FERTILIZER PHOSPHORUS IN SOME FINNISH SOILS

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A large part of the phosphorus applied in mineral fertilizers is accumulated in the soil. The distribution of this phosphorus among the various forms has been the object of numerous investigations. Dean (6) showed that phosphorus applied to acid soils tended to accumulate in the alkali-soluble forms, and phosphorus added to neutral or calcareous soils tended to accumulate in acid-soluble but alkali-insoluble forms. Further studies have corroborated the observations that dressing with soluble phosphates mainly increases the phosphorus bound to aluminium and iron, even in soils with a pH value of 6.7 (5, 18). On the other hand, Nagelschmidt and Nixon (17) found by X-ray diffraction studies that superphosphate which for a century had been applied to a calcareous soil formed apatite. Rock phosphate appears only slowly to react with the soil, and a part of it may remain in its original molecular combination for a considerable period (8, 16). Bray and Dickman showed that rock phosphate increases the »acid-soluble» phosphorus, but any conversion to adsorbed forms is found to occur only in acid soils with a pH value of 5 or less than it. Some increase in the organic phosphorus fraction of soil as the result of fertilization with superphosphate for a longer period has been demonstrated (10, 14, 20).

In some previous works (9, 13) it was proved that in more or less acid Finnish soils the superphosphate phosphorus mainly increases the fractions which are supposed to represent phosphorus bound by aluminium and iron compounds. The rock phosphate, on the other hand, enhanced the calcium bound phosphorus, and only a small increase in the aluminium bound fraction could be detected.

In the present paper some further results are reported on the accumulation of superphosphate and hyperphosphate phosphorus in soils of field trials. Also some incubation experiments were carried out. To get more guidance for the interpreting of the results of the fractionation, the method employed for soil samples was applied to a variety of phosphate fertilizers.

Material

The soil samples were collected from the following four field trials:

Trial 1: Fine sand soil, poor in organic matter, treated with hyperphosphate at the rates of 0, 4000, 8000, and 12000 kg/ha. Samples were taken from each plot down to 6 inches in the middle of June, or about 4 weeks after the fertilizer had been worked in with plough and spade harrow, and about three weeks after the sowing of barley.

Trial 2: Superphosphate applied at the rates of 0 or 1200 kg/ha to a fine sand soil, poor in organic matter, and worked in with spade harrow. Samples were collected from successive layers down to 6 inches about 4 weeks after the application of superphosphate, and about three weeks after barley had been sown.

Trial 3: Loam soil, fairly rich in organic matter, treated with superphosphate at the rates of 0, 500, or 5000 kg/ha five years before the sampling. The experimental crops in these years were sugar beet, barley, and a timothy-red clover ley.

Trial 4: Annual application of superphosphate to a fen peat soil at the rates of 0, 100, 200, or 300 kg/ha for 34 years.

The fertilizers studied were Finnish hyperphosphate containing 12.6 % of P according to the manufacturer's analyses, superphosphate (8.5 % of P), and Kotkaphosphate (9.5 % P as superphosphate and rock phosphate). In addition to the fertilizers also dicalcium phosphate dihydrate was fractionated.

Analytical methods

Phosphorus fractionation was performed by the method introduced by Chang and Jackson (4); only instead of neutral NH_4F a slightly alkaline solution recommended by Fife (7) was used. Organic phosphorus of the soil samples was determined by an acid-alkali extraction (15).

The acetic acid soluble phosphorus was estimated by shaking the soil samples for half an hour in 0.5 N acid in the ratio of 1: 10. Phosphorus soluble in 0.03 N NH_4F — 0.025 N HCl was extracted in the ratio of 1: 10 by shaking for one minute. An approximate idea of the phosphorus concentration in the soil solution was tried to get by shaking the soil samples in 0.02 N $CaCl_2$-solution in the ratio of 1: 5 for 18 hours.

The pH-values refer to suspensions in 0.02 N $CaCl_2$ in the ratio of 1 to 2.5.

Results

Fractionation of fertilizers

The amount of phosphorus extracted by certain solvent from a phosphorus compound largely depends on the ratio of extraction and on the presence of other salts or material capable to disturb the process. Thus, it cannot be claimed that the results of fractionation reported in Table 1 would give any reliable picture in the

Table 1. Fractionation of phosphates by the method of CHANG and JACKSON (Expressed as P mg/g and per cent of total content)

Extracted	Hyperphosphate		Kotka-phosphate		Superphosphate		$CaHPO_4 \cdot 2H_2O$	
by	mg/g	%	mg/g	%	mg/g	%	mg/g	%
NH_4Cl	0.1	—	70	73	81	93	15	8
NH_4F	4	3	2	2	2	2	130	73
NaOH	0.02	—	0.01	—	0.05	—	0.2	—
H_2SO_4	117	97	24	25	4	5	34	19
Total	121		96		87		179	

presence of soil. The data are average values obtained when the fractionation was performed in the ratio of salt to solution of 1 to 50 or 1 to 100.

