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THE USE OF CHEMICAL DATA IN THE PROGNOSIS OF PHOSPHATE DEFICIENCY IN SOILS^{1, 2}

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LACK OF CORRELATION BETWEEN PLANT GROWTH AND ACID-EXTRACTABLE PHOSPHATE

SOIL CHEMISTS have long recognized that there is a certain rationale in extracting soils with acids to determine the capacity of soil particles for releasing ions to the plant. Unfortunately, attempts to correlate the actual amounts of given ions released by acids in the laboratory with the amounts of such ions absorbed by plants have not been highly successful.

Two general types of explanation might account for the discrepancy. The first of these is that, although the release of H ion to the soil by plants and microorganisms is always quantitatively important, the plant can, by absorbing from the liquid phase, shift the equilibrium between the liquid and solid phase without a material change in the H ion concentration of the system. Ions thus released independently of evolution of acid by the plant become a part of the soil solution and can be absorbed by the plant. Moreover, H. Jenny⁵ has shown that the merging of the swarm of ions in the electrical double layer of the soil particle with a similar system at the root-hair surface, is sufficient to cause the removal of an exchangeable cation from the soil to the root hair and that there is no necessity for postulating the presence of a discrete intervening layer

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² This paper was written by the senior author and is based upon experiments formulated in conference by both authors. The experimental work was performed by the junior author.

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⁵ Unpublished data.

of soil solution or the excretion of acids by the plant to account for acquisition of such ions by plants. We suggest that this type of exchange could also take place if the soil particles and root-hair surfaces carry mutually exchangeable anions. That such exchanges may occur, but to widely varying degrees, in practically all soils is extremely probable. Such exchanges could dominate in soils whose colloidal particles approach saturation for particular ions and are in contact with kinds of root surfaces which are likewise highly saturated with ions of appropriate sign of charge (+ or —). This latter condition might be met by some kinds of plant root surfaces and not by others; thus the superior acquisitive power of certain plants for certain ions (for example, rye for phosphate) might be accounted for.

The second type of causes of failure to obtain correlations between acid extractions and growth or absorption (on the part of the plant) is largely of a technical character.

Several causes are rather obvious. Thus, the larger *amounts* of acid solutions necessarily used in the laboratory treatments exceed the buffering capacity of the soil; they produce greater shifts in H ion concentration, and dissolve larger amounts of a given ion—for example, phosphate—than would be likely to dissolve in the field. Moreover, the relative amounts of a given ion extracted from different soils by acid vary with the amounts of acid used and with the magnitude of the shift in H ion in the equilibrium solutions produced by equal amounts of acid.

A good illustration of this is afforded by data previously reported from this laboratory (8):^a Two soils of similar physical properties and approximately equal pH were treated with varied amounts of acid and the soils subjected to displacement in the manner usual in this laboratory (1). When the amount of acid was theoretically equivalent to 1/24 *N*, the first soil shifted the pH of the displaced solution to 5.9, the second to 6.6. The amounts of phosphate brought into solution were 29.5 mg and 5.0 mg respectively, a ratio of 6 to 1.

In a comparative experiment with acid applications equivalent to 4/24 *N*, the first soil shifted the pH of the displaced solution to 4.5, the second to 6.2; and the amounts of PO₄ were 67.6 mg and 6.0 mg respectively, a ratio of 11 to 1.

Again, using the same data, if the results are studied on the basis of the shift in pH instead of amount of added acid, at pH 6.5 the amounts of PO₄ brought into solution were 11.0 mg and 6.0 mg, respectively, or a ratio of about 2 to 1. At pH 5.5, the amounts of PO₄ were 55.0 mg and 3.0 mg respectively (an actual decline from that at pH 6.5), or a ratio

^a Italic numbers in parentheses refer to "Literature Cited" at the end of this paper.

of 18 to 1. Thus, if the figures are used to show the relative differences in supplying power of the two soils, the relation would be :

$$\left\{ \begin{array}{l} 6 \text{ to } 1 \text{ for small amounts of acid} \\ 11 \text{ to } 1 \text{ for larger amounts of acid} \end{array} \right\}$$

or

$$\left\{ \begin{array}{l} 2 \text{ to } 1 \text{ for one increment of shift in pH} \\ 18 \text{ to } 1 \text{ for another increment of shift in pH} \end{array} \right\}$$

These discrepancies are due to the fact that the acid comes in contact with different kinds of particles, and ions released by one kind of particle or compound become subject to secondary reactions. In the field, on the other hand, individual root hairs may influence solution from individual particles and the plant can remove dissolved substances before they have opportunity to react with other types of soil particles, or compounds, or with the free ions in the soil solution. This is also well illustrated by the work referred to above. Thus, it was shown that one of the effects of increasing acidity in a series of equilibrium treatments is to dissolve calcium or other ions, which in turn precipitate phosphate. Thus the phosphate figures so obtained do not reflect the magnitude of the effect of acid produced by H ion at the interphase boundary between a single particle and a root hair.

