ON CHEMICAL METHODS OF DETERMINING PHOSPHORUS AVAILABILITY IN SOILS.

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Weak acid solvents have been extensively employed for differentiating between the available and the non-available portions of the mineral plant food constituents—particularly phosphorus—in the soil. Numerous methods have been proposed by different workers, and in almost every case, a different solvent for extraction has been used. Thus, dilute acetic acid, originally suggested by Liebig, was tried by Deherain (*Ann. Agron.*, 1891, 17, 445); an aqueous solution of carbon dioxide was used by Gerlach (*Landw-Versuchs. Stat.*, 1896, **46**, 201), Schloesing (*Compt. rend.*, 1900, 131, 149) and Mitscherlich (*Landw-Jahrb.*, 1907, **36**, 309; *Bodenkunde*, 1920, p. 201); Hoffmeister (*Landw-Versuchs. Stat.*, 1898, **50**, 363) suggested an ammoniacal solution of humic acid, while Petermann (cited from Hall and Plymen, *see* later) employed a solution of ammonium citrate. Maxwell (*J.A.C.S.*, 1899, **21**, 415) and Emmerling (*Bied. Central.*, 1900, **29**, 75) used 1 per cent. solutions of aspartic and oxalic acids respectively. Hydrochloric acid of varying strengths was also used by some workers (Shedd, *Soil Sci.*, 1923, **15**, 383; Fraps, *Jour. Assoc. Offic. Agric. Chem.*, 1923, **6**, 329; and others). Dyer (*Trans. Chem. Soc.*, 1894, **65**, 115; *Phil. Trans. Roy. Soc.*, 1901, **194**, 234) proposed the use of 1 per cent. citric acid (*cf.* Grupe and Tollens, *Ber.*, 1880, **13**, 1267; Ollech and Tollens, *J. f. Landw.*, 1882, **30**, 519; Stutzer, *Chem. Ind.*, 1884, 7, 37). Schloesing (*Compt. rend.*, 1899, **128**, 1004) and de'Sigmund (*J.A.C.S.*, 1907 **29**, 929) and Fraps (*Texas Agric. Exptl. Stat. Bull.*, No. 126, 1909; *Jour. Amer. Soc. Agron.*, 1915, 7, 33) employed dilute nitric acid. Dirks and Scheffer (*Landw. Jahrb.*, 1928, **67**, 779) recommended an aqueous solution of calcium acid carbonate while Löhse and Ruhnske (*Soil Sci.*, 1933, **35**, 437) used a solution of potassium bisulphate buffered at pH 2.5. Very dilute acetic acid suitably buffered has also been employed by Morgan (*Trans. Third Internat. Cong. Soil Sci.*, Oxford, 1936, **1**, **103**), Hibbard (*Soil Sci.*, 1931, **31**, 437), Demolon and Barbier (*Compt. rend.*, 1929, **189**, 1310), and others. Truog (*Jour. Amer. Soc. Agron.*, 1930, **22**, 874) used a 0.002N sulphuric acid solution buffered at pH 3.0 with ammonium sulphate (*cf.* Arrhenius, *Chem. Abstr.*, 1929, **23**, 2780).

Several other extractants have been suggested from time to time, but of these, the citric acid method of Dyer (*loc. cit.*) has been generally favoured by several workers (König *et al.*, *Landw. Jahrb.*, 1923, **59**, 97; *ibid.*, 1923, **58**, 55; *ibid.*, 1923, **58**, 87; *ibid.*, 1923, **59**, 65; *Z. Pflanz. Düng.*, 1924, **3B**, 497; Lemmermann *et al.*, *Landw. Versuchs-Stat.*, 1921, **98**, 155; *Z. Pflanz. Düng.*, 1923, **2A**, 363; Wood, *Trans. Chem. Soc.*, 1896, **69**, 287; Wood and Berry, *Jour. Agric. Sci.*, 1905, **1**, 114; McGeorge, *Louisiana Planter*, 1924, **72**, 312; Hall and Plymen, *Trans. Chem. Soc.*, 1902, **81**, 117; Malherbe and Myburgh, *Proc. Third Internat. Cong. Soil Sci.*, 1936, **1**, 238, and others), although, it has been found to be thoroughly unsuitable for certain soils, especially calcareous ones (*cf.* Brioux, *Ann. Sci. Agron.*, 1922, **39**, 82; Engels, *Ernährung d. Pflanze.*, 1925, **21**, 172; Das, *Mem. Dept. Agric., India, Chem. Ser.*, 1926, **8**, 69, and others) for which 1 per cent. potassium carbonate solution has been suggested (Das, *Soil Sci.*, 1930, **30**, 33: Hockensmith *et al.*, *Colorado Agric. Exptl. Sta. Tech. Bull.*, No. 2. 1933, and others).

