

EFFECT OF INCUBATION AND LIMING ON THE PHOSPHORUS FRACTIONS IN SOIL

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There exists in the soil a dynamic equilibrium between the forms of phosphorus. RATHJE (12) emphasized the importance of the equilibrium between hydroxylapatite and sesquioxide phosphates which largely depends on the pH of soil. There is also an equilibrium between the organic and inorganic forms of phosphorus controlled e.g. by the activity of microorganisms. Phosphorus added to the soil in fertilizers may disturb these equilibriums, yet, at a slower or faster rate, it will turn over to that form which is most stable under the conditions of the particular soil. The profitable effect of lime on acid soils is partly attributed to the improvement of phosphorus conditions either through the mineralization of organic phosphorus compounds or through the rendering phosphorus bound by iron and aluminium complexes more available (1, 6, 13). Which of these ways is the more important one in different cases, has not yet been indisputably demonstrated.

The laboratory experiments described in this paper were carried out in order to study the changes in the soil phosphorus resulted from a prolonged incubation, and the role lime is playing in these changes. An attempt was also made to trace the fate of fertilizer phosphorus in these incubation experiments.

Material and methods

The soil samples were collected from the surface inch of two field trials in which superphosphate and hyperphosphate were compared (8). In the trial on a loam soil superphosphate had been annually applied as a surface dressing at the rate of 200 kg/ha for three years, in the trial on a silt soil this treatment was repeated in four years. The application of 2 000 kg/ha of hyperphosphate occurred in the trial on the loam soil four years, and in the trial on the silt soil five years before the sampling.

Samples from all the four replicate plots were separately incubated and analyzed. 100 g of air-dry and ground soil was weighed into a glass jar, moistened with distilled water to the field capacity, and incubated at about 20°C for seven months. Before

the moistening, 1 g of calcium carbonate was added to a second set of samples and thoroughly mixed. At the end of the incubation period the samples were air-dried and ground.

The pH-values refer to 1:2.5 water suspension.

P soluble in 0.03 N NH_4F -0.025 N HCl was extracted in the ratio of 1:10 by shaking for one minute. The acetic acid soluble P was determined by using 0.5 N acid in the ratio of 1:10, the shaking period being half an hour.

Phosphorus fractionation was performed by the method introduced by CHANG and JACKSON (3). Instead of neutral NH_4F -solution a slightly alkaline extractant recommended by FIFE (5) was used.

For the determination of organic phosphorus two methods were employed. In the acid-alkali extraction procedure 2 g of soil was treated with 50 ml of 4 N H_2SO_4 in 100 ml Erlenmeyer flask for 18 hours with occasional stirring during the first hour. After filtration and washing with distilled water to give a leachate of 200 ml the filter paper with soil was transferred to a 300 ml Erlenmeyer flask, 200 ml of 0.5 N NaOH was added, and the suspension was left to stand over night with occasional stirring during the first two hours. The thoroughly mixed suspension was centrifuged, or poured into a high glass, and on the following day the clear supernatant extract was analyzed. For the determination of the inorganic P extracted, equal amounts of the acid extract and the alkaline extract were mixed, and the dark organic matter precipitated removed by filtering or centrifuging. The destruction of organic matter for the determination of total P extracted was performed either by dry or wet combustion. In the former case, 10 ml of both extracts were mixed and evaporated to dryness with 3 ml of 2 N NaNO_3 , ignited at 550°C, and heated on a boiling water bath for at least two hours in 21 ml of 1 N H_2SO_4 . The wet combustion was performed with the aid of a mixture containing two parts of 70 % perchloric acid and one part of concentrated sulphuric acid. The difference of the total and inorganic P extracted represents the organic P.

In the ignition method 2 g of air-dry soil was ignited for 1 hour at 550 °C. Both the ignited residue and a 2 g lot of untreated soil were then extracted with 200 ml of 0.2 N H_2SO_4 for two hours. The difference between the P extracted from the ignited and the unignited soil is taken to represent the organic P of the soil.

Since the acid-alkali extraction method probably gives too low results, while the values obtained by the ignition method are likely to be too high, an average of the figures was supposed to be the most reliable estimation of soil organic P.

Results

The effect of incubation and liming on the reaction of the experimental soils is illustrated by the data in Table 1. Both soils are slightly acid, the loam soil somewhat more acid than the silt soil. A marked drop in the pH-values is caused by incubation, while liming has been able to increase the pH-values so much that even at the end of the incubation the soils are neutral.

