NOTE TO USERS

CHARACTERIZATION OF SOIL PHOSPHORUS BY EXCHANGE RESIN ADSORPTION AND P^{32} EQUILIBRATION

by

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INTRODUCTION

For a century, soil chemists have been in continuous search for a laboratory method to evaluate the availability of soil phosphorus to plants. Nearly all the current methods employ some extracting agent to remove part of the inorganic soil phosphorus. The phosphorus thus extracted is probably derived from several different types of compounds, the quantity from each type depending not only on the proportion present, but also on the nature of the extractant and the interaction between extractant and soil. Because of the diverse nature of soils, it is not surprising that the extractants are not of universal applicability.

A fundamentally different approach has been used with P^{32}. When a solution of orthophosphate labeled with P^{32} is added to soil, the added phosphate is diluted immediately with soil phosphate in solution. At the same time, it begins to exchange with the solid-phase soil phosphate in kinetic equilibrium with the phosphate in solution. Knowing the quantity of phosphate in solution, together with the initial and final specific activity, it is possible to compute the quantity of soil phosphorus with which the added phosphorus has equilibrated. This approach has the theoretical advantage that it gives a measure of net behavior of all types of inorganic soil phosphorus. The measure is independent of the accessory characteristics of the soil, except as the latter may influence the behavior of the phosphorus. In addition

to the technical difficulties of measurement, however, the inorganic soil phosphorus that equilibrates with P^{32} suffers a theoretical disadvantage as a measure of phosphate availability. The process of measurement is of course rather different from that by which plants absorb phosphorus. Absorption of phosphate by plants is largely a one-way process. Although electrical neutrality is maintained, the replacing ions are not other phosphate ions. They are perhaps silicate and hydroxyl in acid soils, and silicate, hydroxyl, and carbonate in alkaline soils.

The experimental work reported in the following pages was undertaken with the foregoing ideas in mind. It was thought that the use of an anion exchange resin to remove inorganic phosphorus from soil would largely eliminate both the theoretical and practical disadvantages connected with the P^{32} equilibration method.

REVIEW OF LITERATURE

In 1845, Daubeny (8) used the terms "active" and "dormant" to express the more and less soluble constituents of soil, respectively. Dyer (15) employed a 1 per cent citric acid solution to discriminate between "available" and "unavailable" fractions. It was assumed that the action of 1 per cent citric acid solution simulated that of the acid secretion of plant roots. The conception of the plant root as a secreting and dissolving agent, however, was shortly abandoned, and the method became entirely empirical. Nevertheless, the citric acid method is still used in England and Holland, where a more or less satisfactory working agreement has been established between its solvent action and response of plants to phosphate fertilization in field tests. Since the work of Dyer (15), a number of other acids, including carbonic (17,27), nitric (19,30,32) and sulfuric (2,33), have been used as soil phosphorus extractants.

Several investigators (5,7,12) have suggested that, in addition to acid soluble phosphorus, adsorbed phosphorus should be considered in evaluating the fertility status of the soil. It has been proposed that the so-called adsorbed phosphate can be extracted by sodium hydroxide (7), ammonium fluoride (14), and sodium arsenate (11). Both acid soluble and adsorbed phosphorus are highly empirical,

however. The magnitude of each fraction depends upon the nature, volume, and concentration of the solution and on the time of extraction.

Liberation of phosphate by other anions has been thought to be an anion exchange reaction analogous to cation exchange (11,24,31). McAuliffe, et al. (26), however, studying the distribution of P^{32} added to soils, found that only a small fraction of the sodium hydroxide soluble inorganic phosphorus (9, p. 406), which was presumed to be held in adsorbed or exchangeable form, appears to be in direct equilibrium with the phosphorus in the soil solution. The exchangeable bases of soils are all in equilibrium with the bases in the liquid phase. Thus, the so-called adsorbed phosphorus could no longer be considered exchangeable in the sense of exchangeable bases.

When $P^{32}O_4$ ions are added to a system consisting of soil in equilibrium with its solution, the P^{32} will distribute itself between the solution and solid phase in proportion to the numbers of phosphate ions in solution and in the solid phase with which the $P^{32}O_4$ has equilibrated. McAuliffe, et al. (26), designated the latter as "surface" phosphorus. Such terminology would be suitable if the isotopic exchange reaction were limited only to the surface. The extent of exchange increases with time over a long period (26,35), however, indicating that more than surface phosphate ions participate in the reaction. Further, it is not certain that all phosphate ions on the surface are exchangeable, since the exchanging part of the surface may be much smaller than the geometrical surface (29). In some cases,

only the less restricted surface ions, such as those on edges and corners, may enter into exchange reactions (21).

