Soil solution aluminium in disturbed and undisturbed podzolic profiles at two tilt-ploughed forest sites

Niina Tanskanen[1]*, Timo Kareinen[1], Ari Nissinen[2] and Hannu Ilvesniemi[1]

[1] *Department of Forest Ecology, P.O. Box 27, FIN-00014 University of Helsinki, Finland (*e-mail: niina.tanskanen@helsinki.fi)*

[2] *Finnish Environment Institute, P.O. Box 140, FIN-00251 Helsinki, Finland*

Podzolic soil profiles down to the illuvial (B) horizon are inverted on soil surfaces during ploughing of forest soils (as part of forestry practices). As a result, aluminium once immobilized in the horizon may begin to remobilize. In the present study, soil solution Al concentrations in ploughed podzolic profiles were compared with those of the corresponding undisturbed profiles at two forest sites tilt-ploughed 17 (K1) and 31 (K2) years ago. The soil solution was obtained from fresh soil samples, using a centrifugation drainage technique. Aluminium was fractioned to labile monomeric Al, non-labile monomeric Al and acid-soluble Al. Increased concentrations of various Al fractions were observed in the ploughed profiles at both forest sites, especially in the Bs horizons exposed to the soil surface and in the O horizon buried beneath the tilt at site K1. In those horizons where Al had increased, soil solution pH decreased while the concentration of dissolved organic carbon (DOC) increased, suggesting that remobilization of Al occurred in the ploughed profiles.

Introduction

Ploughing and other mechanical site preparation methods have been used since the late 1960s in regeneration of coniferous forests in Fennoscandia. About 18% 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 (mounded or ploughed). The consequences of intensive tilling on the chemical properties of podzolic forest soils have not, however, been widely studied.

Forest soils in Fennoscandia have undergone podzolization since the retreat of the glacial ice, about 10 000 years ago (Eronen 1983). Variation in the age of podzols has occurred, however, since the different areas were deglaciated and emerged from water due to land uplift at different times. In a podzolic soil profile, the concentration of total aluminium in the soil solution is generally highest in the weathered eluvial (E) horizon, while in the illuvial (B) horizon it decreases due to immobilization (e.g. Dahlgren and Ugolini 1989, Lundström 1993, van Hees *et al*. 2000, 2001). Consequently, this forms a B horizon enriched with metal–humus complexes and secondary Al, Fe and Al-Si oxides and oxyhydroxides.

The stratified structure of the podzolic soil is substantially altered during ploughing of coniferous forest soils, i.e. the soil profile down to the B horizon is inverted on the soil surface (as a tilt).

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
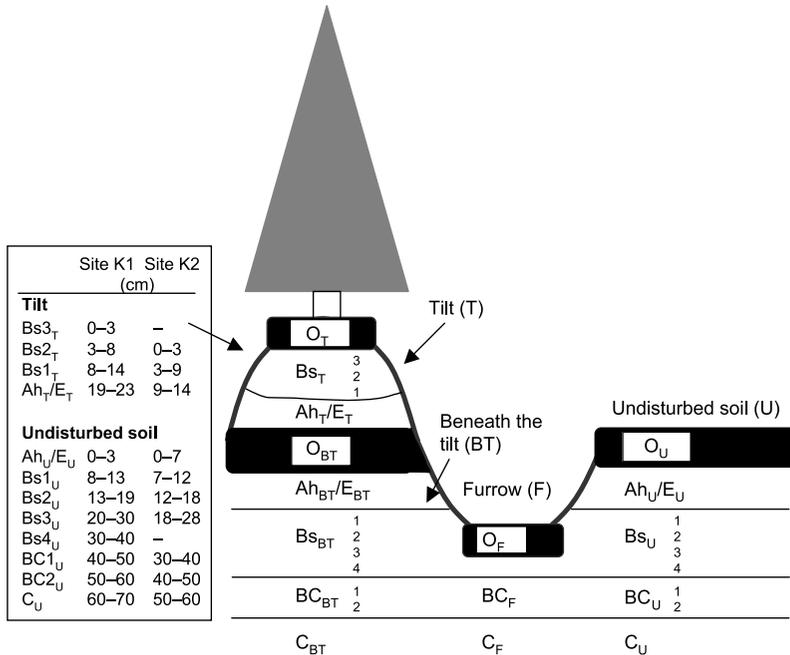
Fig. 1. A schematic presentation of tilt-ploughed soil. Sampling depths of the tilt and the undisturbed soil at both study sites K1 and K2 are shown.

