Inorganic and Organic Phosphorus Fractions in Peat from Drained Mires in Northern Finland

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Soil samples from 15 eutrophic, 26 herb-rich, 15 tall-sedge, and 11 low-sedge drained peatland sites were analysed for easily soluble and aluminum, iron, and calcium bound phosphorus (P) using the Chang and Jackson sequential fractionation method. Compared to earlier investigations, where only total and easily soluble P contents (e.g. NH_4OAc or dilute H_2SO_4 extractable P) in peat have been analysed, significantly higher differences between sites were observed. The eutrophic sites were characterized by four to six-fold greater Ca-bound organic P and two to three-fold greater Ca-bound inorganic P contents than on the other three site type groups, whereas the average Al-bound inorganic P content of the eutrophic sites was only one-third of that at the other site types. Substantial differences between sites were also observed for Fe-bound inorganic P, i.e. two to four-fold greater Fe-P contents were measured at the herb-rich sites compared with the other three site type groups. The stand volume growth in the 67 studied drained peatland sites correlated significantly with Al-bound organic P and Fe-bound inorganic and organic P. The study showed that a detailed fractionation and discrimination of different forms of soil P is important in increasing the understanding of the relationship between P availability and vegetation community types and stand growth on drained peatlands.

Keywords drained peatland forests, phosphorus availability, sequential fractionation, site type classification, tree growth
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1 Introduction

The total area of peatlands and paludified mineral soils in Finland is about 10 million hectares or about one third of the total land area. Over half of this area has been drained for forestry purposes. The drainage has increased the wood resources by >200 mill. m^3 and the annual volume increment by >10 mill. m^3 (Tomppo 1999, Nuutinen et al. 2000, Hökkä et al. 2002). Although the drainage effect generally has been satisfactory, unexpectedly low post-drainage production rates have also been observed, especially in North Finland (Keltikangas et al. 1986).

It has been shown that the production capacity of the tree stand after drainage strongly relates to the original site type (Lukkala 1929, 1937, 1951, Heikurainen 1959, Seppälä 1969, Keltikangas et al. 1986), varying between about 1 $m^3 ha^{-1} yr^{-1}$ (low-sedge and other nutrient-poor ombro-oligotrophic site types) and >7 $m^3 ha^{-1} yr^{-1}$ (the most fertile herb-rich and eutrophic site types). It has long been known that phosphorus is one key-nutrient for satisfactory tree growth on drained peatlands and numerous attempts have been made to explain the differences in tree stand productivity on different site types by their peat P content (Vahtera 1955, Holmen 1964, Valk 1973, Starr and Westman 1978, Westman 1981). Clarification of the relationship between peat P contents and the growth potential of different site types has also been considered important for formulating fertilization instructions for drained peatland forests (Starr and Westman 1978, Heikurainen 1982).

Generally, relatively small differences in the peat P contents between different site type groups have been observed. It has also been found that the correlation between peat P content and stand growth is fairly low (Holmen 1964, Paarlahti et al. 1971, Mannerkoski 1973, Kaunisto and Paavilainen 1988). However, so far only total and easily soluble soil P (e.g. NH_4OAc or dilute H_2SO_4 extractable P) contents have been studied. To better understand the differences in bioavailability of peat P between sites of different fertility, information on biogeochemically important P fractions, such as Al-, Fe- and Ca-bound P, is also needed.

The sequential fractionation procedure (Chang and Jackson 1957, Hedley et al. 1982) has been widely used to investigate the chemical forms of P in soil. In the fractionation procedure, progressively more aggressive extractants are used to remove the different forms of soil inorganic and organic P. In this study, we used the sequential P fractionation procedure to determine the differences in peat P fractions and P availability to trees between drained peatlands of differing fertility.

2 Material and Methods

2.1 Study Sites

For the study, a total of 67 sites were selected from the group of peatland sites, known as the SINKA sites in Finland. The SINKA sites were established in 1984–1987 in North Finland to study the growth of peatland forests and related ecological factors.

