

# Phosphorus sorption properties in podzolic forest soils and soil solution phosphorus concentration in undisturbed and disturbed soil profiles

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Podzol horizons (O, E, B1, B2 and C) from three undisturbed sites were analyzed for phosphorus (P) sorption, P saturation, P fractions, and P concentrations in soil solutions, and three disturbed Podzols for P in soil solution. The threshold concentrations for net sorption were 8000  $\mu\text{g l}^{-1}$  and 700  $\mu\text{g l}^{-1}$  for the O and E horizons, respectively, and 3–6  $\mu\text{g l}^{-1}$  for the B1, B2 and C horizons. Consequently, if water percolates through the B horizon the risk of P leaching is low. Phosphorus saturation degree was 0.2%–25%. Fe-P dominated in the O, E, B1 and B2 horizons, and Ca-P in the C horizon. P was depleted from the E horizon (24  $\mu\text{g g}^{-1}$ ) and enriched in the B1 and B2 horizons (500 and 250  $\mu\text{g g}^{-1}$ ) as compared with that in the C horizon (160  $\mu\text{g g}^{-1}$ ). P in soil solution increased in the topmost 3 cm of the disturbed B horizons.

## Introduction

The podzolization process occurs in cold humid climates, where the annual rainfall exceeds annual evapotranspiration, and a slow microbial decomposition enables the formation and migration of a diverse combination of organic compounds (humic, fulvic, phenolic) which often are acidic. These compounds accelerate the weathering of soil minerals and the downward migration of released ions. The solubility of phosphorus (P) is also increased by organic chelates or by complex formation (Tan 1982). A typical podzolized

profile consists of a layer of an incompletely decomposed organic (O) horizon on the top of an eluviated (E) mineral soil horizon that deeper in the soil profile turns into an illuviated layer (B) enriched with aluminium (Al), iron (Fe) and organic carbon.

Weathering and pedogenesis change the soil P chemistry, i.e. the distribution of inorganic P as well as the P retention properties in the profile. Apatite is the only primary mineral in igneous rocks with a significant P content. During soil formation, this original P pool decreases and secondary forms such as organic P, P sorbed with

Al, Fe and Ca compounds, and occluded forms of P begin to accumulate (Walker and Syers 1976). In a Podzol profile, the original P pool has been depleted from the E horizon and secondary P forms have accumulated deeper in the profile (Land *et al.* 1999, Olson and Melkerud 2000, Tyler 2004). The alteration of P retention properties follows the redistribution of Al and Fe in the profile. In acid mineral soils, such as Podzols, P is mostly retained by Al and Fe (oxyhydr)oxides by the ligand exchange mechanism where the OH or H<sub>2</sub>O groups on the sesquioxide surfaces are displaced by (di)hydrogenphosphate anions (Hingston *et al.* 1967). Consequently, the enrichment of Al and Fe oxides and hydroxides in the illuvial B horizon of Podzols makes it efficient in binding P (Burnham and Lopez-Hernandez 1982, Wood *et al.* 1984, Borggaard *et al.* 1990, Yuan and Lavkulich 1994, Li *et al.* 1999) and the P concentration in the soil solution of the B horizon is therefore low (Piirainen *et al.* 2004). Depletion of Al and Fe compounds in the eluvial E horizon results in a low P retention capacity (Burnham and Lopez-Hernandez 1982, Wood *et al.* 1984, Li *et al.* 1999) and a high P concentration in the soil solution (Piirainen *et al.* 2004). P retention in the organic O horizon is also related to the content of Al and Fe in the layer (Giesler *et al.* 2002, Väänänen *et al.* 2007). However, the connection between the P retention properties in soil and the corresponding soil solution P concentration needs closer examination, especially in the case of low-sorptive surface soil horizons, which receive P input from litter and where other processes, such as biological retention may exceed chemical P retention.

In Finland, approximately 150 000–200 000 hectares of forests are clear-felled annually. Timber harvesting and forest regeneration may cause significant changes in the soil P input. It has been estimated that clear-felling can cause a P release of several kilograms per hectare during the first years following the operation (Bekunda *et al.* 1990, Stevens *et al.* 1995, Ahtiainen and Huttunen 1999, Palviainen *et al.* 2004, Piirainen *et al.* 2004). However, very little, if any, of this release enters water ecosystems from Podzol dominated upland catchments (Stevens *et al.* 1995, Neal *et al.* 2003), which implies that the released P is retained within the catchment,

e.g. in the soil. To estimate the significance of this input on soil P chemistry, detailed data on soil P reserves, both in a soil solution and in a solid form, and P retention ability are needed. However, despite the general understanding of the distribution of inorganic P and P retention properties of Podzol horizons, actual data which could be applied for quantifying the outcome of an elevated P input in a soil in boreal forest conditions are inadequate. Furthermore, even if the fate of P entering the soil system is affected by all the horizons through which the water flows, the cumulative effect of soil horizons on P movement has received little attention.

P sorption in soil is often studied as an equilibrium reaction where the amount of sorbed P is described as a function of solution P concentration. The Langmuir and Freundlich equations (Olsen and Watanabe 1957, Fitter and Sutton 1975) have been widely used to describe this equilibrium. However, these equations describe the chemical P sorption whereas biological factors are more important for P retention in the surface soil horizons O and E (Wood *et al.* 1984) and the applicability of the equations in describing P retention in these surface horizons still needs to be assessed.

Clear-fellings are generally followed by site preparation measures such as ploughing and mounding (Hyvän metsänhoidon suosituksset 2006) that may increase P release by enhanced mineralization of the soil organic matter. In addition, by turning the soil horizons upside down, the site preparation methods may also alter the soil P retention characteristics. The effect of site preparation on P leaching risk needs to be examined.

The aim of our study was to deepen the understanding of the behaviour of P in podzolized soil profiles. We investigated P retention and P retention properties in Podzol horizons using a variety of different methods in order to estimate the changes in percolate P concentrations during its passage through the different soil layers. To provide information on the long-term changes in P reserves in Podzol profiles the distribution of inorganic P forms in Podzol horizons was investigated. In addition, soil solution P concentrations in undisturbed soil horizons as well as the sites scarified with deep ploughing or

mounding were compared to study whether the soil solution concentration is altered when soil horizons are mixed in such a way that the deep horizons are directly exposed to precipitation and above ground litter deposition. Our hypothesis was that the soil P retention properties are reflected in soil solution P concentration and reversing the order of soil layers by site preparation has minor effect on the soil solution P.

## Material and methods

### Site description and sampling of the undisturbed Podzol profiles

The sampling sites are located in Ruovesi in southern Finland (61°50'N, 24°22'E). The studied soil profiles have developed on glacio-fluvial sorted material. The forest harvested five years before the soil sampling had been a 130–140-year-old mixed Norway spruce and Scots pine forest with an average standing volume of 240 m<sup>3</sup> ha<sup>-1</sup> (63% Norway spruce and 37% Scotch pine). Conventional stem-only harvesting, where logging residues are left at the site, was employed.

