FRACTIONATION OF SOIL PHOSPHORUS

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Received for publication October 25, 1956

Inorganic phosphates in the soil can be classified into four main groups: calcium phosphate, aluminum phosphate, iron phosphate, and the reductant-soluble phosphate extractable after removal of the first three forms. Calcium phosphate exists mainly as apatite, but dicalcium, monocalcium, and octacalcium phosphate also exist in small amounts or as transitional forms. Iron, aluminum, and calcium phosphates also include adsorbed and surface-precipitated phosphates associated with the respective types of soil particles. The availability of soil phosphorus to plants depends apparently on the extensity of the phosphate surface of various chemical species (10, 11); conventional methods for the determination of available phosphorus appear to extract a portion of all chemical forms having either higher solubility or high specific surface. In contrast, the system presented herein for fractionation of inorganic soil phosphorus into the total amount of each discrete chemical form permits determination of the chemical status of native soil phosphorus and of the fate of applied phosphate fertilizer with or without the effect of cropping. The development of a system of fractionation of soil phosphorus should thus be helpful in the fields of soil chemistry, soil genesis, and soil fertility.

LITERATURE REVIEW

Previously no method was available for fractionation of the soil inorganic phosphate discretely into the total amount of each of the four principal chemical forms. Fractionation of soil inorganic phosphorus was studied by Fraps in 1906 (8), Fisher and Thomas in 1935 (7), Williams in 1937 (14), Dean in 1938 (6), Ghani in 1943 (9), and Williams in 1950 (13). In these methods iron and aluminum phosphates were combined into the same fraction. Since Turner and Rice in 1954 (12) found that neutral ammonium fluoride can dissolve aluminum phosphate but not iron phosphate, the phosphate extracted from soils by neutral ammonium fluoride by Bray and Kurtz (3) must be largely aluminum phosphate. In some of these methods (9, 13) the acid extraction which preceded the alkali extraction was shown to remove not only calcium phosphate but also considerable aluminum and iron phosphate. The phosphate insoluble in alkali and acid has been shown to be reductant soluble (2)[2], but the nature of this portion of the phosphorus has been only partly characterized.

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[1] This work, supported in part by a grant of funds from the Alumni Research Foundation of the University of Wisconsin, was presented at the North Central Branch of the American Society of Agronomy, August 21, 1956, at Lafayette, Indiana. The senior author is now Professor of Soils, National Taiwan University, Taipei, Taiwan (Formosa).

[2] Lancaster, J. D. Forms of inorganic phosphorus and relations to liming. Ph.D. thesis, *University of Wisconsin*, 1954.

MATERIALS

For control tests of the new system of soil inorganic phosphate fractionation, synthetic iron phosphate, synthetic aluminum phosphate, and apatite of known composition were employed. The methods were then tested with soil samples. The various materials used in these experiments are briefly described as follows:

Iron phosphate. Precipitated by digestion of 10 ml. of *M* $FeCl_3$ with 30 ml. of *M* NaH_2PO_4 in a total volume of 600 ml. of solution on a steam plate for 2 days, having a suggested formula as $FePO_4 \cdot 2H_2O$, and containing 17.2 per cent P.

Aluminum phosphate. Precipitated by digestion of 30 ml. of *M* $AlCl_3$ with 90 ml. of *M* NaH_2PO_4 in a total volume of 600 ml. of solution on a steam plate overnight, having a suggested formula as $AlPO_4 \cdot 2H_2O$, and containing 20.6 per cent P.

Apatite from Florida. Ground to pass a 100-mesh sieve, and containing 17.2 per cent P.

Catalina. A_2 horizon, 12–36 inches, a latosol (probably a low humic latosol) from Puerto Rico, with 18.2 per cent extractable Fe_2O_3, 0.045 per cent total P, and a pH of 6.2.

Wahiawa clay loam. Lower A horizon, 10–18 inches, a dark reddish-brown low humic latosol from Hawaii, with 10.1 per cent extractable Fe_2O_3, and a pH of 6.7.

Miami silt loam. *A_p horizon*, 0–6 inches, a gray brown podzolic soil from Kirwin farm near Madison, Wisconsin, with 0.83 per cent extractable Fe_2O_3, 0.036 per cent total P, and a pH of 7. *C_1 horizon*, 36–42 inches, a gray-brown podzolic soil from Mitchell farm near Madison, Wisconsin, with 1.7 per cent extractable Fe_2O_3, 0.048 per cent total P, and a pH of 4.9.