The SINKA sites were sub-sampled from the data set of the 7th National Forest Inventory of Finland by applying a specific procedure of stratified systematic sampling (for further details, see Penttilä and Honkanen 1986, Hökkä et al. 1997). The main criteria in the set-up of a SINKA site that had to be fulfilled were that three circular plots 40 m apart from each other should have the same site trophic level (using Huikari's (1952) classification system with 6 levels), similar stand development state and history concerning cuttings, drainage etc. The sites that had been drained for forestry but were considered too poor in nutrients for satisfactory tree production by present requirements were rejected.

For studying peat P fractions, the SINKA sites representing oligotrophic (low-sedge types), oligo-mesotrophic (tall-sedge types), mesotrophic (herb-rich types), and eutrophic types were selected (Table 1). However, sites where any kind of fertilizer had been applied during the last 15 years were rejected. Further, sites where any kind of cuttings had been applied during the last 10 years and undrained, pristine sites and those near the regeneration stage were rejected.

For each of the three plots at each site, the peatland site type was determined according to Heikurainen and Pakarinen (1982) using the original, undrained site type. On 57 of the 67 sites there

Table 1. Background information on study sites.

Site type [a)]	Site	Dominant [b)] tree species	Stand volume, $m^3 ha^{-1}$	Stand growth, $m^3 ha^{-1} yr^{-1}$	N_{tot}, % [c)] 5–10 cm peat layer	P_{tot}, % [c)] 5–10 cm peat layer	Peat depth, cm
Eutrophic types							
Eutrophic paludified hardwood-spruce forest	1	P.a.	166	4.8	1.8	0.14	41
	2	P.a.	38	3.2	2.6	0.13	34
	3	P.a.	214	2.0	2.2	0.10	28
Eutrophic hardwood-spruce fen	4	P.a.	15	1.6	2.1	0.12	>100
	5	P.a.	39	2.3	2.3	0.14	98
	6	P.a.	33	4.2	2.4	0.12	>100
	7	P.a.	189	6.7	2.2	0.16	15
	8	P.a.	33	1.4	2.3	0.12	>100
	9	P.a.	27	1.7	2.1	0.08	45
Eutrophic birch fen	10	B.p.	100	4.4	2.8	0.15	>100
Eutrophic pine fen	11	P.s.	24	1.6	2.0	0.17	62
	12	P.s.	62	1.4	3.1	0.11	67
	13	P.s.	7	1.7	2.9	0.08	83
	14	P.s.	34	1.9	3.0	0.16	>100
	15	P.s.	43	4.7	2.4	0.09	>100
Herb-rich types							
Herb-rich hardwood-spruce swamp	16	B.p.	12	2.2	2.5	0.15	57
	17	B.p.	30	3.0	2.7	0.20	57
	18	P.a.	143	7.0	2.3	0.17	26
	19	P.a.	39	2.4	2.7	0.16	55
Herb-rich sedge hardwood-spruce fen	20	P.s.	148	7.3	1.5	0.15	17
	21	B.p.	79	3.9	2.3	0.13	30
	22	B.p.	88	4.5	2.8	0.13	>100
	23	B.p.	17	2.5	2.7	0.14	>100
	24	B.p.	34	2.7	1.5	0.11	>100
	25	B.p.	188	5.3	0.9	0.15	>100
	26	B.p.	62	1.9	2.4	0.11	>100
	27	B.p.	77	3.3	2.4	0.14	>100
Herb-rich sedge birch-pine fen	28	P.s.	54	3.2	2.5	0.20	37
	29	p.s.	118	5.8	2.0	0.12	>100
	30	P.s.	130	7.4	2.2	0.13	>100
	31	P.s.	93	4.2	1.9	0.13	>100
	32	P.s.	137	7.6	2.4	0.18	>100
	33	P.s.	35	4.6	2.3	0.10	>100
	34	P.s.	15	0.5	2.7	0.11	>100
	35	P.s.	72	1.8	2.8	0.13	>100
	36	P.s.	112	2.7	3.0	0.12	>100
	37	P.s.	33	2.7	2.0	0.09	85
	38	P.s.	98	7.0	2.8	0.20	63
	39	P.s.	19	0.8	2.3	0.12	85
	40	P.s.	26	1.5	3.0	0.13	>100
	41	P.s.	87	4.1	2.3	0.17	>100

Table 1 continued.

