

Behaviour of certain phosphorus and potassium compounds in a sedge peat soil

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The solubility of various phosphorus and potassium compounds in a sedge peat soil was studied in an incubation experiment aimed at screening potential fertilizers for the cultivation of fast-growing willows. $(\text{KPO}_3)_n$ proved not to be a source of the slow-release K regarded as most desirable for this kind of cultivation as it was hydrolyzed completely in the soil during incubation. Phosphorus from easily soluble or hydrolyzable compounds (superphosphate, KH_2PO_4 , $(\text{KPO}_3)_n$) was bound in the soil largely by Al and Fe and elevated the level of readily soluble P considerably, whereas rock phosphates were found to be practically unchanged after incubation and did not contribute to the readily soluble P in the soil. Apatites proved to be quite insoluble and are therefore assumed to be unsuitable as P fertilizers for fast-growing willows, which have a high nutrient demand.

Tutkimuksessa käsitellään erilaisten fosfori- ja kaliumlannoitteiden liukoisuutta turvetuotannosta poistuneen suon pohjaturpeessa laboratorioinkubointitestissä. Tavoitteena oli selvittää nopeakasvuisen pajuviiljelmän kannalta edullisin fosforilannoite. Samalla pyrittiin etsimään sopivia hidasliukoisia fosfori- ja kaliumlannoitteita. Inkubointikokeessa $(\text{KPO}_3)_n$ ei osoittautunut hidasliukoiseksi K-lannoitteeksi; kalium hydrolysoitui miltei täysin inkuboinnin aikana. Helppoliukoisten tai hydrolysoituvien P-lannoitteiden (superfosfaatti, KH_2PO_4 ja $(\text{KPO}_3)_n$) fosfaatit sitoutuivat valtaosin alumiiniin ja rautaan, lisäten kuitenkin kasveille käyttökelpoisen fosforin pitoisuutta turpeessa. Sedimenttinen pehmeä raakafosfaatti oli lähes liukenematonta inkuboinnin aikana. Samoin apatiitti saattaa olla liian hidasliukoisia nopeakasvuisen pajujen lannoitukseen.

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1. Introduction

Fast-growing willows have a high biomass production potential, which makes them an attractive plant species for converting solar energy. Consequently their nutrient requirement is higher than that of birch, alder or coniferous trees, a willow stand producing 10–15 t dry matter/ha annually being known to consume 100–200 kg/ha N, 25–40 kg/ha P and 100–200 kg/ha K per year (Kaunisto 1983, Lumme et al. 1984, Saarsalmi 1984). The areas planned to be used for willow cultivation consist mainly of mined peatlands, and it has been estimated that by the end of this century there will be approx. 5 000–10 000 hectares of such land available for this purpose in the northwestern part of Finland. The lower part of the peat layer in virgin peatlands is poor in phosphorus and potassium (Kaila 1956, Kaila and Kivekäs 1956, Lumme et al. 1984, Heikkilä 1985), which means that successful willow cultivation will require both the use of suitable varieties and heavy applications of fertilizers. In addition, virgin peatlands are highly acid, whereas the most suitable pH for willows is estimated to be in the range 5.0–7.0 (Ericsson and Lindsjö 1981). Thus heavy liming (CaCO_3 5–15 t/ha) is also needed.

2. Materials and methods

The phosphorus and potassium compounds tested in the experiment are presented in Table 1.

Superphosphate, consisting mainly of $\text{Ca}(\text{H}_2\text{PO}_4)_2$, and KH_2PO_4 were monomeric compounds, while the others were polymeric and contained only minor amounts of water-soluble orthophosphate (PO_4) and potassium. The Siilinjärvi apatite was a hard magmatic rock phosphate, while the soft rock phosphate, imported from China, was of sedimentary origin. Biotite, a mica-type mineral, was a by-product from the Siilinjärvi phosphate mine.

The Carex peat (H7) used in the experi-

It has been found in field experiments that phosphorus and potassium fertilization may be even more important than nitrogen fertilization on mined peat soils (Hytönen 1986, Lumme and Kiukaanniemi 1987). Willow plantations can be harvested every three to five years, and it would be cost-efficient to apply fertilizers only at the beginning of each such period.