The effects of the type of secondary reactions (chemical and mass-action effects) just referred to, are now generally recognized and must, of course, be taken into account in interpreting data derived from the acid treatment of soil. It would, however, be unsafe and even absurd to conclude that this type of secondary reaction (precipitation) is the exclusive cause of the removal of phosphate from acid extracts. Many workers⁷ have observed that various soil and colloidal clay minerals have great capacity to remove PO_4 from solutions and have ascribed this to an adsorption. Some of the data reported are, unfortunately, subject to the criticism that release of Ca ion by exchange with H ion could have caused the precipitation of phosphate and thus vitiated the conclusion that the effect is an adsorption phenomenon.

A notable attempt to elucidate the rôle of adsorption in phosphate fixation was that of Russell and Prescott (7). These investigators were unfortunate in that their experiments were performed at a time when the importance of the secondary chemical reactions discussed above were not generally recognized. Moreover, their conclusions were largely based on adsorption isotherms conforming to the Freundlich equation. Comber (2) pointed out the possibility of chemical reactions, and Fisher (3) showed the inadequacy of conformity to the Freundlich equation

⁷ See the bibliography in Murphy (5).

as the exclusive test of an adsorption. These criticisms of the conclusions from the particular experiments are, of course, valid, but they do not prove that adsorption may not have played a part in determining the actual experimental results. Whether complexes capable of adsorbing phosphate were present in substantial amounts in these particular soils is perhaps of no general interest at this late date. The point is that an overemphasis of the rôle of secondary chemical reactions, important as these are in many soil types, has prejudiced the interpretation of data from experiments with phosphate in which the secondary reactions may have been caused by adsorption or exchange.

Murphy (5), in the accompanying paper, shows that a certain soil (Aiken clay loam), in which the colloidal clay component was largely of the kaolinitic type (as shown by X-ray diffraction photographs), reacted under experiment in the same manner as would have been expected from the studies of finely ground kaolinite carried on concurrently. In experiments with kaolinite, the material manifested the usual properties of colloidal alumino-silicates characterized by a low silica:alumina ratio. The kaolinite removed cations (K) most effectively from alkaline solutions and anions (PO_4) from acid solutions. The absence of ions capable of precipitating PO_4 precludes any other explanation than that of an adsorption. The similar behavior of the soil definitely points to its natural kaolinite component and to an adsorption reaction as the cause of the negligible amounts of phosphate removed from the soil by acid. Crops planted on the soil manifest all the symptoms of phosphate deficiency and the soil is practically immune to phosphate fertilization except when the applications are beyond economic possibility or where the fertilizer is localized in immediate contact with the absorbing roots. Phosphate adsorbed by this soil (and by the kaolinite) is not brought into solution except to a negligible extent by acid until the amount of acid is sufficient to shift the reaction of the equilibrium solution to about pH 1.0 when the aluminum silicates are breaking down, as demonstrated by the copious solution of Al and the release of soluble and colloidal SiO_2 .

The paper in which these results are reported (5) also demonstrates a substantial phosphate-adsorbing capacity for other types of clay minerals (Volelay and bentonite). The much greater adsorbing capacity of kaolinite depends on its being finely ground. Even when finely ground, however, the kaolinite particles are probably much coarser than the particles of Volelay and bentonite as shown by the physical properties of liquid mixtures, ease of filtration, etc. The clays with high silica:alumina ratio are highly dispersed in water and are probably in a very fine state of subdivision in most soils. The kaolinite in natural soils (6) appears to

vary more in particle size than other clay minerals, and phosphate-adsorbing capacity of kaolinitic soils must therefore vary widely, even between soils of equal kaolinite content.

It is obviously impossible to devise a technique yielding index figures that can be applied with exactness to express the acid solubility of phosphate from the *individual* phosphate-carrying particles of the soil. With the vast majority of arable soils, a variable proportion of the phosphate rendered labile (dissolved) by acid is precipitated or adsorbed. Fairly good correlations between acid-soluble phosphate of soils and the phosphate-fertilizer requirement of plants are sometimes claimed. Such correlations must, however, be limited to slightly buffered soils, containing only small amounts of adsorbing clay minerals or clay minerals of low specific adsorbing capacity or clay minerals which are nearly saturated with phosphate.