As could be expected, by far the largest part of hyperphosphate phosphorus is found first in the acid extract, whereas superphosphate phosphorus is mostly dissolved by ammonium chloride. Kotka-phosphate which contains about 80 per cent of superphosphate and 20 per cent of hyperphosphate gives results in accordance with its composition. It may be noteworthy that ammonium fluoride seems to be able to extract a small amount of hyperphosphate phosphorus. The distribution of phosphorus of dicalcium phosphate dihydrate is of particular interest, since it has been shown that when monocalcium phosphate dissolves in a soil system a part of it is precipitated as this compound (3). According to the present results, about three fourth of the phosphorus in $CaHPO_4 \cdot 2H_2O$ falls into the fraction of ammonium fluoride soluble phosphorus. If this also holds for a fractionation in the presence of soil, it does not seem to be justified to suppose that phosphorus extracted by ammonium fluoride would be only aluminium bound in soils recently treated with fertilizers containing monocalcium phosphate.

Analyses of the soil samples from the field trials

At the sampling time, the hyperphosphate in Trial 1 had been in contact with the soil for only a fairly short period. Thus, a large part of it probably existed as unchanged fertilizer particles. Figures in Table 2 indicate some liming effect which, however, is not quite regularly correlated to the amounts of hyperphosphate applied, possibly owing to the incomplete reaction of the fertilizer with the soil. The application of hyperphosphate has, of course, caused the highest increase in the fraction of acid-soluble phosphorus. No significant increase may be found in the alkali-soluble or iron bound phosphorus. In the ammonium fluoride soluble fraction somewhat higher values for the samples treated with hyperphosphate were obtained. As pointed out above, this cannot offhand be taken to mean that a part of apatite phosphorus had been dissolved and then sorbed by aluminium compounds. It may as well represent unchanged hyperphosphate phosphorus.

The effect of hyperphosphate on the phosphorus test values in this soil were quite in accordance with the results of the fractionation. The following figures were obtained for P soluble in

	0.02 N $CaCl_2$	NH_4F-HCl	Acetic acid
No hyperphosphate	0.03 mg/l	27 mg/kg	19 mg/kg
400 kg/ha	0.04 »	51 »	105 »
8000	0.05 »	59 »	217 »
12000 »	0.07 »	66 »	445 »
L. S. D. at 5 %	0.02 »	24 »	50 »

The P concentration in the $CaCl_2$-extracts has been increased, but even in the soil of the heaviest treatment it is low. The test values for P extracted by NH_4F-HCl show a higher increase due to the treatment with 4000 kg/ha as compared with the increases brought about by further 4000 or even 8000 kg/ha. Acetic acid has been a good solvent for hyperphosphate phosphorus.

Table 2. Fractions of inorganic P in fine sand soil treated with hyperphosphate

Hyperphosphate applied kg/ha	pH	P extracted by					
		NH_4F		NaOH		H_2SO_4	
		ppm	increase	ppm	increase	ppm	increase
0	4.7	34	—	154	—	300	—
4000	4.9	59	25	154	0	557	257
8000	5.0	68	34	180	26	708	408
12000	5.1	74	40	159	5	1062	762
L.S.D. at 5 %	0.1	26		30		240	

The soil samples of Trial 2 were taken from the successive layers down to 6 inches. Thus, it is possible to find out the distribution of superphosphate phosphorus into the different depths. The pH-values measured in $CaCl_2$-suspensions were 4.8 for all the layers and treatments. The first fraction, the phosphorus extracted by

Table 3. Fractions of inorganic phosphorus in a fine sand soil treated with 1200 kg/ha of superphosphate (Expressed as P ppm)

Depth inches	P extracted by								
	NH_4F			NaOH			H_2SO_4		
	0	Super	Difference	0	Super	Difference	0	Super	Difference
0 – 1	20	55	35	46	71	25	434	438	4
1 – 2	18	52	34	44	73	29	426	436	10
2 – 3	15	54	39	42	74	32	433	439	6
3 – 4	13	40	27	41	62	21	429	439	10
4 – 5	15	21	6	50	52	2	418	437	19
5 – 6	16	16	0	43	49	6	441	429	– 12
L.S.D. 5 %		10			15			23	

NH_4Cl was very low, about 0.7—0.9 ppm in the untreated plots, and the superphosphate phosphorus had increased it only to about 2—2.5 ppm. This demonstrates that in this acid soil the water-soluble monocalcium phosphate was rapidly sorbed or changed to less soluble forms. The inorganic phosphorus in the other fractions and the corresponding difference caused by the application of superphosphate are represented by the figures in Table 3.