Site type[a)]	Site	Dominant[b)] tree species	Stand volume, $m^3 ha^{-1}$	Stand growth, $m^3 ha^{-1} yr^{-1}$	N_{tot}, %[c)] 5–10 cm peat layer	P_{tot}, %[c)]	Peat depth, cm
Tall-sedge types							
Tall-sedge hardwood-spruce fen	42	P.s.	52	3.2	1.8	0.09	70
Tall-sedge pine fen	43	P.s.	26	2.8	2.0	0.13	33
	44	P.s.	28	2.9	1.9	0.10	73
	45	P.s.	63	3.5	2.4	0.10	>100
	46	B.p.	12	2.5	1.6	0.12	69
	47	P.s.	18	1.5	2.2	0.11	60
	48	P.s.	22	1.6	2.1	0.11	>100
	49	P.s.	9	0.7	2.0	0.12	>100
	50	P.s.	17	1.2	2.3	0.12	>100
	51	P.s.	48	4.0	2.5	0.14	>100
	52	P.s.	77	4.0	2.4	0.17	31
	53	P.s.	27	0.8	2.2	0.13	>100
	54	P.s.	23	1.1	2.0	0.09	95
Tall-sedge fen	55	P.s.	52	3.5	1.8	0.10	>100
	56	B.p.	21	1.1	2.5	0.20	75
Low-sedge types							
Carex globularis pine swamp	57	P.s.	9	0.5	0.8	0.06	30
	58	P.s.	8	1.0	1.5	0.10	70
	59	P.s.	50	2.2	1.9	0.12	46
	60	P.s.	4	0.7	1.1	0.07	55
	61	P.s.	22	2.2	2.3	0.16	36
Cottongrass-sedge pine fen	62	P.s.	47	2.2	2.0	0.11	>100
	63	P.s.	45	3.1	1.4	0.12	51
	64	P.s.	8	1.2	0.9	0.05	>100
	65	P.s.	28	1.8	1.5	0.08	100
	66	P.s.	54	2.0	2.3	0.15	28
Low-sedge *Sphagnum papillosum* pine fen	67	P.s.	7	0.7	2.7	0.10	>100

a) Nomenclature according to Laine and Vasander (1996).
b) P.s. = *Pinus sylvestris* L., P.a. = *Picea abies* Karst., B.p. = *Betula pubescens* Ehrh.
c) Methods used (Halonen et al. 1983):
N_{tot}; the Kjeldahl method
P_{tot}; dry digestion in HCl and colorimetric determination

were no differences in peatland site type between the three plots. However, on 10 sites one plot had different site type characteristics than the other two and was therefore excluded.

Stand characteristics were measured at intervals of 5 years and stem volume and annual volume increment was computed for each plot and the entire SINKA site using the KPL-software package by Metla (Heinonen 1994). For details of site and tree measurements, see Penttilä and Honkanen (1986) and Hökkä et al. (1997). From each plot on the selected 67 SINKA sites, peat samples were collected from 5 systematically located sampling positions. The peat samples were taken from the lawn surface, not from hollows or hummocks. The sample cores were cut to represent the layer of 5–10 cm below the soil surface, defined as the lower limit of the living (green) ground vegetation, and combined to form a composite sample for each plot. Finally, the