The preceding discussion of data on or conclusions from acid extractions of soils concerned equilibrium extractions with "strong" acid (HCl). Many suppose, however, that the use of "weak" acids remedies some of the defects pointed out above.

The use of buffered acids, of course, prevents the rise of H ion concentration in the equilibrium solution and eliminates the secondary chemical precipitations, which tend to lower the phosphate figures actually obtained by use of unbuffered acid. In the field, however, the H ion concentration about an individual phosphate-carrying particle would rise greatly or little, as a result of CO₂ excretion by the plant, according to the distance of the particles of potentially soluble neutralizers, such as CaCO₃ or Ca-clays, from the phosphate-carrying particle. Thus, if the neutralizing power of a given soil is primarily due to CaCO₃, the amount of phosphate in solution at any one time in the field, as a result of acid excretion by plants, would depend upon the size and distribution of the CaCO₃ particles. In the laboratory at equilibrium, however, the phosphate dissolved by acid would be primarily a function of the total amount of CaCO₃.

Perhaps the most unfortunate occurrence in the history of soil-phosphate investigation was the choice of citric acid as a solvent. Dilute solutions of citric acid *do not dissolve* phosphate from the adsorption complex of soils: the citrate anion *displaces* phosphate from the adsorption complex.

But the plant cannot do this unless it excretes citrate ion, OH ion, or some other ion which is highly adsorbed by the clay complex, or by hydrogels when these are involved. Possibly some plants excrete enough organic acids containing anions which are strongly adsorbed. This spe-

cial ability could account for a relatively greater power of such plants to acquire phosphate from a given adsorption complex. Even if some plants could be shown to do this to a considerable degree, even if the contact phenomenon emphasized by Jenny is accepted *in toto*, it is certain that plants in general acquire adsorbed phosphate with great difficulty unless the individual particles are highly saturated (9) and the number of such particles is great.

We hesitate to use the term "availability," but in the sense in which this term is commonly applied, the phosphate contained in clay minerals is only slightly available,⁸ while that removed by *dissolving* phosphates is extremely available, unless prevented from dissolving by a high buffer power on the part of the soil.

Thus, two soils extracted with citric acid could give equal and relatively large amounts of phosphate (as compared with the great majority of soils), and yet be very different in phosphate-fertilizer requirements. If in one soil, the phosphate in the citric-acid extract were actually derived from solution of phosphate, probably no fertilizer would be required. If, however, the phosphate in the acid extract were derived from an adsorption complex, a need for fertilization would almost certainly be indicated for most plants.

A simple experiment reveals all the facts necessary to the above conclusion. Finely ground kaolinite was partially saturated with phosphate. Five-gram portions, containing 61.45 mg PO_4 , were brought to equilibrium with the respective solutions as noted. The following amounts of PO_4 were removed at equilibrium (1:5 suspensions), out of a possible 61.45 mg:

	pH value	PO_4 removed, mg
0.1 <i>N</i> Citric acid.....	2.27	21.88
0.005 <i>N</i> Hydrochloric acid.....	2.28	1.00
0.1 <i>N</i> Hydrochloric acid.....	1.01	6.84
0.1 <i>N</i> Sodium hydroxide.....	12.00	50.00

Hydrochloric acid (0.1 *N*) dissolves Al from kaolinite and releases small amounts of phosphate. Phosphate is *not displaced* from the adsorbed condition by hydrochloric acid of any pH short of one which breaks down the alumino-silicates of the adsorbing complex. In the pH range possible about an individual particle of clay complex in normal soils, there is no release of adsorbed phosphate as a result of a specific "acid" effect. Under such circumstances, phosphate is released only if the acid is one with a strongly adsorbed anion.

⁸ Unless the particles are highly saturated and the *amounts* of phosphate so held are large.

FACTORS AFFECTING PHOSPHATE AVAILABILITY

From the preceding analysis, we suggest that the points to be determined in laboratory studies of soils in order to predict the need for phosphate fertilizers are as follows:

1. The amounts of phosphate liberated by acids of a type whose anion is not adsorbed by clay minerals or Fe hydrogels.⁹
2. The shift in pH caused by added acid, because this indicates whether increased acidity in the field would or would not be likely to shift the pH enough to cause the solution of phosphate to the extent observed in the laboratory.
3. The degree of phosphate saturation of the adsorbing clay minerals or adsorbing hydrogels.
4. The total phosphate (fusion analysis of the soil).