Barnes silt loam. C horizon, 54–64 inches, the calcareous subsoil of a Chernozem, with 0.93 per cent extractable Fe_2O_3, 0.02 per cent total P, and a pH of 8.

Reagents

N NH_4Cl. 53.5 g. solid dissolved in water and made up to 1 liter.

Neutral 0.5 N NH_4F. 18.5 g. solid dissolved in 1 liter of water; pH adjusted to 7.0 by 4*N* NH_4OH added dropwise.

0.1 N NaOH. 4.1 g. dissolved in 1 liter of water and the solution standardized to 0.1 *N* by addition of water.

0.5 N H_2SO_4. 15 ml. concentrated added to 1 liter of water, and the solution standardized by addition of water.

0.3 M sodium citrate (pH 7.3). 75 g. tribasic sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) dissolved in 900 ml. of warm water and made up to 1 liter.

Sodium dithionite. Reagent grade $Na_2S_2O_4$ (from Amend Drug and Chemical Co., New York).

Saturated NaCl solution. 400 g. suspended in 1 liter of water and shaken repeatedly. (The solubility of NaCl in water is 36 g. per 100 ml. of water at 20°C.)

Standard P solutions (50 ppm. and 5 ppm.). 0.2195 g. reagent KH_2PO_4 dissolved in sufficient water and made up to 1 liter. This stock solution contains 50 ppm.

P. Fifty ml. of this solution is diluted to 500 ml. to make a solution of 5 ppm. P in concentration.

0.8 M boric acid. 50 g. H_3BO_3 dissolved in water with heating and diluted to 1 liter.

Chloromolybdic acid solution. 15.0 g. c.p. $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ dissolved in about 300 ml. of distilled water and warmed to about 50°C. (solution filtered if cloudy). Solution is cooled and 350 ml. of 10 *N* HCl added slowly with stirring. Solution is again cooled, diluted with water to 1 liter, and stored in a brown bottle.

Chlorostannous reductant A. 10 g. $SnCl_2 \cdot 2H_2O$, dissolved in 25 ml. of concentrated HCl. This stock solution is stored in a brown bottle. 3 ml. of this stock solution are freshly diluted to 1 liter not longer than 4 hours before use.

Chlorostannous reductant B. 25 g. $SnCl_2 \cdot 2H_2O$, dissolved in 100 ml. concentrated HCl, diluted to 1 liter, and stored in a brown bottle with a siphon under a 10-mm. layer of white mineral oil.

Sulfomolybdic acid solution. 25 g. $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ dissolved in 200 ml. of water heated to 60°C. and filtered. A 275-ml. volume of arsenic-free and phosphorus-free concentrated H_2SO_4 is diluted to 800 ml. After both solutions have cooled, the ammonium molybdate solution is added to the sulfuric acid solution slowly with shaking, and the solution is made up to 1 liter when cooled.

30 per cent phosphorus-free H_2O_2, reagent grade. Superoxol shaken with kaolinite at the ratio of 1 g. to 10 ml. and the suspension filtered and centrifuged. Three additional treatments in this way decreases the phosphorus concentration to approximately 0.1 ppm. (7).

0.5 M $FeCl_3$. 135 g. of $FeCl_3 \cdot 6H_2O$ dissolved in water and made up to 1 liter.

2 N H_2SO_4. Approximately 55 ml. of concentrated diluted to 1 liter.

2N NaOH. 80 g. dissolved in water and diluted to 1 liter.

2,6 dinitrophenol indicator. 0.25 per cent in water (2,4 dinitrophenol may be substituted).

SOIL PHOSPHORUS FRACTIONATION PROCEDURE

The procedure or system for the extraction and determination of the various discrete chemical forms of inorganic phosphate of soils is described here, and the experimental tests on which the system is based follow.

Extraction and determination of phosphorus in aluminum phosphate

A 1-g. sample of soil is placed in a 100-ml. centrifuge tube and extracted with 50 ml. of 1 *N* NH_4Cl for 30 minutes on a shaking machine to remove water soluble and loosely bound phosphorus and the exchangeable calcium. The suspension is centrifuged and the supernatant solution discarded. The phosphorus in the solution is generally very low. To the NH_4-soil in the centrifuge tube, 50 ml. of neutral 0.5 *N* NH_4F is added and the suspension extracted on a shaking machine for 1 hour. The suspension is centrifuged and the clear supernatant solution is decanted for determination of phosphorus. The soil sample in the tube is saved for extraction of iron phosphate.