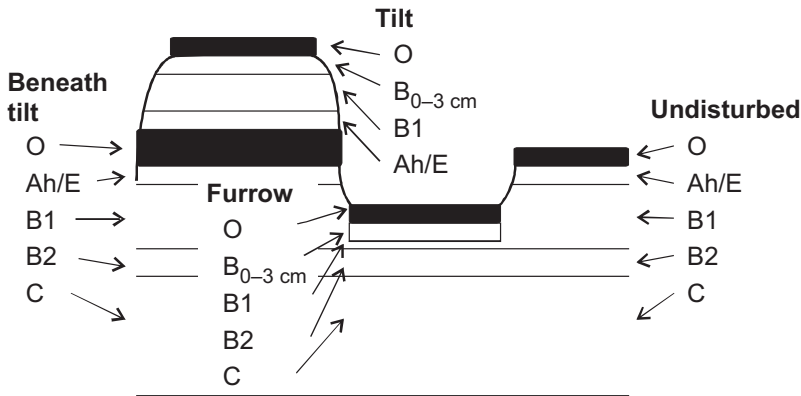
For the determination of inorganic P pools, desorption–sorption isotherms and PO<sub>4</sub>-P in the centrifuged soil water, soil was sampled in autumn 2002 from three points along a slightly descending catena representing three different site fertility classes. The site types, listed from the highest to the lowest site (downwards the slope) in the order of increasing fertility, represented VT (*Vaccinium vitis-idaea*) type, MT (*Vaccinium myrtillus*) type and OMT (*Oxalis maianthemum*) type according to the site classification system used in Finland (Cajander 1926). At each sampling point, the Podzol profile down to the relatively unchanged parent material was exposed by digging a pit to a depth of 50 cm from the mineral soil surface. All profiles were classified as Haplic Podzols (FAO 1998). The soil horizons were visually classified as follows: the humus layer, i.e. the O horizon, the eluvial E horizon, the illuvial B horizon and the parent material, i.e. C horizon. The B horizon was further divided into an upper (B1) and lower section (B2). The average thickness of the O,

E, B1, B2 and C horizons was 6, 5, 12, 12 and 21 cm, respectively. O and E horizon samples were collected from an area of 0.5–1.0 m<sup>2</sup>. To determine the bulk density of these layers separate volumetric subsamples were taken by pressing a volumetric cylindrical sampling device (diameter 46 mm, height 75 mm) vertically into the soil surface and separating the O and E horizons from the sample. Samples from the B1 and B2 horizons were taken from the pit walls by pressing the sampling core horizontally into the middle of the horizons. Three separate samples were taken from each of the four walls of the pit, i.e. a total of twelve samples were taken from both the B1 and B2 horizons. Five volumetric core samples (diameter 46 mm, height 100 mm) were taken from the C horizon from a depth of 40–50 cm. A composite sample was formed by every horizon for each site. The texture of the soils of all the three undisturbed sites was sand, except for the C horizon of the OMT, which consisted mainly of silt.

For soil solution sampling, in each of the three sites, plate type zero tension lysimeters were installed below the O horizon and suction lysimeters (Prenart) below the E horizon and in the middle of the B and C horizons. Weekly lysimeter samples were taken over the growing season in 2002. At each soil depth three lysimeters were placed. The average P concentration in the precipitation and in the groundwater from three groundwater wells, installed on the sites simultaneously with the lysimeters, was also determined. A detailed description of the sampling of the lysimeter water, the ground water and precipitation is given by Westman and Liski (1994).

### Site description and sampling of the ploughed and mounded sites

One site in Karkkila (K1) (60°32'N, 24°16'E) and one site in Kuorevesi (K2) (61°53'N, 24°35'E) were selected to investigate the effects of ploughing, and a site in Kerimäki (K3) (61°51'N, 29°22'E) was chosen to investigate those of mounding on soil solution P concentrations. The K1 site was clear-cut and tilt ploughed 17 and the K2 site 31 years before sampling. The



**Fig. 1.** A schematic representation of tilled soil showing the vertical order of horizons in the tilt, beneath the tilt and the furrow, and in the undisturbed soil.

K1 and K2 sites had been planted with Norway spruce (*Picea abies*) seedlings. The K3 site had been mounded 4 years before sampling and planted with silver birch (*Betula pendula*) one year after mounding. The site type of K2 was MT and the two others represented the OMT site type. The soil at the K1 site was classified as Entic Podzol with a clear Ah horizon (surface mineral soil horizon enriched with organic matter), and the soil at the K2 site as Haplic Podzol with an eluvial E horizon (FAO 1998). The Podzol at the K3 site had entic features, such as an Ah horizon instead of an eluvial horizon. The parent material at the K1 site was glacial till of a silt-loam texture, at the K2 site glacial till of a sandy-loam texture and at the K3 site sandy loam.

For soil and centrifuged soil solution sampling, soil samples were taken from four different positions: undisturbed soil, tilt/mound, soil beneath the tilt/mound and furrow (Fig. 1). From each sampling position, 8 to 11 core samples were taken with a volumetric cylindrical sampling device (46 mm diameter, height 75 mm). The core samples were further divided into soil horizons which were O, Ah or E, B1, B2 and C. The average thicknesses of the O, Ah/E, B1 and B2 horizons at site K1 were 4, 8, 11 and 20 cm, at site K2 5.5, 7, 11 and 10 cm, and at site K3 5.5, 9, 10 and 15 cm, respectively. The samples were combined by horizon to give one set of samples for each sampling position of each study site. Sampling was carried out six times in early summer and autumn in 1996 at the K1 site, four times in 1997 at the K2 site and one time in mid-summer in 1997 at the K3 site. In the ploughed

soil at K1 and K2, a new O horizon had been formed on the top of the tilt and the furrow. Beneath the newly formed O horizons, the top 3 cm of the mineral soil were sampled separately because of its darker colour when compared to the soil beneath, which indicated that the soil properties had changed. A detailed description of the tilt-ploughed soils and the order of soil horizons in the soils is given by Tanskanen *et al.* (2004).

## Laboratory analyses

### Soil solution analyses

Soil samples from the undisturbed Podzol profiles and from the ploughed and mounded sites were stored in +5 °C, and soil solution was extracted within 48 h after sampling. The soil samples were centrifuged at 13 000 rpm for 30 min to separate the soil solution. From the driest samples no soil water could be collected, thus the number of soil solution samples for laboratory analysis varied depending on whether soil water could be extracted or not. After centrifuging, the soil samples were refrigerated until further analyses. PO<sub>4</sub>-P in the centrifuged and filtered (pore size 0.45 μm) soil solution was analyzed spectrometrically using a molybdenum blue method (Standardi SFS 2025 1986), total P with ICP-AES, ARL 3580, and the pH of the solution was also determined. The soil solution samples from the zero tension lysimeters and groundwater wells were filtered (pore size 0.45 μm) and analyzed for total P with ICP-AES, ARL 3580.

## Soil analyses

The soil bulk density for the undisturbed Podzols was determined as the mass of oven-dried (105 °C) soil per volume. Poorly crystalline iron ( $\text{Fe}_{\text{ox}}$ ) and aluminium oxides ( $\text{Al}_{\text{ox}}$ ) were extracted with 0.2 M acid (pH 3) ammonium oxalate (Wang 1981). Fresh soil samples were shaken with the oxalate buffer solution (dry soil to solution ratio of 1/50 w/v) for four hours in the dark and filtered. Extracted  $\text{Fe}_{\text{ox}}$  and  $\text{Al}_{\text{ox}}$  were determined using an atomic absorption spectrophotometer (AAS Perkin Elmer 5100). The total organic carbon ( $\text{C}_{\text{tot}}$ ) content was measured using the dry combustion method (Leco CNS 1000).

Forms of inorganic P in each mineral soil horizon of the three undisturbed profiles, and in the O horizon of the OMT site, were characterized by a modified sequential fractionation procedure of Chang and Jackson (Hartikainen 1979). A  $\text{NH}_4\text{Cl}$  solution was used to remove the easily soluble P, a  $\text{NH}_4\text{F}$  solution was assumed to extract the P bound by Al oxides (Al-P), a NaOH solution for the P bound by Fe oxides (Fe-P) and a  $\text{H}_2\text{SO}_4$  solution for the apatitic Ca-bound P (Ca-P). The accuracy of this procedure in separating distinct P forms is discussed in detail by Hartikainen (1979). The fractionated P was analyzed by the molybdenum blue method as above.