The P test values, also recorded in Table 1, reveal the effect of phosphate fertilizers in the degree that could be expected: the treatment with superphosphate is

Table. 1. pH and phosphorus test values in the original and incubated soil samples

	Loam soil			Silt soil		
	0	Super	Hyper	0	Super	Hyper
Original	5.7	5.6	5.7	5.9	5.7	5.9
Incubated	5.0	5.0	5.1	5.3	5.1	5.3
Incubated with lime	7.0	7.2	7.2	7.3	7.3	7.3
L.S.D. at 5 %		0.1			0.1	
P ppm extracted by 0.03 N NH ₄ F-0.025 N HCl						
Original	22	62	33	14	39	23
Incubated	36	80	59	24	57	37
Incubated with lime	32	65	41	25	51	34
L.S.D. at 5 %		8			9	
P ppm extracted by 0.5 N acetic acid						
Original	8	16	96	12	17	101
Incubated	8	16	85	12	18	99
Incubated with lime	8	20	55	12	24	69
L.S.D. at 5 %		23			29	

not apparent in the acetic acid values, while it is evident from the results of the acid fluoride extraction. The latter numbers also show the treatment with hyperphosphate, although to a far less degree than do the corresponding figures for the acetic acid soluble P. The incubation has increased the acid fluoride soluble P in all the samples, but the treatment with lime has, particularly in the loam soil, reduced this increase. The amount of acetic acid soluble P has not been changed by the incubation. The fact that acetic acid has not dissolved more P from the limed samples may be attributed to the neutralizing effect of lime on the acid: the pH of the extract of the limed samples was about 3.5 while that of the unlimed samples kept at about pH 3.1.

On the basis of these test values it might be concluded that the incubation has probably somewhat improved the availability of phosphorus in these samples. No positive effect of lime is apparent.

The results of the P fractionation give a more thorough picture of the changes brought about by the incubation. The data obtained for the samples from the untreated plots are reported in Table 2. In both soils the incubation has caused an increase in the inorganic P extracted by ammonium fluoride and sodium hydroxide. No changes in the amount of acid soluble P has occurred. The increase in the inorganic P extracted is most likely due to the mineralization of organic P, since a significant decrease in this form is found. The effect of lime is most evident in the reducing of the accumulation of the mineralized P as the alkali-soluble form. Only in the loam soil it has, to some degree, increased the amount of acid-soluble P, in the silt

Table 2. P fractions in the original and incubated samples of untreated soil (Expressed as P ppm)

P fractions	Original	Incubated	Incubated with lime	Increased by		
				incubation	incubation + lime	lime
Loam soil						
Inorganic P extracted by						
NH ₄ Cl	1	2	3	1*	2**	1**
NH ₄ F	33	45	45	12**	12*	0
NaOH	95	112	99	17**	4	-13***
H ₂ SO ₄	264	264	274	0	10***	10**
Total	393	423	421	30*	28*	-2
Organic P	358	332	333	-26***	-25***	1
Silt soil						
Inorganic P extracted by						
NH ₄ Cl	3	2	5	-1	2**	3**
NH ₄ F	18	33	38	15**	20**	5**
NaOH	69	89	75	20**	6**	-14***
H ₂ SO ₄	341	344	346	3	5	2
Total	431	468	464	37**	33**	-4
Organic P	307	285	273	-22**	-34***	-12

soil a slight increase in the fluoride-soluble fraction may be detected. It is of interest to find out that lime did not exert any effect on the mineralization of organic P in these soils.

The P fractions of the soil from the plots treated with superphosphate (Table 3) have undergone changes similar to those found in the untreated samples. Only the effect of lime on the increase of the acid-soluble fraction and the decrease in the alkali-soluble fraction seems to be more marked than in the untreated soils.

In the results obtained for the samples treated with hyperphosphate (Table 4) some new features may be observed. The incubation has brought about in both soils a marked decrease in the acid-soluble P with a corresponding higher increase in the fluoride- and alkali-soluble fractions. Apparently, lime has prevented the turning over of acid-soluble P to the alkali-soluble form, and the organic P mineralized is in the limed samples mainly accumulated in the fraction which is extracted by ammonium fluoride or in the acid soluble form.

Even in the samples from the plots treated with superphosphate or hyperphosphate, the effect of lime on the mineralization of organic phosphorus appears to be negligible.

In all the cases incubation with lime has increased the low amount of P extracted by the first treatment, or by ammonium chloride. In the loam soil, also incubation without lime has improved the solubility of P in this extractant.

