3_T$	0-3	-
$Bs2_T$	3-8	0-3
$Bs1_T$	8-14	3-9
Ah_T/E_T	19-23	9-14
Undisturbed soil		
Ah_U/E_U	0-3	0-7
$Bs1_U$	8-13	7-12
$Bs2_U$	13-19	12-18
$Bs3_U$	20-30	18-28
$Bs4_U$	30-40	-
$BC1_U$	40-50	30-40
$BC2_U$	50-60	40-50
C_U	60-70	50-60

Figure 2. A schematic representation of deep-tilled soil. Sampling depths of the tilt and the undisturbed soil at both sites K1 and K2 are shown.

Ploughing alters the microclimate and microtopography of the site. Improved soil temperature and moisture have been shown to promote the rapid establishment, early growth and increased survival of seedlings at ploughed sites (Mälkönen 1972, Leikola 1974, Pohtila 1977, Ritari and Lähde 1978, Saksa et al. 1990, Kubin and Kemppainen 1994). Decomposition and mineralisation of organic matter has been found to be accelerated in site-prepared soils a few years after preparation (Palmgren 1984, Johansson 1994, Lundmark-Thelin and Johansson 1997), and attributed mainly to increased temperatures (Salonius 1983). Thus, ploughing leads to better and more successful seedling establishment by providing favourable conditions within the tilt for root growth and rich source of nutrients in the form of the buried double humus layer.

As a result of ploughing, the B horizon, which was formed through illuviation processes, is exposed on the soil surface in the tilts and furrows (Figure 2). Upon exposure, the spodic material becomes subject to new environmental conditions, including direct deposition and litterfall that slowly converts to an acid humus layer. Since soil acidification releases Al^{3+} ions into the soil solution as a result of H^+ buffering processes, secondary forms of Al in the inverted B horizons may begin to mobilise. The mobilization of Al and heavy metals was considered one of the negative effects of ploughing (Tikkanen 1985, Mälkönen 1983). Other negative effects of ploughing include the eutrophication of surface waters, leaching of nutrients and suspended loads, the cost, and the aesthetics (the change of natural topography), and were widely discussed during the 1980s. In recommendations for good silviculture, ploughing was not allowed any more unless the plough used can be adjusted to a certain level not exceeding 0.25 m (Hyvän metsänhoidon… 2001). The area annually ploughed decreased substantially during the 1990s, and in 2000, the area ploughed was only 2000 ha out of a total 120 000 ha site prepared (Finnish Forest Research Institute 2001).

2. AIMS OF THE STUDY

The overall aim of this study was to determine long-term effects of deep tilling on the chemical properties of soil and soil solution chemistry in podzolized forest soils. Particular interest was focused on soil Al due to its abundance, its central role in podzolization and soil acidification.

Specific aims were to:

- to determine the mobilisation of Al in ploughed podzols by comparing the chemical composition of soil (Study **I**) and soil solution (Study **II**) in the disturbed and corresponding undisturbed soil.
- to understand and describe the mechanisms behind possible mobilisation of Al by applying various equilibria models to explain the Al^{3+} activity in soil solutions of the disturbed and undisturbed podzolic horizons (Study **III** and Study **IV)**.

Although Al solubility in acid forest soils has been widely studied, the processes controlling release and retention of Al in podzolized soils remain unclear. By examing Al chemistry in deep-tilled podzols, some new insight into processes determining activity of Al^{3+} in soil solutions in acid forest soils might be gained. In Study **III**, Al solubility and its relationship to soil solid phases was examined. The role of exchangeable Al_e in soil cation-exchange reactions and in modelling the weak organic acid dissociation using the extended Henderson-Hasselbach equation were assessed in Study **IV**. Because soil organic matter is one of the key soil properties in podzolic soils and root litter is an important source of SOM in the mineral soil, the distribution of fine-root (< 2 mm) biomass at ploughed sites was also determined.

The studies for this thesis were carried out at two forest sites that had been ploughed 17 and 31 years ago and planted with Norway spruce (*Picea abies* (L.) Karst.) seedlings. Older sites were selected since changes in soil properties are generally slow and may not be detectable in more recently prepared sites. Soil solutions obtained by centrifugation and representing large range in temporal and spatial variation within the sites were used to study the processes determining soil solution Al chemistry.

3. MATERIAL AND METHODS

3.1. Sites

The studies for this thesis were carried out at two sites in southern Finland; one located in Karkkila (60º32’ N, 24º16' E) and referred to as K1, and the other at Kuorevesi (61º53' N, 24º35' E) referred to as K2. The mean temperatures between the decades from site preparation to soil sampling at the nearby meteorological stations were about –5.6 °C in January and 16.7 °C in July for site K1 and –7.4 °C and 15.5 °C for site K2, respectively (Drebs et al. 2002). Yearly precipitation was on average 626 mm for site K1 and 713 mm for site K2 during the period (Drebs et al. 2002).

The K1 site is part of a site preparation and fertilisation experiment (Muokkaus- ja lannoituskoe 608) established by Finnish Forest Research Institute in 1979. The factorial experiment consisted of 40 x 40 m plots subjected to various site preparation and fertilization treatments. For this study, a ploughed and unfertilized plot was selected. The site had been clear-cut and ploughed in 1979 and planted with Norway spruce (*Picea abies* (L.) Karst.) seedlings in 1980. The K2 site belonged to a site preparation experiment established by Finnish Forest and Park Service in 1966. The plot of 30 m x 30 m was clear-cut and ploughed and planted with Norway spruce seedlings in 1966. As a result of ploughing, both forest sites consisted of a series of tilts and furrows with strips of undisturbed soil between. After ploughing, the depth of the furrows had been on average over 30 cm and the height of the tilts about 40 cm as compared to mineral soil surfaces at both sites.

The K1 site was classified as an *Oxalis-Myrtillus* (OMT) type according to Finnish classification of forest types (Cajander 1925), which is fertile. The site K2 was a less fertile *Myrtillus* (MT) type. At the time of sampling, the field layer in the undisturbed soil at site K1 was dominated by *Calamagrostis arundinacea* (L.) Roth and the ground layer by mosses *Pleurozium schreberi* (Brid.) Mitt. and *Dicranum polysetum* Sw.*,* especially in the tilt and furrow. The field layer at site K2 was characterized by the presence of *Deschampsia flexuosa* (L.) Trin. and *Vaccinium myrtillus* L., and the ground layer by *Pleurozium schreberi. Sphagnum girkensohnii* Russ. was variously abundant in the furrow at site K2. Seedlings of *Sorbus aucuparia* L. and *Betula Pendula* Roth. were also occasionally found to grow on the undisturbed strips between the tilts and furrows.

The soil at site K1 was classified as a Cambic Podzol according to the FAO-Unesco (1990), with an Ah horizon. The parent material was glacial till of a silt-loam texture. The bedrock in the area consisted of gabbros and diorites (Geological Map of Finland 1953). The soil at 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 bedrock in the area consisted of coarse-grained porphyritic granite (Geological Map of Finland 1986). 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, and the coarse sand content (> 0.6 mm) was 5% at site K1 and 11% at site K2.

3.2. Sampling

3.2.1. Soil sampling

Soil samples for chemical analyses and extraction of soil solution were taken at four different positions: undisturbed soil (U), tilt (T), soil beneath the tilt (BT), and furrow (F) at both study sites (Figure 2). The undisturbed soil between the tilts was selected to represent the intact soil since spatial variability due to e.g. soil topography was considered greater at the adjacent forest plots than within the plot. From each sampling position (T, BT, F, U), 8 to 11 core samples were taken with a steel auger (0.046 m diameter). The cores were sliced into horizons with the B and BC horizons being further divided into layers as shown in Figure 2. Newly formed O horizon on top of the tilt (O_T) and in the furrow (O_F) was distinguishable (Figure 2). The top three centimetres (0-3 cm) of Bs horizon beneath the O_T and O_F horizons were sampled separately at both study sites, since a darker soil colour compared with the soil beneath indicated the occurrence of changes in the soil. These layers were referred to as $Bs3_T$ at site K1 and $Bs2_T$ at site K2 (Figure 2). Partitioning of the horizons in the ploughed soil was performed by visual examination of the horizons and by comparing the thicknesses to those in the undisturbed soil. The mineral soil beneath the tilt was similar to that of the undisturbed soil. The samples were combined by horizons and layers to give one set of samples for each sampling position of each study site. Mixing of adjacent horizons was observed in a few cores. Horizons showing features of mixing due to ploughing were not included in the bulked sample for that horizon.