P desorption–sorption isotherms were determined by applying the procedure described by Hartikainen (1982). The solution added to the O, E and C horizons contained 0, 0.5, 1.0, 2.5, 5.0, 10.0, 20.0 and 50.0 mg P l<sup>-1</sup> and the solution added to the B1 and B2 horizons 0, 1.0, 2.0, 5.0, 10.0, 20.0, 50.0 and 100.0 mg P l<sup>-1</sup> (made by dissolving  $\text{KH}_2\text{PO}_4$  in water). The moist soil samples were shaken with a P solution (dry soil to solution ratio of 1/40 w/v) in a reciprocating shaker at 180 rpm for one hour and left to equilibrate for 23 hours at 21 °C. Next, the samples were shaken for 10 min at 100 rpm and the solution was filtered through a 0.2- $\mu\text{m}$  membrane filter. The  $\text{PO}_4\text{-P}$  left in the solution phase was analyzed with the molybdenum blue method as above.

## Calculations and statistical analysis

The modified Langmuir equation (Eq. 1) (Har-

tikainen and Simojoki 1997) and Freundlich equation (Eq. 2) (Fitter and Sutton 1975) were fitted to the P sorption data.

$$q = \frac{P_{\text{max}} Kc}{1 + Kc} - q_{0L} \quad (1)$$

$$q = kc^n - q_{0F} \quad (2)$$

where  $q$  is P sorbed (mg g<sup>-1</sup>),  $c$  is P in equilibrium solution (mg l<sup>-1</sup>),  $q_{0L}$  and  $q_{0F}$  are instantly labile P (mg g<sup>-1</sup>),  $P_{\text{max}}$  is a constant describing sorption maximum (mg g<sup>-1</sup>),  $K$ ,  $k$ ,  $n$  are constants.

The intersection point of the isotherm on the concentration axis, i.e. the equilibrium P concentration ( $\text{EPC}_0$ ) at which no net desorption or sorption occurs, was determined graphically using nearest measured points of the intersection in the concentration axis.

The P saturation degree (PSD) of Al oxides was estimated as the molar ratio of  $\text{NH}_4\text{F-P}$  (Al-bound P) to  $\text{Al}_{\text{ox}}$ , and for Fe oxides as the molar ratio of  $\text{NaOH-P}$  (Fe-bound P) to  $\text{Fe}_{\text{ox}}$ . In addition, PSD was calculated for the total amount of Al and Fe oxides in soil (Eq. 3) (Peltovuori *et al.* 2002).

$$\text{PSD} = \frac{[(\text{Labile P}) + (\text{Al-P}) + (\text{Fe-P})]}{0.5(\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})} \quad (3)$$

Spearman's correlation was used to test the correlation between soil solution  $\text{PO}_4\text{-P}$  and soil  $\text{C}_{\text{tot}}$ ,  $\text{Al}_{\text{ox}}$  and  $\text{Fe}_{\text{ox}}$ . Values of  $p$  smaller than 0.05 were considered significant.

## Results

### Inorganic P fractions and P saturation degree of oxides in the undisturbed sites

The B1 and B2 horizons showed an accumulation of Fe and Al, and also  $\text{C}_{\text{tot}}$  in the upper part of the B1 horizon and soil solution pH increased by depth (Table 1).

The highest Fe-P and Al-P concentrations were found in the B1 and the lowest in the E horizons. Fe-P was the dominant fraction in the O, E, B1 and B2 horizons, forming as an average of all sites 45%, 64%, 50% and 45% of the extracted P, respectively (Table 2). Al-P was the second or third most common fraction in the B2

horizon, whereas Ca-P exceeded all other fractions in the C horizons of the VT and MT sites and was the second largest fraction in the E horizons. Easily soluble P formed 30% of the P in the O horizon and 5% in the E horizon, whereas in the deeper horizons its proportion was <0.5%. The total fractionable P was highest in the B1 and B2 horizons, approximately 500  $\mu\text{g g}^{-1}$  and 250  $\mu\text{g g}^{-1}$ , respectively. The corresponding concentrations for the O, E and C horizons were 100, 24 and 160  $\mu\text{g g}^{-1}$ , respectively.

As compared with that in the C horizon, easily soluble (labile) P increased in the E horizon whereas Al-P, Fe-P and Ca-P became depleted (Table 2). In the B1 and B2 horizons, in turn, an enrichment of P into Al- and Fe-bound fractions occurred when compared with the C horizon, but the changes in easily soluble P and Ca-P in those horizons were ambiguous.

When taking into account the varying bulk densities and thicknesses of the horizons, the

pool of fractionable P in the horizons O, E, B1 and B2 amounted to 0.5, 1, 84 and 52  $\text{g m}^{-2}$ , respectively. The corresponding figure for the C horizon, calculated down to the total depth of 50 cm from the mineral soil surface was 47  $\text{g m}^{-2}$ .

The phosphorus saturation degree (PSD) of  $\text{Fe}_{\text{ox}}$  ranged from 3.3% to 25.2%, being the lowest in the O and B2 horizons of the OMT site and highest in the E horizon of the MT site (Table 2). PSD of  $\text{Al}_{\text{ox}}$  was clearly lower, being the lowest in the B1 horizon and highest in the C horizon. PSD for the sum of  $\text{Al}_{\text{ox}}$  and  $\text{Fe}_{\text{ox}}$  indicated a low P saturation degree in all horizons: 6% for the O, and 9%, 3%, 2% and 5% for the E, B1, B2 and C horizons, respectively.

### Phosphorus desorption–sorption properties in the undisturbed sites

P retention in the B1 and B2 horizons was high

**Table 1.** Soil and soil water properties of the undisturbed Podzol horizons (O, E, B1, B2 and C) by site types (OMT, MT and VT). Soil bulk density (BD), total organic carbon ( $\text{C}_{\text{tot}}$ ), oxalate extractable Al ( $\text{Al}_{\text{ox}}$ ) and Fe ( $\text{Al}_{\text{ox}}$ ) were determined from soil samples. The number of soil and centrifuged soil water samples was one for O, E and C horizons and two for the B1 and B2 horizons. Total P concentrations ( $\text{P}_{\text{tot}}$ ) in lysimeter water are presented as mean value  $\pm$  SD over one growing season (number of samples is in parenthesis). Zero tension lysimeters were used to collect water from the O horizon and the samples from E, B and C horizons were obtained with suction lysimeters. Lysimeters were placed in the middle of the B horizon, which is why the value for  $\text{P}_{\text{tot}}$  is shown for the B1 horizon only.

	Soil samples				Centrifuged soil water		Lysimeter soil water $\text{P}_{\text{tot}}$ ( $\mu\text{g l}^{-1}$ )
	BD ( $\text{g cm}^{-3}$ )	$\text{C}_{\text{tot}}$ (%)	$\text{Fe}_{\text{ox}}$ ( $\text{mg g}^{-1}$ )	$\text{Al}_{\text{ox}}$ ( $\text{mg g}^{-1}$ )	$\text{PO}_4\text{-P}$ ( $\mu\text{g l}^{-1}$ )	pH	
OMT							
O	0.10	36.8	2.0	1.7	2814	3.9	268 $\pm$ 107 (25)
E	1.17	1.3	0.2	0.4	160	4.1	203 $\pm$ 61 (43)
B1	1.35	1.5	8.4	20.4	0	5.5	23 $\pm$ 18 (60)
B2	1.35	0.6	5.2	12.4	8	5.9	–
C	1.54	0.1	1.7	2.9	0	6.4	26 $\pm$ 16 (86)
MT							
O	–	–	–	–	6129	3.5	288 $\pm$ 248 (13)
E	0.76	0.8	0.1	0.2	441	4.3	129 $\pm$ 40 (30)
B1	1.31	1.7	5.2	14.7	0	4.8	25 $\pm$ 16 (78)
B2	1.31	0.6	6.1	16.6	0	4.9	–
C	1.42	0.1	0.5	1.5	–	–	34 $\pm$ 32 (34)
VT							
O	–	–	–	–	1005	3.5	101 $\pm$ 60 (28)
E	0.95	0.9	0.2	0.5	123	4.2	171 $\pm$ 50 (63)
B1	1.43	2.1	7.3	39.8	0	5.8	26 $\pm$ 18 (73)
B2	1.43	0.3	4.0	17.2	18	6.2	–
C	1.49	0.1	0.8	2.6	–	–	33

