

XXVII.—*The Determination of Available Plant Food in Soil by the Use of Weak Acid Solvents. Part II.*

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THE use of some weak acid solvent to extract that portion of the mineral plant food in soil, particularly phosphoric acid and potash, which may be regarded as immediately "available" for the use of the crop, has become an established part of soil analysis. It has been shown to yield results in accord with field trials and to be of value in determining the manurial requirements of the soil, although

opinions still differ as to the best method to follow and as to the interpretation of the analytical figures. Of the methods employed, the use of a 1 per cent. solution of citric acid, as suggested by Dyer (Trans., 1894, 65, 115), has become most general; on the other hand, the American chemists have adopted in preference a $N/200$ solution of hydrochloric acid. Dyer's method was based on the idea of obtaining a solvent approximating in composition and strength to the acid sap which is to be found in the roots of most plants, which sap was supposed to have a direct action on the mineral particles with which the roots were in contact. This view, that the root excretes an acid other than carbon dioxide, has now been generally abandoned (see Czapek, *Prings. Jahrb. wiss. Bot.*, 1896, 29, 321; Kossowitsch, *Ann. de la Sci. Agron.*, 2nd S., 1, 1903, 220; Hall, *Proc. Roy. Soc.*, 1905, 77, Series B, 1), and the method should be taken as an empirical one to be judged by its agreement with the evidence afforded by the crop. The theoretical basis for the use of $N/200$ hydrochloric acid is that it extracts from the soil quantities of mineral plant food approximately equal to those removed by an ordinary crop from the same soil. It would be difficult, however, to justify this theory in view of the fact that such extraneous factors as cultivation, supply of water or of nitrogen, and the nature of the crop will make radical variations in the amounts of the constituents in question assimilated by the crop.

To both theories, however, there is one further objection: they regard the material extracted by the solvent as differing essentially from that which is left behind; the one is "available" for the crop, the other not, and when the "available" portion has been removed from the soil there should be nothing left for the crop until weathering, &c., has brought a fresh portion into a more soluble condition (see Ingle, Trans., 1905, 87, 43). In such cases, however, both in the laboratory and in nature, the process of solution must be considered dynamically; there is no fixed point when all the material soluble in the medium employed will have gone into solution, the extraction proceeds until an equilibrium is established between the material in the solid state and that in solution, and if the original material be homogeneous in nature, its mass will not affect the concentration attained by the solution.

Whitney (United States Department of Agriculture, Bureau of Soils, *Bulletin* 22, 1903) has advanced this argument in support of the idea that the soil water, which must be regarded as the culture medium on which all plants feed, possesses a constant composition for all soils, because it is always in equilibrium with the same slightly soluble soil phosphates. Therefore, the addition of more plant food in the form of fertilisers does not supply the plant with further nutrient material, because an equivalent amount of the constituent

added will be thrown out of solution and the original position of equilibrium established. But even assuming that the soil gives rise to a solution of constant concentration, the mass of the constituent in the soil would still come into play by regulating the ease or the frequency with which the solution could be renewed. If, for example, the phosphates in the soil give rise to a solution of phosphoric acid in the soil water, the strength of which is independent of the mass of phosphate present, yet as soon as the crop withdraws phosphoric acid from the solution the equilibrium will be disturbed and more phosphate will be attacked. But the rapidity with which the phosphate will pass into solution, and in its turn to the plant, will be conditioned by the mass of it present, and if the amount is near the limit required for saturation of the soil water, then the solution might not be replenished so often as the plant requires. Thus, even if a particular substance establishes a solution of constant composition in the soil water, its mass will still affect the supply of nutrient to the plant, because with it is bound up the renewal of the solution as it becomes depleted by the growth of the plant.

Again, a soil solution of constant composition would necessitate the identity in all soils of the state of combination of the constituent in question. If, for example, all soils contained a similar tricalcium phosphate and no other compound of phosphoric acid, then the soil water in equilibrium with the soil would attain the same concentration of phosphoric acid, whatever the amount of phosphate in the soil. This identity, however, of the compounds of phosphoric acid in all soils has not been demonstrated.

It was with the view of obtaining more light on the conditions of solution of soil phosphates and kindred substances, both in the soil itself and in the laboratory processes for soil analysis, that the following investigation was undertaken. The method adopted was to attack the soil continuously with the solvent. After equilibrium had been attained with the first portion of solvent, it was removed and renewed to see to what extent similar solutions could be obtained with fresh portions of solvent. The earlier experiments were undertaken with carbon dioxide and water, with the idea of realising thereby as nearly as possible the conditions prevailing in the field, where water charged with carbon dioxide is the great natural solvent. For reasons which will be given, this method of attack was abandoned in favour of repeated extractions with a 1 per cent. solution of citric acid. The investigation was limited to a consideration of the phosphoric acid, since in its progress it became clear that the potash in the soil would be likely to behave in a similar fashion.