Sampling was carried out six times in early summer and autumn in 1996 at site K1 and four times in 1997 at site K2. When the division to soil horizons was taken into account, the total number of bulked soil samples down to and including the Bs3 horizon was 176 representing a large range in temporal and spatial variation.

3.2.2. Soil solution sampling

Soil solution from bulked, fresh soil samples, was obtained by centrifugation drainage technique described by Giesler and Lundström (1993). Giesler and Lundström (1993) preferred unbulked soil samples to bulked ones but in the present study, soil samples were bulked because they were also used to analyse soil chemical properties. The centrifugation drainage technique to obtain soil solution was preferred to zero-tension and suction lysimeters because it is assumed to better reflect nutrient availability and apparent equilibrium conditions at the soil solution-soil interface (Nissinen et al. 2000). A Sorvall RC5C centrifuge with a GSA rotor was used to centrifuge the samples at 13 000 r.p.m. 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. Two subsamples, each containing approximately 120 cm^3 of soil, were centrifuged from each bulked soil sample. The soil solutions obtained were combined prior to the analyses. In practice, the water yield restricted the analysis, especially those from the tilt during autumn. Thus, the number of soil solutions obtained with centrifugation was smaller than the number of soil samples collected per site. A comparison of the water content in soil after centrifugation to soil water retention curves (Figure 3) revealed that the remaining water content was held at tensions between 100 and 1500 kPa (pF 3 and 4.2).

3.2.3. Root sampling

Ten core samples (volumetric samples, core diameter 0.046 m) per sampling position (T, BT, F and U) were taken from both study sites in June 1999 for determination of fine-root biomass and length. The soil cores were divided according to soil horizon and layers as presented in Figure 2. The samples were stored frozen (-18 °C) until analysis.

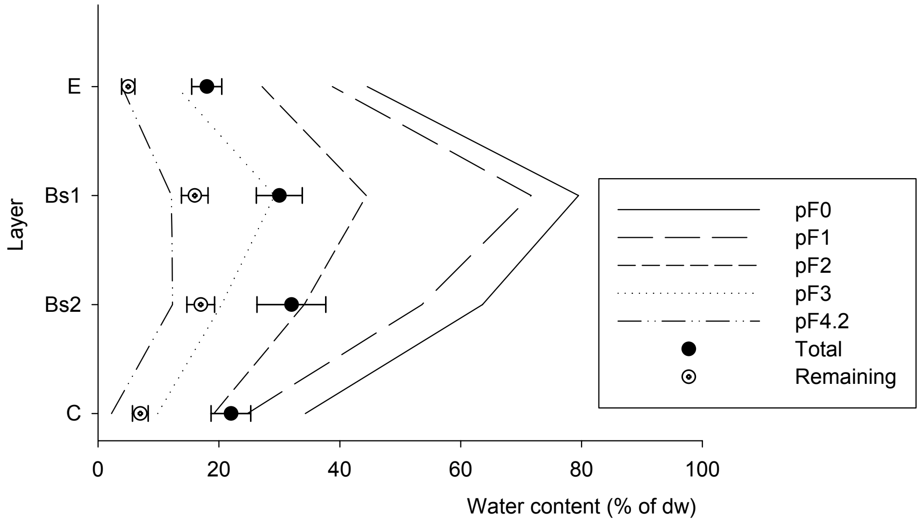


Figure 3. A comparison of the total water content and the remaining water content in soil samples after centrifugation at site K2 (mean and standard error of the mean for all sampling occasions). For comparison are also water retention curves (pF) shown.

3.3. Analyses

3.3.1. Soil samples

The nature of accumulated Fe, Al, and Si in the soils, as outlined in chapter 1.3., was elucidated with selective extractions (Table 3). Oxalate ($_o$) extracts organically complexed Al and Fe, and 'short-range ordered', amorphous compounds of Fe, Al and Si. Pyrophosphate ($_p$) extracts organically complexed forms of Al and Fe. The difference between oxalate and pyrophosphate extractable Al (Al_o-Al_p) is commonly used as a measure of soil amorphous, inorganic secondary Al, and amorphous Al to soil oxalate extractable Si, (Al_o-Al_p)/Si_o, close to 2 indicates that an imogolite-like allophane is present (Parfitt and Childs 1988). Dithionite ($_d$) is known to extract efficiently organically bound Fe and also surface-reactive Fe oxides. In case of Al, dithionite extracts organically complexed Al plus some surface-reactive inorganic Al (Farmer et al. 1983). Considering the ITM in soils, imogolite is completely soluble by oxalate but insoluble by dithionite-citrate, while proto-imogolite allophane is only partly soluble by dithionite-citrate (Farmer et al. 1983).

In all the Al and Fe extractions and in determinations of exchangeable cations and total acidity (Table 3), the supernatants were filtered through a 0.45 µm filter (Millipore HAWP 47 mm) with vacuum. For a more detailed description of the analyses methods used, see Studies **I** and **IV**. All 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.

Table 3. Schematic presentation of the analyses performed on the soil samples.

Soil	Analyte	Method	Designation	Reference
	Amorphous compounds of Al, Fe, Si	0.2 M acid ammonium oxalate, AAS	Al_o, Fe_o, Si_o	Wang (1981)
	Free Fe oxides	Cold dithionite-citrate, AAS	Al_d, Fe_d	van Reeuwijk (1995)
	Organically bound Al, Fe	0.1 M Na-pyrophosphate, AAS	Al_p, Fe_p	van Reeuwijk (1995)
	Organically complexed Al	0.5 M $CuCl_2$, AAS	Al_{cu}	Juo and Kamprath (1979)
	Exchangeable cations	0.1 M $BaCl_2$, ICP-AES, pH-meter	Al_e, Ca_e, Mg_e, Na_e, K_e, Fe_e, H_e	Hendershot and Duquette (1986)
	Exchangeable acidity	0.1 M $BaCl_2$, titrated with 0.01 M NaOH to pH 7	EA	
	Total acidity	$BaCl_2$-TEA buffer pH 8.2	TA	Thomas (1982)
	pH in soil	0.01 M $CaCl_2$	pH_{Ca}	
	Total C, N	Dry combustion, CNS analyser	C, N	

Table 4. Schematic presentation of the analyses performed on the soil solutions.

Soil solution	Analyte	Method	Designation	Calculation
	pH		pH_s	
	Dissolved organic C	Carbon analyser	DOC	
	Total monomeric Al, Non-labile monomeric Al	Pyrocatechol violet; cation-exchange column, FIA	Total mono. Al Non-labile mono. Al	Labile monomeric Al = Total mono. Al – non-labile mono. Al
	Al, Ca, Mg, Na, K, Fe, Si	ICP-AES	Total Al etc…	Acid-soluble Al = Total Al – total mono. Al
	SO_4, Cl, NO_3	HPLC		
	PO_4-P	Molybdenum blue, FIA		

3.3.2. Soil solution samples

Analyses performed on the soil solution centrifugates are represented in Table 4. The concentrations of total monomeric Al and non-labile monomeric Al were measured by reaction with pyrocatechol violet (PCV) with a flow-injection ion analyzer (Lachat Quikchem 8000, Milwaukee, WI, USA). Non-labile monomeric Al was fractionated from total monomeric Al using a cation-exchange column (packed with Amberlite IR-120), based on the method of 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 (organically complexed monomeric Al). The concentrations of acid-soluble Al were calculated as the difference in concentration between total Al (acidified with concentrated HNO_3 and analysed using inductively coupled plasma-atomic emission spectrometry (ICP-AES)) and total monomeric Al. Acid-soluble Al was assumed to consist mainly of strong Al-organic complexes and colloidal polymeric Al. Soil solution was filtered through a disposable syringe filter (Millex-HV) with a pore size of 0.45 µm (Millipore Corporation, Billerica, MA, USA). Some auxiliary samples were taken from the Bs horizons of the undisturbed soil and the tilt at site K1 to analyze also the Si concentrations in the soil solution. The ICP-AES was used to analyze the Si since most of the Si in soil solution, on average 94%, is in monomeric form (van Hees et al. 2000). For a more detailed description of the analysis methods used, see Studies **II** and **III**.

3.3.3. Root samples

In the laboratory, the roots were washed free of soil and classified into living and dead Norway spruce roots. Dead roots were distinguished from living roots on the basis of their colour and consistency. Length of living roots and diameter distribution were measured using the image analysis system WinRHIZOTM V 3.0.2 (Regent Instruments Inc., Quebec, Canada). The separated roots were dried at 70 °C for two days and weighed to determine the oven-dry biomass of Norway spruce fine (< 2 mm) roots and coarse (> 2mm) roots and total necromass.