We now present for analysis the results of a series of experiments with a single soil, carried out in such a manner as to differentiate between precipitation and adsorption effects. All data represent 1:5 equilibrium extracts of 100 grams of a fine sandy loam soil (known as No. 117 in this laboratory) with amounts of acid (or alkali) producing the pH values noted at equilibrium. Series of extracts were made on the soil alone, soil + excess CaCO_3 , soil + 400 mg Ca as CaCl_2 , soil + 1 gram finely ground kaolinite.¹⁰ The soil was chosen as one having no kaolinite and having little buffering power according to standards accepted for soils of this region. The soil does contain other clay minerals, and undoubtedly some of its phosphate is held as adsorbed phosphate. Moreover, the exchange complex does release calcium on acid treatment but not nearly so much as highly buffered soils of this region. When such a soil is extracted with dilute HCl, the resulting figures represent the amount of phosphate derived from solution of individual phosphate-carrying particles minus the phosphate precipitated or adsorbed.

The points on the curve representing the acid side of neutrality (see curve A, fig. 1) are obviously lower than they would have been if the phosphate-carrying particles could have been isolated and these alone extracted. This cannot be done, and calculations of the magnitude of this depressive effect from calcium released or amount of clay present are of little value because of the complexity of the equilibrium solution and lack of knowledge of the amounts of each clay mineral and the specific adsorbing capacity of each such mineral in this particular soil.

The curve (curve A, fig. 1) can, however, be analyzed and the dominating factors which determine it characterized. If the data are plotted in

⁹ Possibly Al hydrogels in some soils at certain pH values.

¹⁰ Data not presented for soil + excess CaCO_3 . All acid treatments with CaCO_3 in excess, gave about equal pH values and equal phosphate figures.

absolute terms (curve *A*, fig. 2), the curve is practically a straight line on the acid side in the H ion range between pH 5.17 and 3.65. The slight change in the slope of the line at the lower pH values can be accounted for either by a small amount of precipitation or by adsorption effects or by both. The straightness of the line, however, indicates that the major effect is solution of phosphate-carrying particles or compounds. On the alkaline side (curve *B*, fig. 2), the curve is apparently logarithmic and

Fig. 1.—Phosphate determined in 1:5 equilibrium extracts from a variously treated slightly buffered soil, by acid and by alkali. Concentrations of HCl and NaOH used were 0.002, 0.004, 0.006, 0.008, and 0.010 *N*. The data for the kaolinite treatment on the alkaline side were essentially the same as for the untreated soil and are omitted to avoid confusion of the lines.

can be shown (if plotted logarithmically) to obey the Freundlich equation. All of the common phosphate compounds, which do not hydrolyze, become less and less soluble with increasing alkalinity. The rise observable with increasing alkalinity could be due to hydrolysis of iron, aluminum, or manganese phosphates (8); or to exchange of OH with PO_4 adsorbed either by clay minerals or by iron or aluminum hydrogels (5). As a matter of fact, an exchange of OH for the PO_4 of the clay minerals is undoubtedly the cause of the increase in this particular soil, but it really does not matter because all three classes (clay minerals, hydrogels,

and iron or aluminum phosphate) of phosphate complex would act in the same manner with OH.

As may be seen from curve *B* of figure 1, addition of 400 mg Ca ion as CaCl_2 to 100 grams of soil depressed the solubility of phosphate throughout the entire range. On the alkaline side, the PO_4 released from the soil minerals by OH exchange is almost completely precipitated by a very

Fig. 2.—Data from curve *A* of figure 1 presented in absolute terms.

small application of Ca ion. In the soil alone (curve *A*, fig. 1) there was not enough dissolved calcium (that is, Ca ion) at pH values above 7 to produce this effect; the phosphate released from the soil minerals therefore remained in solution as determined.