The extractions were all made in 1 litre (half Winchester) green glass bottles containing 100 grams of soil, 10 grams of citric acid, and

1 litre of distilled water. The bottles were placed in a shaker and kept in continual end-over-end rotation for twenty hours, this, as will be seen later, being a sufficient period to establish equilibrium. After settling and filtering off the bulk of the liquid for analysis, the remaining soil was washed free from acid and returned to the bottle together with 10 grams of citric acid and water to the level which had been marked after the first filling. The shaking was then renewed and the process repeated as often as need be.

Solutions in Water charged with Carbon Dioxide.

Preliminary experiments showed that the amount of carbon dioxide in the solution was a factor in determining how much phosphoric acid was dissolved from the soil, hence it was necessary to ensure a solution of approximately constant composition. Distilled water was charged with carbon dioxide in an ordinary selzogene, and the required volume was drawn off and added to the soil in the bottle; the mixture was then shaken for a minute or two and the stopper withdrawn to allow the escape of any excess of carbon dioxide shaken out of the super-saturated solution. In this way, the liquid in the bottle would be approximately saturated under atmospheric pressure and contain, within negligible limits, always the same quantity of carbon dioxide. After shaking for twenty to twenty-four hours and filtration, an aliquot portion of the extract was evaporated and ignited, the residue was dissolved in hydrochloric acid, again evaporated, heated in an air-bath at 120—150° for an hour to render the silica insoluble, and finally taken up with dilute hydrochloric acid before being precipitated with molybdic acid. As the amounts of phosphoric acid which go into solution in the water charged with carbon dioxide are very small, they were estimated by a colorimetric method devised by Pagnoul (*Ann. Agron.*, 1899, 25, 5), which depends on the depth of the brown colour produced when a solution of the phosphomolybdic acid precipitate in ammonia is added to an acid solution containing potassium ferrocyanide. The tint is compared by a method of trial and error with that similarly produced by successive quantities of a standardised solution of phosphoric acid.

The experiments were begun on some of the soils from the Broadbalk Field, Rothamsted, which had been growing wheat under known conditions of manuring since 1843. The treatment of the various plots has repeatedly been described (Dyer, *Phil. Trans.*, 1901, 194, Series B, 235; Hall and Plymen, *Trans.*, 1902, 81, 117); it will be sufficient here to summarise very briefly the important features as regards the annual supply of phosphoric acid.

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TABLE I.—*Description of Soils.*

Plot.	Date at which treatment began.	Annual manuring.	Phosphoric acid. Lbs. per acre in manure.	Total produce. Average lbs. per acre.
<i>Broadbalk Wheat Field.</i>				
2b	1843	Dung	78(?)	6049
3	1843	Unmanured	—	2009
5	1849	Superphosphate; potassium, sodium, and magnesium sulphates	64	2308
7	1849	Superphosphate; alkaline sulphates and ammonium salts	64	5775
8	1852	Superphosphate; alkaline sulphates and ammonium salts	64	6913
10	1845	Ammonium salts only	—	3408
<i>Hoos Barley Field.</i>				
1	1852	Sodium nitrate only	—	3743
2	1852	Superphosphate; sodium nitrate	64	5431
3	1852	Alkaline sulphates; sodium nitrate	—	3987
4	1852	Superphosphate; alkaline sulphates and sodium nitrate	64	5529

Thus, Plots 2, 5, 7, and 8 receive an excess of phosphoric acid every year; on Plot 2 it is applied as dung, on the others as "superphosphate." In the absence of nitrogen, the crop and the loss of phosphoric acid are very small on Plot 5; they are much increased on Plot 7, and still further on Plot 8. Plot 3 receives no phosphoric acid, nor does Plot 10, but in the latter case the loss of phosphoric acid has been greater, because of the use of 86 lbs. of nitrogen every year.

TABLE II. — *Phosphoric Acid dissolved by Water saturated with Carbon Dioxide.*

Milligrams per 100 grams of soil.

Expt.	Plot.	Extractions.							
		1st.	2nd.	3rd.	4th.	5th.	6th.	7th.	8th.
1	Broadbalk, 2b ...	3.9	2.6	3.2	3.3	4.7	3.4	3.4	2.4
2	" 2b ...	3.6	2.6	3.0	3.3	2.8	2.6	3.4	2.7
3	" 3 ...	0.25	0.25	0.16	0.15	0.22	0.28	—	—
4	" 7 ...	2.8	1.9	1.9	4.6	2.2	3.3	—	—
5	" 7 ...	2.6	2.1	2.3	4.6	—	—	—	—
6	" 10 ...	0.26	0.27	0.25	0.18	0.58	0.55	—	—
<i>Calcium carbonate replaced after each extraction.</i>									
7	Broadbalk, 5 ...	5.0	2.8	2.2	1.8	1.4	1.6	1.3	1.2
8	" 8 ...	1.7	1.2	1.0	0.6	0.9	0.7	0.7	0.6

Table II gives some of the results obtained, which are also set out in graphic form in Fig. 1.