The closest estimate of the changes in the fertilizer phosphorus which may be obtained on the basis of this material, is the difference between the corresponding

Table 3. P fractions in the original and incubated samples of soil treated with superphosphate (Expressed as P ppm)

P fractions	Original	Incubated	Incubated with lime	Increased by		
				incubation	incubation + lime	lime
Loam soil						
Inorganic P extracted by						
NH ₄ Cl	3	5	8	2**	5*	3*
NH ₄ F	91	103	105	12**	14**	2
NaOH	138	157	136	19**	- 2	-21**
H ₂ SO ₄	262	260	273	-2	11	13**
Total	494	525	522	31*	28*	- 3
Organic P	370	343	340	-27***	-30***	- 3
Silt soil						
Inorganic P extracted by						
NH ₄ Cl	4	5	10	1	6**	5***
NH ₄ F	57	73	76	16**	19***	3
NaOH	110	132	110	22***	0	-22**
H ₂ SO ₄	349	344	355	- 5*	6	11***
Total	520	554	551	34***	31***	- 3
Organic P	299	272	271	-27*	-28**	- 1

Table 4. P fractions in the original and incubated samples of soil treated with hyperphosphate (Expressed as P ppm)

P fractions	Original	Incubated	Incubated with lime	Increased by		
				incubation	incubation lime +	lime
Loam soil						
Inorganic P extracted by						
NH ₄ Cl	2	3	4	1 ***	2*	1
NH ₄ F	54	82	66	28**	12**	-16*
NaOH	118	139	111	21***	- 7**	-28**
H ₂ SO ₄	486	468	505	-18**	19*	37***
Total	660	692	686	32*	26***	- 6
Organic P	388	356	360	-32***	-28**	4
Silt soil						
Inorganic P extracted by						
NH ₄ Cl	3	4	6	1	3*	2**
NH ₄ F	35	54	54	19***	17**	- 2
NaOH	94	119	91	25***	- 3	-28***
H ₂ SO ₄	538	515	539	-23**	1	24***
Total	670	692	688	22**	18*	- 4
Organic P	290	267	269	-23**	-21**	2

results for the samples from the treated and untreated plots. The tracing of the fate of the applied phosphorus in this way is not theoretically sound, owing to the fact that the samples originated from field trials in which the uptake of phosphorus by plants was not equal from the treated and untreated plots. Yet, in the lack of anything better this approach may be employed to get some idea of the distribution of fertilizer phosphorus in these soils.

The differences in the various fractions of inorganic phosphorus in the samples treated with superphosphate and in the untreated samples are the following:

P ppm extracted by	Loam soil			Silt soil		
	Original	Incubated	Incubated with lime	Original	Incubated	Incubated with lime
NH ₄ Cl	2	3	5	1	3	5
NH ₄ F	58	58	60	39	40	38
NaOH	43	45	37	41	43	35
H ₂ SO ₄	0	0	0	8	0	9

In the unincubated samples of the loam soil the treatment of superphosphate seems to have increased the fractions soluble in ammonium fluoride and sodium hydroxide. The incubation has not caused any changes in the amount of these fractions, and this holds true also with the incubation with lime, since the decrease in the alkali soluble fraction is not statistically significant. The «superphosphate-phosphorus» in the silt soil also accumulated in the fluoride- and alkali-soluble fractions, and no changes in these forms can be detected due to the incubation or the incubation with lime. In this soil the incubation seems to have decreased the low amount of acid-soluble phosphorus which is assumed to originate from the treatment with superphosphate. Incubation with lime has prevented this decrease. The easily soluble part of «superphosphate-phosphorus» was increased in both soils as a result of the incubation with lime.

The corresponding differences in the values for the samples from the plots treated with hyperphosphate and from the untreated plots are the following:

P ppm extracted by	Loam soil			Silt soil		
	Original	Incubated	Incubated with lime	Original	Incubated	Incubated with lime
NH ₄ Cl	1	1	1	0	2	1
NH ₄ F	21	37	21	17	21	16
NaOH	23	27	12	25	30	16
H ₂ SO ₄	222	204	231	197	171	193

As could be expected, in both soils the hyperphosphate phosphorus is accumulated mainly in the acid-soluble fraction. Yet, there seems to be some «fertilizer phosphorus» also in the ammonium fluoride-soluble and the alkali-soluble fractions. Provided, these differences in the phosphorus content of the soil treated with hyperphosphate and the untreated soil really represent fertilizer phosphorus, this would mean that during the four or five years of contact with the soil in the field, some apatite has been dissolved.

Incubation has brought about a significant decrease in the acid-soluble »fertilizer phosphorus» with an increase in the values for the fluoride-soluble phosphorus. The presence of lime has prevented this reaction, and there also seems to be less »fertilizer phosphorus» in the alkali-soluble fraction. In every case, results of this kind of calculation must be treated with caution.

Discussion

In the present incubation experiments liming did not exert any effect on the mineralization of organic phosphorus: the turning over of organic phosphorus into inorganic forms was equally high in samples incubated with or without lime. One possible reason for this result may be found in the fact that neither of the experimental soils was very acid, the pH values being 5.7 and 5.9 respectively. The incubation increased the acidity to pH 5.0 and 5.3, but incubation with lime could keep the pH values as high as 7.0 and 7.3, respectively.