Conflicting results have been obtained by several workers in regard to the different methods of determining phosphate availability in soil (Troug and Dean, *Trans. Third Internat. Cong. Soil Sci.*, 1936, **1**, 106; Hibbard, *Soil Sci.*, 1931, **31**, 437; Hasenbäumer and Balks, *Z. Pflanz. Dung.*, 1930, **9B**, 456; Jessen and Lesch, *ibid.*, 1930, **18A**, 218; Dworak, *ibid.*, 1931, **10B**, 201; Malherbe and Myburgh, *loc. cit.*; de'Sigmund, Zohls and Becker, *Proc. First Internat. Cong. Soil Sci.*, 1928, 1, Commn. I, p. 230; Lemmermann, Fresenius and Lesch, *Z. Pflanz. Düng.*, 1927, **6B**, 163, and others), and there is, generally speaking, a lack of sufficient information regarding the distinction between the more easily available and the less available plant nutrients. In the hope of obtaining some critical results, with regard to the action of dilute acids on the phosphorus compounds of the soil, the present investigation on the factors influencing the availability of phosphorus and the fate of added phosphates in the soil was undertaken. The experiments involved extraction with various solvents after treatment of the soil with varying known amounts of different forms of both soluble and insoluble phosphates. It was thought that the discrepancies in the results of previous investigators due to differences in the nature and composition of the soil would be overcome by using throughout the same soil subjected to different treatments.

EXPERIMENTAL.

Materials and Methods: Soil.—This was a light clay obtained from an adjoining paddy field. The soil was air-dried and ground to pass through the 40-mesh sieve.

Phosphate.—A standard solution of potassium dihydrogen phosphate (KH_2PO_4)—Kahlbaum, A.R. quality—was employed. Each c.c. of this solution corresponded to 1 mg. of P_2O_5. The strength of the solution was checked from time to time.

Phosphate Estimation.—Phosphorus in solution was determined according to a modified Neumann (*Z. Physiol. Chem.*, 1902, **37**, 115;

ibid., 1904, **43**, 35) procedure after removal of silica (Sreenivasan, unpublished).

Fixation of Phosphate by the Soil.—The fixing power of the soil for phosphate has been studied by a number of workers (*vide* Sreenivasan, *Proc. Ind. Acad. Sci.*, 1936, **3B**, 283). The extent to which added phosphate is retained by the soil in the present investigations was studied under different conditions and it was observed that the amount of soil, the quantities of added phosphate, the volume of extractant, the time of shaking and the temperature were among the factors governing the extent of fixation. It was observed that even addition of soluble phosphates, corresponding to 10 mg. of P_2O_5 per 100 g. of soil, resulted in more than 80 per cent. of the same being converted into water-insoluble forms.

Extraction of Phosphate by Different Solvents.—In soils which are free from soluble precipitants, such as salts of iron and aluminium, it may be assumed that added soluble phosphates would be completely available immediately after application to the soil. If, therefore, any suitable method can be developed for recovering the entire quantity of such a phosphate immediately after addition to the soil, then it can be successfully applied as a procedure for the estimation of available phosphorus in soils. With this end in view, the soil (50 g. lots) was first treated with 10 c.c. of the phosphate solution (corresponding to 10 mg. P_2O_5) and allowed to stand for 15 minutes. The soil-phosphate mixtures were then transferred to shaking bottles, treated with 200 c.c. each of the different extractants as given in Table I below, and shaken in an end-over-end shaker for 30 minutes and filtered. In each case, phosphate in aliquots of the filtrate was estimated and from this, the total amounts in the extracts were calculated. The results, after allowing for the amounts of phosphate extracted from the untreated soil by the different extractants, are given in Table I.