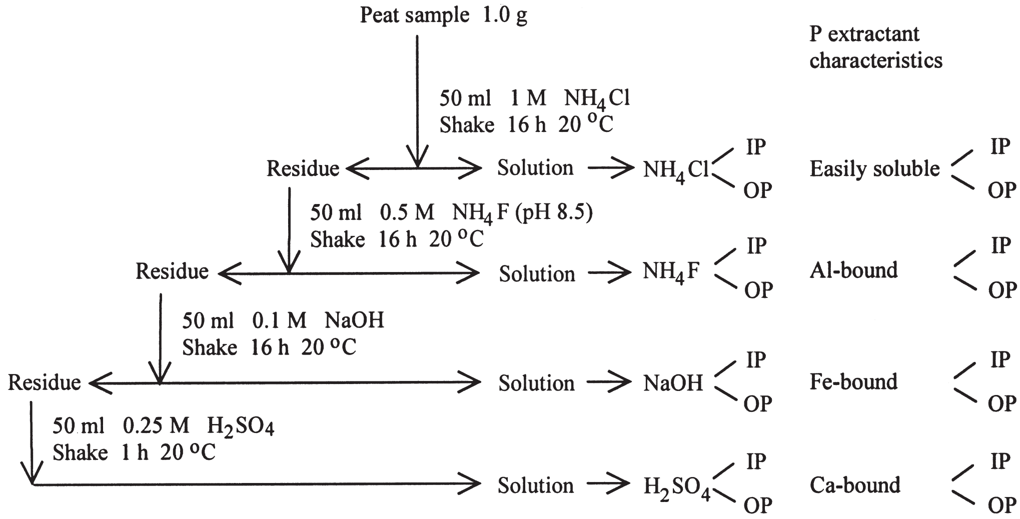

Fig. 1. Flow chart of the fractionation of peat phosphorus into various inorganic (IP) and organic (OP) fractions.

samples from the different plots were combined to represent the entire SINKA site.

2.2 Laboratory Analyses and Calculations

The peat samples were dried to a constant mass at 60 °C and homogenized in a stainless steel mill (sieve mesh diameter 2 mm). Peat P was fractionated into easily soluble, and Al-, Fe-, and Ca-bound forms according to the procedure of Chang and Jackson (1957). This involved sequential extraction of 1.0 g peat with 50 ml of 1 M NH_4Cl, 0.5 M NH_4F, 0.1 M NaOH, and 0.25 M H_2SO_4. The pH of the NH_4F reagent was adjusted to 8.5 according to Fife (1959). In each step of the fractionation procedure, both inorganic (IP) and organic P (OP) were extracted. The IP content of each extract was determined by the modified molybdenum blue method (Kaila 1955). The humus in the NH_4F extracts interfering with the colorimetric determination of P was removed according to the method of Hartikainen (1979). Total P (TP) was determined with ascorbic acid method after potassium peroxodisulphate digestion (Vesihallinnon analyysimenetelmät 1981). The organic P was calculated by difference TP-IP. The flow chart of the fractionation procedure and the resulting P fractions, along with their hypothetical availability, are presented in Fig. 1.

The data were tested for the significance of differences in different P fractions between the sites of different site type by one-way-analysis of variance and Tukey's test. Simple Pearson correlation analysis was used to examine the dependence of tree growth on peat P fractions.

3 Results

Minor differences occurred in total P in peat between the studied peatland site type groups (see P_{tot} in Table 1). The average P_{tot} concentration was about 0.12% at both the eutrophic and tall-sedge sites sites, 0.14% at the herb-rich sites, and about 0.10% at the low-sedge types. In contrast, major differences occurred in different P fractions between site type groups (Table 2). The eutrophic sites were characterized by four to six-fold greater $H_2SO_{4\text{-}OP}$ and two to three-fold greater $H_2SO_{4\text{-}IP}$ concentrations than the other three site types, whereas the $NH_4F_{\text{-}IP}$ content of the eutrophic sites averaged to only one-third of that at the other site types. The NaOH extractable P contents were particularly high for the herb-

Table 2. Mean P fractions ($mg\,kg^{-1}$) ± s.e. in peat from different site type groups. Means followed by the same letter are not significantly different ($P>0.05$). For different fractions, see Fig. 1.