The working in of superphosphate by spade harrow has mixed the fertilizer into the four highest inches which is a fairly good result (cf. 9). In these layers, the superphosphate phosphorus has increased both the fraction extracted by NH_4F and that extracted by NaOH, the former probably slightly more than the latter. No significant increase in the acid-soluble phosphorus may be found in any layer. The amount of superphosphate applied to this soil corresponds to about 80 mg of P per kg of soil in a layer of 4 inches. This amount is almost completely recovered in the four fractions determined. Superphosphate increased the P concentration in the 0.02 N $CaCl_2$-extract by 0.03—0.06 mg/l. The increase in acetic acid soluble P was barely significant, while a marked increase was found in the phosphorus extracted by NH_4F-HCl.

The fate of superphosphate phosphorus in a less acid soil than that of Trial 2, and five years after the application, may be traced by examining the results of fractionation obtained for Trial 3. These are reported in Table 4. 500 kg/ha of superphosphate is an amount too low to exert any noticeable residual effect on the phosphorus content of the soil. The heavier dressing, however, has markedly increased both the NH_4F-soluble and the NaOH-soluble fractions. Also in the acid-soluble fraction a tendency to a higher level may be detected, although, owing to the large variation between the replicate plots, the difference is not statistically quite significant at the 5 per cent level. It cannot be proved, on the basis of these results, that any accumulation of superphoshate as apatite-like phosphates had occurred in this slightly acid loam soil during the period of five years. Attention must also be paid to the fact that even a part of dicalcium phosphate may get into the acid soluble fraction.

Table 4. Residual phosphorus in a loam soil treated with superphosphate five years before the sampling

	Superphosphate applied kg/ha			L.S.D. 5 %
	0	500	5000	
pH	6.3	6.2	6.4	0.2
P extracted by NH_4F, ppm	95	95	138	24
P » » NaOH »	193	198	239	35
P » » H_2SO_4 »	465	457	489	26

In the fen peat soil of Trial 4 the annual application of superphosphate for 34 years resulted in the increase of phosphorus content of several fractions (Table 5).

Table 5. Phosphorus fraction in a peat soil treated with superphosphate for 34 years (Expressed as P ppm)

	Total amount of P applied				L.S.D. 5 %
	0	270	540	810	
Inorganic P					
extracted by NH_4F	11	15	31	77	11
» » NaOH	48	64	102	196	21
» » H_2SO_4	38	71	80	82	23
reductant soluble	61	58	68	68	11
occluded, NaOH	8	8	8	8	2
Organic P	730	780	860	930	50

The only exceptions are the fractions of reductant soluble and occluded phosphorus which are known to be very little affected by recent fertilizer applications (5). These fractions, apparently, are unavailable to plants, and not mobilizable. The NH_4F-soluble fraction is small in this soil, and not markedly increased by the lower rates of superphosphate treatment. The richness of this soil in iron (12) is in accordance with the considerable accumulation of fertilizer phosphorus in the alkali-soluble fraction. It is of interest to notice that the acid-soluble fraction is equal in all the treated samples and significantly higher than in the untreated one. Yet, the largest difference between the treated and untreated samples is found in the fraction of organic phosphorus. It represents 36—46 per cent of the total increase in the phosphorus content of the samples brought about by the fertilization.

This accumulation of fertilizer phosphorus in organic form may be due to the activity of microorganisms. It is, however, more likely that the larger amounts of plant residues in the fertilized plots account for the corresponding higher content of organic phosphorus in soil. The possible differences in the mobilization rate of organic phosphorus in these samples was studied by performing a couple of incubation experiments.

Incubation experiments

The incubation experiments were carried out at 18—20° C. 2 g of the peat samples from Trial 4 were weighed into 100 ml Erlenmeyer flasks; three of the replicates were moistened with distilled water, the other three were kept dry until the samples were analyzed for organic phosphorus after an incubation period of four months.

The mineralization, or the increase in the inorganic phosphorus content and the decrease in the content of organic phosphorus, in these samples was found to be the following:

org. P mineralized	0	P	2P	3P
ppm	35	65	70	85
% of org. P	5	8	9	9

Thus, there is a tendency for a higher rate of mineralization of the organic phosphorus from the plots annually treated with 100, 200, or 300 kg/ha of superphosphate (P, 2P, and 3 P respectively) as compared with that of the untreated one.

It is possible that the main part of the organic phosphorus mineralized during the incubation originated from plant residues. At the sampling time the experimental crop in this trial was a nine year old timothy ley, the root system of which had probably produced a large amount of organic material in the soil. This supposition may be corroborated by the results obtained when samples from successive layers of this soil were incubated. These figures are reported in Table 6.