For determination of aluminum phosphate in the extract, an aliquot (usually 10 ml.) is placed in a 50-ml. volumetric flask. Ten ml. of distilled water, 15 ml. of 0.8 *M* boric acid and 10 ml. of chloromolybdic acid solution are added, the solution being well mixed after each addition. Then 5 ml of chlorostannous reductant A is added to develop the color. Water is added to make up the volume and the solution is well mixed. The color is measured on an photoelectrocolorimeter at 660 mμ within 5–20 minutes. The extract may have a light color due to organic matter, but it does not interfere with reading at 660 mμ. If the color is strong, an aliquot may be prepared without the reductant and used as a blank.

Extraction and determination of phosphorus in iron phosphate

The soil sample saved after the extraction of aluminum phosphate is washed twice with 25-ml. portions of saturated NaCl solution. It is then extracted with 50 ml. of 0.1 *N* NaOH on a shaking machine for 17 hours. The soil suspension is centrifuged for 15 minutes at 2400 rpm. and recentrifuged, if necessary, to obtain a clear solution which is decanted into another centrifuge tube. The soil sample is saved for extraction of calcium phosphate. For surface soils the decanted extract is usually highly colored with considerable organic matter, in which case 2 ml. of 2 *N* H_2SO_4 are added to the solution and then one or a few drops of concentrated H_2SO_4 until the organic colloids begin to flocculate. The suspension is then centrifuged and the clear solution collected.

To determine the phosphorus in the clear solution, an aliquot (usually 2 ml.) is placed in a 50-ml. volumetric flask. Water is added to give about 20 ml. The solution is adjusted to about pH 3 by addition of 2 *N* NaOH until 2, 6 dinitrophenol indicator color turns to yellow and then is brought back to colorless by addition of 2 *N* H_2SO_4. Then 2.0 ml. of sulfomolybdic acid solution is added and water is added to make 48 ml. and the solution mixed. Three drops of chlorostannous reductant B are added to develop the color. Water is added to volume and the solution mixed. The color is measured within 5–10 minutes at 660 mμ.

Extraction and determination of phosphorus in calcium phosphate

The soil sample saved after extraction of iron phosphate is washed twice with 25-ml. portions of saturated NaCl solution. It is then extracted with 50 ml. of 0.5 *N* H_2SO_4 for 1 hour on a shaking machine. The suspension is centrifuged to get the solution and the sample is saved for extraction of reductant soluble iron phosphate.

The solution thus obtained is generally colorless. A suitable aliquot (usually 1 to 5 ml.) is placed in a 50-ml. volumetric flask. Water is then added to about 25 ml. The solution is adjusted to about pH 3 by addition of 2 *N* NaOH until 2,6 dinitrophenol indicator color turns to yellow and the solution is brought back to colorless by addition of 2 *N* H_2SO_4. The color is then developed and measured as for iron phosphate. To test the noninterference of ferric ions, two identical aliquots are taken. To one enough standard phosphorus solution is added to give a final concentration of 0.2 ppm. of the added phosphorus. Then phosphorus is determined in both aliquots. The complete recovery of the added phosphorus establishes the noninterference of the ferric ions in the solution. Lower recovery, indicating ferric ion interference, can be diminished by additional chlorostannous acid or by use of Jones reductor.

Extraction and determination of reductant soluble iron phosphate

The soil sample saved after the extraction of calcium phosphate is washed twice with 25-ml. portions of saturated NaCl. It is then suspended in 40 ml. of 0.3 *M* sodium citrate solution and then 1.0 g. of solid $Na_2S_2O_4$ is added. The suspension is heated in a water bath at 80–90°C. with constant stirring for 15 minutes. The supernatant solution after centrifugation is collected in a 100-ml. volumetric flask. The soil is washed twice with 25-ml. portions of saturated NaCl solution, the washings being combined with the extract in the 100-ml. flask. The sample is saved for extraction of occluded aluminum phosphate.