This study forms part of a larger project run by the Research Institute of Northern Finland, University of Oulu, Kemira Oy and the Academy of Finland aimed at developing practices for the cultivation of fast-growing willows. The present work is concerned with evaluating the solubility of various phosphorus and potassium compounds in an incubation experiment and tracing in detail the reactions of the fertilizer phosphorus in the soil. The authors wish to thank Mrs Kirsi Haasala, M. A., for performing the necessary laboratory work, Mr Malcolm Hicks, M. A., Technology Center of Oulu for correcting the English manuscript and Professor Eero Paavilainen, head of the Department of Peatland Forestry at the Finnish Forest Research Institute and Dr. Jukka Laine of the Department of Peatland Forestry, University of Helsinki, for making valuable corrections to the manuscript.

ment originated from Hirvineva near Oulu (location 64°42'N, 25°20'E). When peat mining at the site came to an end about 80 cm of surface peat had been removed and about 20 cm was left. For the experiment, the peat was mixed carefully and 313 g of moist peat, corresponding to 79 g of air-dried peat, was weighed into plastic boxes. The fertilizers added corresponded to 386 mg P and/or 486 mg K per kilogramme of air-dried peat (assuming the fertilizers to be mixed in the 0–20 cm peat layer with a bulk density of 200 g/l, the amount of fertilizers would correspond to 155 kg of P/ha and 195 kg of K/ha). Five replicates were run without liming and five

Table 1. Phosphorus and potassium content of the compounds used in the incubation experiment.

Compound	Tot P %	Water soluble P %	Tot K %	Water soluble K %
Superphosphate	8.7	8.1	–	–
(KPO_3) _n	26.4	0.4	31.1	6.8
KH_2PO_4	22.8	22.8	28.7	28.7
Siilinjärvi apatite	14.2	<0.1	–	–
Soft rock phosphate	13.2	<0.1	–	–
Biotite	0.5	<0.1	5.0	n.d.
n.d. = not determined				

with an admixture of 2.0 g $\text{Ca}(\text{OH})_2$. The pots were watered to a moisture content of 80 % and incubated at 20–25 °C for one year.

After incubation the samples were dried, ground and extracted with 0.5 M CH_3COOH –0.5 M CH_3COOH – NH_4 (pH 4.65) (Vuorinen and Mäkitie 1955). This solution, abbreviated here as AAAC, is routinely used in agricultural fertility testing in Finland. The extracts were then analyzed for P, K, Ca and Mg. The pH of the samples was measured in a water suspension with a soil-solution ratio of 1:20 (v/v). Inorganic P was

fractionated according to the procedure of Chang and Jackson, as modified by Hartikainen (1979). Organic P was determined by the method by Kaila (1962). Amorphous Fe and Al were extracted with 0.05 M ammonium oxalate solution (pH 3.3), given a soil-solution ratio of 1:20 (w/v) and a shaking time of two hours. The cation exchange capacity (CEC) of the unfertilized samples was determined using 1 M AAAC (pH 7) (Kaila and Rytö 1968). The bulk density of the samples was also measured.

3. Results

Liming to the extent of 16 t CaCO_3 per hectare raised the exchangeable Ca content to a high level (Table 2), but the soil pH only by about one pH unit, indicating that the soil had a very high pH buffer capacity. As usual for peat, the samples had a high CEC (135 mekv/100 g at pH 7.0) Liming increased the percentage of base cations (Ca, Mg, K) from 25 % to 56 %, implying that a considerable proportion of the cation exchange sites were occupied by Al^{3+} and H^+ even after heavy liming. The peat concerned seemed to contain large amounts of Mg, the solubility of which was not influenced by liming. Instead liming reduced the extractability of Al and Fe.

Native K was very low, indicating an extreme K deficiency. KH_2PO_4 and (KPO_3)_n increased the amount of exchangeable K equally effectively, practically all the K added being exchangeable after the year of incubation. Due to an experimental error, only the results from the limed biotite treatment samples were available. These showed that the biotite had released about half of its K in exchangeable form during the incubation.

The original amount of readily soluble P was also extremely small (Table 2), and superphosphate, (KPO_3)_n and KH_2PO_4 all increased the amount effectively to a moderate level, whereas neither apatite had much effect. Magmatic apatite had no effect what-

Table 2. AAAC-soluble phosphorus, exchangeable potassium (mg/l) and pH in soils subjected to various treatments.