– not measured.

as compared with that in the horizons above and below them (Fig. 2). In the O and E horizons, sorption increased linearly with an increasing equilibrium concentration. The threshold concentration above which net sorption occurred ( $EPC_0$ ) was  $8000 \mu\text{g l}^{-1}$  and  $700 \mu\text{g l}^{-1}$  for the O and E horizons, respectively (Table 3). With lower solution P concentration, P was desorbed from the O and E horizons. In contrast, desorption from the B1, B2 and C horizons was insignificant and sorption started at significantly lower concentrations ( $3\text{--}6 \mu\text{g l}^{-1}$ ) (Table 3). The isotherms for these horizons were non-linear, but the level of maximum sorption ( $P_{\text{max}}$ ) was not achieved at the applied concentration range. As compared with that in the B1 and B2 horizons, sorption by the C horizon was low.

The modified Freundlich (Fitter and Sutton 1975) and Langmuir (Hartikainen and Simojoki 1997) types of equilibrium equations were fitted separately for each soil horizon (Fig. 2) and the corresponding parameters are presented in Table 3. The  $P_{\text{max}}$  showed similar pattern of depth distribution at the OMT and VT sites, where it was

highest for the B1 horizon. However, the MT site showed the highest  $P_{\text{max}}$  for the E horizon.

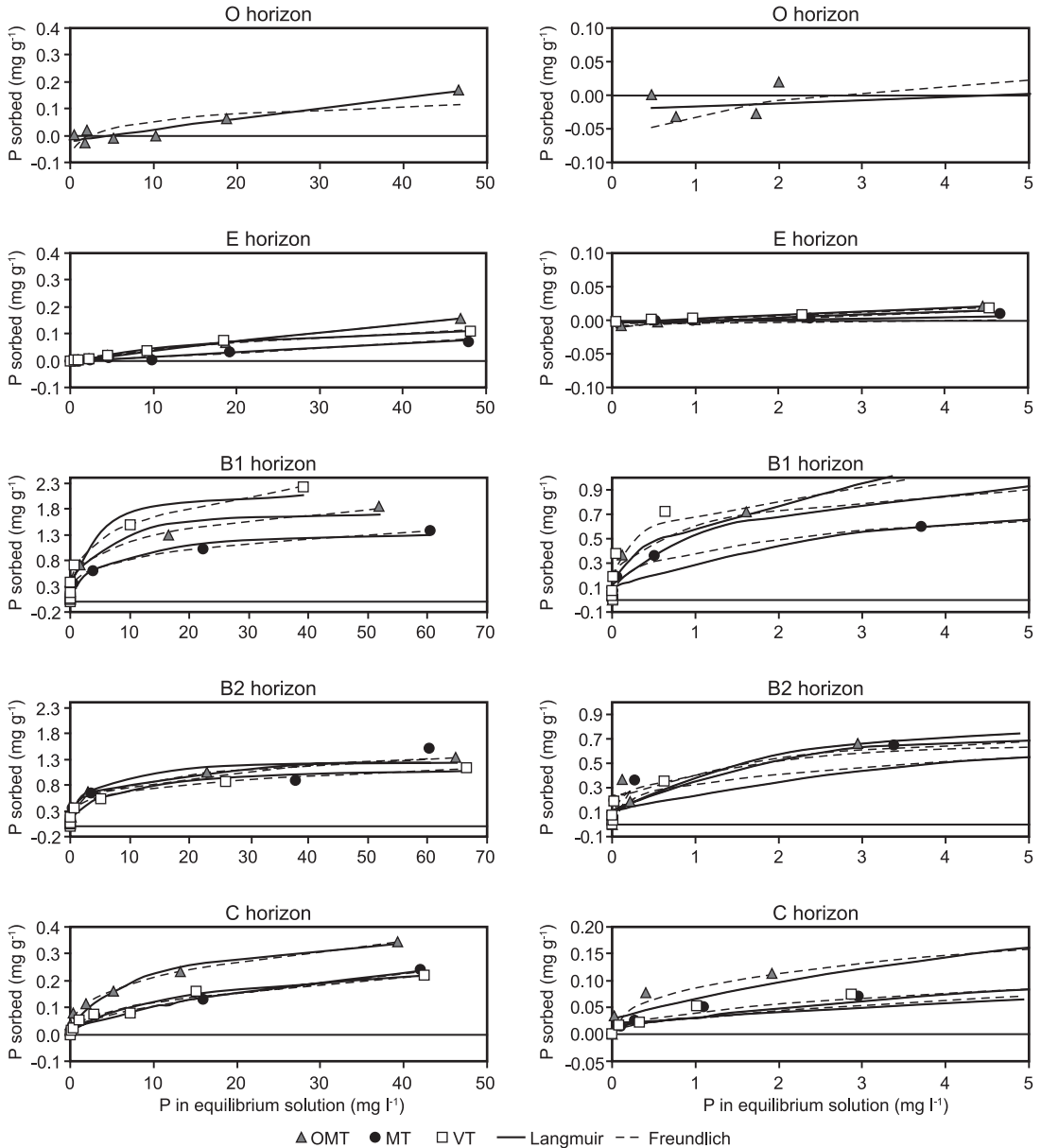
## Soil solution phosphorus concentration

### Undisturbed sites

In the O horizon, the  $\text{PO}_4\text{-P}$  concentration in centrifuged soil solution varied between  $1005$  and  $6100 \mu\text{g l}^{-1}$  and for the E horizon between  $123$  and  $441 \mu\text{g l}^{-1}$  (Table 1). The variation within the same soil horizon between the sites did not correlate with site fertility; the highest concentrations were found at the medium fertile MT site. The average total P concentrations in the lysimeter solutions varied between  $100$  and  $300 \mu\text{g l}^{-1}$  in the O and E horizons and between  $23$  and  $34 \mu\text{g l}^{-1}$  in the B1 and C horizons (Table 1). The lysimeter solution total P concentration in the O horizon of the VT site was lower than that at the two other sites, but no obvious between-site differences were observed for the B1 and C horizons. Especially in the O horizon, the total P

**Table 2.** Inorganic soil P fractions and phosphorus saturation degree (PSD) of Al and Fe compounds of the undisturbed Podzol horizons (O, E, B1, B2 and C) by site types (OMT, MT and VT). O horizon samples were analyzed only from the OMT site. The number of soil samples was one for the O, E and C horizons and two for the B1 and B2 horizons. PSD was calculated as the molar ratio of Al-bound P (Al-P) to oxalate extractable Al ( $\text{Al}_{\text{ox}}$ ), as the molar ratio of Fe-bound P (Fe-P) to oxalate extractable Fe ( $\text{Fe}_{\text{ox}}$ ) and as the molar ratio of the sum of labile P, Al-P and Fe-P to the halved sum of  $\text{Al}_{\text{ox}}$  and  $\text{Fe}_{\text{ox}}$ .