Thus, as a result of the ploughing, the exposed B horizon is located on top of the tilt, while the E and O horizons are buried within the tilt above the original soil surface (Fig. 1).

Al is released from soil solids in a response to increased acidity in the soil (McBride 1994). Due to inversion on the soil surface, Al enriched in the 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. Thus, secondary Al exposed to the soil surface in the tilt and in the furrow may begin to mobilize and thus the concentration of Al in the soil solution to increase. Solution Al^{3+} at high concentrations is known to be toxic to plants (e.g. Cronan and Grigal 1995). The soil solution in podzolic forest soils contains, however, a wide variety of organic solutes such as organic acids that are known to form stable complexes with Al (Dahlgren and Ugolini 1989, van Hees *et al.* 2000). Thus, the concentrations of free Al^{3+} in solution tend in general to be considerably lower than those of the total Al. Lundström and Giesler (1995) used Al species composition in the soil solution as an indicator of acidification and stated that leaching of inorganic Al from the B horizon indicates that the process of podzolization is perturbed.

In the present study, soil solution Al concentrations in the tilt-ploughed podzolic profiles were compared with those of the corresponding undisturbed profiles. The aim of the study was to determine whether the concentrations of Al in the soil solution increase when the soil profile is perturbed.

Material and methods

Site description

The study site K1 was located in Karkkila (60°32´N, 24°16´E) and K2 in Kuorevesi (61°53´N, 24°35´E), 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* (L.) Karst.). At the time of sampling at site K1 in 1996, the field layer was dominated by *Calamagrostis arundinacea* (L.) Roth and the ground layer by mosses *Pleurozium schreberi* (Brid.) Mitt. and *Dicranum polysetum* Sw., espe-

cially in the tilt and furrow. The field layer at site K2 in 1997 was characterized by the presence of *Deschampsia flexuosa* (L.) Trin. and *Vaccinium myrtillus* L., and the ground layer by *Pleurozium schreberi*. *Sphagnum girgensohnii* Russ. was variously abundant in the furrow.

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 (FAO-Unesco 1990) 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.

Soil sampling

Sampling was carried out six times at site K1 and four times at site K2; during each, 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^3 per soil layer sampled. The samples were collected in early summer and autumn 1996 at site K1 and 1997 at site K2.

The O, Ah, Bs, BC and C horizons were found in the undisturbed soil at site K1 and the O, E, Bs, BC and C horizons at site K2 (O_U, Ah_U/E_U, Bs_U, BC_U and C_U). 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 to that of the undisturbed soil. No horizon showing features of mixing (due to ploughing) was included in the bulked sample from this horizon. Mixing of the adjacent horizons was, however, found only on a few occasions. A new O horizon was formed in the ploughed soil on top of the tilt (O_T) and in the furrow (O_F) (Fig. 1). The first three centimetres (0–3 cm) of the exposed 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. Consistent with the division to subhorizons in the undisturbed soil, these horizons were referred to as Bs3 at site K1 and Bs2 at site K2. Thus, inverted Bs3, Bs2, Bs1 and Ah horizons could be found in the tilt at site K1 ($Bs3_T$, $Bs2_T$, $Bs1_T$, Ah_T), whereas at site K2 the tilt consisted of the horizons Bs2, Bs1 and E ($Bs2_T$, $Bs1_T$, E_T) (Fig. 1). In the furrow, the horizons were Bs3, BC and C at site K1 ($Bs3_F$, BC_F, C_F) and the same plus Bs2 ($Bs2_F$) at site K2. The mineral soil beneath the tilt was similar to that of the undisturbed soil and included the O horizon buried beneath the tilt (O_{BT}).

The thickness of the undisturbed O horizon (O_U) at site K1 ranged from 2 to 6 cm (mean 4 cm). The range in the O_{BT} horizon was 3–12 cm (mean 6 cm). The range in the newly formed O horizon was 0–1 cm in the tilt (O_T) and 0.5–2.5 cm in the furrow (O_F). The O_T layer was, however, formed mainly of undecomposed litter residues of needles and graminoids. The range in the O_U horizon at site K2 was 3–10 cm (mean 5.5 cm) and in the O_{BT} horizon 5–16 cm (mean 8 cm). The O_T and O_F horizons ranged from 0 to 5 cm and 1 to 6 cm, respectively.