TABLE I.

Extractant	Mg. P_2O_5 in solution
Water	1·8
N/5 Sulphuric acid	5·2
N/5 Nitric acid	3·3
N/5 Hydrochloric acid	3·6
N/5 Citric acid	4·7
N/5 Ammonium citrate	4·4

It may be observed (*Table I*) *that considerably* larger quantities of phosphate are brought into solution by the dilute acids compared to extraction with water. Sulphuric and citric acids give the maximum amounts of phosphate in the extracts.

Use of acids stronger than N/5 resulted in the structure of the soil particles being partially affected while more dilute acids gave lower values for phosphorus in solution. Thus with N/10 and N/50 sulphuric acids, the corresponding values for phosphorus in solution were 3.8 and 2.1 mg. P_2O_5 respectively, while N/100 and N/200 acids gave still lower values.

Repeated extraction with successive 200 c.c. portions of the different extractants gave logarithmically decreasing amounts of phosphorus in solution (*cf.* Hall and Amos, *Trans. Chem. Soc.*, 1906, **89**, 205). *Thus, with N/5 sulphuric* acid, the second, third and fourth extraction of the soil gave respectively, 2.8, 1.6 and 1.0 mg. of P_2O_5 in solution. Besides, there did not appear to be any sharp line of distinction between the available and the unavailable forms of phosphorus in the soil.

Effect of Volume of Extractant.—Increasing the volume of extractant invariably gave higher values for the amounts of phosphorus brought into solution. But, as was expected, varying values were obtained for the different extractants. The values obtained in a few cases using 50 g. lots of soil treated with 10 c.c. of phosphate solution are given in Table II.

TABLE II.

Extraction with	Mg. P_2O_5 in solution
1 litre of N/5 sulphuric acid for 15 minutes ..	9·6
2 litres of N/20 sulphuric acid for 15 minutes ..	8·0
1 litre of 1 per cent. citric acid for 15 minutes ..	5·4
1 litre of 1 per cent. ammonium citrate for 15 minutes	5·0

Successive leaching of the soil-phosphate mixture on the Buchner with small quantities of the extractant also removed larger quantities of phosphate into solution (Table III).

TABLE III.

Extractant	Volume of leachate	Mg. P_2O_5 in solution
N/5 Sulphuric acid	500 c.c.	9·7
N/20 Sulphuric acid	1000 ,,	5·1
N/50 Sulphuric acid	1000 ,,	4·1
N/50 Sulphuric acid buffered to pH 3·0 with ammonium sulphate	1000 ,,	5·8
1 per cent. citric acid	750 ,,	8·3

Hibbard (*loc. cit.*) found none of the single extraction methods satisfactory compared to some form of relative solubility (*cf.* Lemmermann, *Landw.-Versuchs. Stat.*, 1917, **89**, 100; *Handbuch. d. Bodenlehre,* 1931, **8**, 174; Lemmermann and Fresenius, *Z. Pflanz. Düng.*, 1930, **15A**, 249; *ibid.*, 1930, **9B**, 1; Van der Spuij, *ibid.*, 1925, **5A**, 281; Vanstone, *Jour. Agr. Sci.*, 1925, **15**, 460; *vide also* Crowther, *Ann. Repts. Soc. Chem. Ind.*, 1928, **13**, 501) expressing the relation of the amounts of phosphate extracted under two different conditions. There has been considerable discussion on the value of single or repeated extraction with water or solutions of carbon dioxide or calcium acid carbonate for characterising the readily soluble phosphates (*vide* Crowther, *Ann. Repts. Soc. Chem. Ind.*, 1931, **16**, 495).

Influence of Time of Shaking.—The soil-phosphate mixture (50 g. soil + 10 mg. P_2O_5) was shaken for varying periods of time with different strengths of sulphuric acid. The quantities of phosphorus thus brought into solution are given in Table IV.