	Eutrophic sites	Herb-rich sites	Tall-sedge sites	Low-sedge sites
NH_4Cl_{-IP}	19 ± 8a	17 ± 6a	33 ± 8a	67 ± 10
NH_4Cl_{-OP}	13 ± 2a	16 ± 2a	13 ± 2a	15 ± 2a
NH_4F_{-IP}	18 ± 10	57 ± 7a	61 ± 10a	68 ± 12a
NH_4F_{-OP}	47 ± 12a	94 ± 9b	89 ± 12b	67 ± 14ab
$NaOH_{-IP}$	31 ± 13a	123 ± 10	64 ± 13a	48 ± 15a
$NaOH_{-OP}$	159 ± 15a	220 ± 11b	209 ± 15b	139 ± 17a
H_2SO_{4-IP}	42 ± 6	20 ± 4a	15 ± 6a	24 ± 7a
H_2SO_{4-OP}	71 ± 8	16 ± 6a	18 ± 8a	11 ± 10a

Table 3. Correlation coefficients between peat P fractions and stand growth. Coefficients followed by ** are statistically significant ($P<0.01$). For different fractions, see Fig. 1.

	Growth
NH_4Cl_{-IP}	–0.19
NH_4Cl_{-OP}	0.15
NH_4F_{-IP}	0.18
NH_4F_{-OP}	0.40**
$NaOH_{-IP}$	0.37**
$NaOH_{-OP}$	0.35**
H_2SO_{4-IP}	–0.08
H_2SO_{4-OP}	–0.12

rich types, i.e. two to four-fold greater $NaOH_{-IP}$ contents were measured compared to the other three site type groups. The tall-sedge types were not characterized by particularly high contents of any of the eight P fractions, but significant differences from one or two of the other three site type groups were observed for all other P forms besides NH_4Cl_{-OP}. The low-sedge types had two to four-fold greater NH_4Cl_{-IP} contents than the other three site types.

Correlation analysis showed that the stand volume growth in the 67 drained peatland sites in the present study most strongly correlated to NH_4F extractable (Al-bound) OP (Table 3). High and statistically significant correlations were also observed for NaOH extractable (Fe-bound) IP and OP. However, neither the NH_4Cl nor the H_2SO_4 extractable soil P contents correlated with stand growth.

4 Discussion

The differences in peat P contents between the peatland site types in this fractionation study were significantly higher than in earlier investigations, where only differences in total P or easily soluble P between the sites had been studied (Vahtera 1955, Holmen 1964, Valk 1973, Starr and Westman 1978, Westman 1981). This indicates that the detailed fractionation and discrimination of different forms of soil P is important in increasing the understanding of the relationship between vegetation community types and P availability.

The eutrophic types were characterized by 2 to 6-fold higher H_2SO_4 extractable (Ca-bound) P concentrations than in the other three site type groups, whereas the NH_4F (Al-bound) and NaOH (Fe-bound) extractable P contents of the eutrophic sites were very low. The dominance of Ca-bound P over Fe- and Al-bound may simply be due to very high Ca concentrations in eutrophic types (Heikurainen 1953). However, the differences in the amounts of Ca-, Al-, and Fe-P may also be related to their differing response to soil acidity. The Fe and Al phosphates have an increasing solubility with increasing pH, whereas Ca phosphates have a decreasing solubility. Under relatively high pH levels, such as typical for eutrophic peat soils (Heikurainen 1953), Ca-bound P may thus be the most insoluble form of P.