3.4. Calculations

3.4.1. Processes controlling activity of Al^{3+} in soil solution

To study the processes controlling Al solubility in the podzols two models were applied: 1) equilibrium of Al^{3+} with secondary Al solid phases and 2) Al complexation reactions with solid-phase organic matter (Study **III**).

If the activity of Al^{3+} in soil solution is in equilibrium with the secondary Al solids, the calculated ion-activity product (IAP) in solution is equal to the equilibrium constant of the secondary mineral studied, that is $\log(\mathrm{IAP}) = \log{}^{*}K_s^0$. Log(IAP) values for several solid Al phases were calculated, including crystalline gibbsite, amorphous Al-hydroxide, imogolite, proto-imogolite, kaolinite and soil imogolite and $Al(OH)_3$ as determined by Gustafsson and co-workers (1998). The thermodynamic data of the solid phases are presented in Table 2. The van't Hoff equation (Eq. 2 in chapter 1.2) was used to correct the equilibrium constants for the temperature (5 °C) used in centrifugation.

If the activity of Al^{3+} in soil solution is controlled by complexation reactions with SOM, as outlined in Eq. 6 in chapter 1.3.1., Al^{3+} ion activity is a function not only of H^+ ion activity but also of the degree of saturation of the organic complexation sites by Al ions. In the present study, the degree of saturation of complexation sites was described by the molar ratio of pyrophosphate-extractable Al to soil C (Al_p/C), as proposed by Wesselink and coworkers (1996).

In addition to processes controlling Al solubility in the studied soils, the role of exchangeable Al_e in soil cation-exchange reactions and in modelling the weak organic acid dissociation by the extended Henderson-Hasselbach equation were examined in Study **IV**. In considering the apparent cation-exchange equilibria involving Al^{3+} ions as represented in Eq. 12 for Al^{3+} - Ca^{2+} exchange, two criteria were used: (i) the coefficient of determination (R^2) should be high, i.e. much of the variation in log S is explained by 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 a constant selectivity coefficient can not be applied. Gaines-Thomas selectivity coefficients were estimated for the Al^{3+} - Ca^{2+}, Al^{3+} - Mg^{2+}, Al^{3+}- K^+, Al^{3+}- Na^+ and Al^{3+}- H^+ exchange reactions (Study **IV**). Aluminium was selected as the reference cation because it is a dominate cation on soil exchange sites in podzolized forest soils (e.g. Tamminen and Starr 1990). The charge fraction of each exchangeable cation was calculated as Me_e/CEC_e, in which Me_e was the exchangeable cation (H_e, Al_e, Ca_e, Mg_e, K_e and Na_e) and effective cation exchange capacity (CEC_e) was the sum of all exchangeable cations H_e, Al_e, Ca_e, Mg_e, K_e and Na_e. Exchangeable Fe_e was also determined but not included in the calculation of CEC_e because the Fe_e content was less than 0.7% of CEC_e in the majority of the soil samples (0.3 ± 0.03%, mean and standard deviation (SD).

When the role of exchangeable Al_e in modelling the weak organic acid dissociation using the extended Henderson-Hasselbach equation (Eq. 16 in chapter 1.3.1) was studied, the relationships between pH_s and effective base saturation ($BS_e = (Ca_e+Mg_e+K_e+Na_e)/CEC_e$) and effective base saturation calculated with exchangeable Al_e ($BS_e^* = (Ca_e+Mg_e+K_e+Na_e+Al_e)/CEC_e$) were examined.

Ion activities in soil solution were calculated using the extended Debye-Hückel expression (Lindsay 1979). Labile monomeric Al was assumed to consist of Al^{3+}, and different Al-hydroxy species and Al sulphate complexes as presented in Table 1. The van't Hoff equation was used to correct the equilibrium constants for the temperature (5 °C) used in centrifugation.

3.4.2. Statistical analysis

A One-way analysis of variance, a Kruskall-Wallis test and a Wilcoxon rank-sum test were used to compare the concentrations of elements and logarithms of cation-exchange selectivity coefficients (log K) in different sites, horizons and treatments (T, BT, F, U). The nonparametric tests, Kruskall-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, 12, and 16 representing Al solubility control by organically bound Al, cation-exchange reactions of Al and weak organic acid dissociation. Statistics were computed using SAS version 6.12. Differences with a P value ≤ 0.05 were considered to be significant.

4. RESULTS

4.1. Aluminium in soil

Depth gradients in the undisturbed soil (U) for each of pH_{Ca}, organic C, CEC_e and selectively extracted Al and Fe were similar at both study sites: concentrations of organic C and CEC_e were highest in the O_U and Ah/E_U horizons while the soil pH_{Ca} and concentrations of extractable Al and Fe increased with depth in the Bs horizon (Table 5). Concentrations of pyrophosphate extractable Al (Al_p) were highest in the upper part of the Bs horizon while the concentrations of inorganic secondary Al (Al_o-Al_p) reached highest values deeper in depth (Figure 4). The higher contents of oxalate extractable Al (Al_o) than pyrophosphate extractable Al in the Bs horizons indicated that the studied soils were characterised by accumulation of inorganic secondary Al (Al_o - Al_p), as is found in other boreal podzols (Gustafsson et al. 1995, Karltun et al. 2000). The Al_o-Al_p/Si_o ratio in the Bs horizons varied between 2.0 and 3.3, which is consistent with the studies where the predominance of ITM in oxalate-extractable Al minerals has been shown (Gustafsson et al. 1995, Zysset et al. 1999, Karltun et al. 2000). Concentrations of organic C and CEC_e in the Bs horizons were relatively low (Table 5) and, consequently, the exchangeable Al_e pool was minor as compared to those pools of selectively extracted Al (Figure 4).

The soil chemical properties (pH_{Ca}, C, CEC_e and selectively extracted Al and Fe) in the disturbed mineral soil profiles were mostly not significantly different from those in the corresponding horizon in the undisturbed soil (Table 5). The horizon showing significant differences at site K1 was the exposed Bs subhorizons in the tilt and furrow, where the concentrations of exchangeable Al_e, CEC_e and soil organic C were significantly greater and the soil pH_{Ca} lower than in the corresponding undisturbed Bs subhorizon (Table 5). Concentrations of extractable Al (Al_o, Al_d) were also significantly lower in the exposed Bs horizons while concentration of pyrophosphate extractable Al was lower in the Bs_T subhorizon beneath (for (Al_o-Al_p) see also Figures 2 and 4 in Study **I**). At the site K2, few statistically significant differences were observed, but the number of samples from each subhorizon was less (*n*=4) than at site K1 (*n*=6) and the concentrations of extractable Al in the Bs horizons varied substantially within the site thereby complicating the comparison (see e.g. Table 1 in Study **I**). However, consistent with site K1, increased concentrations of exchangeable Al_e and organically complexed Al_p were observed in the buried O_{BT} horizon at the K2 site when the concentrations of Al_e were compared to those found in the undisturbed horizon at the K1 site and those reported for O horizons from 65 sites in southern Finland (mean 18.9 $mmol_c$ Al_e kg^{-1} with a range from 0.5 to 72 $mmol_c$ kg^{-1}; Tamminen and Starr 1990). Moreover, exchangeable Al_e and organically complexed Al_p in the newly formed O_F horizon in the furrow and undisturbed O_U horizon at site K2 were exceptional high (Table 5). Concurrently, effective base saturation BS_e in these horizons was relatively low as compared to those reported for O horizons in southern Finland (mean 77%, with a range from 50 to 95%; Tamminen and Starr 1990).

Table 5. Soil chemical properties expressed as mean values for each horizon in the undisturbed soil (U), tilt (T), in the O horizon buried beneath the tilt (BT) and furrow (F) at site K1 and site K2. Data in individual horizons that differ from the corresponding undisturbed horizon ($P < 0.05$) are marked with an asterisk (*). The number of samples within each subhorizon was six at site K1 and four at site K2. (n.d. not determined).