As the extractions proceeded, the process became disturbed by the difficulty of filtration; with the first and second extractions it was easy, the finer particles of the soil being kept in a flocculated condition by the presence of calcium bicarbonate and other salts in the solution. But as soon as all the calcium carbonate in the soil had been removed by the carbonated water, filtration became exceedingly slow, and it was almost impossible to obtain a clear filtrate. The presence of even a small quantity of fine soil in the extract would add a quantity of

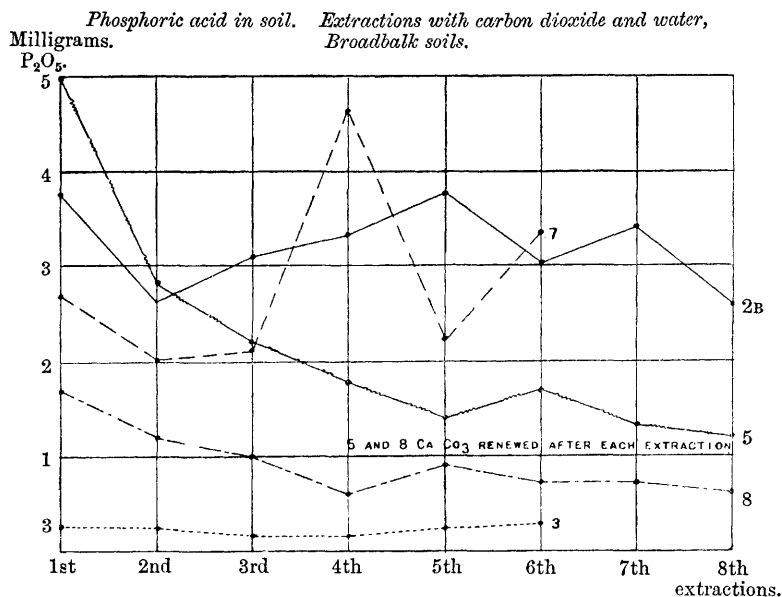


FIG. 1.

phosphoric acid too great to be neglected, and the introduction of even soluble flocculators, such as calcium chloride or magnesium sulphate, seemed to precipitate some of the soluble phosphoric acid with the sediment. Putting aside the expenditure of time the process began to involve, such a fertile source of errors was thus introduced in the determination of the very small quantities of phosphoric acid that in view of the trend of such results as could be trusted it was decided to abandon the process.

A consideration of the results and curves shows that in most cases less phosphoric acid is extracted by the second than by the first extraction; a steady equilibrium is not immediately attained, indicating

that soil phosphate which is first attacked is not combined in the same way as the rest. After a falling off in the second extraction, a rise in the amount of phosphoric acid going into solution is generally observed, and this rise coincides with the complete removal of calcium carbonate from the soil. Evidently at each extraction a somewhat complex condition of equilibrium is attained, in which the free carbon dioxide, the calcium carbonate, and the soil phosphates all are variable factors. This is made more clear by a consideration of experiments 7 and 8, in which, after each extraction, an amount of calcium carbonate was returned to the soil equivalent to that removed by the previous extraction. It will be seen that after the initial decline in the first two or three extractions practically a constant condition is attained, and the state of equilibrium between the soil phosphates, the calcium carbonate, and the free carbon dioxide is repeated indefinitely.

Looking at the results as a whole, it may be concluded that the soil produces with carbon dioxide and water a characteristic solution of phosphoric acid which does not vary greatly in concentration when the solution is renewed. This position of equilibrium is, however, different for each soil, and since it does fall off considerably from the first to the second extraction, and as again it bears no particular relation to the total amount of phosphoric acid in the soil, it would seem to be determined by the nature rather than the mass of the soil phosphates. The concentration of the solution, however, reflects the manurial treatment the soil has received, so that if we may take these laboratory solutions as a guide to the composition of the soil water, the fertilisers applied in the past, so far from being without effect, condition wholly the concentration in phosphoric acid of the soil water, and in consequence the supply of this constituent to the roots of the plant.