The solution in the flask is made up to volume and aliquots taken for phosphorus (and Fe, if desired) analysis. A suitable aliquot (usually 1 to 5 ml.) taken for phosphorus determination is placed in a 150-ml. conical flask. About 10 ml. of distilled water and 5–10 ml. of the 30 per cent P-free H_2O_2 (5 ml. for 1–2 ml. aliquot and 10 ml. for 3–5 ml. aliquot) are added and the solution gently heated over a burner; vigorous splashing must not occur. The burner is moved under or away from the flask as needed. One drop of 0.5 *M* $FeCl_3$ (or 10 ml. of 100 ppm. Fe solution) is added to moderate the oxidation. The cessation of foaming (gas evolution) and beginning of ordinary boiling indicate the completion of oxidation. Complete drying must be avoided before the oxidation is complete, otherwise the very concentrated H_2O_2 and high temperature will ignite the organic matter, leaving some carbon particles. Small amounts of distilled water are added as necessary. After completion of oxidation, the solution is boiled for an additional 1 or 2 minutes and then dried on a steam plate. About 10 ml. of 2 *N* NaOH is added. The solution is boiled for 1–2 minutes and digested on a steam plate for 5 minutes. The suspension is poured into a 15-ml. centrifuge tube and centrifuged to throw down the iron oxide precipitate; the supernatant liquid is then decanted into a 50-ml. volumetric flask. The original 150-ml. flask is washed with 10 ml. of water into the same 15-ml. centrifuge tube and centrifuged. The supernatant solution is poured into the same 50-ml. volumetric flask. The flask washing is repeated once more and the supernatant solution is placed in the same volumetric flask. The combined supernatant solutions are made to volume and the phosphorus determined by the same method as for iron phosphate.

Extraction and determination of phosphorus in occluded aluminum phosphate

For soils high in iron oxide, the residue is extraced with neutral NH_4F to remove occluded aluminum phosphate. Alternatively, the residue is extracted with 0.1 *N* NaOH to remove occluded aluminum-iron phosphate (barrandite-like). The phosphorus in the solution is determined in the same way as aluminum phosphate or iron phosphate, respectively.

In a complete system of fractionation of soil phosphorus, total phosphorus and organic phosphorus are determined on two separate samples.

SOLUBILITY OF PURE PHOSPHATES

The separate extraction methods, in part adapted from the literature, were systematized in proper sequence in a complete system of fractionation (table 1) to remove the respective discrete chemical form of inorganic phosphate. In control studies, pure phosphates in amounts indicated (table 2) were treated as specified in the respective procedures. The percentage of phosphate dissolved in the fluoride solution (table 2) increased continuously with the decrease of the solid-solvent ratio. When the ratio decreased to 1 mg. P to 50 ml. solvent (1000 ppm. of P, 1 g. soil), aluminum phosphate was completely dissolved. Since 1 g. soil ordinarily contains less than 0.1 mg. or 100 ppm. P as aluminum phosphate (4), it is evident that its aluminum phosphate is completely soluble in 50 ml. of extract. This has been tested to be true whether the soil aluminum phosphate is in the form of synthetic aluminum phosphate or as natural minerals in -50-μ particle sizes such as variscite, taranakite, or wavellite. The soil aluminum phosphate formed largely from weathering processes is assumed, however, to be most similar to the synthetic form. A small percentage of iron phosphate also was dissolved in the NH_4F, and the amount increased with decrease of solid-solvent ratio (table 2). For a soil containing 50–200 ppm. iron phosphate or 0.05–0.2 mg. P per gram of soil, not over 5–10 per cent (7.5 per cent extrapolated for 0.1 mg. P) of the iron phosphate would be dissolved during the extraction of aluminum phosphate. To correct for this, a second extraction with NH_4F may be made and the amount of P thus extracted subtracted from the aluminum phosphate obtained in the first extraction and added to the subsequent iron phosphate ex-

TABLE 1

Phosphorus fractionation into discrete chemical forms

Phosphorus Fraction	Extractant	Forms of Phosphate Extractable	Method Adapted From*
1. Al-phosphate	Neutral 0.5 *N* NH_4F	Al-phosphate completely Fe-phosphate slightly	(3)
2. Fe-phosphate	0.1 *N* NaOH	Al-phosphate Fe-phosphate Organic phosphorus	(13)
3. Ca-phosphate	0.5 *N* H_2SO_4	Ca-phosphate completely Al- and Fe-phosphate considerably	(6)
4. Reductant soluble Fe-phosphate (iron oxide occluded)	$Na_2S_2O_4$-citrate	Fe-phosphate completely Al-phosphate negligibly	(1)
5. Occluded Al-phosphate	Neutral 0.5 *N* NH_4F	Al-phosphate completely	—
6. Occluded Al- Fe-phosphate	0.1 *N* NaOH	(Alternative or addition to *5*) Al- and Fe-phosphate completely	—

* Figures in this column represent references at end of this paper.

tracted by NaOH. For convenience, 10 per cent of the iron phosphate as obtained by subsequent NaOH extraction may be subtracted from aluminum phosphate and added to the iron phosphate. In this investigation, the latter method was employed. The result obtained in this way would not differ from the true value by more than a few ppm.