As may be seen from curve *C*, figure 1, 1 gram of kaolinite in 100 grams of soil removes a large proportion of the PO_4 released by acid, the adsorption increasing with increasing H ion (decreasing pH) at first, but later rising. This latter rise is evidently due to the fact that, at the lower pH values, the clay mineral is approaching saturation. That this is so is

shown (curve *D*, fig. 1) by the supplementary experiment: 2 grams of kaolinite removes all of the phosphate released by acid. *Evidently then, the degree of saturation and the amount* of adsorbing clay minerals in a soil is what determines their ability to conceal the true acid solubility of soil phosphate. Moreover, the degree of saturation of the clay mineral particles and the number of those particles in immediate contact with potentially acid-soluble phosphate particles must determine the amount of phosphate that is actually dissolved in the soil by biologically produced acids. If the clay minerals are only slightly saturated with phosphate and very numerous as compared with other phosphate-carrying particles, the excretion of acids by the plant will merely move the phosphate from the acid-soluble particles to the practically insoluble adsorption complex. If the plant gets phosphate from this complex, it does so, not by acid solution, but as a result of exchanges, as suggested by Jenny for cations. Here again, the amount of phosphate the plant can get from the adsorption complex is determined by degree of saturation and amount of adsorbed phosphate.

An interesting point is whether any factor other than pH in the complex mixture of ions in the acid extracts has any effect upon the adsorbing capacity of the clay minerals. At pH 3.6, the amount of phosphate released by the soil was 23.5 mg (curve *A*, fig. 1). The amount of phosphate *not* removed by the kaolinite was 3.4 mg (curve *C*). The kaolinite had, therefore, adsorbed 20.1 mg and was in equilibrium with a solution containing 3.4 mg. We, accordingly, made up a number of solutions, all containing 23.5 mg of PO_4 (from KH_2PO_4) in 500 cc, after adjusting the H ion concentration to give values of about pH 3.6 when 500 cc of solution was brought to equilibrium with 1 gram of kaolinite. One of these equilibrium mixtures, with a pH of 3.69, had approximately the same PO_4 ion content as the soil-kaolin-acid mixture, as shown below:

Equilibrium mixture	pH	Phosphate adsorbed, mg	Phosphate in solution, mg	Total phosphate, mg
100 grams soil + 1 gram kaolinite + 500 cc dilute HCl. . . .	3.60	20.1	3.4	23.5
1 gram kaolinite + 500 cc dilute KH_2PO_4 solution.	3.69	19.3	4.2	23.5

The distribution of phosphate between kaolinite and solution is essentially the same in the two mixtures, which are otherwise very different. Apparently the only factors which affect the phosphate-adsorbing capacity of the clay minerals are PO_4 concentration and pH.

INFORMATION REQUIRED TO DIAGNOSE PHOSPHATE DEFICIENCY

In the preceding discussion, the points emphasized are the importance of determining the degree of saturation of the adsorbing complexes (minerals, hydrogels, etc.) ; the specific capacity of potentially soluble phosphate particles to dissolve in acid ; the effect of buffers (Ca ion, etc.) in lowering the apparent solubility of these particles ; and the total phosphate content of the soils. How are these factors to be determined, and how can they be evaluated ?

The degree of saturation of the adsorbing constituents of the soil can be readily calculated if the amount of adsorbed phosphate actually present in the soil is known, together with the amount of phosphate the adsorbing minerals *could* hold at saturation, that is, the adsorption capacity. These figures can be ascertained from 0.1 *N* NaOH equilibrium extracts¹¹ of the soil itself and of the soil *after* saturation with PO_4 . The actual concentration of the NaOH is not important provided it is uniform for both treatments, is sufficiently concentrated to overcome buffering on the alkaline side of neutrality, and produces a high pH in the equilibrium solution.

The adsorption capacity of an adsorption complex is, of course, affected by the pH at which the adsorption takes place (and the concentration of phosphate in the treating solution), but if concentrated solutions of KH_2PO_4 at pH 4.5 are used in the proportion of 500 cc to 100 grams of soil, the pH of the equilibrium solution will usually lie between 4.5 and 7.0 and the absolute amounts adsorbed will not vary greatly. Moreover, in those soils in which adsorption effects are important, the adsorbing capacity for PO_4 is very great as compared with the amounts actually in the adsorbed condition ; so that a considerable variation in the determined adsorption capacity could not materially affect the calculated values of what we call the "degree of saturation," or the "adsorption deficit."

The specific capacity of phosphate-carrying particles to dissolve in acids cannot be determined exactly except in soils having no buffer capacity and which are also free from adsorbing complexes. The general order of magnitude of this factor can, however, be inferred from the amounts of phosphate extracted by acid and the determined buffer capacity of the soil. Five volumes of 0.01 *N* HCl to 1 gram of soil will shift the pH more than any plant could do, but not enough to overcome the buffering

¹¹ Equilibrium extracts do not give the entire amount of adsorbed phosphate, but they give almost all, and all that need be considered in these relations.

power of soils. The shift in pH actually observed by this treatment gives an appropriate measure of the buffer capacity of the soil.