It is more reasonable to designate the phosphorus fraction found by P^{32} equilibration in terms of the process used in measurement. Thus, the portion of the soil phosphorus capable of isotopic exchange with phosphorus in solution under prescribed experimental conditions may be designated as exchangeable phosphorus. Such a definition involves no assumptions about the nature or location of the phosphorus compounds involved.

The behavior of soil phosphorus that equilibrates with P^{32} is not analogous to that of exchangeable bases in soils. The bases commonly used in cation exchange work are, for the most part, freely interchangeable. The same is not true of phosphate and other anions. The reason for the difference appears to be that exchangeable bases are more strongly dissociated from the soil than are phosphate groups. Phosphate forms relatively insoluble compounds with soil constituents. It exchanges with other anions that form insoluble compounds with the same soil constituents, but not with those that do not. In this respect, the behavior of soil phosphate is similar to that of oxalate in the calcium oxalate precipitate. Kolthoff and Sandell (22) found that sulfate, iodate, and hydroxyl, but not chloride, would exchange with the oxalate on the surface of calcium oxalate monohydrate.

Another difference between exchange of bases and of phosphorus appears to be the change in rate with respect to time. If exchange-

able calcium on keonlinite, for example, is measured by exchange with Ca^{45}, the equilibration is essentially completed within a period of about 2 hours (3). Exchange of soil phosphorus with P^{32} shows a similar rapid initial reaction, but in addition shows a slow reaction that apparently continues for a long time (26,35). The rapid reaction is presumably due mainly to the phosphorus held in superficial positions, although it may be due in part to phosphate in the interior of discrete particles of phosphate compounds that are in rapid kinetic equilibrium with the solution. The slow reaction is presumably due mainly to phosphorus held in interior positions, although it may be due in part to less ionized phosphorus held in superficial positions. Apatite (18) and precipitated ferric phosphate (35) both exhibit the rapid and slow phosphate exchange characteristic of soils. No published data are available on isotopic exchange of bases in solution with those in the soil solid phase. It would be expected, however, that the course of the reaction might vary between the behavior described for calcium in kaolinite and phosphorus in soils. Isotopic exchange of potassium in soils having considerable illite, for example, would be expected to approach the behavior found for phosphorus.

The phosphate exchange reaction in soils is in sharp contrast to that in exchange resins. Wiklander (35) obtained complete isotopic exchange within 10 minutes with an anion exchange resin. Exchange of phosphorus in this case followed the behavior of exchangeable calcium in kaolinite.

MATERIALS AND PROCEDURES

Radiochemical Measurements

The P^{32} employed in this investigation was obtained from the Oak Ridge National Laboratory. It was a dilute solution of H_3PO_4 containing 0.025 mgm. of P^{31} per millicurie of P^{32}. The P^{32} was free from radioactive impurities, as indicated by checking the activity for a 14.3-day halflife. Phosphomolyhdate precipitation (28) indicated that 94.65 per cent of the P^{32} was in orthophosphate form.

All radioassays were made by means of a solution counter with a background of 0.7 ct./sec. Correction for counter fluctuation was made by counting a standard solution. The statistical counting error was reduced to about 1 per cent by recording 10,000 counts. Suitable quantities of P^{32} were used so that the solutions counted about 40 ct./sec.

Soils

The study was made on soils from the north central region which had been tested in the cooperative uniform phosphorus experiments of 1951 (10). Samples of these soils were sent to Beltsville and Ames. A greenhouse experiment was conducted in Beltsville to evaluate the phosphorus fertility status of the soils. "Available" phorphorus was

determined on both sets of samples by the Iowa State College Soil Testing Laboratory using Bray's (6) 0.03 N NH_4F - 0.025 N HCl extractant. The results on the two sets of samples agreed closely for 16 of the 23 soils. Samples of these 16 soils were used. They represented soils from North Dakota, South Dakota, Minnesota, Nebraska, Michigan, Illinois, and Kansas.

Anion Exchange Resin Dowex 2

Dowex 2 (Nalcite SAR) is a strongly basic anion exchange resin produced by the Dow Chemical Company, Midland, Michigan. According to Wheaton and Bauman (34), it is a quaternary ammonium salt ($RR'R''R'''N^+ . A^-$), in which one of the R's is cross linked with divinylbenzene to render the resin insoluble in aqueous and nonaqueous media. The product is a highly dissociated organic base, in which the large cationic body is limited in movement and the relatively small and mobile anions are free to exchange over a wide pH range. The hydroxide form is a strongly ionized base. Strong mineral acids will react with the hydroxide form of the resin to give water and the neutral salt form. The latter is comparable to the neutral salt resulting from the reaction of sodium hydroxide and a strong mineral acid (25).