As much as 4.1 and 3.4 mg. P in the form of aluminum phosphate and iron phosphate, corresponding to 4100 and 3400 ppm. P in a gram of soil, is completely dissolved in 50 ml. of 0.1 *N* NaOH (table 2), while the solubility of apatite in the same extractant is negligible. Therefore, on the sample from which aluminum phosphate was removed, the separation of iron phosphate is complete.

Apatite in amount of 3.4 mg. or 3400 ppm. P in a gram of soil is completely dissolved in 50 ml. of 0.5 *N* H_2SO_4, but a very large quantity of aluminum phosphate and iron phosphate can also be dissolved in it. This shows that the NH_4F and NaOH extractions *must* be carried out in the procedure *before* the acid extraction.

EXTRACTION OF Al-, Fe-, AND Ca- PHOSPHATE FROM SOILS

Two soil samples, an iron-rich latosol (Catalina) and a gray-brown podzolic soil (Miami) were used to test the method for fractionation of aluminum, iron,

TABLE 2

Solubility of phosphates

Amount of Phosphates Taken	Total P	
	Taken	Dissolved
mg./50 ml.	*mg.*	*%*
Extractant = neutral 0.5 N NH_4F		
Al-phosphate:		
20	4.1	57.2
10	2.1	88.4
5	1.0	100.5
Fe-phosphate:		
20	3.4	2.2
10	1.7	2.8
5	0.9	3.1
2.5	0.4	4.1
0.5*	0.1	7.5
Apatite:		
20	3.4	0.9
10	1.7	1.0
5	0.9	0.9
Extractant = 0.1 N NaOH		
Al-phosphate: 20	4.1	100
Fe-phosphate: 20	3.4	100
Apatite: 20	3.4	trace
Extractant = 0.5 N H_2SO_4		
Al-phosphate: 20	4.1	39
Fe-phosphate: 20	3.4	46
Apatite: 20	3.4	100

* By extrapolation.

and calcium phosphorus. One gram of each sample, after treatment with NH_4Cl, was extracted successively with neutral 0.5 *N* NH_4F, 0.1 *N* NaOH, and 0.5 *N* H_2SO_4 for one to three times each (table 3).

The Catalina latosol contains a negligible amount of aluminum phosphate and also a relatively small amount of iron phosphate. The second and third extractions with NH_4F dissolved, therefore, only a negligible amount of phosphate. The Miami silt loam contains relatively large amounts of aluminum and iron phosphates. The phosphate dissolved in the second and third extractions with NH_4F, as shown above, can be attributed to iron phosphate. The next extraction with NaOH, therefore, gave only 94 ppm. phosphorus in comparison with 128 ppm. in the second sample (table 3) given only one extraction of NH_4F.

Considerable iron phosphate was dissolved in the second and third extractions

TABLE 3

Amount of soil phosphorus extracted by successive extractions with each extractant

Extractants	Extractions	Catalina Latosol A_1 Horizon		Miami Silt Loam C_1 Horizon, 36–42 in.	
		Successive extractions	One extraction	Successive extractions	One extraction
		ppm.	*ppm.*	*ppm.*	*ppm.*
Neutral 0.5 *N* NH_4F	1st	2.5	0	72	77
	2nd	0		12	
	3rd	0		10	
0.1 *N* NaOH	1st	37	42	94	128
	2nd	11		10	
	3rd	6.2		10	
0.5 *N* H_2SO_4	1st	7.8	6.3	113	—
	2nd	6.5		3.5	

with NaOH in both Catalina latosol and Miami silt loam. Phosphorus in synthetic iron phosphate (equivalent to 3400 ppm. in 1 g. soil) can be completely dissolved in one extraction of NaOH (table 2), yet successive NaOH extractions of soils which contain much less P continuously dissolve a portion of iron phosphate in the second and third extractions (table 3). Where does the P in the second and third extractions come from? The Catalina latosol and the Miami silt loam contain about 320 ppm. and 150 ppm. P, respectively, in reductant soluble (occluded) iron phosphate (table 4). The portion of iron phosphate dissolved in the second and third extracts must come from the occluded form, through diffusion or from the freshly exposed iron phosphate surface formed by the breaking of particles during the 17-hour shaking. The occluded form is only physically different from that unoccluded so the distinction between them would not be very sharp. The sudden drop from amount of phosphorus dissolved from the first extraction to that of the second extraction fully justifies placing the iron phosphate dissolved in the first extraction in a different category from that of subsequent extractions. One single extraction with NaOH was adopted, therefore, to separate the iron phosphate from occluded phosphorus. The second extraction with H_2SO_4 also dissolved a small amount of phosphorus, attributed also to slow removal of some occluded phosphate.