	Inorganic P fractions					PSD		
	Labile P ( $\text{mg kg}^{-1}$ )	Al-P ( $\text{mg kg}^{-1}$ )	Fe-P ( $\text{mg kg}^{-1}$ )	Ca-P ( $\text{mg kg}^{-1}$ )	Sum ( $\text{mg kg}^{-1}$ )	Al-P/ $\text{Al}_{\text{ox}}$ (%)	Fe-P/ $\text{Fe}_{\text{ox}}$ (%)	(Labile P + Al-P + Fe-P) / $0.5(\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})$ (%)
OMT								
O	27	18	44	9	98	0.9	4.0	5.8
E	2	3	23	9	37	0.7	23.0	10.7
B1	0	75	274	171	520	0.3	5.9	2.4
B2	0	69	81	49	199	0.5	3.3	1.8
C	0	38	51	45	133	1.1	5.2	4.1
MT								
E	1	1	11	3	17	0.6	25.2	10.4
B1	1	131	270	114	516	0.8	9.4	4.1
B2	0	73	150	57	280	0.5	5.3	2.4
C	1	24	29	138	192	1.4	10.5	5.6
VT								
E	1	1	12	4	19	0.3	13.2	4.9
B1	1	82	206	211	499	0.2	5.1	1.2
B2	1	46	118	89	254	0.7	5.5	3.3
C	1	20	24	126	170	2.1	5.2	6.3



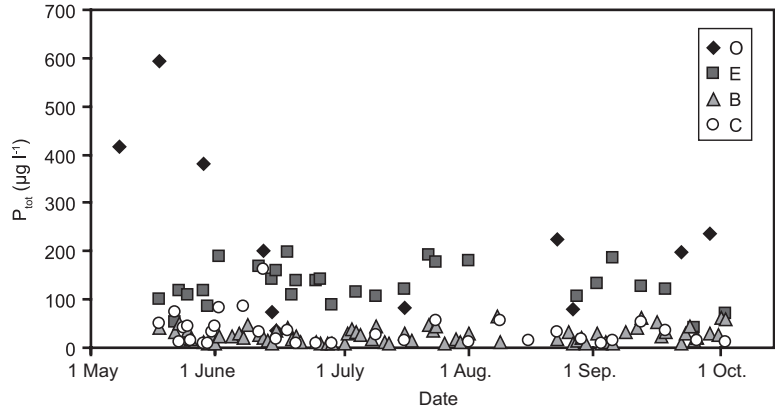
**Fig. 2.** Modified Langmuir and Freundlich equations were fit to measured data to achieve desorption-sorption isotherms for each horizon (O, E, B1, B2 and C) of the Podzol profiles. A different scale in the concentration and sorption axis has been applied for the horizons. On the left, sorption is presented for the whole range of measured equilibrium concentrations. On the right, figures are focused on the equilibrium concentration range of 0–5 mg l<sup>-1</sup>.

concentrations in lysimeter solution were lower than the PO<sub>4</sub>-P in the centrifuged soil solutions.

PO<sub>4</sub>-P in soil water showed negative correlation with the sum of Al<sub>ox</sub> and Fe<sub>ox</sub> in soil ( $r = -0.581$ ,  $p = 0.011$ ,  $n = 18$ ). Significant correlation with C<sub>tot</sub> could not be detected.

With regard to total P concentrations in the soil solution of the different soil horizons, there was no significant variation between the OMT, MT and VT sites. The MT site represented typical variation in the P in the soil solution over one growing season (Fig. 3). The highest concentra-





**Fig. 3.** The seasonal variation of P concentration in lysimeter soil solution in the soil horizons O, E, B and C of the undisturbed Podzol profile at the medium fertile MT site.

tions were found below the O horizon in spring, when the concentrations varied between 400 and 600  $\mu\text{g l}^{-1}$ . Later in the season the concentrations were lower, varying between 100 and 200  $\mu\text{g l}^{-1}$ , and nearly equalling the concentrations found in the eluvial layer. In the B and C horizons, the total P concentrations were almost consistently below 50  $\mu\text{g l}^{-1}$ .

The average  $\text{PO}_4\text{-P}$  concentration of the groundwater wells over one growing season was  $7.2 \pm 7.7 \mu\text{g l}^{-1}$  ( $n = 33$ ), and the average  $\text{PO}_4\text{-P}$

concentration in precipitation  $10.5 \pm 7.5 \mu\text{g l}^{-1}$  ( $n = 8$ ).

**Disturbed (ploughed and mounded) sites**

In all the ploughed and mounded sites the B1 horizon was enriched with  $\text{Fe}_{\text{ox}}$  and  $\text{Al}_{\text{ox}}$ , and the pH increased with soil depth (Tables 4, 5 and 6).

As for the undisturbed soil horizons, the  $\text{PO}_4\text{-P}$  concentrations in the centrifuged soil solu-

**Table 3.** Equilibrium phosphorus concentration ( $\text{EPC}_0$ ) and parameter values of the fitted modified Langmuir equation ( $q_{0L}$ ,  $P_{\text{max}}$  and  $K$ ) and Freundlich equation ( $q_{0F}$ ,  $k$  and  $n$ ) for the undisturbed Podzol horizons (O, E, B1, B2 and C) by site types (OMT, MT and VT). O horizon samples were analyzed only from the OMT site.

	$\text{EPC}_0$ ( $\mu\text{g l}^{-1}$ )	Langmuir fit			Freundlich fit		
		$q_{0L}$ ( $\text{mg g}^{-1}$ )	$P_{\text{max}}$ ( $\text{mg g}^{-1}$ )	$K$	$q_{0F}$ ( $\text{mg g}^{-1}$ )	$k$	$n$
OMT							
O	8305	0.021	1.404	0.003	0.225	0.201	0.138
E	851	0.003	0.935	0.004	0.006	0.007	0.833
B1	4	-0.125	1.671	0.283	0.135	0.764	0.237
B2	6	-0.106	1.188	0.303	0.130	0.605	0.211
C	2	-0.029	0.382	0.105	0.003	0.094	0.357
MT							
E	777	0.003	2.659	0.001	0.001	0.001	1.118
B1	5	-0.101	1.314	0.161	0.086	0.502	0.258
B2	2	-0.112	1.200	0.241	0.066	0.512	0.240
C	5	-0.022	0.456	0.022	-0.009	0.027	0.572
VT							
E	524	0.004	0.181	0.036	0.010	0.014	0.555
B1	9	-0.149	2.061	0.339	0.023	0.773	0.293
B2	2	-0.103	1.058	0.147	0.042	0.409	0.247
C	2	-0.017	0.278	0.062	0.002	0.046	0.423

tion from the ploughed and mounded sites were significantly lower in the mineral soil horizons than in the organic layers (Tables 4, 5 and 6). In the scarified mineral soil layers, the PO<sub>4</sub>-P concentrations in the soil solution were in the same range as measured in the corresponding layers of the non-scarified locations. However, in the top 3 cm of the tilt or furrow the average concentrations at the sites K1 and K2 were higher than in the corresponding unaltered layers (Tables 4 and 5). The soil material of these exposed layers originated from the B1 horizon. The colour of this B<sub>0-3 cm</sub> horizon was darker than the corresponding unaltered layer, but the carbon concentration of this newly formed uppermost mineral soil horizon had not changed significantly.

PO<sub>4</sub>-P in soil water correlated positively with C<sub>tot</sub> ( $r = 0.549$ ,  $p = 0.001$ ,  $n = 160$ ) and a weak

negative correlation could be detected with the sum of Al<sub>ox</sub> and Fe<sub>ox</sub> ( $r = -0.203$ ,  $p = 0.010$ ,  $n = 160$ ).