	C	pH$_{Ca}$[b]	Al$_e$[c]	Ca$_e$[c]	CEC$_e$[c]	BS$_e$	Al$_p$[d]	Al$_o$[e]	Al$_d$[f]
	(%)		(mmol$_c$ kg^{-1})			(%)	(mmol kg^{-1})		
Site K1									
Undisturbed									
O$_U$	24	3.54	27	112	194	74	48	57	n.d.
Ah$_U$	7.4	3.60	44	21	80	38	89	92	87
Bs1$_U$	2.7	4.24	17	5	23	29	178	226	207
Bs2$_U$	2.2	4.51	8	5	14	48	196	345	280
Bs3$_U$	1.6	4.68	4	5	10	51	148	337	241
Tilt									
O$_T$	27	3.97	24	176	249	82	79	106	n.d.
Bs3$_T$	2.9*	4.22*	12*	6	20*	40	136	278*	202*
Bs2$_T$	2.3	4.39	12	4*	17	28*	154*	278	224*
Bs1$_T$	2.3	4.29	14	3	19	22	159	279	217
Ah$_T$	5.9	3.70	44	18	75	33	124	137	126
O$_{BT}$	19	3.21 *	55*	118	228	60*	92*	87*	n.d.
Furrow									
O$_F$	23	4.02	24	104	173	79	94*	141*	n.d.
Bs3$_{(0\text{-}3)F}$[a]	2.7	4.27*	15	5	23	33	124	236*	171*
Bs3$_{(3\text{-}8)F}$[a]	2.1	4.24	11	5	17	36	147	287	203
Site K2									
Undisturbed									
O$_U$	39	3.09	140	65	264	32	198	226	n.d.
E$_U$	1.6	3.88	19	2	24	12	29	31	24
Bs1$_U$	3.4	4.39	17	2	21	16	256	480	315
Bs2$_U$	2.5	4.60	9	2	12	20	226	451	335
Bs3$_U$	1.8	4.67	5	1	6	29	159	452	288
Tilt									
O$_T$	38	3.79	16	197	273	86	50*	76	n.d.
Bs2$_T$	4.6	4.24	21	5	29	22	204	444	293
Bs1$_T$	4.2	4.30	20	1	23	10	247	610	398
E$_T$	2.5	3.85	25	2	30	11	38	42	35
O$_{BT}$	32	3.29	86	135	301	50	115	133	n.d.
Furrow									
O$_F$	44	3.49	152	34	216	23	291	372	n.d.
Bs2$_F$	2.8	4.30	15	2	19	14	152	366	233*
Bs3$_F$	2.3	4.48	11	1	14	17	148	385	222

[a] Two subhorizons in the furrow were referred to as the Bs3 horizon at site K1.
[b] Soil pH in 0.01 M $CaCl_2$. [c] Extracted with 0.1 M $BaCl_2$. [d] Extracted with pyrophosphate.
[e] Extracted with acid ammonium oxalate. [f] Extracted with dithionite citrate.

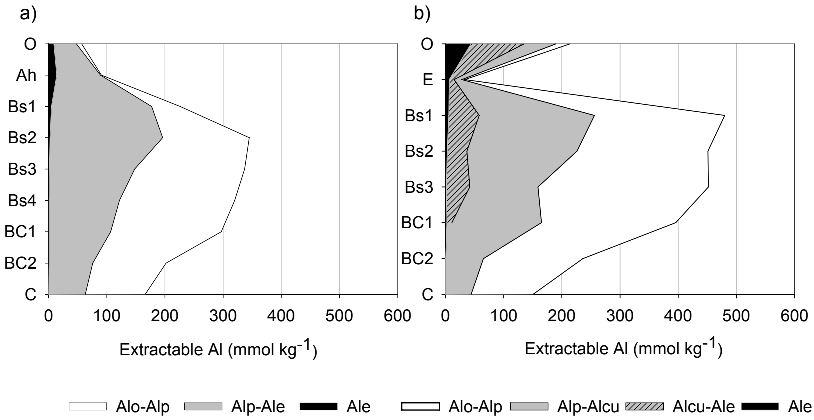


Figure 4. Distribution of extractable Al pools in the undisturbed soil a) at site K1 and b) at site K2. Al_o – extracted with oxalate, Al_p – extracted with pyrophosphate, Al_e – extracted with 0.1 M $BaCl_2$. Copper chloride was also used to extract Al (Al_{cu}) from K2 soil samples.

4.2. Aluminium in soil solution

Concentrations of Al fractions in soil solution were highest in the O horizon and lowest in the Bs horizon (Table 6) and consistent with the soil solution Al concentrations found in southern Finland (Nissinen et al. 1998, Derome et al. 2001, 2002). Most of soil solution Al (mean 78%, with a range from 44 to 97%) was organically bound (non-labile monomeric Al and acid-soluble Al, Table 6).

At both sites, the concentrations of labile monomeric Al in soil solution from the exposed Bs horizons were higher than in solution from the corresponding undisturbed horizon (Table 6). Concurrently, soil solution pH_s was slightly lower and concentrations of DOC higher than in the intact horizons. At the site K1, labile monomeric Al concentration from the O_{BT} horizon beneath the tilt was also higher than that from the O_U horizon.

In general, Al and other element concentrations in soil solutions from the Bs_T horizons of the tilt were similar to those observed in the undisturbed $Bs1_U$ horizon at the K1 site while at the K2 site, Bs_T horizon solution concentrations were similar to those in the undisturbed E_U horizon (Table 6). On only one sampling occasion in November (when the soil had started to rewet after the dry autumn) elevated concentrations of total Al within the tilt at site K1 were found reaching the highest concentration (1250 µmol dm^{-3}) in the Ah_T horizon.

Table 6. Soil solution properties expressed as mean values (and standard error of the mean in parenthesis) for each horizon in the undisturbed soil (U), tilt (T), in the O horizon buried beneath the tilt (BT) and furrow (F) at site K1 and site K2. Data in individual horizons that differ from the corresponding undisturbed horizon (*P* < 0.05) are marked with an asterisk (*). The number of soil solution samples within each subhorizon varied between one to six at site K1 and between one to four at site K2 depending on the water yield during centrifugation. (n.d. not determined, < l.d. value below limit of detection.)

	Labile monomeric Al	Non-labile monomeric Al	Acid-soluble Al	pH	DOC	Ca^{2+}	K^+
		$\mu mol\ dm^{-3}$			$mmol\ dm^{-3}$	$\mu mol\ dm^{-3}$	
Site K1							
Undisturbed							
$\mathrm{O_U}$	9 (2)	33 (3)	49 (15)	3.92 (0.08)	53 (19)	504 (150)	625 (231)
$\mathrm{Ah_U}$	19 (2)	31 (3)	37 (6)	4.10 (0.11)	14 (5)	253 (95)	114 (42)
$\mathrm{Bs1_U}$	14 (3)	17 (6)	29 (11)	4.87 (0.07)	5 (2)	94 (12)	23 (5)
$\mathrm{Bs2_U}$	4 (1)	6 (3)	13 (5)	5.19 (0.07)	2 (0.4)	68 (7)	< l.d.
$\mathrm{Bs3_U}$	2 (0.7)	2 (1)	8 (2)	5.40 (0.10)	2 (0.2)	76 (9)	< l.d.
Tilt							
$\mathrm{O_T}$	19	42	55	4.81	n.d.	566	703
$\mathrm{Bs3_T}$	16 (5)*	16 (6)*	24 (9)	4.87 (0.07)*	8 (2)*	97 (23)	178 (67)
$\mathrm{Bs2_T}$	16 (4)	7 (2)	10 (2)	4.95 (0.09)	4 (1)	36 (6)*	88 (38)
$\mathrm{Bs1_T}$	19 (2)	8 (1)	18 (9)	4.84 (0.09)	2 (1)	26 (2)*	35 (19)
$\mathrm{Ah_T}$	34 (13)	30 (0.1)	26 (2)	4.03 (0.19)	23 (18)	462 (357)	140 (97)
$\mathrm{O_{BT}}$	70 (28)*	93 (18)	120 (35)	3.56 (0.09)*	50 (15)	1149 (556)	132 (26)
Furrow							
$\mathrm{O_F}$	13 (4)	40 (12)	111 (25)	4.38 (0.20)*	55 (22)	614 (145)	1000 (247)
$\mathrm{Bs3_{(0-3)F}}$[a]	6 (2)	6 (2)	19 (4)	4.84 (0.18)	6 (1)*	101 (2)	157 (43)
$\mathrm{Bs3_{(3-8)F}}$[a]	5 (0.3)	4 (0.6)	9 (0.6)	5.01 (0.11)	5 (2)	66 (9)	82 (18)
Site K2							
Undisturbed							
$\mathrm{O_U}$	51 (23)	49 (12)	67 (21)	3.72 (0.11)	40 (19)	202 (52)	611 (153)
$\mathrm{E_U}$	17 (5)	19 (9)	28 (13)	4.42 (0.08)	6 (1)	70 (35)	108 (37)
$\mathrm{Bs1_U}$	7 (2)	4 (2)	10 (3)	4.93 (0.10)	5 (1)	31 (7)	98 (35)
$\mathrm{Bs2_U}$	3 (1)	2 (0.5)	8 (2)	5.09 (0.08)	4 (1)	23 (1)	42 (4)
$\mathrm{Bs3_U}$	1 (1)	1 (0.4)	3 (1)	5.27 (0.11)	2 (1)	24 (3)	23 (4)
Tilt							
$\mathrm{O_T}$	26 (14)	64 (18)	129 (22)	3.80 (0.19)	126 (43)	1494(203)	1817 (445)*
$\mathrm{Bs2_T}$	16 (5)*	14 (4)*	35 (5)*	4.80 (0.04)*	14*	99 (10)*	299 (36)*
$\mathrm{Bs1_T}$	27	8	13	4.65 (0.02)	8	47 (9)	204 (45)
$\mathrm{E_T}$	45 (6)	31 (13)	46 (36)	4.03 (0.11)	8 (1)	108 (20)	148 (48)
$\mathrm{O_{BT}}$	18 (2)	48 (5)	65 (35)	3.80 (0.10)	19 (10)	336 (241)	106 (25)
Furrow							
$\mathrm{O_F}$	30 (7)	32 (6)	71 (18)	4.32 (0.06)*	21 (5)	93 (16)	659 (122)
$\mathrm{Bs2_F}$	7 (0.4)*	6 (0.6)*	15 (2)*	4.95 (0.04)	7 (1)*	26 (4)	173 (26)*
$\mathrm{Bs3_F}$	2 (0.2)	2 (0.4)	6 (3)	5.08 (0.08)	4 (1)	21 (6)	58 (16)