Analyses

The soil solution was extracted 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 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 in between. 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.

The amount of water in the O horizon obtained by centrifugation was 42% ± 17% (mean ± S.D.) of the total water content in the soil sample. In the mineral horizons, the extraction efficiency was 57% ± 1%. In practice, the

water yield restricted the analysis, especially within the tilt during autumn. Thus, in many cases the number of soil solutions obtained with centrifugation was smaller than the number of soil samples collected per site (Table 1).

Immediately after centrifugation, the pH of each subsample was measured with a combined pH glass electrode (6.0216.100, Metrohm 605, Herisau, Switzerland). The remaining solution was filtered through a disposable syringe filter (Millex HV13) with a pore size of 0.45 μm (Millipore Corporation, Billerica, Mass., USA). The concentrations of total monomeric Al and non-labile monomeric Al were measured by reaction with pyrocatechol violet (Henshaw *et al.* 1988) with a flow-injection ion analyzer

(Lachat Quikchem 8000, Milwaukee, WI, USA). Non-labile monomeric Al was fractionated from total monomeric Al using 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

Table 1. Concentrations of total monomeric Al and total Al at site K1 and site K2. Mean, standard error of the mean (S.E.) and the number of samples (in parentheses) are given. Those concentrations in each horizon that differ from the undisturbed horizon are marked with different letters.

| | Total monomeric Al (μmol dm^{-3}) | | | | | | Total Al (μmol dm^{-3}) | | | | | |
| | Site K1 | | | Site K2 | | | Site K1 | | | Site K2 | | |
	Mean	S.E.	n	Mean	S.E.	n	Mean	S.E.	n	Mean	S.E.	n
Undisturbed soil (U)												
O_U	42[a]	4	(5)	100	29	(4)	91[a]	17	(5)	167	49	(4)
Ah/E_U	50	5	(5)	37	13	(4)	87	10	(5)	64	25	(4)
$Bs1_U$	30	9	(5)	11	4	(4)	56	16	(6)	21	6	(4)
$Bs2_U$	9	3	(6)	4[a]	2	(4)	22	8	(6)	12[a]	2	(4)
$Bs3_U$	4[a]	2	(5)	2	1	(4)	12[a]	4	(4)	5	2	(4)
$Bs4_U$	2	1	(3)				7	1	(3)			
Tilt (T)												
O_T	34	27	(2)	90	32	(4)	116		(1)	188	28	(3)
$Bs3_T$[1]	23[b]	9	(5)				47[b]	18	(5)			
$Bs2_T$[2]	15	6	(5)	30[b]	4	(4)	25	7	(5)	63	8	(3)
$Bs1_T$	27	3	(2)	34		(1)	33	15	(3)	38	9	(2)
Ah/E_T	64	13	(2)	193	74	(4)	366	295	(4)	123	55	(2)
Soil beneath the tilt (BT)												
O_{BT}	142[b]	22	(3)	66	7	(4)	262[b]	40	(3)	121	45	(2)
Ah/E_{BT}	70	18	(4)	57	13	(4)	247	66	(6)	91	28	(3)
$Bs1_{BT}$	21	6	(5)	14	3	(4)	42	13	(6)	23	3	(3)
$Bs2_{BT}$	4	1	(5)	6	2	(4)	15	5	(6)	8	2	(3)
$Bs3_{BT}$	1	0.2	(5)	3	0.5	(4)	6	0.1	(5)	8	2	(3)
$Bs4_{BT}$	1	0.1	(5)				7	1	(5)			
Furrow (F)												
O_F	53	16	(4)	62	10	(4)	164	37	(4)	133	27	(4)
$Bs2_F$[2]				13[b]	1	(4)				28[b]	2	(4)
$Bs3_{F(0-3)}$[1]	12	4	(5)				30	6	(5)			
$Bs3_{F(3-8)}$[3]	9	1	(2)	6	1	(4)	25	6	(3)	13	4	(4)
$Bs4_F$	2	1	(5)				10	2	(6)			