The determination of total phosphate by fusion analysis presents no difficulty. This datum is necessary to give weight to the quantity factor, in supplementing conclusions drawn from the data showing the degree of saturation.

APPLICATION OF CHEMICAL DATA TO PROGNOSIS OF PHYSIOLOGICAL PHOSPHATE DEFICIENCY

The evaluation of the criteria suggested will obviously depend upon comparisons between the known physiological responses to phosphate fertilization of individual soils, and the figures or indexes obtained from such soils by the methods outlined.

This we believe we have accomplished for a group of fourteen soils of widely different characters. The minor defects of our correlations are apparently due to the incompleteness of the physiological data and to variation in the specific capacity of different plants to acquire phosphate from particles of equal degree of saturation. The first defect can be overcome by obtaining further evidence of physiological deficiency in the particular soils. The second defect can never be entirely eliminated, but its elimination is not necessary if the data are not interpreted too narrowly. Fertilizers are not so valuable that the most effective dosage must be predicted with a high degree of accuracy. To be able to say that for the generality of crops such and such a soil will probably respond to phosphate applications, is sufficient.

Many of the soils used in these experiments are the same as those used by Hibbard (4), who gives additional data on them.

Phosphate-deficient Soils.—By referring to table 1, the reasons why the soils manifesting great phosphate deficiency are unable to supply the plant are perfectly obvious. Soils 103, 69A, and 64 yield practically no acid-soluble phosphate: their unsatisfied adsorption capacity is so great (adsorption indexes, 3.28, 1.54, and 0.93) as compared with their phosphate content, and the degree of saturation is so small that the adsorption complex holds phosphate with great avidity, and the plant cannot easily remove it.

Soil 78 can yield practically no acid-soluble phosphate; this is definitely referable to its high adsorption index. The degree of saturation is high and individual particles of adsorption complex could be expected to yield phosphate well to the plant, but the low total phosphate, the effect of which is reflected in adsorption index, prevents plants from getting phosphate rapidly.

TABLE 1
CHEMICAL DATA (PO₄) FROM SOILS OF KNOWN PHYSIOLOGICAL RESPONSE

Soil No. and description	PO ₄ per 100 grams of soil		Present degree of saturation ($\frac{\text{col. 1}}{\text{col. 2}}$)	PO ₄ per 100 grams of soil		Adsorption index ($\frac{\text{col. 4}}{\text{col. 5}}$)	PO ₄ per 100 grams soil, acid-soluble [§]	pH of acid equilibrium	Mineral characteristics†	Buffering ability	Phosphate deficiency indicated by plant growth
	Adsorption capacity,*	In adsorbed condition†		Adsorption deficit (col. 1 - col. 2)	Total‡						
	1	2	3	4	5	6	7	8	9	10	11
	mg	mg	per cent	mg	mg		mg	pH			
103. Aikin clay	547	22.0	4	525	160	3.28	0.2	4.78	Kaolinite	Moderate	Extreme
69A. Sites clay loam	290	44.0	15	246	160	1.54	0.8	3.89	Kaolinite	Moderate	Great: extreme for tomatoes, etc., but not for fruit trees
78. Fine sandy loam	105	30.4	29	75	45	1.67	1.2	2.74	Kaolinite and montmorillonite	Slight	Great: extreme for tomatoes; moderate for barley; none for fruit trees
64. Vina silt loam	174	16.4	9	158	170	0.93	0.6	4.81	Kaolinite	Moderate	Great: marked for tomatoes; moderate for alfalfa
38. Vina silty clay loam	181	23.6	13	157	250	0.63	4.8	5.22	Kaolinite	Substantial	Intermediate: none for some time
36. Farwell sandy loam	126	13.6	11	112	250	0.45	1.9	6.19	Kaolinite and montmorillonite	Substantial	Intermediate: marked for tomatoes
40. Altamont-Olympic-loam wash	172	41.6	24	130	330	0.39	13.4	4.86	Mineral X and montmorillonite	Moderate	None
37. Nord sandy loam	51	10.4	20	40	240	0.17	5.5	8.50	Faintly kaolinite	Extreme	Intermediate: moderate for tomatoes, much less than No. 36 at first
1C. Yolo silty clay loam	55	26.6	48	28	200	0.14	5.1	7.09	Montmorillonite	Substantial	None
68A. Tuiunga fine sand	23	4.4	19	19	140	0.14	17.9	3.50		Slight	Unknown, no information
53. Delhi sand	29	18.0	62	11	80	0.14	46.7	2.86		Slight	None for first crop; later marked for tomatoes
30. Fresno fine sandy loam	32	6.0	19	26	160	0.16	40.6	3.00		Slight	None for some time; after several crops, moderate for tomatoes
75. Yolo loam	87	12.8	15	74	232	0.32	9.1	6.25	Montmorillonite	Substantial	None
80. Hanford fine sandy loam	8	4.4	55	4	115	0.04	0.6	7.75	Mineral X	Extreme	Great: very marked for tomatoes; largely corrected by making soil acid