[a] Two subhorizons in the furrow were referred to as the Bs3 horizon at site K1.

4.3. Soil Al chemistry

4.3.1. Aluminium solubility

To study the processes controlling activity of Al^{3+} in soil solution of the podzolic horizons, $Al(OH)_3$ solubility, defined as $\log(Al^{3+}) + 3$ pH (Eq. 4), was plotted against the soil Al_p/C ratio in Figure 5. In the undisturbed O_U and Ah/E_U horizons, Al solubility was lower than gibbsite solubility and related to soil Al_p/C ratio (according to Eq. 6), indicating that the Al solubility in these organic rich surface horizons was controlled by organically complexed Al. The Al solubility in the buried O_{BT} horizons was similar to that of the undisturbed O_U horizons but in some of the newly formed O_T and O_F horizons on top of the tilt and furrow, the solubility was higher, indicating a shift from organic complexation to a control by a $Al(OH)_3$ phase (Figure 5, for further details of Al organic complexation see also Figure 4b in Study **III**).

The Al solubility in the undisturbed and disturbed Bs horizons was not related to the Al_p/C ratio (Figure 5), although a shift to the left along the x-axes (to lower Al_p/C ratios) was observed for the samples of the exposed Bs_T and Bs_F horizons of the tilts and furrows. Relatively constant $\log(Al^{3+}) + 3$ pH values across a range of Al_p/C values indicated that Al solubility in the undisturbed and disturbed Bs horizons was controlled by a mineral phase. The calculated log(IAP) value (9.58 ± 0.05 at 5 °C, mean ± standard error of the mean (SE)) for all Bs horizons samples (n=92) was relatively close to that of soil $Al(OH)_3$ (log K_s^0 of 9.61 at 5 °C; Gustafsson et al. 1998). In some of the soil solutions, log(IAP) value for ITM (7.89 ± 0.08 at 5 °C) was, however, relatively close to that of soil imogolite (log K_s^0 of 7.89 at 5 °C; Gustafsson et al. 1998), especially in those soil solutions where the pH was over 5 (see also Figure 3 in Study **III**).

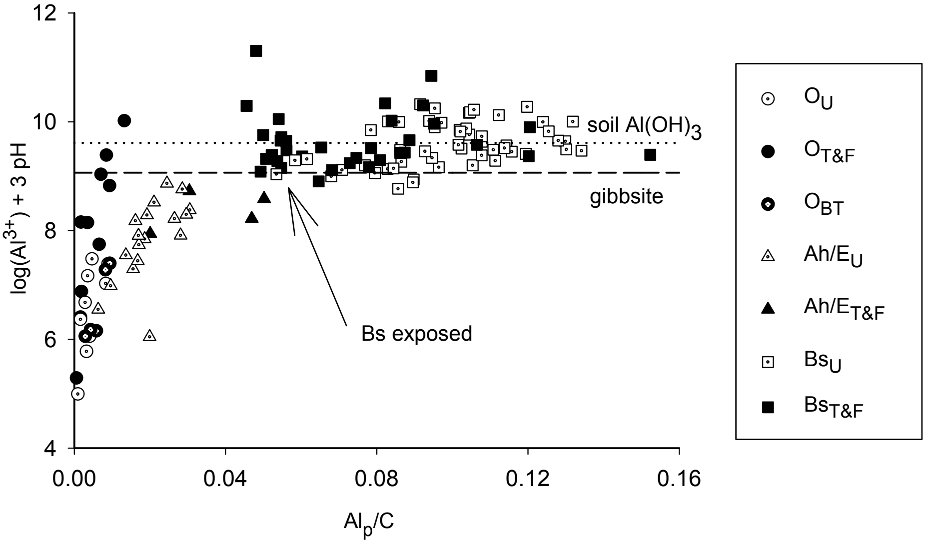


Figure 5. Aluminium solubility in terms of $\log(Al^{3+}) + 3$ pH plotted as a function of the Al_p/C ratio in the disturbed (T&F; tilt and furrow) and undisturbed (U) soil horizons. The broken lines indicate the solubility of gibbsite (log K_s^0 = 9.06 at 5 °C; Palmer and Wesolowski 1992), and $Al(OH)_3$ in soil (log K_s^0 = 9.61 at 5 °C; Gustafsson et al. 1998).

4.3.2. Apparent cation-exchange equilibria involving Al^{3+} ions

The fit of the Gaines-Thomas cation-exchange equation (Eq. 12) for Al^{3+} and Ca^{2+} exchange is illustrated in Figure 6. The two criteria used to study the apparent cation-exchange equilibria as outlined in chapter 3.4.1. were fulfilled: the R^2 value of the modeled regression for Al^{3+} - Ca^{2+} exchange in the O horizon was relatively high (0.88) and the slope (*b*) was not significantly different from unity and, thus, the intercept (-0.56) could be taken as an estimate of log $K_{\text{Al-Ca}}$ (Figure 6a). This suggests that the Gaines-Thomas cation-exchange equation (Eq. 12) successfully described the Al^{3+} - Ca^{2+} exchange reactions in the O horizon of tilts, furrows and undisturbed soil (see also Table 2 in Study **IV**).