During the progress of these experiments, the tile drains beneath the plots yielding the soils under investigation began to run for the first time after a long period of dry weather. Samples of the water were taken for the determination of phosphoric acid, the concentration of which, however, was far below that obtained in the carbonated water in the laboratory, being in most cases only about one-tenth as much. Plot 5 yielded 0.00044 per cent. of phosphoric acid, Plot 7, 0.0003 per cent., and Plot 3 a trace too small for estimation. The samples were taken at hourly intervals during the day when the drains were running and then mixed; probably the more concentrated early runnings, which represent the true soil solution, had become much diluted by the later water running rapidly through the soil. The composition of these samples, then, settles nothing as to whether the carbon dioxide solutions obtained in the laboratory can be taken to represent the soil water. These experiments with carbon dioxide and water as a

solvent may be taken to demonstrate that a hard and fast line cannot be drawn between the phosphoric acid going into solution and that which remains behind. The solution can be renewed repeatedly, and although it will diminish somewhat in concentration with successive extractions, the change is such as would indicate the presence in the soil of an indefinite series of phosphoric acid compounds, akin to one another and only varying slightly in composition. For practical purposes, the average position of equilibrium obtained in the first six extractions would supply a very fair index to the character of the soil as judged from its past history, but there is no indication that any beyond empirical conclusions can be drawn from the results. Since the difficulties of manipulation put the process out of question as a working method of analysis, the further use of carbon dioxide was abandoned in favour of the 1 per cent. solution of citric acid.

Extractions with 1 per cent. Solution of Citric Acid.

The process adopted was exactly similar to that previously described. One hundred grams of the air-dried soil were shaken for twenty hours with 10 grams of citric acid and 1 litre of water, the solution being filtered and the phosphoric acid determined in the usual way. The washed soil was then returned to the bottle and the process repeated. No attempt was made to restore the original calcium carbonate, most of which was removed by the first extraction. It has been shown that the presence of calcium carbonate does diminish the amount of phosphoric acid, &c., dissolved by the citric acid solution (Cousins and Hammond, *Analyst*, 1903, **28**, 238), but to add a further amount of citric acid equivalent to the calcium carbonate in the soil seems to introduce a fresh source of error. The Rothamsted soils only contain about 3 per cent. of calcium carbonate, and the amount does not vary greatly in the particular plots under examination, so that it was not considered necessary to attempt any correction on this score.

It has already been stated that an extraction of from twenty to twenty-four hours with continual shaking has been adopted instead of digestion for one week with occasional shaking, as originally recommended by Dyer (*loc. cit.*, p. 142). In experiment 11, each extraction proceeded for five days with continual shaking; in 10, the same soil was extracted for twenty hours only. Other experiments with carbon dioxide led to the same conclusions. The results are practically the same whether the extraction proceeds for one or five days; by twenty hours, the solution has come into equilibrium with the soil, and will dissolve no more phosphoric acid however long the contact continues. It does not, however, follow, as subsequent

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extractions show, that all the phosphoric acid soluble in the citric acid has been removed in the first extraction. In view of the fact that phosphoric acid continues to be dissolved with each separate extraction, it was not considered necessary to study the time factor further.

The soils already described from the Broadbalk Field were examined, and, in addition, four soils from the Hoos Field, which has carried barley under the same system of manuring since 1852. Four other

TABLE III.—*Phosphoric Acid dissolved by 1 per cent. Solution of Citric Acid.*

Milligrams per 100 grams of soil.

Expt.	Field.	Period.	Extractions.						Sum of first 5 extractions only.	Ratio of first to last col.
			1st.	2nd.	3rd.	4th.	5th.	6th.		
9	Broadbalk, 2b ...	5 days	—	1·6	6·2	6·0	—	—	—	—
10	„ 2b ...	20 hours	47·7	14·2	7·5	6·1	4·4	—	—	—
11	„ 2b ...	5 days	51·0	15·8	8·8	—	—	—	—	—
		Mean...	49·3	15·3	7·5	6·0	4·4	—	82·5	59·8
12	Broadbalk, 7 ...	20 hours	56·4	22·0	8·9	6·5	4·4	4·4	—	—
13	„ 7 ...	20 „	55·8	23·6	—	—	—	—	—	—
		Mean...	56·1	22·8	8·9	6·5	4·4	4·4	98·7	56·8
14	Broadbalk, 3 ...	20 hours	6·6	6·6	4·0	3·5	2·4	—	—	—
15	„ 3 ...	20 „	6·2	7·0	3·8	2·6	2·7	—	—	—
		Mean...	6·4	6·8	3·9	3·0	2·5	—	22·6	28·3
16	Broadbalk, 5 ...	20 hours	69·0	28·0	11·3	7·3	4·5	2·3	120·1	57·5
17	„ 8 ...	20 „	46·3	18·9	7·8	5·3	4·0	3·0	82·3	56·4
18	„ 10 ...	20 „	7·7	5·2	3·3	2·7	2·7	2·7	21·6	35·7
19	Hoos, 1AA ...	20 „	6·3	3·5	2·2	1·9	2·0	1·2	15·9	39·6
20	„ 2AA ...	20 „	52·2	21·2	8·9	6·5	3·8	2·9	92·6	56·4
21	„ 3AA ...	20 „	6·3	2·7	2·3	2·1	1·9	1·5	15·3	41·2
22	„ 4AA ...	20 „	53·5	10·6	6·4	4·9	4·5	3·8	79·9	67·0
23	Shenington ...	20 „	7·4	2·6	2·2	1·8	1·3	1·2	15·3	48·4
24	Saxmundham ...	20 „	7·2	5·8	5·3	4·1	3·1	2·1	25·5	28·2
25	Cockle Park ...	20 „	14·3	8·0	7·4	5·2	4·3	3·8	39·2	36·5
26	Bramford ...	20 „	72·6	28·4	19·5	—	5·2	3·2	(125·7)	(57·8)