These differences in the reaction and calcium carbonate content of the samples incubated without or with lime were reflected in the changes observed in the fractions of inorganic phosphorus. In the unlimed samples the phosphorus released from the organic compounds apparently was accumulated in the fractions extracted by ammonium fluoride and sodium hydroxide, or fractions which are supposed to represent aluminium bound and iron bound phosphorus, respectively. Yet, the former fraction may also contain dicalcium phosphate (9), and the latter one phosphorus dissolved from aluminium complex and adsorbed by iron oxide (2). When the samples were incubated with lime, the mineralized phosphorus mainly tended to enhance the ammonium-fluoride soluble fraction. In one case also an increase in the acid-soluble fraction was detected. This holds true both in regard to the samples from untreated plots and from the plots treated with superphosphate.

In the samples originating from the plots to which hyperphosphate was applied some years before the sampling, the incubation with its increase in the acidity of the soil resulted in a considerable increase in the ammoniumfluoride and sodium hydroxide soluble phosphorus accounted not only to the mineralisation of organic phosphorus but also to a marked decrease in the acid-soluble fraction. This suggests that a part of the apatite of the hyperphosphate was dissolved and turned over to fluoride- and alkali-soluble forms. Liming prevented also in these samples the accumulation of the mineralized phosphorus as the alkali-soluble form, and it kept the acid-soluble fraction from decreasing.

An attempt to calculate on the basis of the results obtained the amounts of fertilizer phosphorus in various fractions could not, of course, lead to very reliable results. It seemed that incubation with or without lime did not change the distribution of the »superphosphate-phosphorus» which mainly occurred in the fractions extractable by ammonium fluoride or sodium hydroxide. The incubation without lime appears to have reduced the acid-soluble fraction of hyperphosphate phosphorus and caused some increase in the fluoride-soluble forms.

The phosphorus test values obtained by the extraction with 0.03 N NH_4F — 0.025 N HCl were in accordance with the picture found by the fractionations. If

these values are supposed to indicate the availability of phosphorus to plants, it must be concluded that liming did not in any case improve the availability more than the incubation did. The test values for acetic acid soluble phosphorus proved to be rather worthless as the indicator of the phosphorus conditions of the present soil samples.

The results of these experiments are mostly in accordance with what has been previously published (4, 7, 10, 11). Only the complete failure of liming to increase the mineralization of organic phosphorus was somewhat surprising. Also the apparent accumulation of mineralized organic phosphorus into the ammonium-fluoride soluble fraction in the limed soils deserves attention. It may be taken to indicate either that aluminium oxide and hydroxide is able to bind phosphate also in the presence of calcium carbonate, or that this fraction may contain e.g. dicalcium phosphate.

S u m m a r y

Samples from two field trials were incubated at 20°C for seven months with or without an addition of 1 per cent CaCO₃. Both the samples of loam soil and silt soil originated from the surface inch of plots treated with no phosphate, superphosphate or hyperphosphate, resp.

It was found that liming did not in any case increase the amount of organic phosphorus mineralized during the incubation. Its effect was observed in the distribution of this phosphorus in the various fractions of inorganic phosphorus. In the distinctly acid samples which were incubated without lime the mineralized phosphorus seemed to accumulate as the ammonium fluoride-soluble and alkali-soluble forms, while in the neutral samples incubated with lime an increase only in the former fraction was detected. When the samples from the hyperphosphate plots were incubated without lime, apparently some apatite of the fertilizer was dissolved and sorbed as the ammonium fluoride soluble or alkali-soluble forms. No decrease in the acid-soluble fraction of these samples incubated with lime did occur.

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SELOSTUS

MUHITUKSEN JA KALKITUKSEN VAIKUTUKSESTA MAAN FOSFORIIN

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Tutkimuksessa selostetaan kahden superfosfaatin ja hienofosfaatin vertailukokeen maanäytteiden muhituksessa saatuja tuloksia. Todettiin, ettei kalkitus kummassakaan maassa lisännyt muhituksessa mineraloituvan orgaanisen fosforin määrää. Sen sijaan se vaikutti tämän fosforin sitoutumismuotoon: kun kalkitsematta muhitetuissa ja selvästi happamissa näytteissä vapautuva fosfori lisäsi sekä ammoniumfluoridiin että emäkseen liukenevaa fosforia, kalkituissa näytteissä havaittiin vain edellisen fraktion kasvaneen. Hienofosfaattiruutujen näytteitä muhitettaessa ilman kalkkia liukeni ilmeisesti lannoitteen apatiittia, joka pidättyi ammoniumfluoridiin ja emäkseen liukenevana fosforina. Kalkituissa näytteissä ei havaittu happoonliukenevan fraktion pienentyvän.