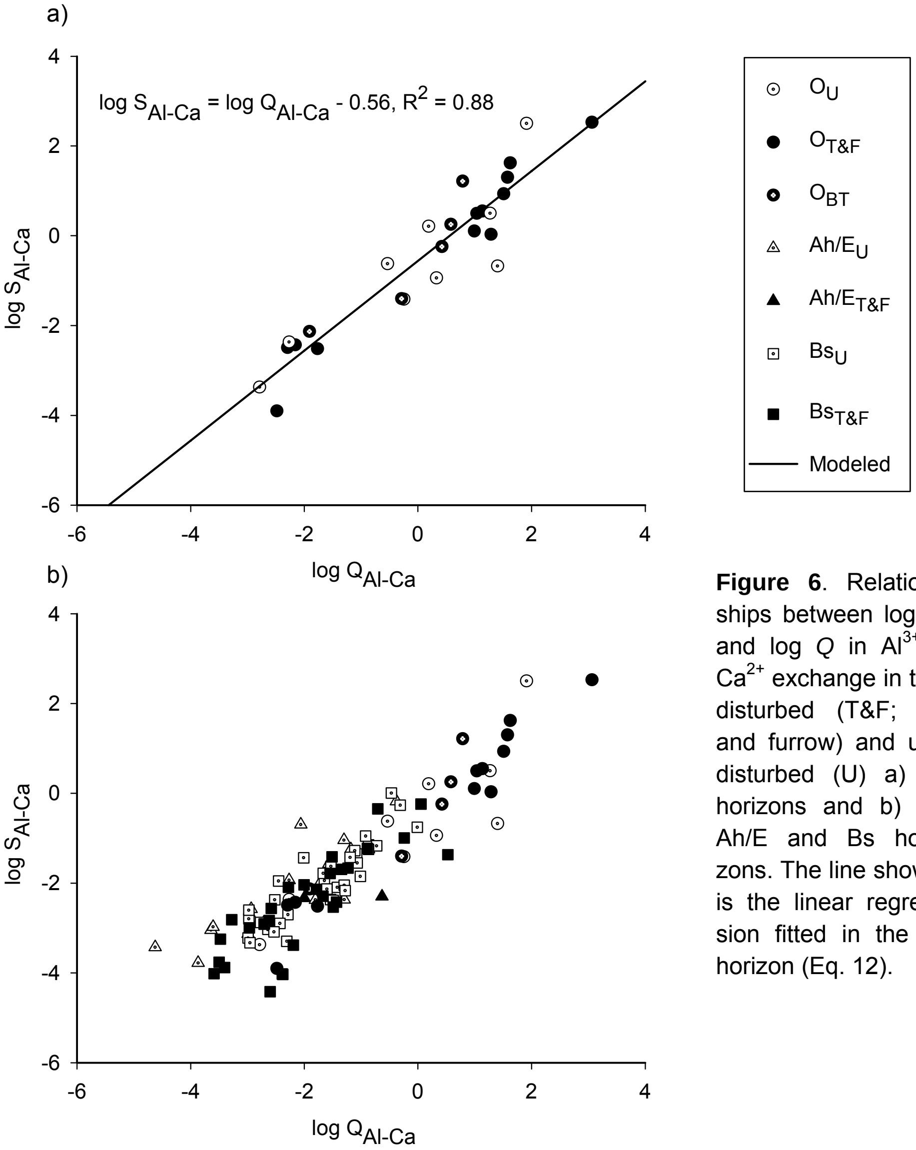


Figure 6. Relationships between log *S* and log *Q* in Al^{3+} - Ca^{2+} exchange in the disturbed (T&F; tilt and furrow) and undisturbed (U) a) O horizons and b) O, Ah/E and Bs horizons. The line shown is the linear regression fitted in the O horizon (Eq. 12).

The calculated Al^{3+} - Ca^{2+} exchange selectivity coefficient in the undisturbed and disturbed Bs horizons (log $K_{\mathrm{Al\text{-}Ca}}$ = -0.39 ± 0.54, mean ± SD) was not significantly different from that in the O horizons (log $K_{\mathrm{Al\text{-}Ca}}$ = -0.56 ± 0.59, see also Table 2 in Study **IV**). Since the CEC_e in the Bs horizons was positively correlated to soil organic C at both study sites (R^2=0.66, and the intercept of the modeled regression did not significantly differ from zero P = 0.87; Study **IV**), SOM was the predominant source of exchange sites in the Bs horizons and inorganic surfaces made an insignificant contribution.

Also in the undisturbed and disturbed E and Ah horizons, results from fitting Eq. 12 were similar to those of the O and Bs horizons (Figure 6b), but the estimated slope was significantly lower than unity (Table 2 in Study **IV**).

In the exchange reactions between Al^{3+} and other cations (Mg^{2+}, K^+, Na^+, and H^+), R^2 values for fitting Eq. 12 were high and the slope was near unity in the O horizons (Table 2 in Study **IV**) while the R^2 values for the mineral horizons were, however, clearly lower than that for the O horizon.

4.3.3. Exchangeable Al_e in modelling weak organic acid dissociation

The role of exchangeable Al_e in explaining soil solution pH_s by the weak organic acid dissociation was examined by assuming that effective base saturation (BS_e) or effective base saturation computed with exchangeable Al_e (BS_e^*) described the fraction of dissociated R-COO^- functional groups (in Eq. 16). The pH_s in the O horizons of tilts, furrows and undisturbed soil was positively correlated to $\log(BS_e^*/(1 - BS_e^*))$ where BS_e^* included exchangeable Al_e (Figure 7a). The range in the x-axis in Figure 7a varied between 0.6 and 1.6 corresponding to a range in BS_e* from 0.80 to 0.98. The BS_e* in most of the newly formed O_T and O_F horizons was greater than in the undisturbed O_U horizon, but all O horizons followed a common relationship (Figure 7a). When the linear regression was fitted to the relationship (Eq. 16), R^2 value was 0.85 and a, an estimate of pK_{app}, was 2.59 (Figure 7a).

For the mineral horizons, the relationship between pH_s and $\log(BS_e^*/(1 - BS_e^*))$ was clearly weaker than for the O horizons (Figure 7b, see also Table 3 in Study **IV**), indicating that the weak acid dissociation by assuming that exchangeable Al_e had nonacidic properties similar to those of base cations did not succeed in detemining the pH_s values in the studied mineral horizons.

4.4. Distribution of Norway spruce fine roots

Norway spruce fine roots (< 2 mm) were found throughout the ploughed sites, but not evenly distributed (Figure 8). The fine-root biomass was highest in the tilt at both study sites and lowest in the undisturbed soil at site K1 and in the furrow at site K2 (Figure 8). Some 70% of the fine-root biomass at site K1 was in the tilt, 20% in the furrow and 10% in the undisturbed soil assuming 60% of the soil surface was disturbed during ploughing, half of which is tilt and the other half furrow (Kellomäki 1972, Ferm and Pohtila 1977, Saksa et al. 1990). At the site K2, the fine roots were more evenly distributed: 50% in the tilt, 17% in the furrow and 33% in the undisturbed soil. The tilts at the K2 site were lower, which may partly explain the more even distribution of fine roots at the site K2 than at the K1 site. The estimated average fine-root biomass at the ploughed sites, 268 g m^{-2} at the K1 site and

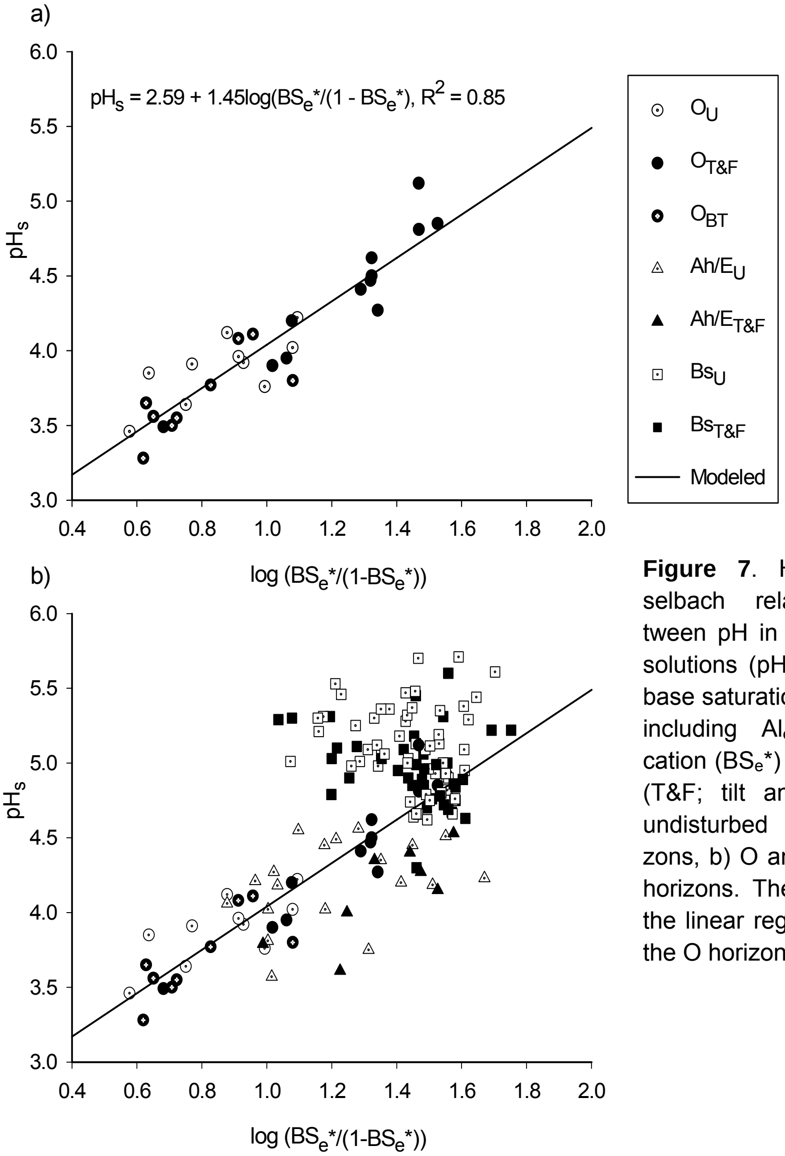


Figure 7. Henderson-Hasselbach relationships between pH in centrifuged soil solutions (pH_s) and effective base saturation calculated by including Al_e as a base cation (BS_e*) in the disturbed (T&F; tilt and furrow) and undisturbed (U) a) O horizons, b) O and Ah/E and Bs horizons. The line shown is the linear regression fitted in the O horizon (Eq. 16).

248 g m^{-2} at the K2 site, were, however, at the same level to those reported (182 - 528 g m^{-2}) for a boreal zone Norway spruce forest (Helmisaari and Hallbäcken 1999, Taskinen et al. 2003).