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soils were used, two of which, Bramford and Saxmundham, have long been under experiment by the Cambridge University Department of Agriculture (*Report on Experiments, East Suffolk, 1904*). They are in sharp contrast, Saxmundham giving a very pronounced return for applications of phosphoric acid, which on Bramford show no return in the crop. Cockle Park is another soil on which field experiments have been repeatedly tried (Northumberland Education Committee, *Seventh*

Phosphoric acid in soil. Extractions with 1 per cent. solution of citric acid, Broadbalk soils.

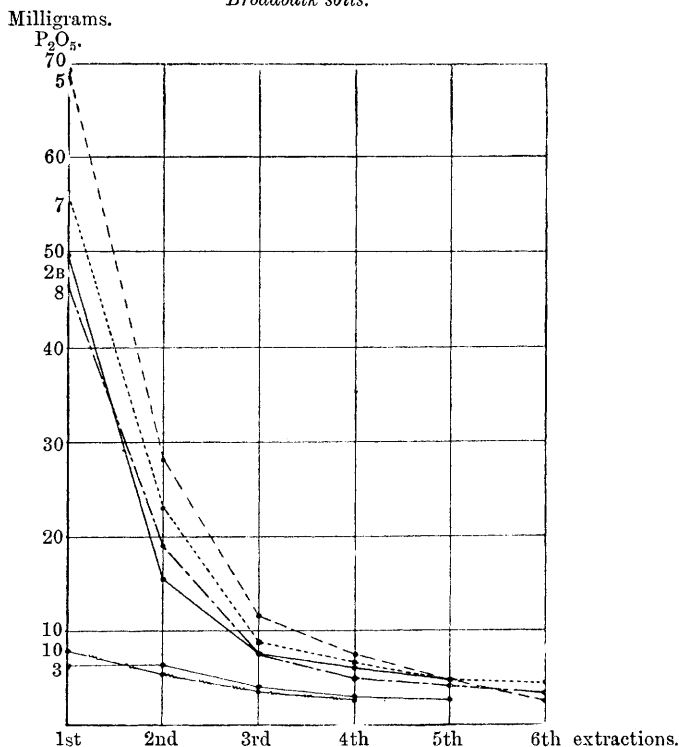


FIG. 2.

Report on Experiments, 1903); it shows a normal, but no marked, response to phosphatic manures. Shenington is again a very exceptional soil, for although it contains as much as 0.84 per cent. of phosphoric acid, crops grown on it stand in great need of phosphatic manuring, probably because the soil contains the wholly exceptional amount of 28.16 per cent. of ferric oxide (Hall, *Jour. Agri. Sci.*, 1905, 1, 85). The results obtained are set out in Table III and in Fig. 2.

It will at once be seen that all the results partake of the same general character; in the second extraction, there is obtained something less than half the phosphoric acid dissolved by the first extraction, the third extraction yields about half of the second, in the fourth the amount dissolved does not fall so much, whilst eventually, about the sixth extraction, the amount going into solution shows a tendency to become constant. When the amount of phosphoric acid dissolved is plotted against the number of extractions, the curve shows at first a steep descent, then the fall becomes less

Phosphoric acid in soil. Logarithms of amounts extracted by 1 per cent. solution of citric acid.

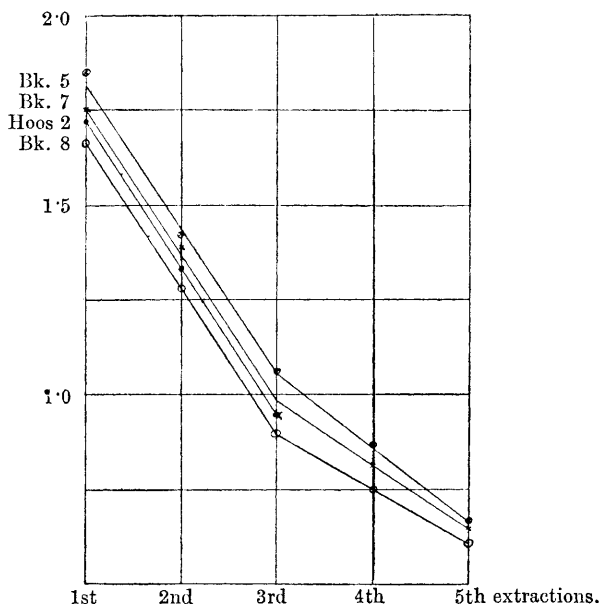


FIG. 3.

and less until the curve becomes practically parallel to the axis. The position of the curve throughout differs for each soil, and the relative character of the curves agrees very well with what is known of the cropping and manuring of the plots from which the soils were drawn.