[1] Subhorizon exposed to a soil surface at site K1.
[2] Subhorizon exposed to a soil surface at site K2.
[3] Two subhorizons in the furrow were referred to as Bs3 at site K1.
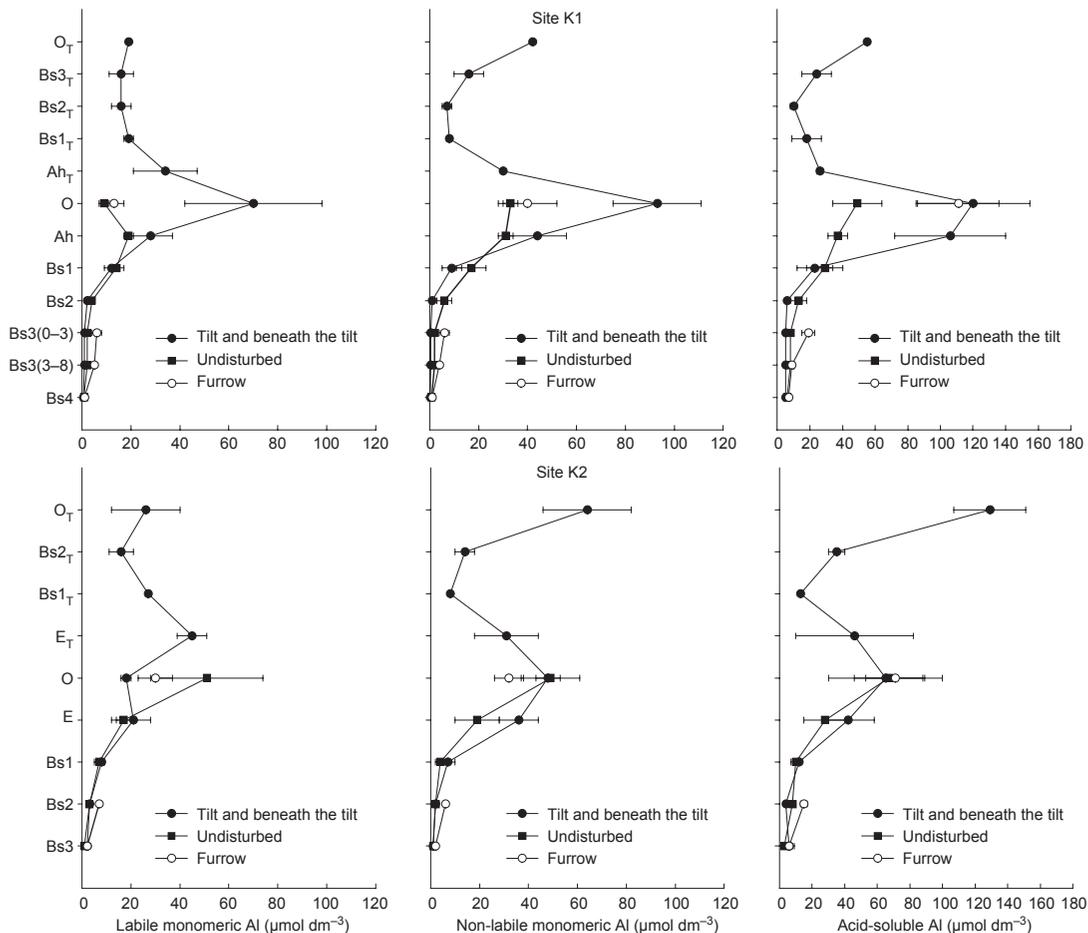
Fig. 2. Concentrations of various Al fractions (mean and S.E.) in soil solution of the tilt, furrow, and undisturbed soil. Two subhorizons (0–3 cm, 3–8 cm) in the furrow were referred to as the Bs3 horizon at site K1.

Al. Ion chromatography (HPLC, Waters, Milford, Mass., USA) was used to determine the concentration of chloride (Cl), while the concentration of dissolved organic carbon (DOC) was determined with a carbon analyser (Shimadzu TOC 5000, Japan).

Statistics

The Wilcoxon rank-sum and Kruskall-Wallis tests were used to compare the concentrations of Al in individual soil horizons at different sampling positions; Kendall's tau-*b* was used for correlations. These nonparametric tests were chosen because the variances were not equal and the data distribution was not normal, except for

that of pH. The statistics were analysed using SAS version 6.12. Significant differences refer to the 0.05 level.