The shallowing rooting nature of Norway spruce was observed in the present study. Over 80% of all the fine roots in the undisturbed soil was in the O_U and underlying Ah/E_U horizons at both study sites (Figure 8). In the furrow, the majority of the fine roots were in the neo-formed O_F horizon and in the 3-cm-thick Bs_F subhorizon beneath. In the tilt, 68% at site K1 and 54% at site K2 of all the fine-root biomass was in the neo-formed O_T horizon

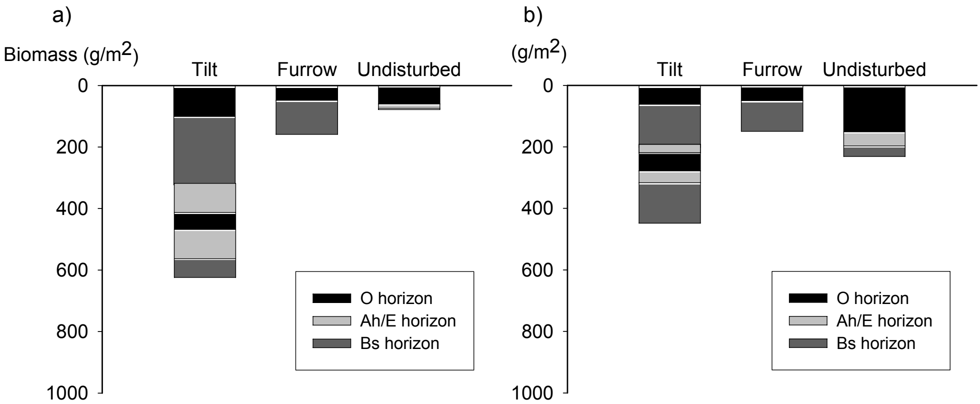


Figure 8. Norway spruce fine root biomass (< 2 mm) in the tilt and beneath the tilt, furrow and undisturbed soil at (a) site K1 and (b) site K2.

and inverted mineral horizons (Figure 8). The proportion of fine roots in the buried O_{BT} horizon of the tilt was 9% at both study sites.

Consistent with fine-root biomass, total Norway spruce necromass was highest in the tilt (average 2484 g m^{-2} at site K1 and 2910 g m^{-2} at site K2) and lowest in the furrow (386 g m^{-2} at site K1 and 639 g m^{-2} at site K2). A substantial proportion of the dead roots in the tilt was in the buried O_{BT} horizon (37% at site K1 and 57% at site K2) and in the adjacent Ah_T and Ah_{BT} horizons at site K1 (42%). At both sites, the high necromass with relatively low fine root biomass in the buried O_{BT} horizons indicate that this horizon has formerly played a significant role in nutrient supply but was in the long run less important for nutrient uptake.

5. DISCUSSION

5.1. Aluminium in ploughed podzols

The two sites in this study had been ploughed in the 1960s and 1970s — 17 and 31 years before sampling — and represented the time period when ploughing was commonly done in Finland. The disturbed soil profiles retained their chemical properties compared to undisturbed soil. Values of soil pH_{Ca}, carbon, CEC_e, and selectively extractable Al and Fe were mainly similar in the same corresponding major horizons in the tilt, furrow and undisturbed soil.

However, the decreased concentrations of extractable Al, consisting mainly of inorganic secondary Al in the exposed Bs horizons of the tilt and furrow, and increased concentrations of organically bound Al in the buried O_{BT} horizons indicate that some Al was mobilised in the ploughed soil.

Aluminium is released from soil solids as a response to increased acidity in soil. Seventeen and 31 years after ploughing, a newly formed organic horizon had developed on top of the tilt and furrow. The concurrent increase in the soil C in the exposed Bs horizons and decrease in soil pH imply that ecosystem internal processes such as organic acids excreted by roots or released during decomposition of above- and belowground litter most likely explain the mobilization of Al in the tilts and furrows. The Norway spruce fine-root biomass observed in the restricted space of the tilts was high indicating that the increase observed in soil C in the exposed Bs horizons was mainly due to the developing Norway spruce trees. Ground vegetation consisting mainly of grasses and herbs, which occupies the tilts within a few years after ploughing (Kellomäki 1972), may have also formerly played a role in C accumulation but at the time of sampling, the Norway spruce canopies were closed and the ground layer in the tilts consisted mainly of dead needles.

Chemical and physical properties of soil under the influence of plant roots differ from the rest of the soil (Killham 1994). The changes observed in soil chemical properties in the exposed Bs horizons — the increase in soil organic C, CEC_e and exchangeable Al_e but maintaining simultaneously relatively high BS_e — were similar to those properties that were found to increase in the rhizosphere soil when properties of rhizosphere were compared to those of the podzolized soil under a Norway spruce stand in Sweden (Gobran and Clegg 1996).

Substantial amounts of organic matter are transferred to soil when roots die. Compared to coarse roots, fine roots contribute more to soil organic matter accumulation because they stay alive for only a short period and produce large amounts of fast-decaying organic matter annually (Vogt et al. 1991). Fine roots also contribute to soil organic pools while they are alive in the form of organic exudates. Increased carbon availibility due to root exudation and sloughing results in higher bacterial and fungal populations and higher microbial activity in the vicinity of plant roots thereby enhancing mineralisation (Killham 1994). Organic acids excreted by roots, mycorrhizal fungi and microorganisms are also known to accelerate weathering (Manley and Evans 1986). Thus, the abiotic and biotic processes in the vicinity of plant roots have a major influence on the chemical and physical properties of soil.

In the present study, an estimated 0.5 kg C m^{-2} had accumulated in the exposed Bs horizons of the tilt and furrow and in the neo-formed O_T and O_F horizons at site K1 in 17 years and 0.9 kg C m^{-2} at site K2 in 31 years, corresponding an average annual rate of 29 g C m^{-2} at both sites. Decomposition rates and C fluxes in soil after harvest have been studied in Finland (e.g. Piirainen et al. 2002, Palviainen et al. 2004, Pumpanen et al. 2004), but studies of changes in C pools in growing sapling and pole-stage stands are scarce (Ilvesniemi et al. 2002, Hytönen et al. 2004). Hytönen and co-workers (2004) reported that 0.3 kg C m^{-2} was sequestrated in forest floors in 9-25 years old afforested arable land that corresponds to the amount of C in the neo-formed O_T horizon at site K1 (0.27 kg C m^{-2}) in 17 years. Ilvesniemi and co-workers (2002) reported an increase in soil C stores around 0.5 kg C m^{-2} within 12-27 years after the clear-cutting. The results of the present study support those of Ilvesniemi et al. (2002) and further indicate that C input from above- and belowground litter in young stands and subsequently its effect on soil properties at ploughed forest sites may be of greater significance than previously anticipated.

Aluminium concentrations in soil solution of the Bs horizons of the tilts and furrows were mostly similar to those concentrations found in the upper part of the undisturbed mineral soil (in the $Bs1_U$ and E_U horizons, respectively). On one sampling occasion a total Al concentration of 1.25 mmol dm^{-3} was observed within the tilt at site K1, which is clearly higher than the total Al concentration ranges (from 0.003 to 0.357 mmol dm^{-3}) found commonly in soil solutions in podzolic forest soils in southern Finland (Nissinen et al. 1998, van Hees et al. 2000, Derome et al. 2001, 2002). The high total Al concentration within the tilt also substantially exceeded the potentially toxic Al threshold concentrations (from 0.05

mmol to 0.2 mmol dm^{-3}) for tree seedlings found in nutrient solution cultures and pot trials (reviewed by Cronan and Grigal 1995). However, it has to be beared in mind that most of the total Al in soil solution of podzolic soils is organically bound, which has been shown to be non-toxic to plants (Hue et al. 1986). Nygaard and de Wit (2004) and de Wit and co-workers (2001) also showed that potentially toxic Al concentrations that have been associated with reduction of root growth and root mortality in hydroponic studies did not affect tree growth or fine root growth in mature Norway spruce stands. Thus, although high concentrations of Al in soil solution of the ploughed soils might occasionally exist it is not likely that these concentrations have a negative impact on fine-root growth.