New light is thrown on the character of the curves if, instead of the amounts dissolved at each extraction, their logarithms are plotted, Fig. 3, whereupon it is seen that a series of straight lines is obtained from the Broadbalk and Hoos plots which have been similarly

manured with superphosphate every year. The first three extractions yield points which fall in a straight line, and the straight lines obtained for each plot are parallel. After the third extraction, there is a sudden change of direction, but straight lines are again obtained; at this stage, however, the quantities dealt with are so small that the experimental error forbids any detailed discussion of the results. The logarithmic decrement of the amount of phosphoric acid extracted from Plots 5, 7, and 8 indicates that in each case there exists a particular quantity of phosphoric acid of which a certain fraction goes into solution at the first extraction; of the remainder, the same fraction goes into solution at the second extraction, and again the same fraction of what is still left dissolves at the third extraction. The fraction of the whole which goes into solution approximates very closely to 0.6; by taking this coefficient, the following comparison between the calculated and observed amounts of phosphoric acid going into solution is obtained.

TABLE IV.—*Phosphoric Acid dissolved at Successive Extractions.*
Milligrams per 100 grams of soil.

	Plot.	Calculated.			Found.		
		First.	Second.	Third.	First.	Second.	Third.
Broadbalk.....	5	70.2	28.0	11.3	69.0	28.0	11.3
„	7	55.8	22.3	8.9	56.4	22.0	8.9
„	8	46.8	18.7	7.5	46.3	18.9	7.8
Hoos	2	52.2	20.7	8.5	52.2	21.2	8.9

Only the plots which have been continually receiving the same superphosphate manure show this logarithmic rate of decrement in the amounts of phosphoric acid going into solution; with Plot 2*b*, which receives the variable phosphates contained in dung, Plot 3, which is unmanured, and Bramford, which is farmed in the ordinary way, the results when plotted do not fall into straight lines. But as regards the four Rothamsted soils receiving superphosphate, the strength of the solution of phosphoric acid obtained is the product of the active mass of a particular phosphoric acid compound present and a coefficient which is the same in each case.

The exact significance of the observed regular partition between the solvent and the soil of one portion of the phosphoric acid of the soil on these plots is not as yet apparent; it does not fall under any of the recognised laws of chemical dynamics of a solid going partially into solution. There is doubtless a somewhat complex condition of equilibrium set up between the dissolving acid, the phosphoric acid, and the various bases in the soil, which can only be interpreted by a study, now in hand, of the similar action of the solvent on various

pure phosphates in the presence of such bases as are found in the soil. It can hardly be doubted, however, that the logarithmic portions of the curves represent a single phosphoric acid compound in the soil, which has been almost wholly removed after the third extraction, and that the non-logarithmic character of the curves yielded by the other soils indicates that their phosphoric acid is present in a more varied and irregular state of combination, as, indeed, would be expected from the history of the treatment of the plots.

We are indebted to Mr. R. D. Watt, B.Sc., Carnegie Scholar of the University of Glasgow, for some further experiments on the conditions of equilibrium set up between phosphoric acid, the citric acid solution, and soil.

One possible factor is the action of the surface of the soil particles, which is very large, from 10 to 40 square metres for 100 grams of the soils employed. Accordingly, 1 gram of basic slag was shaken with the citric acid solution alone and with the citric acid solution to which had been added 100 grams of "slimes," or kaolin, or soil. The "slimes" consists of the finest portions of the crushed gold-bearing rock from the Rand; the particles vary in size from 0.04 to 0.002 mm. in diameter, and are mainly quartz with a little felspathic material. This crushed rock had previously been treated with strong hot hydrochloric acid.

The following results show the amounts of phosphoric acid going into solution in 1 litre of 1 per cent. citric acid solution.

TABLE V.—*Phosphoric Acid dissolved by 1 litre of 1 per cent. Citric Acid Solution.*

Expt.		Phosphoric acid.
27	1 gram of basic slag alone.....	0.2117 gram
28	" " plus 100 grams of "slimes".....	0.2085 "
29	" " " " kaolin	0.2080 "
30	" " " " soil (Hoos 1)...	0.1428 "
31	100 grams of soil (Hoos 1) alone	0.0059 "

The amount retained by the "slimes" and the kaolin is inappreciable, so that surface actions may be dismissed from consideration, but the presence of the soil withdraws about 35 per cent. of the phosphoric acid which would otherwise have gone into solution. In a second series of experiments, pure dicalcic phosphate was employed as being wholly soluble in the citric acid solution, and the following results were obtained :

TABLE VI.—*Phosphoric Acid dissolved by 1 litre of 1 per cent. Citric Acid Solution.*

Expt.		Phosphoric acid.
32	1 gram of dicalcic phosphate alone	0.486 gram
33	„ „ „ with 0.64 per cent. of citric acid ...	0.470 „
34	„ „ „ plus 100 grams of Woburn soil (R)*.	0.435 „
35	„ „ „ „ „ (2A).	0.429 „
36	„ „ „ „ „ 100 grams of Shenington soil...	0.252 „
37	Shenington soil alone	0.0128 „

* A light sandy soil from the Stackyard Field of the Woburn Experimental Farm.