TABLE IV.

Time of shaking (mins.)	N/5 H_2SO_4 (500 c.c.)	Extraction with N/10 H_2SO_4 (1 litre)	N/20 H_2SO_4 (1 litre)
		Mg. P_2O_5 in solution	
5	4·4	..	..
15	6·5	9·2	7·5
30	6·3	9·0	7·6
60	5·2	8·4	7·0
120	5·0	..	..
240	4·8	7·8	6·4
360	3·8	..	..

It may be observed that, if the shaking is prolonged to beyond 15–30 minutes, there is a definite fall in the values obtained for phosphorus in solution. Russell and Prescott (*Jour. Agric. Sci.*, 1916, **8**, 65) observed that when acids of low concentration are allowed to act on soil, the amount of phosphorus compounds extracted decreases with time and that the seat of this reverse action is probably in the soil. It is likely that in the foregoing experiments with added phosphate, the fall in phosphorus values after 30 minutes is due to a refixation of dissolved phosphate by the soil adsorbing complex. Such refixation increases with the concentration of acid. Refixation was also greater at higher temperatures of extraction. Thus, in a parallel series of experiments, when the soil-phosphate mixture was extracted with 200 c.c. of N/5 sulphuric acid at about 90°C., only 4.4 mg. of P_2O_5 was brought into solution at the end of 30 minutes, while the corresponding figure at the end of 1 hour was 3.8 mg.

Influence of Reaction of Soil on Phosphate Retention.—The pH of the soil was adjusted in the alkaline and acid ranges by addition of alkali or acid as the case may be. The soils so obtained were then treated with different quantities of the phosphate solution at the rate of 20 mg. of P_2O_5 for every 100 gm. of soil. The phosphate in solution was estimated in each case after extraction with water (Table V).

TABLE V.

Mg. P_2O_5 added	pH of soil		
	4·4–4·6	6·8–7·0	8·0–8·2
	Mg. of P_2O_5 in solution		
5·0	0·6	1·4	3·8
10·0	0·7	2·5	4·3
15·0	0·9	3·4	5·6
20·0	1·0	4·1	7·4

It is seen that the extent of phosphate recovery decreases with increase in the acidity of the soil (*cf.* Mattson, *Proc. First Internat. Cong. Soil Sci.*, 1927, Commn. II, p. 199; *Soil Sci.*, 1931, **32**, 343; Gordon *et al.*, *Soil Sci.*, 1922, **14**, 1,441, 449; *ibid.*, 1923, **15**, 157; Vanstone, *Trans. Far. Soc. Symp.*, 1924, p. 614; McCool, *Proc. First Internat. Cong. Soil Sci.*, 1927, Commn. VI, p. 1207; Sreenivasan, *loc. cit.*)

Influence of Neutral Salts on Phosphate Retention.—Addition of small quantities (5 c.c. of 0.5 per cent. solution) of neutral salts such as sodium chloride, potassium sulphate, magnesium sulphate, etc., to the soil (50 g. lots) prior to treatment with phosphate (10 mg. P_2O_5) did not have any appreciable effect on the recovery of water-soluble phosphate. Salts of calcium, iron and aluminium, however, had a definite effect on the extraction of phosphate from combination.

The results obtained with soil (50 g. lots) treated with 5 c.c. of 0.1 per cent. aqueous solutions of calcium chloride, ferric chloride and aluminium sulphate respectively, prior to addition of phosphate, followed by extraction with water are given in Fig. 1 in the form of a 'solubility-rate curve' (Vanstone, *loc. cit.*, 1925; Simon, *Soil Sci.*, 1930, **29**, 71).