Considering the theories of podzolization, Anderson et al. (1982) and Gustafsson et al. (1995) have suggested that the podzolic Bs horizon is transformed into a Bhs horizon with no ITM if the supply of organic acids is increased. Thus, the occurrence of changes in the exposed Bs horizons — the increase in soil organic C and the decrease in soil inorganic secondary Al — were consistent with that theory of podzolic Bhs horizon formation (Anderson et al. 1982, Gustafsson et al. 1995), and further support the importance of organic matter as a driving variable in the podzolization process (Lundström et al. 2000b). It may be assumed that the exposed Bs horizons beneath the newly formed O horizons are subject to soil post-disturbance development and in the course of time, new spodic horizons will develop as the soil formation processes proceed. Although the time scale in this study — 17 and 31 years after ploughing — was a relatively short period, the results of the present study were consistent with studies where soil development after disturbance has been evaluated. Scalenghe et al. (2002) studied pedogenesis in disturbed alpine soils and suggested that vegetation plays a key role in soil development: soil formation under a coniferous forest leads to the appearance of podzol-like features (Scalenghe et al. 2002). 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). Buurman and Jongmans (2005) suggested recently an amended podzolization theory in which root-derived organic matter has a predominant role in the accumulation of carbon 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 may offer an unique opportunity to study the importance of plant-soil interactions in modifying the properties of boreal podzols.

5.2. Processes controlling activity of Al^{3+} in soil solution

Processes controlling activity of Al^{3+} in soil solution in the disturbed soil profiles were generally similar to those observed in the undisturbed profiles indicating that irrespective of the change in the stratified structure of a podzolic soil, no major changes have occurred in these mechanisms.

In the Bs horizons, Al solubility was controlled by a secondary mineral phase, consistent with the predominance of soil inorganic secondary Al observed. The estimated log(IAP) values showed that Al solubility was relatively close to soil $Al(OH)_3$, which Gustafsson and co-workers (1998, 2001) found to prevail in spodic Bs horizons containing ITM. Gustafsson et al. (2001) further stated that imogolite probably does not control Al solubility in the short term due to its relatively slow formation and dissolution kinetics. The calculated log(IAP) for soil imogolite, however, showed that in some of the soil solutions, Al solubility was relatively close to that of soil imogolite (Gustafsson et al. 1998, Zysset et al. 1999), especially, in those soil solutions with the pH_s values over 5.

In the organic matter rich surface horizons, Al cations form complexes with SOM and Al solubility is dominated by organically bound Al (Cronan et al. 1986, Walker et al. 1990, de Wit et al. 1999). The importance of organically bound Al in controlling the Al solubility in the B horizons of podzolised soils has been emphasised in a number of studies, e.g. Mulder and Stein (1994), Wesselink et al. (1996), Simonsson and Berggren (1998) and Skyllberg et al. (2001). In the present study, organically complexed Al using the Al_p/C ratio according to Eq. 6 (Wesselink et al. 1996) explained the Al solubility in the O and Ah/E horizons but not in the exposed Bs horizons (where the increase in soil C was observed) and in the undisturbed $Bs1_U$ horizons. In the latter case, the soil $(Al_o\text{-}Al_p)/Al_p$ ratio (0.27) was below the range (0.3 to 0.7) where organic complexation reactions of Al are likely to predominate (LaZerte and Findeis 1995). Most of the studies using Al_p/C (or Al_p/C_p) ratio for describing the organic complexation reactions of Al were, however, conducted in the podzolized soils in temperate regions (Mulder and Stein 1994, Wesselink et al. 1996, Simonsson and Berggren 1998), where the amount and quality of the accumulated C and secondary Al in the B horizon may differ from that in the boreal podzols (Buurman and Jongmans 2005). In the studied soils, the poorer fit of Eq. 6 in describing the Al solubility control by organically bound Al in the undisturbed $Bs1_U$ horizons may also be due to lack of precision in measuring the concentrations of organic Al using pyrophosphate since pyrophosphate is known to extract $Al(OH)_3$ phases (Kaiser and Zech 1996). Extraction with copper chloride ($CuCl_2$) may give a more precise measure of organically bound Al (Juo and Kamprath 1979). In the present study, 0.5 M $CuCl_2$ solution was used to extract adsorbed Al from K2 Bs horizon samples, but no relationship between the Al_{cu}/C and pH and - $\log(Al^{3+})$ was found (according to Eq. 6, unpublished data).

Although Al complexes with SOM in the Bs horizons did not determine activity of Al^{3+} in soil solution, SOM via cation exchange reactions had a role in influencing the activity of Al^{3+} in the Bs horizon soil solutions as indicated by the close relationship between the organic C and CEC_e in the Bs horizons and, moreover, by the success in describing the apparent Al^{3+} - Ca^{2+} cation-exchange equilibria in the Bs horizons (according to Eq. 12). Thus, although the pool of exchangeable Al_e in the podzolic horizons was small as compared to pools of organically complexed Al (Al_p, Al_{cu} in Figure 4), cation-exchange reactions had an important role in explaining cation concentrations in soil solution. The results of the present study support those presented by Nissinen and co-workers (1998) that Gaines-Thomas selectivity coefficients are applicable to podzolic forest soils.

The importance of SOM and exchangeable cations in determining cation concentrations in O horizon soil solutions was additionally supported by the success in describing the relationship between base saturation and soil solution pH_s using the extended Henderson-Hasselbach equation and assuming that exchangeable Al_e had nonacidic properties due to a low pH (Skyllberg 1994, Ross et al. 1996). Consequently, weak organic acid dissociation explained the pH_s in O horizon soil solutions and indicated that exchangeable cations, displaced by a neutral salt extract, adequately described the pools of these dissociated and undissociated functional groups. The higher pH_s observed in the neo-formed O horizons than in the undisturbed and buried O horizons (Figure 7) suggests that the newly accumulated organic matter is less humified, thereby producing higher pH_s in the soil solution. However, the estimated pK_{app} value in the neo-formed, buried and undisturbed O horizons was the same (2.59), indicating that organic matter behaved similarly. Equilibria of weak acids has been shown to determine the H^+ activity in salt extractions of soils in laboratory experiments (Nissinen et al. 1999, Johnson 2002). In the present study, equilibria of weak acids was shown to explain the activity of H^+ in soil solutions representing a large range in temporal and spatial variation in the field conditions.

In the mineral horizons, the relationship between base saturation and soil solution pH_s using the extended Henderson-Hasselbach equation was clearly weaker than in the O horizons. Thus, the results of this study did not support the use of the weak organic acid dissociation model in predicting pH_s values in the mineral horizons, which contrats with suggestions made by Johnson (2002) for acid mineral soils and Skyllberg (1999) for podzolic E horizons. In the studied mineral horizons, the organic acid dissociation may be overridden by other processes such as Al solubility control by a $Al(OH)_3$ phase in the Bs horizon. Other reactions such as hydrolysis of exchangeable and nonexchangeable Al were also likely to occur at the pH_s values observed. Additionally, soluble organic acids may contribute to the control of the activity of Al^{3+} in the soil solutions of the E and B1 horizons (van Hees et al. 2000).

6. CONCLUSIONS

In the present study, long-term effects of deep tilling on the chemical properties of soil and soil solution chemistry were evaluated at two forest sites that had been ploughed 17 and 31 years ago and planted with Norway spruce seedlings.

Decreased concentrations of selectively extracted Al in the mineral horizons of tilts and furrows and increased concetrations of Al in the buried O horizons suggest that some Al was mobilised at the ploughed forest sites. Accumulation of organic C on top of the tilts and furrows with the relatively high Norway spruce fine root biomass in the tilts indicated that the release of Al was mainly due to acidity produced by ecosystem internal processes such as organic acids excreted by roots or released during decomposition of above- and belowground litter.

Ploughing did not affect the processes controlling activity of Al^{3+} in soil solution. In the undisturbed and disturbed Bs horizons, Al solubility was controlled by secondary minerals while in the O and Ah/E horizons, solubility control by organically bound Al was observed. Although the exchangeable Al_e pool was small in the studied podzolic horizons, cation-exchange reactions also had an important role in explaining the cation concentrations in soil solution. In the O horizons, exchangeable Al_e had nonacidic properties similar to those of base cations, and consequently, the soil solution pH_s was explained by weak organic acid dissociation. In the present study, soil solution was obtained from fresh soil samples using centrifugation. It is noteworthy that, in these soil solutions collected from the field and representing a large range in temporal and spatial variation, near-equilibria conditions consistent with those equilibria conducted under laboratory experiments (e.g. Gustafsson et al. 1998, 2001, Zysset et al. 1999) were found to prevail. The equilibria found in the present study support the use of centrifugation drainage technique in studying the conditions in the soil solution-soil interface.

The changes observed in soil chemical properties in the ploughed soil were consistent with the processes determining the Al chemistry in soil solution. It may be expected that soil formation processes will in the course of time result in the development of a new spodic horizon in the tilts and furrows. Although the time elapsed since ploughing was only a few decades in this study, the occurrence of changes observed suggest that plant-derived organic matter and plant-soil interactions are already modifying the properties of ploughed podzols.

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