The choice of Dowex 2 among other strongly basic anion exchangers was based on the relative ease with which it could be regenerated. The resin is supplied in the chloride form in 20 to 50-mesh spherical

particles, light yellow in color, with a density of 1.15, and about 40 per cent moisture content. Before use, the resin was air dried and sifted through a 32-mesh screen. Only the fraction retained on the screen was employed in this investigation.

Recovery of Phosphorus from the Resin

The phosphorus adsorbed on the resin could not be completely recovered by leaching with reasonable amounts of salt solutions. A wet digestion method was developed to obtain 100 per cent recovery. This method was suitable for use only in cases where no soil was involved because of apparent adherence of minute quantities of soil to the resin. Phosphorus present in adherent soil would dissolve during digestion and contribute erroneously to the phosphorus adsorbed on the resin. Accordingly, a leaching procedure was adopted for the resin-soil experiments. Details of both procedures are given below.

Wet digestion procedure

The size of the resin samples was limited to 1 gm. to reduce the amount of reagent and time required to complete the digestion. The phosphorus-treated resin was transferred to a 250-ml. flat-bottom flask with spout. Sufficient sulfuric acid was added to wet the sample; 3 ml. was usually sufficient. The flask was covered with a watch glass, and set on an electric hot plate turned to medium heat.

A blank containing 1 gm. of untreated resin was started at this point. Heating on the hot plate was continued until the resin was charred and dense white fumes of sulfuric acid appeared. The flask was then removed from the hot plate, tilted, and 3 ml. of phosphorus-free* 30 per cent hydrogen peroxide was added. After the vigorous reaction had subsided, the flask was returned to the hot plate until the white fumes reappeared. The process of adding hydrogen peroxide and heating to white fumes was repeated three more times. When the white fumes of sulfuric acid appeared after the fourth addition of hydrogen peroxide, 0.5 ml. of perchloric acid was added, and the hot plate was set to high heat. The digestion was continued until the acid became colorless. The digestion usually took approximately 90 to 120 minutes. If the solution did not become colorless within this time, 2 to 3 ml. of hydrogen peroxide was added, and digestion was carried to the colorless stage. After digestion was completed, the flask was cooled, and the

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*Hydrogen peroxide was freed from phosphorus by immersing in the reagent bottle a sieve cloth sack containing 2 gm. of Dowex 2. The sack was tied by glass thread held against the mouth of the bottle by a rubber stopper with a hole in it to release excess gas pressure. After shaking the bottle on a wrist-action shaker for about 20 minutes, the sack was replaced by another one containing fresh resin. After repeating the procedure for three or four times, the reagent became practically free of phosphorus.

cover watch glass was rinsed. The solution was filtered through Whatman No. 30 filter paper; the filtrate was collected in an Erlenmeyer flask. Excess acid was neutralized with ammonium hydroxide (1 + 1) using 2-4 dinitrophenol as an indicator. An appropriate aliquot was taken for phosphorus determination.

Leaching procedure

The quantity of resin added to the soil was always fixed at 1 gm. After separating the resin from the soil by washing with water on a screen, the resin was transferred quantitatively to a 250-ml. Erlenmeyer flask. Twenty-five ml. of a 10 per cent sodium chloride solution was added and the flask was set on a steam plate for 45 minutes. Contents of the flask were transferred to Whatman No. 30 filter paper, and the filtrate was collected in a 100-ml. volumetric flask. Resin on the filter paper was leached with extra portions of 10 per cent sodium chloride solution until the volume of the filtrate totaled 100 ml. Appropriate aliquots of the filtrate were diluted with distilled water so that the final concentration of sodium chloride did not exceed 5 per cent. Phosphorus was determined in the diluted solution by the Dickman and Bray (13) procedure using standards that contained the same concentration of salt as the unknowns.

The above procedure gave about 98 per cent phosphorus recovery with the Dowex 2 (Batch No. 919) employed in the experimental work reported. Since all batches of the resin may not be identical, it was

found advisable to check the recovery with each batch. This was done by allowing 1 gm. of the resin to adsorb a known quantity of phosphorus. The procedure described above was then followed in extracting and determining the phorphorus adsorbed.

Phosphorus Determination

Phorphorus was determined by the colorimetric method of Dickman and Bray (13). An Evelyn photoelectric colorimeter employing a 660 m μ filter was utilized.