REDUCTANT SOLUBLE IRON PHOSPHATE

The portion of phosphorus not extracted by the NH_4F, NaOH, and H_2SO_4 treatments (sometimes termed "insoluble" phosphorus, or attributed to "lattice" phosphorus by various workers) is almost completely dissolved by the dithionite-citrate reduction-chelation procedure of Aguilera and Jackson (1) for dissolving free iron oxide coatings. The reduction-chelation treatment was given separately to 20 mg. each of synthetic iron phosphate and aluminum phosphate. Within the analytical error, 100 per cent of the iron phosphate and a negligible amount of the

TABLE 4

Reductant soluble phosphorus, and NaOH or NH_4F soluble phosphorus after reductant extraction

Treatments of Reduction Chelation	Wahiawa Latosol	Catalina Latosol	Miami Silt Loam	
			A_p:0–6 in.	C_1:36–42 in.
	ppm.	*ppm.*	*ppm.*	*ppm.*
One treament	504	320	150	158
Total of two treatments	—	325	138	150
NaOH after one treatment	119	48	8	9
NH_4F after one treatment	97	40	6	—

aluminum phosphate dissolved. The soil phosphorus dissolved by this treatment may properly be termed, therefore, reductant soluble iron phosphate. An iron oxide precipitate apparently is formed on the surface of iron phosphate and on the surface of aluminum-iron phosphate (barrandite-like) in the course of chemical weathering in soils by hydrolysis of iron phosphate and other iron salts. The relative insolubility of iron oxide in the NH_4F, NaOH, or H_2SO_4 extraction must

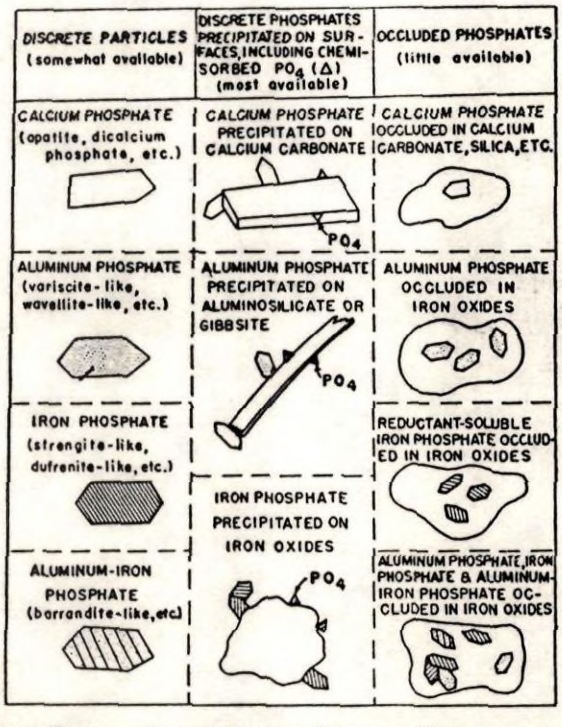

FIG. 1. DIAGRAMMATIC REPRESENTATION OF THE PHYSICAL DISTRIBUTION OF THE DISCRETE CHEMICAL FORMS OF INORGANIC PHOSPHATES PRESENT IN SOILS

[*solubility of each chemical form in NH_4F, NaOH, H_2SO_4, and $Na_2S_2O_4$-citrate is given in text and summarized in table 1; solubility of dufrenite in NaOH has been established (6, 13).*]

account for the fact that the phosphate thus covered can only be dissolved after the removal of the iron oxide coating.

The Wahiawa latosol, the Catalina latosol, and a Miami silt loam after removal of aluminum, iron, and calcium phosphate by successive extraction with NH_4F, NaOH, and H_2SO_4 were treated once with sodium dithionite-citrate and yielded 504, 320, and 150 ppm. of reductant soluble phosphorus, respectively, (table 4). Since two such treatments with dithionite applied to a second sample of the latter two soils did not extract materially more phosphorus, one treatment would appear to be sufficient to complete extraction of the reductant soluble iron phosphate.