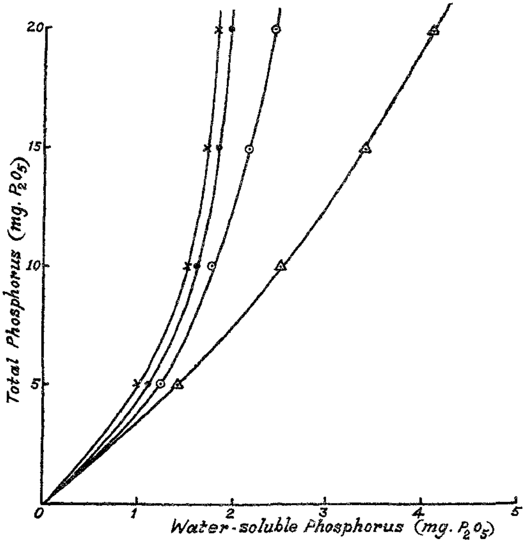

FIG. 1. Influence of Ca, Al and Fe salts on phosphate retention by soil.

△—△ Soil untreated control
⊙—⊙ „ treated with Ca salt
●—● „ „ Al salt
×—× „ „ Fe salt

It may be seen that the curves for the iron- and aluminium-treated soils lie nearest the axis of ordinate, *i.e.*, they have the least soluble phosphorus. With calcium chloride, however, the curve recedes greatest from the vertical axis, showing that calcium does not have such an adverse effect on phosphate solubility. It may be observed in this connection that earlier workers (Deherain, *loc. cit.*; Stoddart, *Wis. Agric. Expt. Sta. Repts.*, 1906, p. 172,; Vanstone, *loc. cit.*, 1925: Simon, *loc. cit.*; Lemmermann and Fresenius, *Z. Pflanz. Düng.*, 1923, **2A**, 363; Hall, *The Soil*, 1921, p. 265; Mckibbin, *Proc. Second Internat. Cong. Soil Sci.*, 1932, **2**, Commn. II, 81, and others) have found more soluble phosphorus in limed than in acid soils and that addition of calcium increases the availability of phosphate in the soil, probably because, lime phosphates are more soluble than iron and aluminium phosphates (Hall, *loc. cit.*). Stephenson and Powers (*Soil Sci.*, 1924, 18, 317) have shown that additions of elemental sulphur to soil cause decrease in the amounts of soluble phosphorus in the soil solution.

Effect of Nature of Soil on Solubility of Added Phosphate.—Specimens (50 g. each) of different types of soil (air-dried, 40 mesh) were treated with known amounts of phosphate and the amounts of the latter extracted by water and by N/5 sulphuric acid respectively, determined as before. The results, together with the description of the soils, are given in Table VI.

TABLE VI.

Soil	Extraction with					
	200 c.c. of water (shaking 30 mins.)			200 c.c. N/5 sulphuric acid (shaking 15 mins.)		
	Mg. of P_2O_5 added					
	0 (Control)	10	20	0 (Control)	10	20
	(P_2O_5 in solution mg.)					
Sandy soil—Travancore ..	Traces	5·5	11·9	1·3	7·2	14·9
Sandy loam—Travancore ..	,,	3·1	9·6	0·9	5·2	13·7
Red loam—Bangalore ..	,,	0·7	2·2	1·0	5·3	10·7
Light clay—Bangalore ..	,,	2·1	2·8	0·6	5·2	10·9
Alluvial—S. Bihar ..	,,	1·2	2·5	1·0	2·7	9·4
Farmland—Alkaline-Sindh ..	,,	0·8	1·3	0·6 (1·2)	1·2 (5·8)	2·7 (6·4)
Black cotton—Nagpur ..	,,	1·2	2·6	0·8 (1·6)	1·1 (6·1)	3·5 (6·9)
Kari—Travancore ..	,,	Traces	Traces	0·9	2·8	5·7

It would be seen that the different soils with more or less the same level of phosphate supply, show varying degrees of retention both in presence of water and with N/5 sulphuric acid. The latter extracts much larger quantities of phosphate from the soil than water alone.

The two soils from Nagpur and Sindh respectively, were alkaline in character and had, besides, a high buffering capacity; the low values for phosphorus, obtained with sulphuric acid extraction in these cases may be due to a part of the acid having been used up by the soils prior to dissolution. Separate extractions were therefore carried out with these soils after addition of enough acid to bring the reaction to neutral in each case. The results are included in brackets in Table VI above and are found to be higher than without previous neutralisation of the soils.