	pH	Ca	Mg	K	P	Fe	Al
O	4.0 ^b	870 ^d	10 ^c	280 ^b	1.5 ^c	179.3 ^a	95.6 ^a
O+Ca(OH) ₂	4.7 ^a	2500 ^c	5 ^c	300 ^a	1.6 ^c	128.44 ^b	80.0 ^{bc}
Superphosphate	3.8 ^b	960 ^d	20 ^c	275 ^b	7.5 ^c	177.5 ^a	87.4 ^a
Superphosphate+Ca(OH) ₂	4.7 ^a	2600 ^b	15 ^c	310 ^a	9.1 ^{ab}	143.5 ^b	78.5 ^{bc}
(KPO ₃) _n	3.8 ^b	905 ^d	130 ^a	285 ^b	9.0 ^{ab}	190.7 ^a	71.9 ^{cd}
(KPO ₃) _n +Ca(OH) ₂	4.8 ^a	2600 ^b	125 ^a	305 ^a	10.2 ^a	127.3 ^{bc}	74.1 ^{bcd}
KH ₂ PO ₄	3.8 ^b	895 ^d	135 ^a	288 ^b	8.1 ^{bc}	177.5 ^a	89.6 ^a
KH ₂ PO ₄ +Ca(OH) ₂	4.8 ^a	2640 ^{ab}	125 ^a	310 ^a	9.4 ^{ab}	130.2 ^{bc}	68.9 ^{cd}
Siilinjärvi Apatite	3.8 ^b	935 ^d	10 ^c	285 ^b	1.6 ^c	182.1 ^a	96.2 ^a
Siilinjärvi Apatite+Ca(OH) ₂	4.8 ^a	2665 ^{ab}	15 ^c	300 ^a	1.5 ^c	131.0 ^{bc}	83.0 ^b
Soft rock phosphate	3.8 ^b	930 ^d	15 ^c	280 ^b	3.2 ^d	185.3 ^a	94.0 ^a
Soft rock phosphate+Ca(OH) ₂	4.7 ^a	2615 ^b	15 ^c	310 ^a	1.7 ^c	127.3 ^{bc}	70.3 ^{cd}
Biotite+Ca(OH) ₂	4.8 ^a	2710 ^a	79 ^b	310 ^b	1.6 ^c	123.4 ^c	63.7 ^d

Values within a given column not sharing a letter (a, b, c, d,) are significantly different at p<0.05 by the Waller-Duncan test.

Table 3. Inorganic and organic P (mg/kg air dry soil) in the incubated peat samples.

	Inorg. P mg/kg extracted with			Sum of fractions mg/kg	Org. P mg/kg
	NH ₄ F	NaOH	H ₂ SO ₄		
O	46 ^g	24 ^g	19 ^d	89 ^d	529 ^d
O+Ca	40 ^g	24 ^g	25 ^d	89 ^d	555 ^{cd}
Superphosphate	192 ^a	177 ^{cd}	85 ^c	454 ^a	552 ^{cd}
Superphosphate+Ca	144 ^{cd}	155 ^c	87 ^c	385 ^b	582 ^{bcd}
(KPO ₃) _n	175 ^b	204 ^b	30 ^d	409 ^b	624 ^{abcd}
(KPO ₃) _n +Ca	132 ^{cd}	185 ^{bc}	67 ^c	384 ^b	703 ^a
KH ₂ PO ₄	147 ^c	225 ^a	25 ^d	397 ^b	660 ^{ab}
KH ₂ PO ₄ +Ca	126 ^d	166 ^{de}	81 ^c	346 ^b	652 ^{abc}
Siilinjärvi Apatite	73 ^f	51 ^g	136 ^b	260 ^c	533 ^d
Siilinjärvi Apatite+Ca	58 ^g	47 ^g	190 ^a	295 ^c	594 ^{bcd}
Soft rock phosphate	103 ^e	112 ^f	141 ^b	356 ^b	570 ^{bcd}
Soft rock phosphate+Ca	46 ^g	46 ^g	133 ^{ab}	225 ^c	614 ^{abcd}
Biotite+Ca	35 ^g	30 ^g	48 ^{cd}	113 ^d	555 ^{cd}

Values within a given column not sharing a letter (a, b, c, d, e, f, g) are significantly different at p<0.05 by the Waller-Duncan test.

soever on AAAC-extractable P, but the sedimentary apatite had obviously dissolved slightly in the unlimed peat.

Detailed analysis of soil P (Table 3) re-

vealed that the majority of this anion in the original soil sample had been bound in the organic matter, the pool of inorganic P, that principally available to plants, being very

Table 4. Recovery of exogenous P (mg/kg air dry soil) in different fractions.

	NH ₄ F mg/kg	NaOH mg/kg	H ₂ SO ₄ mg/kg	Sf mg/kg	Organic mg/kg	IO+O mg/kg	Total Recovery %
Superphosphate	146	153	66	365	23	388	100
+ Ca	104	131	62	297	26	323	83
(KPO ₃) _n	129	180	11	320	76	396	102
+ Ca	92	161	42	295	148	443	115
KH ₂ PO ₄	101	201	6	308	132	440	114
+ Ca	86	142	56	284	80	364	94
Siilinjärvi Apatite	27	27	117	171	4	175	45
+ Ca	18	23	165	206	39	245	63
Soft rock phosphate	57	88	122	267	41	308	80
+ Ca	6	22	108	136	23	159	41

small. Addition of P to the soil increased the size of the various inorganic fractions, but had only a slight influence on the pool of organic P. Liming did not affect the distribution of P.