After one dithionite-citrate treatment of the soils, further extraction with either NaOH or NH_4F dissolved appreciable amounts of phosphorus. Since only aluminum phosphate is soluble in either NaOH or neutral NH_4F, most of the residual phosphate must be aluminum phosphate. The somewhat higher amount extracted by NaOH than by NH_4F (table 4) indicates that there is also some iron phosphate left after the reduction-chelation, most likely in aluminum-iron phosphate (barrandite-like) since any pure iron phosphate would have dissolved in the dithionite-citrate extraction. The physical distribution of the various discrete chemical forms of soil inorganic phosphates is summarized in figure 1.

FRACTIONATION OF PHOSPHORUS

The phosphorus of soils belonging to the latosol, gray-brown podzolic, and chernozem groups were fractionated (table 5). The results of the replicated samples are in good agreement. Iron phosphate, particularly the reductant sol-

TABLE 5

Fractionation of soil phosphorus in replicated samples

Fraction	Catalina Latosol A_1 Horizon 12–36 in.			Miami Silt Loam A_p Horizon 0–6 in.			Barnes Silt Loam C Horizon 54–65 in.	
	a*	b*	c*	a	b	c	a	b
NH_4Cl, pH 7.0	0	0	0	1	1	1	0	0
Al-phosphate	0	0	2	17	15	17	6	7
Fe-phosphate	42	44	42	76	79	77	3	4
Ca-phosphate (apatite)	6	7	9	55	62	58	185	190
Reductant soluble Fe-phosphate	320	309	325†	150	125	138†	0	0
Occluded Al–Fe phosphate	48	52	45§	8	8	6	0	0
Organic P**	8	8	8	52	52	52	—	—
P in residue	15	15	15	4	4	4	—	—
Added total P	*439*	*435*	*446*	*362*	*341*	*352*	*194*	*201*
*Total P***	*450*	*450*	*450*	*364*	*364*	*364*	—	—

* a, b, and c = replicated samples.

† Treated twice.

§ Follows treatment twice with $Na_2S_2O_4$-citrate.

** Organic phosphorus and total phosphorus are determined on two separate samples.

uble form, dominates highly-weathered soils, but these forms are also the most abundant in the gray-brown podzolic (Miami) soil. Aluminum phosphate and calcium phosphate occur in significant amounts in the latter soils, while calcium phosphate is dominant in the calcareous subsoil of the Chernozem (Barnes) soil. The ratio of aluminum phosphate to iron phosphate varies from 0.2 in Miami soil to 2 in the little-weathered Barnes subsoil, and in this connection fractionation of phosphorus in several soil profiles (4) was found to vary even more widely as a function of the degree of chemical weathering.

The fusion analysis of the residual samples of both Catalina latosol and Miami silt loam after all extractions yielded 15 and 4 ppm. of P respectively. The difference between the added total and determined total amount of P in the soils is within the cumulative experimental error.

SUMMARY

A procedure was developed for fractionation of soil phosphorus into the discrete chemical forms, calcium phosphate, aluminum phosphate, iron phosphate, reductant soluble (iron oxide coated) iron phosphate, and occluded aluminum-iron phosphate, based on the selective solubility of phosphates in various extractants. Strengite, variscite, and apatite were used for control study. Neutral ammonium fluoride in a single extraction dissolves aluminum phosphate completely, iron phosphate slightly, and apatite negligibly, when the phosphate-extractant ratio corresponds to that of 1 g. soil to 50 ml. extractant. Sodium hydroxide completely dissolves both aluminum phosphate and iron phosphate but apatite not at all. Sulfuric acid dissolves apatite completely and aluminum phosphate and iron phosphate considerably. The fluoride and alkali extractions, therefore, must precede the acid extraction to obtain complete separation of these three chemical forms of phosphate. The reductant soluble iron phosphate is dissolved by reduction-chelation treatment with sodium dithionite-citrate after fluoride, alkali, and acid extractions. Soils rich in iron oxides sometimes contain a significant amount of occluded aluminum-iron phosphate (barrandite-like) which is not extracted by dithionite-citrate. The occluded aluminum phosphate is extracted with neutral fluoride and the total of the barrandite-like aluminum-iron phosphate is removed by NaOH. Good reproducibility of results for the various discrete chemical forms of soil phosphates was obtained among replicated soil samples.

REFERENCES

(1) Aguilera, N. H., and Jackson, M. L. 1953 Iron oxide removal from soils and clays. *Soil Sci. Soc. Amer. Proc.* 17: 359–364; 18: 223, 350.

(2) Bauwin, G. R., and Tyner, E. H. 1954 The nature and distribution of nonextractable phosphorus in some Gray-Brown Podzolic, Prairie, and Planosol soil profiles. *Agron. Abstracts*, p. 11, American Society of Agronomy, Madison Wis.