Results

Concentrations of Al in the soil solution

The concentrations of Al in the soil solution of the ploughed soil profiles differed from those observed in the undisturbed profiles at both study sites (Fig. 2 and Table 1), especially in the exposed Bs_T horizons and at site K1 in the O_{BT} horizon. In the exposed Bs_T horizons ($Bs3_T$ at site K1 and $Bs2_T$ at site K2), the concentrations of different Al fractions (labile monomeric

Al, non-labile monomeric Al and acid-soluble Al) were higher than in the corresponding Bs_U subhorizons (Fig. 2). The concentrations of Al were slightly higher throughout the tilt at site K2 (Table 1), whereas at site K1 only the concentration of labile monomeric Al was higher, especially in the $Bs2_T$ horizon (Fig. 2). Consequently, the percentage of labile monomeric Al of the total Al in the $Bs2_T$ horizon was also higher ($43\% \pm 4\%$, mean ± S.E.) than in the $Bs2_U$ horizon ($18\% \pm 4\%$).

The changes in concentrations of the Al fractions in the exposed Bs_F horizons of the furrow ($Bs3_{F(0–3)}$ at site K1 and $Bs2_F$ at site K2) were similar to those found in the exposed Bs_T horizons: the concentrations of Al were higher than in the corresponding intact horizon (Fig. 2). The concentrations of Al were, however, lower in the furrow than in the tilt.

At site K1, the concentrations of total Al in the O_{BT} horizon beneath the tilt were three to five times higher (Table 1) than those in the O_U horizon (67 ± 2 μmol dm^{-3}, $n = 3$) during the same season. In contrast to the findings at site K1, the concentrations of Al fractions in the O_{BT} horizon at site K2 were similar to those of the O_U horizon, and in the case of labile monomeric Al even lower beneath the tilt (Fig. 2). At both study sites, the concentrations of Al in the newly formed O_T and O_F horizons were similar to or higher than in the O_U horizon (Fig. 2 and Table 1).

In general, the concentrations of Al were more often higher in autumn than in summer but no apparent seasonal pattern was observed. The maximum concentration of total Al, as high as 1250 μmol dm^{-3}, was observed in the inverted Ah_T horizon at site K1 in November (*see* the high mean and S.E. in this horizon, Table 1).

Soil solution concentrations in relation to Al

The soil solution pH was lower (3.71 ± 0.18) and DOC concentration slightly higher (50 ± 15 mmol DOC dm^{-3}) in the buried O_{BT} horizon at site K1 where the increased concentrations of Al were observed, than in the intact horizon (pH 4.08 ± 0.09, 24 ± 8 mmol DOC dm^{-3}) during the same season. The Cl concentrations ranged between 80 and 225 μmol dm^{-3} beneath the tilt and between 165 and 415 μmol dm^{-3} in the O_U horizon.

The Cl concentrations in the Bs horizons of the tilt and furrow were closely related to the concentrations of the various Al fractions (Fig. 3), with the correlation coefficients ranging between 0.48 and 0.58 ($p < 0.001$, $n = 28–33$). The Al fractions were also correlated with the DOC concentrations ($r = 0.49–0.66$, $p < 0.001$, $n = 25–30$) and pH ($r = –0.73$ for the labile monomeric Al, $p < 0.0001$, $n = 31$; and $r = –0.31$ for the acid-soluble Al, $p < 0.01$, $n = 35$, Fig. 3). When the effect of DOC on the Al concentrations was eliminated by Kendall partial correlation, the correlations with Cl decreased to a range of 0.12–0.18. Correspondingly, when the effect of Cl was eliminated, the correlations with DOC decreased slightly to a range of 0.33–0.44. The relationships of Al fractions with the pH were not affected either by DOC or Cl, except with acid-soluble Al.

To further study the pH–Al relationship, the ion activity product of labile monomeric Al relative to the Al(OH)$_3$ solid phase was estimated. If Al^{3+} in the soil solution is in equilibrium with the Al(OH)$_3$ phase

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O \qquad (1)$$

$$\log K = \log Al + 3pH \qquad (2)$$

the logAl + 3pH value is equal to the logK value. A *logK$_s$° value of 7.74 at 25 °C was reported for crystalline gibbsite (Palmer and Wesolowski 1992). Using the van't Hoff equation, this value is 9.06 at 5 °C. The estimated logK was 9.57 ± 0.04 (mean ± S.E.) in the Bs_T horizons of the tilt.