The Woburn and Shenington soils contain no calcium carbonate to neutralise the citric acid solution, although in the latter case the oxide of iron reduced the acidity of the solution. But on acting on 1 gram of the dicalcic phosphate alone with a citric acid solution of this reduced strength, there was but little fall in the amount of phosphoric acid dissolved.

These results show very clearly that when the citric acid solvent is in contact with the soil, the solution of phosphoric acid which is attained represents a state of equilibrium between that which goes into the acid solution and that which remains combined with the soil bases. The action of the citric acid is not simply to dissolve the whole of one or more phosphoric acid compounds present in the soil; in the cases just cited, experiments 30 and 36, phosphoric acid already seen to be soluble in the acid is retained in a solid state by the soil.

Mr. Watt also attempted to ascertain the nature of the soil phosphates attacked by the successive citric acid solutions by determining the bases which were simultaneously dissolved, with the following results:

TABLE VII.—*Bases dissolved by 1 per cent. Citric Acid Solution.*

	Broadbalk, Plot 3.			Broadbalk, Plot 5.		
	CaO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	Fe ₂ O ₃ .	Al ₂ O ₃ .
First	1.92	0.090	0.398	1.74	0.080	0.343
Second	0.127	0.056	0.074	0.129	0.064	0.059
Third	0.042	0.068	0.055	—	0.054	0.041

These experiments, however, lead to nothing; there is always more of each base dissolved than would be necessary to combine with the whole of the phosphoric acid in solution at the same time.

Reviewing the experiments as a whole, it may be concluded that the soil contains compounds of phosphoric acid of varying solubility; the more easily dissolved compounds removed in the first few extractions are present in comparatively small amounts, so that the amounts

going into solution fall rapidly with each extraction. After the fourth or fifth extraction, a point is reached when the compound remaining in the soil seems to be uniform, as shown by the approximately constant concentration in phosphoric acid which the later solutions now attain. This constant equilibrium point is not, however, the same for all soils; it is evidently determined by certain differences in the nature of the phosphoric acid compounds which are characteristic of each soil.

The results lend no support to Whitney's theory, that all soils will form in nature solutions of approximately constant composition, representing an equilibrium between the soil phosphoric acid and the solvent water which is independent of the mass of the former, for although the 1 per cent. solution is a much more drastic solvent than the natural soil water, there is no reason to suppose that its action will be essentially different in kind; indeed one of us has already attempted to show that all weak acid solvents attack the soil in a very similar fashion (Hall and Plymen, *loc. cit.*). The present results indicate that there are essentially different compounds of phosphoric acid in different soils, possessing initially different points of equilibrium with solvents, and the more soluble of these compounds are present in such comparatively small amounts that their mass becomes a factor in the maintenance of the strength of the solution. In other words, the soil water will be of varying concentration in phosphoric acid in different soils, and when the crops remove this phosphoric acid by their growth, the soils will again differ in their power of renewing the solution, because of variations in the mass as well as the nature of the phosphate which gave rise to the original solution.

There remains the practical question of how far these results obtained by repeated extractions of phosphoric acid from a soil with the dilute citric acid solution bear on the practice of soil analysis, in which one extraction only is attempted. It may be assumed that all the "available" or readily soluble phosphoric acid will be represented by the sum of the phosphoric acid going into solution in the first four or five extractions, until the low, but fairly constant, equilibrium is attained between the solvent and the large mass of "dormant" soil phosphates. In the case of the Rothamsted soils manured with superphosphate, it is also easy to determine from the curve the original amount of phosphoric acid which divided itself between solvent and soil bases according to the ascertained coefficient. In Table VIII (p. 220) these two sets of quantities are set out as percentages and as pounds per acre in the first nine inches of soil, below which depth Dyer has shown (*Phil. Trans., loc. cit.*) the manurial applications of phosphoric acid do not sink, even when soluble in water. Against them are set

TABLE VIII.—*Phosphoric Acid dissolved by 1 per cent. Citric Acid compared with that supplied by Manure.*