RESULTS AND DISCUSSION

Equilibration of Soil Phosphorus with P^{32}

As mentioned before, P^{32} added to soil in equilibrium with its solution will distribute itself between the phosphorus in solution and the solid phase with which it exchanges. The exchange reaction may be represented as follows:

$$P^{31}_{soil} + P^{32}_{solution} \rightleftharpoons P^{31}_{solution} + P^{32}_{soil} \qquad (1)$$

The equilibrium constant for this isotopic exchange reaction is very nearly 1. Hence

$$\frac{P^{31}_{soil}}{P^{31}_{solution}} = \frac{P^{32}_{soil}}{P^{32}_{solution}} \qquad (2)$$

The rate of reaction (1) was measured for two soils, Fargo clay and Waukegan silt loam. The procedure used was similar to that adopted by McAuliffe, et al. (26) for "surface" phosphorus determination. Duplicate 5-gm. soil samples were weighed into 250-ml. glass-stoppered Erlenmeyer flasks. Twenty-five ml. of distilled water was added, and the flasks were agitated on a wrist-action shaker for 3 to 4 days. Then 1-ml. aliquots of P^{32} solution were introduced, and the flasks were shaken for various lengths of time. The phosphorus concentration

of the P^{32} solution added was similar to that of the soil solution. At the end of each reaction period, samples of the solution were obtained by centrifuging the suspension twice with a high-speed centrifuge and filtering through Whatman No. 30 filter paper. Aliquots were taken from each solution for determining phosphorus content and specific activity. It was found necessary to determine the phosphorus concentration of each solution separately because of differences between samples. The amount of soil phosphorus that exchanged with P^{32} was calculated from equation (2), taking P^{32}_{soil} as the difference between P^{32} added and P^{32} remaining in solution.

Results are given in Table 1. It is apparent that equilibrium was not established after 24 hours' shaking. The rate of exchange, however, decreased with time. The results are in general agreement with those obtained by McAuliffe, et al. (26) and Wiklander (35) for isotopic exchange of phosphorus in soils.

Adsorption of Phosphorus by Exchange Resin

In removing phosphorus from soil by resin adsorption, it is desirable to attain a quantitative or proportional removal of the fraction subject to release from the soil. Only if results of this type are obtained can a suitable comparison of results be made between soils. To obtain information on these points, the equilibrium and kinetics of adsorption of phosphorus from solution by the anion exchange resin Dowex 2 were investigated.

Table 1. Soil phosphorus exchanged with P^{32} in solution during different intervals of time

Time, hours	Soil phosphorus exchanged, p.p.m.	
	Fargo clay	Waukegan silt loam
1/4	18.3	26.1
1/2	19.5	31.3
1	24.2	36.4
2	29.1	43.5
4	35.2	50.3
8	36.4	54.8
12	38.4	58.9
24	44.6	69.7

Adsorption from solutions

Before proceeding with any further work, the first problem was to determine whether or not the resin would adsorb phosphate from solutions having the low phosphate concentrations found in soils. Preliminary work showed that the resin removed small quantities of phosphorus almost quantitively from dilute solutions ranging in pH from 4 to 9. These results indicated that the resin was capable of adsorbing phosphate from solutions over the pH range of agricultural soils. Adsorption was reduced in solutions having pH values below 4. Additional experiments were then conducted to investigate (a) the equilibrium concentration of phosphorus as affected by the quantity adsorbed, (b) the rate of phosphorus adsorption as affected by phosphorus concentration, and (c) the process controlling the rate of phosphorus adsorption.

Equilibrium of exchange. The purpose of this experiment was to find the concentration of phosphorus in solution at equilibrium with resin containing different quantities of adsorbed phosphorus. Potassium dihydrogen phosphate solutions of 1, 5, 25, and 50 p.p.m. concentration with respect to phosphorus were prepared. One gram of resin and 200 ml. of each solution were introduced in 500-ml. Erlenmeyer flasks. Thus, the solutions in contact with the resin contained 0.2, 1, 5, and 10 mgm. of phosphorus. The flasks were stoppered and shaken on a wrist-action shaker overnight. Preliminary experiments had shown that almost 99 per cent of the phosphorus was adsorbed within 30 minutes. In this experiment, however, a longer time was allowed to

ensure complete equilibrium. At the end of the reaction period, the solution was decanted from the resin. An aliquot portion was analyzed for phosphorus. The difference between the quantities of phosphorus present in solution initially and at equilibrium was taken as the quantity of phosphorus adsorbed on the resin.