(3) Bray, R. H., and Kurtz, L. T. 1945 Determination of total, organic and available phosphorus in soils. *Soil. Sci.* 59: 39–45.

(4) Chang, S. C., and Jackson, M. L. 1958 Soil phosphorus fraction in some representative soils. *J. Soil Sci.* In press.

(5) CHANG, S. C., AND JACKSON, M. L. 1956 Removal of phosphorus from hydrogen peroxide by kaolinte. *Science* 124: 1209.

(6) DEAN, L. A. 1938 An attempted fractionation of soil phosphorus. *J. Agri. Sci.* 28: 234–246.

(7) FISHER, R., AND THOMAS, R. P. 1935 The determination of forms of inorganic phosphorus in soils. *J. Amer. Soc. Agron.* 27: 863–873.

(8) FRAPS, G. S. 1906 Availability of phosphoric acid of the soil. *J. Amer. Soc. Agron.* 28: 823–834.

(9) GHANI, M. O. 1943 Fractionation of soil phosphorus: I. *India J. Agri. Sci.* 13: 29–45.

(10) KITTRICK, J. A., AND JACKSON, M. L. 1956 Electron microscope observations of the reaction of phosphate with minerals, leading to a unified theory of phosphate fixation in soils. *J. Soil Sci.* 7: 81–89.

(11) OLSEN, S. R., AND WATONABE, F. S. 1957 A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. *Soil. Sci. Soc. Amer. Proc.* 21: 144–149.

(12) TURNER, R. C., AND RICE, H. M. 1954 Role of fluoride ion in release of phosphate adsorbed by Al and Fe hydroxide. *Soil Sci.* 74: 141–148.

(13) WILLIAMS, C. H. 1950 Studies on soil phosphorus: I. *J. Agri. Sci.* 40: 233–242.

(14) WILLIAMS, R. 1937 The solubility of soil phosphorus and other phosphorus compounds in sodium hydroxide solution. *J. Agri. Sci.* 27: 260–270.

CALCIUM UPTAKE BY TOMATOES AS INFLUENCED BY NATURE AND PER CENT OF CALCIUM SATURATION OF Ca-H-CLAY SYSTEMS

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Received for publication October 8, 1956

Soils differ greatly in ability to supply nutrient cations to a given crop and because of the complex nature of soil an evaluation of factors influencing availability of nutrient cations to a given plant species is difficult. For example, soils are composed of both organic and inorganic cation-exchange colloids, and many soils have two or more types of these inorganic colloids (clays). Plant uptake of nutrient cations from a definite clay system offers an approach to the elimination of complex soil variables.

The tenacity or energy with which a cation as calcium is attracted to clay colloids is determined by the type of colloid, the per cent saturation, and the nature of complementary cations present. Albrecht (1) reported that Ca availability to plants increased with an increase in per cent Ca saturation of Putnam (montomrillonitic) clay. Allaway (2) reported great differences in Ca availability from different types of clay colloids as measured by soybean uptake of Ca. The nature of the colloid influenced Ca uptake more than per cent Ca saturation. At 40 per cent Ca saturation, kaolinite supplied soybeans with more Ca than did Mississippi bentonite at 80 per cent Ca saturation. Mehlich and Colwell (9) reported that yield and Ca content of soybeans and cotton, grown on a montmorillonitic soil colloid, increased with each increase in per cent Ca saturation, reaching a maximum at the highest level used, that is, 80 per cent Ca saturation. Equal amounts of Ca were supplied at each per cent saturation. When a kaolinitic clay was used, however, growth and Ca content of cotton increased only with the increment of 20 to 40 per cent Ca saturation. With soybeans on kaolinitic clay, growth increased with the 20 to 40 per cent Ca increment, but with the 40 to 60 per cent Ca increase in one case it decreased and in another it increased slightly. It should be noted that at each per cent Ca saturation both soybeans and cotton obtained more Ca from the kaolinitic than from the montmorillonitic colloid (9).

In a related study Mehlich and Colwell (10) reported that Ca uptake by peanuts from kaolinitic clay was more directly related to total Ca present than to per cent Ca saturation. For montmorillonitic clay, however, Ca uptake was more directly related to per cent Ca saturation. These results clearly show that there are important differences in the Ca-supplying power of kaolinitic as compared to montmorillonitic clays.

Mattson (7) and Elgabaly and Wiklander (4) described the interaction and

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[1] Contribution No. 1073 of the University of Massachusetts, College of Agriculture, Experiment Station, Amherst.