In the sequential fractionation method of Chang and Jackson (Hartikainen 1979) the inorganic P bound by Al compounds is extracted with an NH₄F solution and P attached to Fe compounds with a NaOH solution. These fractions reflect the amount of potentially soluble phosphates. The fertilizer P remaining in the soil accumulates in these two fractions. H₂SO₄ is assumed to dissolve the unweathered native apatite, which is very slightly soluble under normal soil conditions.

The phosphorus added in the superphos-

phate, (KPO₃)_n and KH₂PO₄ was recovered almost completely (Table 4), the greatest additions being found in the fractions extractable with NH₄F (i.e. Al-bound) and NaOH (i.e. Fe-bound). Superphosphate also showed some increase in the H₂SO₄-extractable fraction. The same phenomenon was also observed in the (KPO₃)_n and KH₂PO₄ treatments in the presence of liming.

The recovery of apatite P was only 33–78 %, the fractions of Fe and Al-bound P having scarcely increased at all upon either apatite treatment. Most of the P recovered was found in the H₂SO₄-extractable fraction. This shows that the apatites had not dissolved during incubation nor in the extractants used.

4. Discussion

Despite its high cation exchange capacity, peat does not retain K as tightly as do clay soils. Consequently part of the exchangeable potassium can be lost through leaching in spring and autumn, when floods can occur, especially if large amounts of readily soluble K salts are added (Ahti 1983). If all the K needed by willows during the growth period

of three to five years were to be given in one dose, slowly soluble K fertilizers would be of use. The main problems with these are whether the fertilization effect is long enough and whether it is great enough for any one growing season compared with annual applications of readily soluble fertilizers.

Although chemical analysis showed

(KPO₃)_n to contain practically no water-soluble K, it seemed to be hydrolyzed in the soil so quickly that it resulted in the same amount of exchangeable K at the end of the incubation as did the readily soluble K compound KH₂PO₄. This suggests that the (KPO₃)_n species tested could not serve as a slow-release K fertilizer. Biotite seemed to be a much more promising source of slow-release K, as its K was only partially exchangeable after one year of incubation. Biotite has indeed proved to be a good source of slow-release K in grassland fertilization (Zitting 1980).

Finnish peat soils have a high capacity for fixing P in forms unavailable to plants. Hence earlier Finnish field experiments pointed to peat soils as showing the greatest response to P fertilization (Salonen and Tainio 1957). The P in readily soluble compounds (i.e. superphosphate and KH₂PO₄) and the readily hydrolyzable (KPO₃)_n was mainly recovered in the Al-bound and Fe-bound fractions after incubation, the latter dominating. These compounds also substantially increased the amounts of AAAC-extractable P.

"Fe-P" is usually considered less soluble than "Al-P" (Hartikainen 1982), so that it is likely to contribute to P uptake by plants less than "Al-P". This has the consequence that peat soils very rich in amorphous Fe may have an exceptionally high requirement for P fertilization (Puustjärvi 1953).

The soft rock phosphate had dissolved to a considerable extent in the present unlimed pots, as seen in the elevated content of AAAC-extractable P and in an increase in the Al and Fe-bound P fractions. Liming reduced its solubility markedly. Even so, by far the largest proportion of the P added to the soil in both rock phosphates was recovered in the Ca-bound fraction. This means that the rock

phosphate had dissolved only slightly during incubation. Hänninen and Kaila (1960) and Kaila (1961) have also shown that soft rock phosphate used in a five-year field experiment remained mostly in the Ca-bound fraction by the end of the period. Tainio (1958) has suggested that on average 2.5 times more soft rock phosphate needs to be used in order to obtain the same yield increase as with a given amount of superphosphate P. Paarlahti and Karsisto (1968) also found in a two-year field experiment that growth enhancement in a young pine forest on peat soil was clearly lower with rock phosphates than with superphosphate.

The rock phosphate from Siilinjärvi showed hardly any tendency to dissolve even in the unlimed soil. Salonen (1968) has shown that the same kind of rock phosphate could well serve as a phosphate fertilizer for pine and oats in raw sphagnum peat of pH 3.9, but liming of the soil to pH 5.0–6.0 reduces its fertilization effect drastically. The effect of rock phosphates may be sufficient for traditional forest cultivation (Paarlahti and Karsisto 1968), but the biomass production of fast-growing willows entails a much higher requirement for P. The necessity for liming also contributes to the assumption that rock phosphates may not be successfully used as P fertilizers for fast-growing willows. A similar conclusion has been made by Hytönen (1986).

If one tries to convert the results obtained here to field conditions it should be noted that the temperature in the laboratory was much higher and also moisture content of the peat was more stable than in the field. It can therefore be assumed that the solubility of the compounds tested here may be lower over one year period under field conditions than in the laboratory.

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