Plot.	Total of five extractions.		Amount calculated from the first extraction and the coefficient.		Supplied in manure.	Removed in crop.	Surplus.
	Per cent.	Lbs. per acre.	Per cent.	Lbs. per acre.			
Broadbalk, 3 ...	0·0226	565	—	—	0	550	— 550
„ 5 ...	0·1201	3000	0·117	2925	3960	790	3170
„ 7 ...	0·0987	2470	0·093	2325	3810	1370	2440
„ 8 ...	0·0823	2055	0·078	1950	3810	1520*	2290*
„ 2b ...	0·0825	2060	—	—	4780	1650	3130
Hoos, 1.....	0·0159	400	—	—	0	555	— 555
„ 2	0·0926	2315	0·087	2175	3390	1200	2190
„ 4.....	0·0799	2000	—	—	3390	1240	2150

* Approximate estimate. The crop of Plot 8 has seldom been analysed.

the total applications of phosphoric acid in the manure since the beginning of the experiments together with the amounts removed in the crop, so as to show the surplus accumulated in the soil. These surpluses agree very closely with the total amounts of phosphoric acid soluble in citric acid. On the one hand might be deducted the amount of soluble phosphoric acid supplied by the unmanured soil itself to the citric acid solution, and on the other the amount contained in the crop grown by the unmanured plot without any applications of manure, but as these two quantities of phosphoric acid happen to coincide very closely it is unnecessary to attempt the correction.

For the dunged plot, the agreement between the phosphoric acid dissolved by the citric acid and the surplus of the manurial phosphoric acid over that removed by the crops is by no means so close, but in this case the amount of phosphoric acid supplied in the manure is but an approximate estimate, and some of it is, without doubt, combined in forms less attackable by the citric acid than are the compounds formed when superphosphate is precipitated in the soil.

It may be concluded that the repeated extractions in citric acid do eventually dissolve all the phosphoric acid which has been added to the soil in the shape of soluble phosphates for the previous fifty years or so. But the total amount of such readily soluble phosphoric acid bears a fairly constant ratio to that which is dissolved in the first extraction, as may be seen from the last column in Table III. Since

also the numbers obtained for citric acid soluble phosphoric acid can only be interpreted empirically by comparison with the results yielded by soils the response of which to phosphatic manures has been determined by field trials, then for ordinary analytical purposes the single extraction is likely to give as much information as repeated attacks with the same solvent.

Particularly on the majority of soils under ordinary cultivation which have not been regularly manured year after year in the same manner, the attack of the citric acid is not a sharply defined action, bringing into solution one or two definite compounds of phosphoric acid which can be termed "available," but is, instead, a complicated process in which equilibrium is established between the solvent and a large number of compounds of varying grades of solubility, so that for practical purposes it is useless to repeat the extractions until more knowledge is attained of the separate actions which go to make up the observed results. For the present, the process of extraction with citric acid must still be regarded and interpreted empirically. Probably the solvent process is parallel to the actions going on in nature, which render the soil phosphoric acid available for the plant, but this cannot be decided *a priori*; it must be determined by the agreement between the results yielded by the solvent and the response of the crop on the same soil to phosphatic fertilisers.

General Conclusions.

The conclusions reached in this examination of the process of attacking a soil with weak acid solvents may be summarised as follows.

1. The solvent does not at once remove all the phosphoric acid capable of going into solution in the particular solvent employed; instead an equilibrium is established between the phosphoric acid in the solvent and in the soil.

2. The concentration of the solution in equilibrium with the soil falls with each successive attack of the soil by the same solvent. This indicates the presence in the soil of several compounds of varying solubility, the mass of the more soluble being small and of the same order as the amounts going into solution in the earlier extracts. When these more soluble compounds have been removed, an approximate constant equilibrium is attained between the phosphoric acid remaining in the soil and that going into solution at each extraction, indicating that after the more soluble compounds have been removed there remains a phosphate in each soil of such low solubility that the amount going into solution at each extraction is independent of the mass present in the soil.

3. With soils which have been for many years manured with a

particular phosphate, the amounts of phosphoric acid going into solution in successive extractions with 1 per cent. citric acid solution follow a logarithmic law of decrement, indicating the presence of one particular phosphate which dissolves in proportion to the mass of it present in the soil. This law does not, however, hold for ordinary soils which have been variously manured.

4. In the case of the Rothamsted soils, the sum of the phosphoric acid dissolved out by the first five extractions with citric acid approximates very closely to the known surplus of phosphoric acid accumulated by the additions of manure to the soil.

5. Assuming that the solvent actions of the soil-water and of the weak acid solvents employed in the laboratory are comparable, the evidence lends no support to the theory that all soils give rise to a natural soil solution of approximately constant composition, which is not disturbed by the use of fertilisers containing phosphoric acid.

6. For the practical purposes of soil analysis, the evidence afforded by a single extraction of the soil for twenty hours with continual shaking is very similar to that obtained from a series of successive extractions by the same solvent and leads to the same conclusions as to the manurial requirements of the soil.