Determination of Phosphate Availability by Some Well-known Methods.—The clay soil used in earlier experiments was treated in 50 g. lots with the same amount of KH_2PO_4 solution (10 mg. P_2O_5) and the amounts of available phosphorus as estimated by several of the well-known methods are given in Table VII together with the details of extraction.

TABLE VII.

Extractant	Per cent. of added phosphate in the extract
Dyer's 1 per cent. citric acid	25·3
Frap's 0·2 N nitric acid	21·0
Truog's 0·002 N sulphuric acid	65·0
Das's 1 per cent. potassium carbonate	36·0
Egner's calcium lactate-hydrochloric acid	20·0

It may be seen from the above that different values for availability are obtained for the soil containing originally the same level of phosphate supply.

Effect of Addition of Different Forms of Phosphate to the Soil.—The soil in 50 g. lots was treated with equivalent amounts (10 mg. P_2O_5) of KH_2PO_4, and bone meal respectively; the former was added in solution as in earlier experiments, while the latter was mixed intimately with the soil after being finely pulverized to pass through the 100 mesh sieve. The quantities of phosphorus brought into solution by different extractants after shaking for 15 minutes were then determined and the results together with the details of extraction are given in Table VIII.

TABLE VIII.

Extractant	P_2O_5 in solution from 10 mg. added as	
	KH_2PO_4	Bone meal
N/5 Sulphuric acid (1*l*)	9·6	10·0
N/20 ,, (1*l*)	5·2	9·9
N/100 ,, (2*l*)	6·4	9·0
Truog's extractant (2*l*)	4·3	5·9
Dyer's 1 per cent. citric acid (500 c.c.)	5·8	7·5

It may be noted that consistently higher values for phosphorus in solution are obtained in the experiments where insoluble phosphate was added compared to those with the soluble phosphate. The following experiments were performed with a view to explaining the foregoing observations which had first appeared difficult to explain. 50 g. lots of the soil were treated with equivalent quantities (corresponding to 10 mg. of P_2O_5) of KH_2PO_4, rock phosphate and bone meal respectively, followed by 1 litre of N/100 sulphuric acid in each case. The mixtures were then shaken for definite lengths of time in an end-over-end shaker after which the phosphorus in solution was determined as before (Table IX).

TABLE IX.

P_2O_5 added as	P_2O_5 in solution (mg.)		
	Period of shaking		
	15 mins.	3 hours	6 hours
KH_2PO_4	3·8	2·5	2·0
Rock phosphate	5·6	2·8	2·3
Bone meal	5·9	4·4	2·6

When a soluble phosphate is added to the soil, most of it is held fixed by the soil colloids. An insoluble phosphate, on the other hand, is present merely in an admixed state with the soil. Hence, addition of an acid-solvent extracts most or all of the added insoluble phosphate within the first 15 mins. Since in the other case, the added soluble phosphate is held adsorbed almost immediately after addition, only a smaller quantity, depending on the nature of the solvent, is brought into solution. If, however, the mixture is allowed to remain for longer periods as such, there will be a gradual refixation of phosphate from solution as has been already observed in earlier experiments (*cf.* Table IV), until at the end of six hours, more or less the same values are obtained in all the cases (Table IX).

With a view to verifying the foregoing explanations, another set of experiments was performed in which 50 g. lots of the soil were treated with equivalent amounts (10 mg. of P_2O_5) of the different forms of phosphate, but previously dissolved in one litre of N/100 sulphuric acid. The phosphate in solution was then determined at the end of 15 mins. and 3 hours respectively (Table X).

TABLE X.

Form of phosphate (as P_2O_5 in 1 litre of solution) in contact with soil (50 g.)	P_2O_5 in solution At the end of 15 mins.	P_2O_5 in solution At the end of 3 hours
KH_2PO_4	4·8	4·3
Rock phosphate	5·2	4·5
Bone meal	5·6	4·8

The differences in the quantities of phosphate in solution in the cases of the soluble phosphate and the insoluble phosphates are not as pronounced as in the earlier experiments.