## Discussion

### P sorption properties of undisturbed profiles

As expected, a sharp distinction between the horizons O and E with low P retention and the B1 and B2 horizons with high P retention was apparent. This is attributable to the considerably higher amount of sorption components (Al and Fe oxides) in the B1 and B2 horizons (*see e.g.* Hingston *et al.* 1967, Li *et al.* 1999). Despite the different origin of the soil material in the O

**Table 4.** Total soil organic carbon (C<sub>tot</sub>), oxalate extractable Al (Al<sub>ox</sub>) and Fe (Fe<sub>ox</sub>), and centrifuged soil water phosphate phosphorus (PO<sub>4</sub>-P), total phosphorus (P<sub>tot</sub>) and pH at site K1 17 years after ploughing. Samples were taken by soil horizons from undisturbed soil, tilt, beneath tilt and furrow. The horizon B<sub>0-3 cm</sub> refers to the top 3-cm subhorizon of the B1 horizon. The different horizons are in the vertical order in which they were found after disturbance. Figures are mean values ± SD and the numbers of samples are given in parentheses.

	Soil samples			Centrifuged soil water		
	C <sub>tot</sub> (%)	Al <sub>ox</sub> (mg g <sup>-1</sup> )	Fe <sub>ox</sub> (mg g <sup>-1</sup> )	PO <sub>4</sub> -P (µg l <sup>-1</sup> )	P <sub>tot</sub> (µg l <sup>-1</sup> )	pH
<b>Undisturbed</b>						
O	23.6 ± 8.1 (6)	1.5 ± 0.6 (6)	2.5 ± 0.9 (6)	275 ± 183 (5)	848 ± 621 (5)	4.0 ± 0.2 (6)
Ah	7.4 ± 2.4 (6)	2.5 ± 0.9 (6)	4.9 ± 1.1 (6)	37 ± 22 (5)	327 ± 198 (3)	4.2 ± 0.3 (5)
B1	2.2 ± 0.6 (18)	8.2 ± 2.0 (18)	6.5 ± 1.5 (18)	5 ± 2 (15)	177 (1)	5.2 ± 0.3 (17)
B2	1.1 ± 0.3 (8)	8.3 ± 1.3 (8)	2.7 ± 0.8 (8)	3 ± 1 (5)	–	5.7 ± 0.3 (5)
C	0.5 ± 0.1 (8)	5.0 ± 0.7 (8)	1.6 ± 0.2 (8)	8 ± 10 (5)	–	5.6 ± 0.2 (5)
<b>Tilt</b>						
O	27.4 ± 8.9 (6)	2.9 ± 1.4 (5)	2.5 ± 1.4 (5)	214 (1)	875 (1)	4.8 (1)
B <sub>0-3 cm</sub>	2.9 ± 0.6 (6)	7.2 ± 0.7 (5)	4.8 ± 0.6 (6)	8 ± 4 (5)	–	4.9 ± 0.2 (5)
B1	2.7 ± 1.4 (11)	7.1 ± 1.5 (11)	5.9 ± 0.7 (11)	4 ± 2 (6)	181 ± 40 (2)	5.0 ± 0.3 (8)
Ah	5.9 ± 1.6 (6)	3.7 ± 1.2 (6)	5.2 ± 0.8 (6)	10 ± 5 (4)	705 (1)	4.2 ± 0.4 (4)
<b>Beneath tilt</b>						
O	19.2 ± 5.8 (5)	2.3 ± 0.4 (6)	3.4 ± 0.5 (6)	103 ± 11 (3)	534 ± 178 (3)	3.6 ± 0.3 (6)
Ah	5.9 ± 0.8 (6)	3.3 ± 1.0 (6)	5.6 ± 0.8 (6)	16 ± 4 (6)	250 ± 59 (5)	4.0 ± 0.3 (6)
B1	1.9 ± 0.6 (17)	7.9 ± 1.6 (17)	6.1 ± 2.0 (17)	3 ± 2 (16)	182 (1)	5.1 ± 0.3 (17)
B2	0.9 ± 0.3 (10)	7.0 ± 1.6 (10)	2.4 ± 0.9 (10)	4 ± 2 (7)	–	5.7 ± 0.3 (7)
<b>Furrow</b>						
O	23.0 ± 12.8 (6)	3.8 ± 1.8 (6)	2.4 ± 1.0 (6)	240 ± 125 (4)	826 ± 450 (4)	4.6 ± 0.5 (4)
B <sub>0-3 cm</sub>	2.7 ± 0.8 (6)	6.4 ± 0.5 (6)	4.1 ± 0.5 (5)	10 ± 6 (5)	–	5.1 ± 0.6 (6)
B1	2.1 ± 0.2 (3)	7.7 ± 0.7 (3)	4.4 ± 1.2 (3)	4 ± 2 (2)	–	5.1 ± 0.2 (3)
B2	1.1 ± 0.5 (12)	7.3 ± 1.3 (12)	2.5 ± 1.1 (12)	4 ± 2 (10)	–	5.6 ± 0.4 (12)
C	0.6 ± 0.2 (9)	5.3 ± 1.5 (9)	1.6 ± 0.4 (9)	4 ± 1 (8)	–	5.7 ± 0.3 (8)

– not measured.

and E horizons, i.e. organic *versus* mineral soil, there were similarities in their P retention properties. The most noticeable difference between the O and E horizons was the higher desorption from the O horizon, indicating the presence of instantly labile P, probably originating from decaying organic matter on the soil surface. The clear-cut performed in the area prior to our study has apparently contributed to this labile pool, as soluble P is easily released from cutting residues left on the site (Stevens *et al.* 1995, Palviainen *et al.* 2004). The low amount of sorption components (i.e. Al<sub>ox</sub> and Fe<sub>ox</sub> on volume basis) and the competition between released organic substances and P for sorption sites (Hartikainen 1979) result in reduced sorption ability of humus following clear-cutting as was shown by Väänänen *et al.* (2007). The low P retention in the O and E hori-

zons suggested that water flowing through these horizons would result in higher P leaching as compared with that caused by percolation vertically through the B horizon.

The Langmuir equation has been widely applied to describe P retention in soil, probably because the parameter  $P_{\max}$  represents the theoretical P sorption maximum in the soil. As could be expected from the between-horizon differences in Al and Fe contents, the  $P_{\max}$  values were highest in the B1 and B2 horizons at the OMT and VT sites. However, the MT site showed the highest  $P_{\max}$  values for the E horizon, where the Al and Fe contents were significantly lower than for the other horizons. Visual interpretation of the isotherms also indicated that the fitting of the Langmuir equation sometimes gave the highest  $P_{\max}$  values for soils where the sorption capacity

**Table 5.** Total soil organic carbon (C<sub>tot</sub>), oxalate extractable Al (Al<sub>ox</sub>) and Fe (Fe<sub>ox</sub>), and centrifuged soil water phosphate phosphorus (PO<sub>4</sub>-P), total phosphorus (P<sub>tot</sub>) and pH at site K2 32 years after ploughing. Samples were taken by soil horizons from undisturbed soil, tilt, beneath tilt and furrow. Horizon B<sub>0-3 cm</sub> refers to the top 3-cm subhorizon of the B1 horizon. The different horizons are in the vertical order in which they were found after disturbance. Figures are mean values ± SD and the numbers of samples are given in parentheses.