Results obtained are given in Table 2. Column 4 shows the percentage of added phosphorus adsorbed on the resin at equilibrium. Within experimental error, removal of phosphorus from solution was complete at the two lower initial concentrations but not at the higher concentrations. This behavior suggests that the mass-action law constant varies with the phosphorus adsorbed on the resin. The equilibrium of the exchange adsorption of phosphorus by the resin chloride may be described by

$$R^+Cl^- + H_2PO_4^- \text{ solution} \rightleftharpoons R^+H_2PO_4^- + Cl^- \text{ solution} \qquad (3)$$

where R^+ is the large cationic immobile body of the resin and $H_2PO_4^-$ and Cl^- are the highly dissociated anions. The mass-action equilibrium constant is given by

$$K = \frac{[\overline{H}_2PO_4^- \text{ resin}]\,[\overline{Cl}^- \text{ solution}]}{[\overline{Cl}^- \text{ resin}]\,[\overline{H}_2PO_4^- \text{ solution}]} \qquad (4)$$

where the brackets represent equilibrium concentrations of ions in the solution or resin phase. With small additions of phosphorus, $[\overline{H}_2PO_4^- \text{ resin}]$ is small and $[\overline{H}_2PO_4^- \text{ solution}]$ approaches zero, thus leading to high

Table 2. Phosphorus adsorbed by Dowex 2 from solutions containing different quantities of phosphorus

P in 200 ml. of original solution, mgm.	P in solution at equilibrium, mgm.	P adsorbed on resin, mgm.	Percentage of added P adsorbed on resin
0.20	0.00	0.20	100
1.00	0.00	1.00	100
5.00	0.13	4.87	97.4
10.00	2.02	7.98	79.8

values for K. With large additions of phosphorus, $[H_2PO_4^-$ resin$]$ and $[H_2PO_4^-$ solution$]$ get larger, with smaller values for K as a result. Ekedahl, et al. (16) obtained analogous results with the exchange of silver ions in solution with hydrogen ions on a cation exchanger. They found K to vary from values around 30, where there was little silver adsorbed on the resin, to around 3, where the resin was nearly saturated with silver.

The effect of initial concentration on the equilibrium concentration at constant phosphorus addition was studied also. The resin was equilibrated with different volumes of solutions varying in concentration so that the total addition of phosphorus was kept at 5 mgm. The initial concentrations were 5, 25, 50 and 100 p.p.m. with respect to phosphorus, and the volumes used were 1000, 200, 100 and 50 ml., respectively. The results in Table 3 show that essentially the same equilibrium concentration was attained regardless of initial phosphorus concentration in solution. Similar results were obtained by Kressman and Kitchener (23) for univalent cations on a synthetic phenolsulphonate resin.

The presence of neutral salt in the form of sodium chloride was found to decrease phosphorus adsorption by the resin. One gram samples of resin were shaken overnight with 200 ml. of phosphate solutions containing 200 γ of phosphorus and having a concentration of 0, 100, 1000, and 5000 p.p.m. with respect to chloride. Phosphorus left in solution was 0, 2, 70, 176 γ respectively. Thus, an almost quantitative

Table 3. Phosphorus adsorbed by Dowex 2 from solutions containing 5 mgm. of phosphorus at different concentrations

P in original solution, p.p.m.	P in solution at equilibrium, mgm.	P adsorbed on resin, mgm.	Percentage of added P adsorbed on resin
5	0.07	4.93	98.6
25	0.13	4.87	97.4
50	0.14	4.86	97.2
100	0.14	4.86	97.2

removal of phosphorus from solutions was obtained in the presence of 100 p.p.m. of Cl^- or less. This concentration is approximately equivalent to 165 p.p.m. of sodium chloride. Salt content of cultivated soils is usually less than 3000 p.p.m. (1). Accordingly, if the soil is diluted 100 times with water, the salt concentration of the suspension will almost invariably be low enough to allow a quantitative adsorption of phosphorus released from the soil.

The foregoing results indicate the possibility of essentially complete removal of phosphorus released from soil where the quantities of phosphorus involved are small and salt concentration is low.

Rate of exchange. Preliminary work showed that there is rapid adsorption of phosphorus on Dowex 2. This experiment was undertaken to study the effect of phosphorus concentration upon the rate of exchange.