* The adsorption capacity represents the phosphate removed by 0.1 N NaOH (1:5, 1-hour equilibrium suspensions); from soil subjected for 15 hours to a KH₂PO₄ solution (1:5) containing approximately 3 mg of PO₄ per cc and having a pH of 4.5. The free KH₂PO₄ present in the soil was leached out with distilled water before applying the NaOH treatment.

† Direct determination on soil—0.1 N NaOH (1:5) 1-hour equilibrium suspension.

‡ Fusion analyses.

§ Determined from X-ray photographs.

Soil 80 has a negligible adsorption deficit and negligible amounts of adsorbed phosphate. Plants suffer because the potentially acid-soluble phosphate is prevented from coming into solution as a result of the high buffer capacity of the soil.

Soils of Intermediate Phosphate-supplying Power.—Of this group, soil 36 shows early physiological deficiency. Soils 37 and 38 show deficiency in subsequent crops. Soil 36 yields very little acid-soluble phosphate, primarily owing to its substantial buffering capacity, aided by a substantial capacity to adsorb phosphate (adsorption capacity 126, adsorption index 0.45). In soils 37 and 38, the amounts of acid-soluble phosphate are greater than for No. 36 but are not large, owing entirely to buffering in soil 37 and primarily to adsorption in soil 38. The buffering of No. 37 is capable of being remedied by (acidic) applications in the field, but the acid-soluble phosphate of No. 38 should decline under cropping, as indicated by the high adsorption index (0.63).

Soils of Good Present Supplying Power.—The lack of present physiological deficiency for plants in soils 40, 53, and 30 is easily accounted for by the comparatively large figures for acid-soluble phosphate. The relatively lower acid-soluble figure of No. 40 as compared with Nos. 53 and 30 is referable to the higher adsorption index (0.39 as against 0.14 and 0.16); inasmuch as the soil is only moderately buffered.

Soils 30 and 53 both manifest phosphate deficiency after a relatively small number of crops have been grown. This cannot be explained on the basis of a transfer of potentially acid-soluble phosphates to the adsorption complex, for the adsorption indexes are low; it must be otherwise accounted for. This we believe can be done as follows: The very high figures for acid solubility (*in vitro*) reflect a high acid solubility for both the soils. The buffering power of both of these soils is negligible, so that their individual phosphate-carrying particles could not be prevented from delivering PO_4 to the soil solution with normal CO_2 excretion by plants. This means a concentrated soil solution, with respect to phosphate,¹² and a "luxury" adsorption of phosphate by the plant. The total phosphate in soil No. 53 is very low and the total phosphate in No. 30 is subaverage. The total phosphate in both soils should decline rapidly because of luxury consumption by the plant and cause an absolute deficiency in a very few years.

Soils 1C and 75 give sufficient acid-soluble phosphate to account for a reasonably good supplying power in spite of substantial buffering. Since the soils are buffered, the adsorption complex could play little part in

¹² Soil No. 30 had originally the highest phosphate concentration of displaced solution of all encountered in this laboratory.

lowering the acid-soluble phosphate actually accessible to the plant even if the adsorption deficits were much higher than they are in both cases.

The physiological efficiency of soil No. 68A is unknown, but the comparatively high acid-soluble figures and low buffering capacity with the negligible adsorption capacity (adsorption index 0.14) indicates that the soil cannot be physiologically deficient at the present time.

We refrain from further analysis of these data because we realize that the limited number of soils and the incompleteness of our data with respect to the physiological supplying power of the soils could lead to erroneous conclusions as to the significance of specific figures obtained in the laboratory. We hope to present further evidence at a later date from larger numbers of soils, the physiological response of which is determined with three types of plants—plants with great acquisitive power for adsorbed phosphate, plants with slight acquisitive power, and plants with what may be called “average acquisitive power.”