	Soil samples			Centrifuged soil water		
	C <sub>tot</sub> (%)	Al <sub>ox</sub> (mg g <sup>-1</sup> )	Fe <sub>ox</sub> (mg g <sup>-1</sup> )	PO <sub>4</sub> -P (µg l <sup>-1</sup> )	P <sub>tot</sub> (µg l <sup>-1</sup> )	pH
<b>Undisturbed</b>						
O	36.6 ± 7.8 (5)	5.8 ± 2.7 (5)	2.6 ± 1.0 (5)	234 ± 172 (3)	813 ± 195 (4)	3.8 ± 0.2 (4)
E	1.2 ± 0.1 (4)	0.9 ± 0.3 (5)	1.1 ± 0.8 (5)	17 ± 9 (4)	180 ± 94 (5)	4.5 ± 0.2 (5)
B1	5.0 ± 7.7 (12)	12.2 ± 3.2 (15)	13.4 ± 10.0 (15)	4 ± 2 (12)	100 ± 62 (15)	5.1 ± 0.3 (15)
B2	1.3 ± 1.8 (8)	8.5 ± 5.3 (10)	3.9 ± 4.5 (10)	2 ± 1 (6)	40 ± 43 (10)	5.3 ± 0.3 (10)
C	0.3 ± 0.2 (4)	4.9 ± 2.7 (5)	2.8 ± 1.7 (5)	–	16 ± 0 (2)	5.4 ± 0.2 (2)
<b>Tilt</b>						
O	43.4 ± 6.8 (2)	2.1 ± 1.1 (4)	1.9 ± 1.0 (4)	1988 ± 1156 (3)	3878 ± 2 207 (3)	4.0 ± 0.6 (3)
B <sub>0-3 cm</sub>	4.8 ± 1.2 (3)	12.0 ± 2.5 (4)	8.7 ± 2.1 (4)	14 ± 7 (3)	212 ± 65 (3)	4.8 ± 0.1 (4)
B1	4.3 ± 0.8 (3)	16.5 ± 3.0 (4)	13.6 ± 3.9 (4)	–	78 ± 18 (2)	4.7 ± 0.0 (2)
E	2.5 ± 0.4 (4)	1.8 ± 1.2 (4)	2.0 ± 1.9 (4)	14 ± 4 (2)	184 ± 131 (2)	4.1 ± 0.3 (4)
<b>Beneath tilt</b>						
O	32.9 ± 5.5 (3)	3.6 ± 1.5 (4)	1.9 ± 0.5 (4)	103 ± 78 (2)	410 ± 181 (2)	3.8 ± 0.2 (3)
E	1.6 ± 0.1 (3)	0.8 ± 0.2 (4)	1.0 ± 0.8 (4)	30 ± 21 (3)	244 ± 90 (3)	4.3 ± 0.2 (4)
B1	2.8 ± 1.5 (12)	15.6 ± 5.4 (13)	12.5 ± 7.7 (13)	5 ± 1 (8)	67 ± 35 (9)	5.0 ± 0.2 (12)
B2	0.5 ± 0.1 (4)	5.0 ± 1.0 (5)	2.0 ± 0.3 (5)	4 ± 0 (2)	27 ± 7 (5)	5.4 ± 0.2 (5)
C	0.2 (1)	2.7 ± 0.7 (2)	1.5 ± 0.5 (2)	4 (1)	103 (1)	5.3 (1)
<b>Furrow</b>						
O	44.2 ± 0.3 (3)	10.0 ± 3.0 (4)	2.6 ± 1.3 (4)	106 ± 98 (4)	623 ± 314 (4)	4.3 ± 0.1 (4)
B <sub>0-3 cm</sub>	2.8 ± 0.5 (3)	9.9 ± 1.6 (4)	7.2 ± 3.8 (4)	11 ± 6 (3)	148 ± 41 (4)	5.0 ± 0.1 (4)
B1	1.5 ± 1.2 (8)	9.0 ± 3.3 (8)	5.0 ± 3.6 (8)	6 ± 4 (5)	66 ± 37 (8)	5.1 ± 0.1 (8)
B2	0.3 ± 0.1 (7)	4.6 ± 2.2 (7)	2.0 ± 0.5 (7)	3 ± 0 (4)	25 ± 13 (7)	5.2 ± 0.2 (7)

– not measured.

was actually the lowest. In the B1, B2 and C horizons sorption appeared to approach  $P_{\max}$ , whereas the sorption in the E and O horizons increased linearly without any saturation tendency. This lack of saturation is probably the explanation for why the Langmuir equation failed to result in reliable estimates for maximum sorption in these horizons. Therefore, the parameter value  $P_{\max}$  of the Langmuir equation may be a reliable estimate of maximum P retention only for the B1, B2 and C horizons. The modified Langmuir equation sometimes produced negative values of the parameter  $q_{0L}$  (instantly labile P), which also indicates that the parameter values obtained with the Langmuir equation are not necessarily reasonable estimates of soil P sorption. The problems were less obvious when a modified Freundlich equation was fitted to the data but according to the study by Peltovuori (2007) the confidence levels of the parameter values obtained with the Freundlich equation may be wide and therefore the interpretation of the outcome should also be made with caution.

The phosphorus saturation degree (PSD) of Al and Fe oxides and hydroxides in the soil (the molar ratio of Al-P to  $Al_{ox}$  and Fe-P to  $Fe_{ox}$ ) was low in all Podzol horizons indicating considerable potential to retain further P inputs. However, the sorption–desorption isotherms indicated that the O and E horizons had no P retention capacity at all at the concentration ranges typically occurring in nature. It has been suggested that  $0.5(Al_{ox} + Fe_{ox})$  would represent a hypothetical maximum for the P sorption capacity, and already a saturation of 20% of this capacity may indicate saturated soil (Beauchemin & Simmard 1999, Peltovuori *et al.* 2002) but calculating the P saturation as  $(\text{labile P} + \text{Al-P} + \text{Fe-P})/0.5(Al_{ox} + Fe_{ox}) \times 100$  (%) (Peltovuori *et al.* 2002) still gave much higher P sorption potential than was indicated by the isotherms. Therefore, we conclude that the P saturation degree may not be a suitable index for the available P retention capacity of forest soil.

Even though the use of the parameter values of the fitted sorption equations and phosphorus saturation degree index may have its limits in

**Table 6.** Total soil organic carbon ( $C_{tot}$ ), oxalate extractable Al ( $Al_{ox}$ ) and Fe ( $Fe_{ox}$ ) and centrifuged soil water phosphate phosphorus ( $PO_4\text{-P}$ ), total phosphorus ( $P_{tot}$ ) and pH at site K3 4 years after mounding. Samples were taken by soil horizons from undisturbed soil, tilt, beneath tilt and furrow. Horizon  $B_{0-3\text{ cm}}$  refers to the top 3-cm subhorizon of the B1 horizon. The different horizons are in the vertical order in which they were found after disturbance. Figures are mean values  $\pm$  SD and the numbers of samples are given in parentheses.