The apparatus used for rate determination permitted a rapid separation of the resin from the solution. An electrically-driven glass stirrer was employed which had two legs at its free end. The legs were 2.5 cm. long, and were separated by a 60° angle. A sieve cloth sack* was fitted over both legs of the stirrer, and was tied to the stem with a nylon drawstring. The resin was placed in the sack. As the stirrer rotated, the solution passed rapidly over the resin, which was forced to the corners of the sack. The reaction was

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*The sack was made of sieve cloth (#S-74615 Sargent and Company) having 82 meshes per linear inch. Dimensions were 4 x 7 cm. Before use, the sack and nylon drawstring were shaken several times with 10 per cent sodium sulfate solution to free them from contaminating phosphorus.

started by lowering the rotating stirrer into the solution. It was stopped after the appropriate interval of time by raising it, still rotating, out of the solution. An aliquot portion of the solution was then analyzed for phosphorus.

The weight of resin taken in every run was 1 gm., 100, 500, and 1000 γ of phosphorus were present in the aqueous phase in the form of 1000 ml. of 0.1, 0.5, and 1 p.p.m. solutions. To each solution 1 gm. of chloride was added in the form of sodium chloride. This concentration of salt considerably reduced the rate of adsorption of phosphorus. Without the salt, the phosphorus concentration changed too rapidly for the purpose of the present experiment. The reproducibility of the rate measurements was checked and found to be good. The quantities of phosphorus removed from solution were the same when the resin was agitated freely in the solution as when it was contained in the sack.

Results in Table 4 show that the rate of phosphorus adsorption increased with concentration. There was little change in percentage of added phosphorus adsorbed with concentration. At equilibrium, which was reached within 120 minutes agitation, there seemed to be a slight decrease in percentage of added phosphorus adsorbed with increase in concentration.

The above experiment indicates that, at any particular time, the percentage of the phosphorus removed by the resin should vary relatively little with the quantity of phosphorus released from soil. This behavior would permit the use of the resin for comparing different soils with

Table 4. Rate of phosphorus adsorption by Dowex 2 at different phosphorus concentrations in the presence of excess chloride

Time, minutes	P adsorbed from solution having indicated initial concentration					
	0.1 p.p.m. P		0.5 p.p.m. P		1.0 p.p.m. P	
	P adsorbed,	Percentage of added P adsorbed	P adsorbed,	Percentage of added P adsorbed	P adsorbed,	Percentage of added P adsorbed
5	13	13	62	12	153	15
10	17	17	87	17	173	17
20	22	22	106	21	197	20
120	25	25	113	23	213	21

respect to their phosphorus release.

Kinetics of exchange. According to Boyd, et al. (4), the rate of exchange between an ion in solution and another ion adsorbed on the resin may depend on one or more of a series of consecutive steps. For reaction (3), which describes the exchange of phosphate in solution with chloride on the resin, the steps are (1) diffusion of $H_2PO_4^-$ through the solution up to the resin particles, (2) diffusion of $H_2PO_4^-$ through the resin, (3) chemical exchange between $H_2PO_4^-$ and R^+ at the exchanging positions in the interior of the particles, (4) diffusion of Cl^- out of the interior of the exchanger (reverse of Step 2), and (5) diffusion of the displaced Cl^- through the solution away from the adsorbent particles (reverse of Step 1). It is evident, therefore, that the rate of exchange will be governed either by diffusion or by the actual exchange process. The diffusion processes involved may be either inside or outside the resin particles. If the rate of reaction is slow enough, vigorous agitation may maintain the same concentration of solute at the resin-solution interface as in the body of the solution. Dependence of adsorption rate on external diffusion processes will thereby be eliminated. On the other hand, if the rates of actual exchange and internal diffusion are fast enough, a concentration gradient may remain in the external solution despite vigorous agitation.

Whether diffusion in the film of solution surrounding the resin particles or internal diffusion limits the rate of reaction can be

tested by appropriate techniques. Boyd, et al. (4) found that the rate of exchange adsorption on the basis of a boundary-film diffusion mechanism is described by the equation,

$$- \log \left(1 - \frac{Q_t}{Q_\infty}\right) = kt \qquad (5)$$

where in terms of equation (3) Q_t is the $H_2PO_4^-$ exchanged after time t, Q_∞ is the $H_2PO_4^-$ exchanged when equilibrium has been reached, and k is a constant. It is evident that a plot of $- \log \left(1 - \frac{Q_t}{Q_\infty}\right)$ against t will give a straight line if boundary-film diffusion controls the adsorption rate. On the other hand, if diffusion in the resin particles is rate-determining, the equation is

$$\frac{Q_t}{Q_\infty} = ct^{\frac{1}{2}}$$

where Q_t, Q_∞ , t are the same as above and c is another constant. A plot of $\frac{Q_t}{Q_\infty}$ against $t^{\frac{1}{2}}$ will give a straight line if internal diffusion is rate determining.