In another set of experiments, the soil (50 g.) was treated with 5 c.c. of a 0.1 per cent. solution of ferric chloride prior to treatment with soluble phosphate. The phosphate in solution was then determined both in the water extract and in the N/20 sulphuric acid extract after shaking for 15 mins. in each case, the volume of extractant used being four times that of the soil (Table XI).

TABLE XI.

Treatment	Water extract		N/20 acid extract	
	Without $FeCl_3$	With $FeCl_3$	Without $FeCl_3$	With $FeCl_3$
	P_2O_5 in solution			
50 g. soil + 10 mg. P_2O_5 ..	1·8	1·5	2·9	3·2
75 g. soil + 15 mg. P_2O_5 ..	2·6	2·2	4·1	4·5

The results show that phosphorus in solution in the water extract is lower in the presence of iron while the reverse is the case with the weak acid extract. This is due to the fact that, in presence of added iron salt, part of the added phosphate is converted into insoluble ferric phosphate while the rest is present in an adsorbed state; as shown in the foregoing experiments, the adsorbed compound is less readily extracted by the acid solvent than the insoluble one.

DISCUSSION.

From the results of the experiments detailed above, it would appear that chemical methods may not give reliable indications of phosphate availability in soils. An important consideration affecting the application to fertiliser practice of the results of tests of phosphate deficiency is the fixing power of the soil for that element. Many of the soils are capable of fixing all the phosphorus added to the soil, when the amount involved is of the magnitude of ordinary fertiliser applications (Table VI). The availability of the fixed phosphate will no doubt be determined, among other things, by the form in which it is fixed. The amount of phosphorus brought into solution by any extractant is governed by the nature of the soil, the volume of extractant, the period of shaking, temperature and the level of phosphate supply. Different soils with the same level of phosphate supply show varying degrees of phosphate deficiency as assessed by any particular chemical extractant (Table VI). In a like manner, different values for availability are indicated for the same soil treated with different extractants (Table VI). Again, in acid soils, the phosphorus compounds are less readily extracted than in neutral or alkaline ones (Table V). Since the buffering capacity of soils may be very different, the same solvent may extract the phosphates from them in varying amounts at different H-ion concentrations. In equilibrium extraction, the products of the action of weak acid solvents, particularly iron, aluminium and calcium, may tend to affect the solubility of phosphates (Fig. 1) (*cf.* Teakle, *Soil Sci.*, 1928, **25**, 143; Hibbard, *Soil Sci.*, 1931, **31**, 437). The extent to which different extractants remove the phosphates from the soil into solution will thus depend on the concentration of other cations in solution.

The studies on soil treated with different forms of phosphates, both soluble and insoluble, have shown that chemical extractants remove more phosphate into solution in the latter case than in the former. Indeed, in field practice, where an insoluble phosphatic fertiliser is added to the soil, the latter is brought into solution by the decomposing organic matter of the soil and, when the crop is on, it may be enabled to take up the phosphorus through its root system as and when it is being rendered soluble, although to a certain extent, the dissolved phosphate may also be held fixed by the soil adsorbing complex. The application of a soluble phosphate would however be immediately followed by its adsorption by the soil colloids and hence the plant may not be able to utilise the adsorbed phosphate so well as when the latter is originally present in an insoluble condition. The better fertiliser value of superphosphate compared to other forms of phosphates may indeed be due to its conversion into an insoluble calcium phosphate immediately after application to the soil.

It is now well known that in the large majority of soils, most of the phosphorus exists as calcium and basic iron and aluminium phosphates; when the pH of the soil is about neutral or alkaline, the soil will naturally be richer in calcium phosphates than in the other forms; when the pH is lower, the tendency is for most of the phosphorus to be in the form of complex iron and aluminium phosphates. Phosphates of calcium are generally readily dissolved in weak acids including carbonic acid and hence, the availability of calcium phosphates may be more, compared to the other forms of phosphates usually present in the soil. In soils, saturated with calcium ions, or containing a free supply of lime, it is probable that added soluble phosphates are converted into insoluble calcium salts instead of being adsorbed by the soil colloids and thus rendered less available. These will explain the observations in regard to the influence of soil reaction on phosphate availability (Table V) and the beneficial effects of calcium ions. In presence of excess of calcium carbonate or with calcareous soils, the availability of the calcium phosphates may even be depressed. Thus there is evidence (*cf.* Das, *Agric. & Livestock in India,* 1933, **3**, 166) to show that gypsum may depress the availability of phosphorus in calcareous soils, probably by rendering calcium phosphates less soluble.