Discussion

Increased concentrations of Al were observed in the ploughed soil profiles, especially in the exposed Bs_T horizons and in the O_{BT} horizon at site K1. The concurrent increase in concentrations of Cl implied that the elevated concentrations of Al could be explained by an enrichment in solute concentrations due to transpiration.
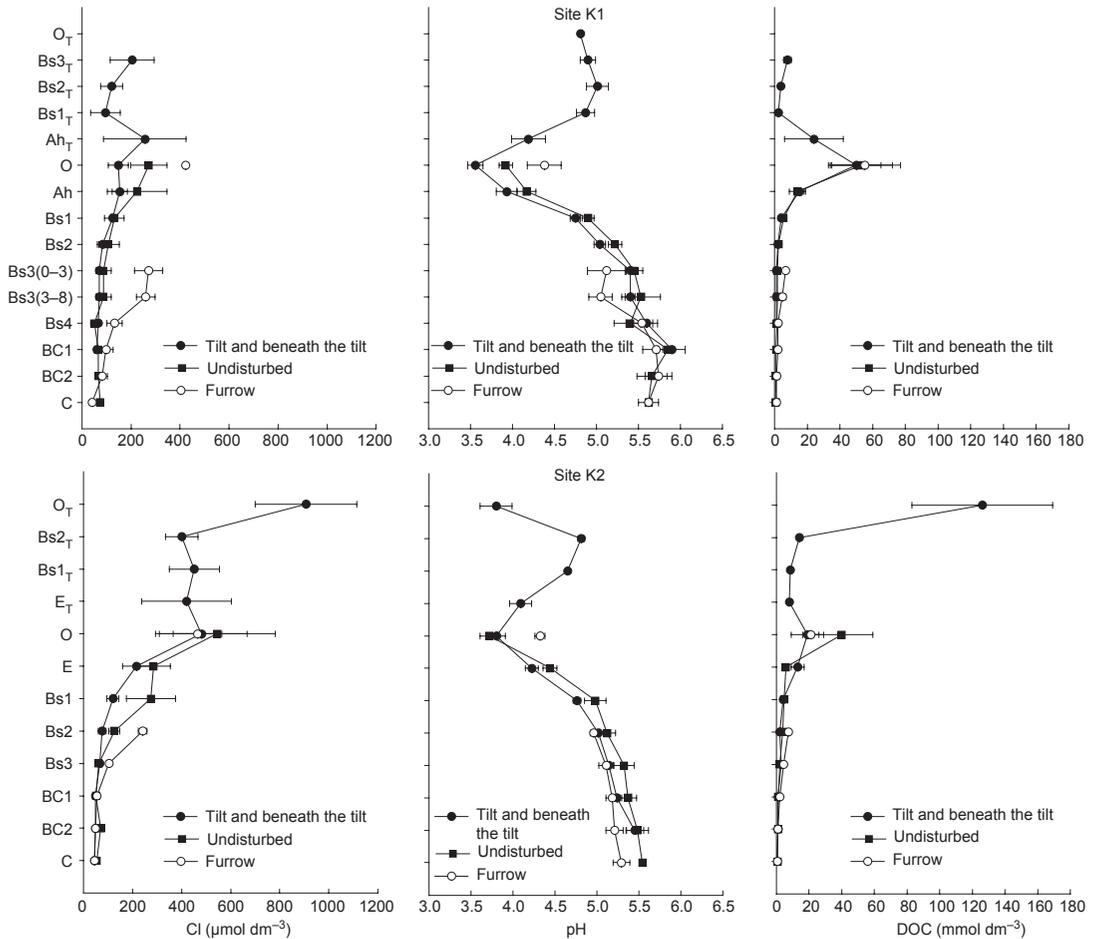
Fig. 3. Soil solution Cl, pH and DOC (mean and S.E.) in the tilt, furrow and undisturbed soil. Two subhorizons (0–3 cm, 3–8 cm) in the furrow were referred to as the Bs3 horizon at site K1.

Higher transpiration from the tilt than from the undisturbed soil could be expected, since seedlings were planted on top of the tilt. The low concentrations of Cl in the buried O_{BT} horizon and decreased correlations between Al and Cl in the mineral soil (when the effect of DOC was eliminated), however, indicated that enrichment of the soil solution due to transpiration was not sufficient reason to explain the increased concentrations in Al.