The primary factors that may decide which mechanism applies in a given system are (1) particle size, (2) the equilibrium distribution coefficient, (3) temperature and (4) concentration. As an example of concentration effects, Boyd, et al. (4) found that $Na^+ - K^+$ exchange was limited by diffusion in the boundary liquid film in a 0.001 M solution and by diffusion in the adsorbent in a 0.1 M solution.

In the present work, the nature of the process governing the rate of exchange adsorption of phosphorus from dilute solutions in

contact with Dowex 2 was of concern. The apparatus used was the same as that employed in the previous rate experiment. Twelve liters of 1 p.p.m. phosphorus solution was placed in a glazed earthenware jar. The solution was adjusted with HCl to approximately pH 2.8 to reduce the rate of adsorption. For each run, a 1 gm. sample of resin was placed in the sieve cloth sack, and the sack was tied to the stirrer and rotated in the solution for the desired interval of time. At the end of each time interval the stirrer was raised, and the sack and resin was washed quickly with a stream of distilled water. The resin was air dried and analyzed for phosphorus by the wet digestion procedure. Although the same phosphorus solution was used for all runs, the concentration was not materially changed. The initial concentration was 1 p.p.m., and the final concentration was 0.96 p.p.m.

Table 5 shows the results. In calculating Q_t/Q_∞, the phosphorus adsorbed after 120 minutes was taken as Q_∞. This length of time was ample for establishment of equilibrium. As shown in Figure 1, a straight line was obtained when $-\log(1 - Q_t/Q_\infty)$ was plotted against t. A curve was obtained when Q_t/Q_∞ was plotted against $t^{1/2}$. This agreement with equation (5) indicates that the rate of the exchange adsorption of phosphorus by Dowex 2 from dilute solutions is not determined by diffusion in the resin particle, but by diffusional transport across a thin liquid film enveloping the resin particles.

Thus on mixing the soil with resin and agitating, the phosphorus released from the soil will be transported to the film surrounding the resin particles. As soil solutions are normally low in phosphorus

Table 5. Exchange adsorption of phosphorus on Dowex 2 as a function of time

Time, minutes	P adsorbed on resin, γ (Q_t)	Q_t/Q_∞	$-\log\left[1 - \frac{Q_t}{Q_\infty}\right]$
1	35.33	0.468	0.223
2	44.52	0.592	0.389
3	54.82	0.729	0.567
4	61.70	0.820	0.745
5	65.61	0.872	0.893
6	68.74	0.914	1.065
7	71.17	0.946	1.297
10	74.41	0.989	1.959
120	75.24*		