CONCLUSIONS

The phosphate-carrying particles of natural soils may be divided into two sharply defined classes—those which dissolve in acids (that is, both ions enter solution) and those which do not dissolve in acid, but which either hydrolyze in alkaline solutions or release phosphate only as a result of anion exchange. The phosphate accessible to plants (derived from acid-soluble particles) depends upon the PO_4 -ion concentration of the soil solution¹³ to a minor degree, and upon the amounts of PO_4 brought into solution by H ion at the interphase boundary between the root hair and the individual phosphate-carrying particle. The phosphate accessible to plants (derived from hydrolysis or from adsorbed phosphate) depends upon the degree of saturation of the hydrogels or adsorbing clay minerals and the amount of phosphate so held.

The phosphate brought into solution from the individual soil particles by acid cannot be exactly determined, but can be inferred from acid extractions, supplemented by a knowledge of the buffer capacity of the soil.

The amounts of phosphate on the hydrogels and clay minerals can be determined by extracting the soil with alkali. The degree of saturation of particles holding phosphate in this manner can be determined by comparing amounts of PO_4 extracted by alkali from the soil before and after saturation with phosphate.

We believe it possible to obtain limiting figures from chemical data, easily obtainable in the laboratory, which will indicate degrees of physio-

¹³ As defined in this laboratory, that is, ions free to move in the water of the soil independently of solid phase or colloidal particles.

logical deficiencies in soils. We suggest certain preliminary and tentative figures and magnitudes, subject to change as a result of further studies of a larger group of soils and for plants of different sensitivities: If acid-extractable phosphate is high¹⁴ (9 mg or more per 100 grams of soil), most plants will have no present difficulty in obtaining phosphate from the soil. If acid-extractable phosphate is low (about 1.0 mg or less), plants will usually acquire phosphate with difficulty, but the difficulty will be greatly enhanced if the buffer capacity is low and the adsorptive index is high. If the acid-extractable phosphate is intermediate, plants will probably have difficulty in acquiring phosphate when the buffer capacity is extremely high (compare soil 37 and soil 1C); or even in the absence of extreme buffering capacity, when the adsorption index is high.

The effect of a high adsorptive power (high adsorption index) in preventing a plant from acquiring potentially acid-soluble phosphate in the field is directly associated with the buffering power of the soil: (a) if the adsorption index is high and the buffering capacity is low, the conditions are highly adverse; (b) if the buffer capacity is high, the adsorption index is of no import in this connection.

The ability of a soil having a high adsorption index to deliver PO_4 from the adsorption complex to the plant in the field may be substantial for certain plants, provided that the degree of saturation and the number of particles carrying adsorbed phosphate is great, and if such plants can give off anions (for example, citrate) capable of being adsorbed. That plants with superior acquisitive power for phosphate have this power for the reason indicated is highly probable, particularly if the amount of contacts (root hair to soil particle) are great as a result of an extensive root development on the part of the plants.

Until further studies by the methods outlined have been performed with soils of very high organic-matter content, and on soils whose buffering capacity (or alkalinity) is due to sodium instead of calcium, we prefer to exclude such soils from our interpretation. We have data in hand which indicate that certain of our methods are applicable to peat soils, but the interpretations we have ventured above may have to be modified in some respects for this type of soil material.

SUMMARY

The causes of failure to obtain correlations between plant growth and the acid-extractable phosphate of soils are partly inherent and partly technical.

The rôles of adsorption complexes, hydrogels, and acid buffers, as

¹⁴ By our technique.

affecting the analytical figures obtained by acid extraction of soils, are outlined.

The specific "acidity effect" of reagents cannot be measured in soils containing substantial amounts of adsorbing colloids if the anion of the reagent is itself adsorbed by the soil.

The kinds of chemical determination necessary in the prognosis of phosphate deficiency are announced.

A critical analysis of the quantitative effects of Ca ion and kaolinite in determining the phosphate solubility of a type soil is presented.

Hydrogen-ion concentration, phosphate concentration, present degree of saturation, and adsorption capacity of the adsorbing complex determine the removal of acid-dissolved phosphate both *in vitro* and in the field.

Chemical data on fourteen soils are analyzed in the light of these findings to illustrate how the present physiological supplying power of the soil could be deduced from the data.

Tentative standards represented by figures and magnitudes are suggested as a basis for predicting the current phosphate-supplying power of soils.

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