Further work on (*a*) the comparative fertiliser value of soluble and insoluble forms of phosphates in field practice, (*b*) the nature of interaction between soil and superphosphate, and (*c*) the mechanism of the action of calcium in increasing the availability of phosphates in soils, is necessary in order to substantiate these views. A study of the behaviour of PO_4 ion in presence of varying concentrations of cations such as Ca, Fe and Al and at different pH may also throw useful light on the above and related questions.

Although chemical methods of determining phosphate availability in soils are fundamentally defective in several respects and no single method can ever be evolved which will be applicable to diverse types of soil, crop and climatic conditions with even approximately uniform success, it may yet be possible that by some grouping of soils according to physical and other characteristics, and by the application of suitable methods of extraction, indications of phosphate availability may be obtained, which would compare favourably with crop response or field behaviour of the soil. As it is, it is possible that the water extract (*cf.* Burd and Martin, *Jour. Agric. Sci.*, 1923, **13**, 265; Nemec, *Dtsch. Landw. Presse*, 1926, **53**, 463; Dirks and Scheffer, *Landw. Jahrb.*, 1930, **71**, 74; von Wrangell and co-workers, *Landw. Jahrb.*, 1926, **63**, 627, 669; *ibid.*, 1926, **63**, 707; *ibid.*, 1926, **63**, 677; *ibid.*, 1926, **63**, 739; *ibid.*, 1930, **67**, 149; *ibid.*, 1930, **71**, 149; Hibbard, *Soil Sci.*, 1935, **39**, 337; and others) differentiates better than any acid-extraction methods, the truly available phosphorus in the soil, though not the total amount of available phosphorus.

SUMMARY.

1. Addition of a soluble phosphate to the soil in quantities corresponding to ordinary fertiliser applications (3 to 4 cwt. per acre) results in more than 80 per cent. of the phosphate being converted into water-insoluble forms.

2. Extraction, with dilute acids, of soil treated with a soluble phosphate brings into solution considerably larger amounts of phosphate than mere water extraction. The quantities of dissolved phosphate depend on the nature of the extractant. Sulphuric acid, and, to a less extent, citric acid, give the maximum amounts of phosphate in the extracts (this observation may not apply to calcareous soils).

3. The quantities of phosphates brought into solution by the same extractant are shown to depend upon the nature of the soil, the volume of extractant, the time of shaking and the amount of phosphate in the soil.

4. With most soils, there is observed a refixation or conversion into insoluble forms, of extracted phosphate after about 30 minutes; the extent of such refixation varies with different solvents and increases with the time of extraction. Refixation is also greater at higher temperatures of extraction.

5. The extraction of phosphate from soil depends upon the reaction of the soil, being less in acid soils than in alkaline ones.

6. The presence of small quantities of iron and aluminium salts in soils increases the extent of phosphate retention by soil; the effects due to calcium salts are, however, less pronounced.

7. Different soils, treated with equivalent amounts of soluble phosphate, show widely varying degrees of retention, both in presence of water and with acid extractants.

8. With soil, treated with equivalent amounts of soluble and insoluble forms of phosphate, it is found that weak acid extractants invariably remove larger quantities of phosphorus into solution in the latter case than in the former. This difference in the behaviour of weak acids towards insoluble and soluble forms of phosphate in the presence of soil has been explained and evidence presented to show that adsorbed phosphorus compounds are less easy of extraction by solvents than insoluble ones.

9. The limitations of chemical methods of determining phosphorus availability in soils have been discussed in the light of the foregoing and other observations.

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