Table 6. Mineralization of organic phosphorus of peat samples in incubation experiment

Depth inches	Org. P ppm				Decrease in org. P due to the incubation							
					ppm				% of org. P			
	0	P	2P	3P	0	P	2P	3P	0	P	2 P	3P
0–2	770	940	1040	1060	60	120	140	140	8	13	13	13
2–4	740	840	880	950	50	50	70	90	7	6	8	10
4–6	720	840	850	850	40	40	50	50	6	5	6	6
6–8	800	820	980	920	20	40	50	70	3	5	5	8

In all the treatments the highest amount of organic phosphorus was found in the top inches where also the decrease in it due to the incubation tended to be both absolutely and relatively the largest. It may be mentioned that in the deeper layers, from 20 to 28 inches, no mineralization of organic phosphorus could be detected in incubation experiments. The fact might also be taken into account that during the experimental period the yields and therefore the amount of plant residues were very low in the untreated plots.

Discussion and summary

In the present paper it is tried to trace the fate of fertilizer phosphorus in soil by comparing the analyses of soils from treated and untreated plots of field trials. This indirect approach cannot be expected to provide exact values, but it is likely to give an approximate answer.

The results reported above do not in any marked degree change our present conception of the forms in which fertilizer phosphorus accumulates in soils. In the acid soils studied (pH 4—6.4 in 0.02 N $CaCl_2$) superphosphate tended to increase the fractions which were extracted by NH_4F or NaOH. Hyperphosphate phosphorus was mostly found in the acid-soluble fraction. During a longer period of dressing with phosphate an increase in the organic phosphorus content of a peat soil could be detected.

In the incubation experiments the mineralization of organic phosphorus occurred at a higher rate in the samples from the plots treated with superphosphate than in those from the untreated one. It might be supposed that the organic phosphorus mineralized mainly originated from the plant residues.

It seems that the fractionation method developed by Chang and Jackson (4) for the estimation of discrete forms of soil phosphorus is not quite satisfactory for tracing the fertilizer phosphorus in soils recently dressed with phosphates. In particular, it may be fallacious to conclude that the fraction extracted by NH_4F would only represent phosphorus bound to aluminium and its compounds. At least in the absence of soil, a large part of phosphorus in dicalcium phosphate dihydrate falls into this fraction, and also a small amount of hyperphosphate phosphorus may be found in it.

The test values for »available» phosphorus showed the effect of fertilizers in accordance with previous observations (9, 13). Acetic acid soluble P revealed the treatment with hyperphosphate, but only slightly the application of superphosphate. The test value for the sorbed P of Bray and Kurtz (2), or phosphorus extracted by 0.03 N NH_4F-0.025 N HCl, distinctly indicated the addition of superphosphate, and also to some extent the presence of hyperphosphate phosphorus. Thus, even these results furnish a supplement to the data (11, 19) which prove that acids are not recommendable for the estimation of »available» phosphorus in Finnish soils. Probably, the use of ammonium fluoride would give a more reliable picture, provided, it is on the whole possible to characterize the phosphorus condition of soil with this kind of test values.

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SELOSTUS:

LANNOITEFOSFORIN KERTYMISESTÄ MAAHAN

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Käyttämällä Changin ja Jacksonin (4) kehittämää fosforin fraktioimismenetelmää yritettiin seurata hienofosfaatin ja superfosfaatin fosforin kertymistä maahan. Todettiin, että tutkituissa neljän kenttäkokeen enemmän tai vähemmän happamissa maissa superfosfaatti lisäsi lähinnä ammoniumfluoridiin ja natriumhydroksidiin uuttuvia fraktioita, kun taas suurin osa hienofosfaatin vaikutuksesta ilmeni happoon liukenevassa fraktiossa. Pitkäaikaisessa turvemaan lannoituskokeessa lisääntyi myös orgaaninen fosfori, joka osoittautui helpommin mineraloituvaksi lannoitetuissa kuin lannoittamattomassa koejäsenessä.

Lannoitteiden fraktioimisen tulokset viittaavat siihen, että ammoniumfluoridiin uuttuva fraktio voi äskettäin lannoitetussa maassa sisältää aluminiumin sitoman fosforin lisäksi myös esimerkiksi dikalsiumfosfaattia, jonka tiedetään olevan ensimmäisiä maassa todettavia surperfosfaatista muodostuvia yhdisteitä.

Tulokset vahvistavat käsitystä happamien uuttonesteiden sopimattomuudesta maittemme fosforin tarpeen määrittämiseen. Sen sijaan ammoniumfluoridin käyttö voinee antaa luotettavampia tuloksia, mikäli yleensä on mahdollista määrittää maan fosforitilannetta tällaisilla testeillä.