Al is released from soil solids in response to increased acidity in soil (McBride 1994). In those Bs horizons where the concentrations of Al had increased, the soil solution pH decreased and DOC concentrations increased, implying that remobilization of Al occurred in the ploughed soil profiles. The estimated logK (calculated using the concentrations of labile monomeric Al) was higher (9.57 ± 0.04) than the value of 9.06 for crystalline gibbsite at 5 °C (*logK$_s$° 7.74 at 25 °C, Palmer and Wesolowski 1992). The logK was, however, similar to the value of 9.61 at 5 °C (*logK$_s$° 8.29 at 25 °C) found by Gustafsson *et al*. (2001) to prevail in podzolic Bs horizons. Al solubility relatively close to that of gibbsite indicated that dissolution of inorganic secondary Al in the ploughed Bs horizons, most likely explained the increased concentrations of Al in the soil solution. Gustafsson *et al*. (2001) stated that it is the Al(OH)$_3$ phase (with a logK$_s$ value of 8.29 at 25 °C) that controls Al solubility in moderately acid Bs horizons.

Increased acidity in soil may originate from ecosystem internal processes such as organic acids released by roots and microbes or anthropogenically derived acid deposition. Increased percentages of labile monomeric Al (predominantly inorganic Al) in the $Bs2_T$ horizon at site K1 were similar to those reported in areas where the process of podzolization may have been perturbed due to anthropogenically derived acidic loads (van Hees *et al*. 2001). In contrast to that study (30 mmol sulphate m^{-2} yr^{-1} and 27 mmol nitrate m^{-2} yr^{-1}), deposition in southern Finland has been lower, averaging 16 mmol sulphate m^{-2} yr^{-1} and 18 mmol nitrate m^{-2} yr^{-1} during recent decades (e.g. Leinonen and Juntto 1992). Since the concentrations of DOC in the soil solution had increased and the proportions of the various Al fractions in the exposed horizons of the tilt were similar to those found in the undisturbed soil, the increased concentrations of Al were probably due to dissolution caused by ecosystem internal processes.

Increased concentrations of Al were observed in the buried O_{BT} horizon at site K1, while at site K2 the Al concentrations in the O_{BT} horizon were similar to those of the undisturbed horizon. In both these horizons at site K2, the concentrations of total Al were clearly higher than those reported earlier in centrifuged solutions of mor layer (20–70 μmol dm^{-3}) (van Hees *et al*. 2000). The plough used at site K2 had turned up mineral soil on both sides of the furrow (T. Ylinen pers. comm.). Subsequently, incorporation of Bs horizon material into the undisturbed O_U horizon occurred. DOC is known to promote weathering of soil minerals, e.g. by complexing Al and Fe (Manley and Evans 1986, Lundström and Öhman 1990). Thus, it may be assumed that dissolution and *in situ* weathering of this material within the surface O horizon was likely to occur and probably explained the high concentrations of Al present. The relatively high concentrations of Al in the newly formed O_T and O_F horizons may also have been due to similar processes in the interface between the exposed Bs horizons and accumulating organic material.

The high Al concentrations in the buried O_{BT} horizons may also have been due to *in situ* dissolution and weathering because during ploughing, slash, litter and humus are buried in the tilt, and organic material is also mixed with inverted mineral soil (Ritari and Lähde 1978). It may further be assumed that if Al is dissolved in the mineral soil of the tilt, some released Al could migrate downward, e.g. during peak flows, and subsequently be retained in the O_{BT} horizon beneath the tilt. If the amount of Al held in the complexation sites within the horizon is increased, solute concentrations would, in turn, be affected (Cronan *et al*. 1986). In the present study, the soil solution was obtained by centrifugation; thus, the fluxes of water through the soil profile could not be evaluated. Centrifugation was, however, preferred since it enables extraction of soil solution from soil samples well defined in time and space. It is further assumed to reflect better nutrient availability and apparent equilibrium conditions in the soil solution-soil interface than zero-tension and suction lysimeters (Giesler *et al*. 1996).

Conclusions

Soil solution Al concentrations in ploughed podzolic profiles were compared with those of the corresponding undisturbed profiles at two forest sites tilt-ploughed 17 (K1) and 31 (K2) years ago. Increased concentrations of various Al fractions were observed in the ploughed profiles at both forest sites, especially in the exposed Bs_T horizons and in the buried O_{BT} horizon at site K1. The soil solution pH decreased in those horizons where Al had increased, while the concentration of DOC increased, suggesting that remobilization of Al occurred in the ploughed profiles.

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