The very high easily soluble IP (NH_4Cl_{-IP}) concentrations in peat from low-sedge mires (Table 2), known as the least productive site type group among the sites of this study, may at first seem surprising, since one would expect higher concentrations for productive sites. Negative correlations between stand growth and easily soluble P contents in peat (NH_4Cl or NH_4OAc extractable) as found in the present study and some earlier investigations (Mannerkoski 1973, Kaunisto and Paavilainen 1988) may also seem to be unexpected. However, it should be noted that, besides peat residues, the peat samples always contain plant roots and other living organisms. Extracts used for easily soluble soil P, such as NH_4Cl and NH_4OAc, are likely to release some P from these. Due to their low P sorption capacity (Cuttle 1983, Nieminen and Jarva 1996), most of the P released will end up in the solution when low productive soils are extracted. Productive soils generally have high P sorption capacity and the P released from roots during extraction is retained in the soil portion. This "plant releasable P" and the differences in P sorption between productive and nutrient-poor sites may thus explain why the extracts supposed to dissolve easily soluble/available P pool often give confusing results.

The post-drainage tree growth of herb-rich mires is often higher than on eutrophic mires among which considerable variation in tree productivity may occur (Keltikangas et al. 1986). The significantly higher $NaOH_{-IP}$ contents in peat from herb-rich sites compared with the other three site type groups would thus indicate that Fe-bound IP is important for high productivity. The correlations between peat P fractions and the stand volume growth also indicated that Fe-bound IP is important for tree productivity, although Fe- and Al-bound OP ($NaOH_{-OP}$ and NH_4F_{-OP}) fractions also correlated significantly with stand growth. Given the very high differences in peat P fractions between different site type groups, one might have expected higher correlations between P fractions and the stand volume growth. It should be noted, however, that in a systematically collected data set, such as the present, a number of factors other than a particular peat P fraction (drainage intensity, age and development stage of the tree stand, soil temperature etc.) affect stand volume growth. A more uniform data concerning "these other factors" might have given higher correlations between peat P fractions and stand growth.

The higher availability to trees of Fe- and Al-bound P fractions as compared with easily soluble (NH_4Cl-P) and Ca-bound (H_2SO_4-P) P (Table 3) deserves some further explanation. The low correlation of NH_4Cl-P with stand growth has been discussed earlier, the probable reason is that NH_4Cl extracts "easily plant releasable P" rather than "easily available soil P". The true easily available pool may be extremely low in acutely P deficient sites such as peat soils. The low bioavailability of Ca-P has also been discussed: this is because the Ca-bound P fraction is high only in eutrophic soils where its solubility is low due to high pH. If the Al- and Fe-P fractions are the main source of P to trees, the question arises: what are the mechanisms controlling their bioavailability?

One of the mechanisms by which plants extract P from less readily available forms, such as Al- and Fe-bound complexes, is thought to be through excretion of organic acids or anions from their roots (Hinsinger 2001). It is believed that this mechanism is especially important for perennial and long-living species, such as trees, whose survival and productivity depend on close association between host trees and ectomycorrhizal fungi. Oxalate anions released to the rhizosphere by tree root/fungi association were shown to effectively enhance the availability of sparingly soluble P forms in a mineral soil forest (Griffiths et al. 1994). However, whether these root exudates are important in P acquisition in peat soils is poorly understood. Because of their decreasing solubility with increasing acidity, the solubility of Al- and Fe-P is probably very low for most peat soils. The activity of plants and fungi may therefore play an important role also in peat soils, but further research is needed to fully understand the processes controlling the availability of peat P.

In a number of studies, substantial leaching of fertilizer-P from drained peatland forests has been observed (Harriman 1978, Kenttämies 1981, Ahti 1983, Malcolm and Cuttle 1983, Nieminen and Ahti 1993, Renou et al. 2000). The application of Fe or Al together with P has been shown to be an effective means of increasing adsorption and reducing leaching from peat soils (Larsen et al. 1959, Fox and Kamprath 1971, Scheffer and Kuntze 1989, Nieminen 2002). It is not known, however, whether the phosphate fertilizers sorped by Al and Fe remain available to trees. According to the present study, the Fe-P and Al-P complexes may be an effective source of P to trees. However, should Al- or Fe-containing fertilizers be used to decrease leaching losses, their effectiveness compared with traditional apatite-fertilizers ought to be clarified.

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