	Soil samples			Centrifuged soil water		
	$C_{tot}$ (%)	$Al_{ox}$ ( $mg\ g^{-1}$ )	$Fe_{ox}$ ( $mg\ g^{-1}$ )	$PO_4\text{-P}$ ( $\mu g\ l^{-1}$ )	$P_{tot}$ ( $\mu g\ l^{-1}$ )	pH
<b>Undisturbed</b>						
O	36.9 $\pm$ 7.8 (2)	0.8 $\pm$ 0.2 (2)	1.1 $\pm$ 0.4 (2)	3079 (1)	4719 $\pm$ 388 (2)	4.3 $\pm$ 0.1 (2)
Ah	5.8 (1)	1.8 $\pm$ 1.2 (2)	2.3 $\pm$ 2.1 (2)	33 $\pm$ 37 (2)	336 (1)	4.3 (1)
B1	1.6 $\pm$ 0.7 (3)	7.8 $\pm$ 0.8 (3)	5.1 $\pm$ 1.0 (3)	6 $\pm$ 1 (3)	33 $\pm$ 15 (3)	4.8 $\pm$ 0.2 (3)
B2	0.6 (1)	4.9 (1)	1.8 (1)	5 (1)	17 (1)	5.1 (1)
<b>Tilt</b>						
$B_{0-3\text{ cm}}$	1.7 $\pm$ 0.1 (2)	8.3 $\pm$ 2.1 (2)	6.5 $\pm$ 1.2 (2)	6 (1)	20 (1)	5.6 (1)
Ah	3.7 (1)	3.3 (1)	3.5 (1)	–	–	–
<b>Beneath tilt</b>						
O	19.1 (1)	2.6 (1)	3.0 (1)	–	1608 (1)	4.0 (1)
Ah	6.2 (1)	1.9 $\pm$ 1.2 (2)	2.7 $\pm$ 2.0 (2)	34 $\pm$ 33 (2)	312 (1)	4.3 (1)
B1	2.0 (1)	7.8 $\pm$ 2.7 (2)	5.9 $\pm$ 4.3 (2)	5 $\pm$ 1 (3)	25 $\pm$ 14 (3)	5.3 $\pm$ 0.3 (3)
B2	–	3.8 $\pm$ 1.1 (2)	2.0 $\pm$ 0.8 (2)	3 $\pm$ 0 (2)	19 $\pm$ 4 (2)	5.6 $\pm$ 0.1 (2)
<b>Furrow</b>						
$B_{0-3\text{ cm}}$	–	6.6 (1)	4.0 (1)	4 (1)	29 (1)	5.5 (1)
B1	0.4 (1)	5.6 $\pm$ 1.5 (2)	3.1 $\pm$ 0.7 (2)	3 $\pm$ 1 (2)	16 $\pm$ 0 (2)	6.0 $\pm$ 0.3 (2)
B2	0.1 $\pm$ 0.0 (2)	1.8 $\pm$ 0.5 (2)	1.2 $\pm$ 0.4 (2)	6 $\pm$ 2 (2)	16 $\pm$ 0 (2)	6.4 (1)

– not measured.

describing P retention in soil, some of the laboratory measurements can be applied to describe the differences in P retention or release potential between Podzol horizons. For example, the  $EPC_0$  value, i.e. the change from desorption to sorption in the adsorption isotherms can be used as an estimate of the threshold concentration of P in soil water above which a soil starts to retain dissolved P. The soluble P concentrations in centrifuged O horizon soil water were within the same range as concentrations determined from a percolate beneath the O horizon after clear-cutting (Pirainen *et al.* 2004). According to the isotherm data, if a solution with such P concentrations percolates through the E horizon, the P concentration would remain almost unchanged, whereas a further percolation through the B1 and B2 horizons would reduce the concentration to approximately  $3\text{--}30 \mu\text{g l}^{-1}$ . Comparison of these estimates with the P concentrations from centrifuged soil water and suction lysimeter data suggested that laboratory measurements underestimated the retention in the E horizon, but reliably predicted the retention in the B horizon. An explanation could be that the isotherms measure only chemical sorption, which is the main P retention process in the B1 and B2 horizons, but ignore the biological assimilation of P, which has a larger impact on P removal from solution phase in the E horizon (Wood *et al.* 1984).

### Inorganic P fractions in undisturbed profiles

As compared with those in the C horizon, the Al-P, Fe-P and Ca-P fractions decreased in the E horizon, but only the Al-P and Fe-P fractions increased in the B1 and B2 horizons. Under acidic conditions, such as those prevailing in the B1 and B2 horizons, the high concentrations of Al and Fe favour P retention on oxide surfaces (Sample *et al.* 1980). Of the oxide-bound fractions, Fe-P was more abundant even though Fe oxides and hydroxides in the B1 and B2 horizons were less common than Al. This preference for the formation of Fe-P apparently prevails in acid Fe-rich soils (Kaila 1965). Moreover, the proportion of Fe-P can increase over time as a result of a shift from Al-P to more stable forms of Fe-P

(Chang and Chu 1961, Kaila 1965, Aura 1980). In the C horizon, the high proportion of Ca-P as compared with that of Fe-P and Al-P can be interpreted as being indicative of a low degree of weathering (Walker and Syers 1976, Peltovuori *et al.* 2002) and large total storage of unweathered P in the soil.

The sum of the measured P fractions in all the horizons was lower than the average total P in till soils in Finland,  $750 \mu\text{g g}^{-1}$  (The Geochemical Atlas of Finland 1992), indicating that the fractionation method extracts only a part of the total P in the soil. The part that was not extracted probably consists of the remaining apatite in the mineral matrix, organic P and reductant soluble and occluded P (*see* Walker and Syers 1976).

### P in soil solution in undisturbed and in disturbed sites

In the undisturbed sites, the phosphate ( $\text{PO}_4\text{-P}$ ) concentrations in centrifuged water samples of the O horizon were more than 30-fold higher than the total P concentrations in zero tension lysimeters from the respective horizon. One probable explanation for this is that the P concentrations in zero tension lysimeters are diluted by the relatively unchanged precipitation water (with low phosphate concentrations) that percolates through large pores and channels, while the centrifuged samples represent more the actual soil solution in smaller soil pores, where the soil solution P concentrations are more strongly influenced by the exchange reactions between solid phase and solution.

In the soil horizons of scarified and mounded sites, the distribution of soil solution P was similar to that in the undisturbed sites, i.e. high P concentrations in the O, E or Ah horizons with low Al and Fe and low soil water P in the Al- and Fe-rich B1, B2 and C horizons irrespective of whether these horizons were in reversed order or buried. The slight increase in soil solution P in the top 3 cm soil on tilt and on furrow suggests that the P retention properties of the B1 horizon turned on a soil surface may slowly change towards those of the E or Ah horizon. The difference between  $\text{PO}_4\text{-P}$  and  $P_{\text{tot}}$  in centrifuged soil solutions suggests that significant part of P in

soil solution is in an organic form, which is typically determined as the difference between  $P_{\text{tot}}$  and  $PO_4\text{-P}$  (e.g. Olsen and Sommers 1982).

At all the studied sites, the more the horizon contained the P sorbing Al and Fe components the lower the P concentration in the soil solution was. This connection was less clear in the disturbed sites and P in the soil solution also depended on the soil carbon content. The disturbed sites contained more carbon in the soil, which is partly explained by the differences in the soil types but mostly because organic matter had been mixed in the profile. This suggests that if soil Al and Fe are not altered, soil preparation as such has little impact on P in the soil solution and thus soil P retention properties of Podzol horizons. However, soluble P in soil may increase if the mineralization of soil organic matter is increased by site preparation.

### Representativeness of the results

In all site types the distribution of carbon, oxalate extractable Fe and Al and soil solution pH was typical for Podzol profiles. Soils in this study represented forest site types that comprise approximately 74% of the forest land in Finland (Finnish Statistical Yearbook of Forestry 2005). In addition, soil physical and chemical properties, such as horizon thickness, total inorganic carbon, Al, Fe and P content and distribution in the studied profiles was similar to previously studied Podzols in the Nordic countries (Kubin 1983, Tamminen and Starr 1990, Westman 1990, Land *et al.* 1999, Melkerud *et al.* 2000), which renders our conclusions applicable for a wider range of Podzols than studied here; however, more data are needed especially to confirm parameter values of sorption equations and their relation with soil properties.

### Conclusions

The P retention potential of the Podzol profile is large and mostly attributed to the B horizon. Therefore, if water flows in contact with the B horizon the risk of P leaching is minor. However, in the case of lateral flow through the O and

E horizons the reduction in P concentration in discharge water is limited. An increased P load after clear-cutting may increase the P saturation degree in the O and E horizons, but the effects of clear-cutting on the B horizon are negligible. The soil solution P concentration is not significantly increased even if the soil profile is turned upside down and new mineral soil layers are exposed. However, the accumulation of litter on top of soil starts to change the properties of the exposed B horizon to resemble those of the eluvial layer.

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