*Q_∞

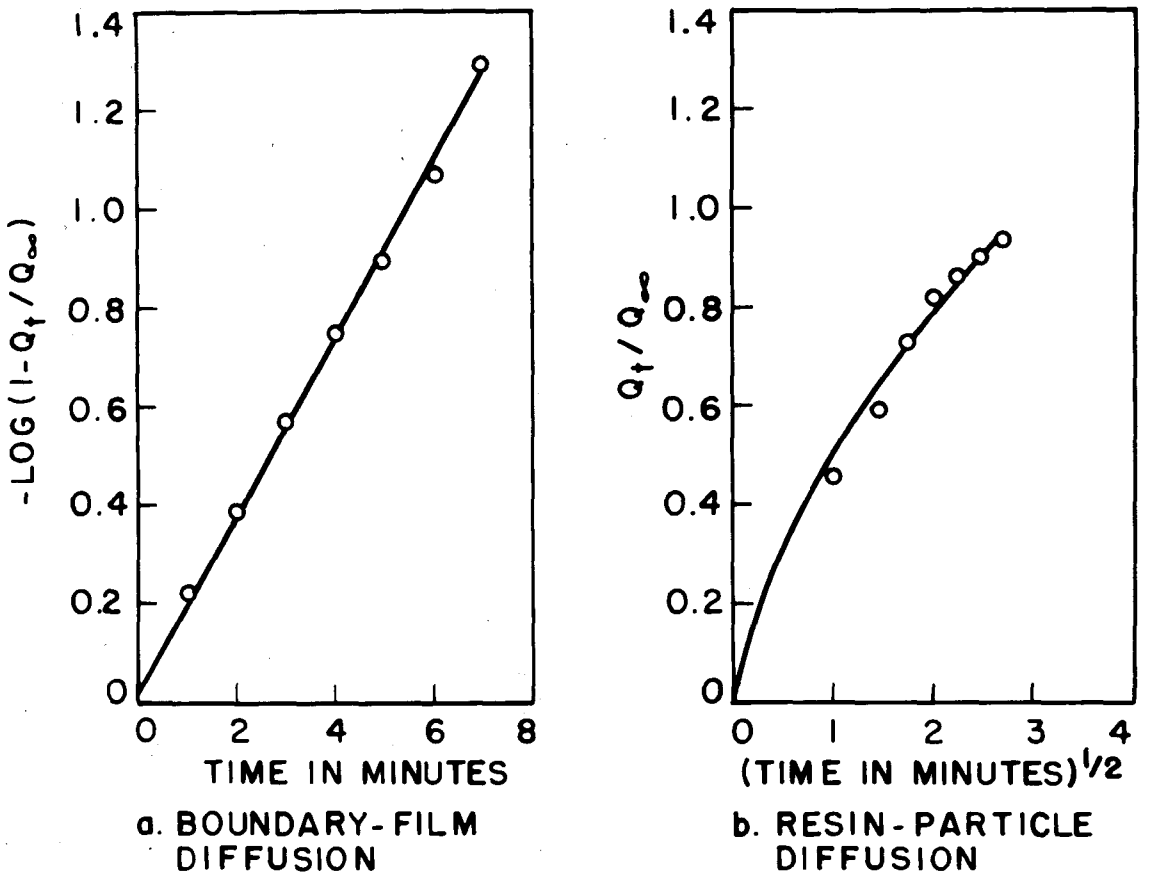

Fig. 1. Tests for rate-controlling process in adsorption of phosphorus from dilute solutions by Dowex 2

concentrations, the rate of phosphorus removal by the resin is expected to be film controlled. Accordingly, the rate at which phosphate ions are adsorbed by the resin in an agitated resin-soil suspension depends on the rate at which phosphate ions enter the surface film. This is the desired behavior from the standpoint of adsorption of phosphate from soils.

Adsorption from soils

The study of phosphorus adsorption from solutions by the resin Dowex 2 indicated the suitability of the latter for removing phosphorus from soils. Judging from the behavior found with solutions, the small quantities of phosphorus released from soil could be removed almost quantitatively over a pH range covering that encountered in agricultural soils. Even if complete removal were not attained, a certain percentage would be removed. This would still permit comparing different soils with respect to their phosphorus release. Further, the rate of phosphorus removal by the resin was found to be controlled by the supply of phosphorus at the surface of the resin particles, and not by a resin characteristic such as internal diffusion. Thus, if a sufficient number of resin particles is present, the rate of phosphorus removal by the resin in an agitated aqueous suspension of soil and resin should be a measure of the rate of phosphorus release from soil.

To determine the experimental conditions necessary to make the rate of phosphorus adsorption by the resin a function of the rate

of release of phosphate from the soil, the following points were investigated: (a) the quantity of resin required to obtain the maximum adsorption rate in the presence of unit quantity of soil; (b) the effect of method of shaking on the adsorption rate.

To permit a convenient separation of resin and soil, the resin used consisted of particles retained on a 32-mesh screen, and the soil was ground to pass a 100-mesh screen. The general procedure was to introduce the appropriate quantities of soil and resin into a 250-ml Erlenmeyer flask, and to start the reaction by adding 100 ml. of distilled water and shaking instantly. At the end of the reaction period, the flasks were taken off the shaker. The resin was separated from soil by pouring the suspension through 82-mesh sieve cloth (No. 8-74615, Sargent and Company) and washing with distilled water to remove the remaining soil. The apparatus for separation was made by sealing a circular piece of sieve cloth to a rubber gasket in a Buchner funnel with paraffin wax. The soil was discarded, and the separated resin was air dried and leached with sodium chloride solution for phosphorus recovery. Correction was made for the percentage recovery by the leaching procedure.

Ratio of resin to soil. To find the appropriate ratio, one-gram samples of resin were shaken with 1/2, 1, 2, 3 and 5-gram samples of soil in the presence of 100 ml. distilled water for 2 hours on a wrist-action shaker at medium speed. The technique followed otherwise was the same as that mentioned above. Two soils were used, Langdon

loam and Fargo clay.

Results in Table 6 show that the phosphorus removed increased with the ratio of resin to soil. However, there seems to be no difference in the quantity of phosphorus removed when the ratio was 1 or 2. It was concluded therefore, that a ratio of 1 gm. of resin to 1 gm. of soil would bring about the maximum possible removal of phosphorus released from soil. This ratio was adopted in all succeeding experiments.

Method of shaking. Three methods of shaking were tested: wrist-action shaking at medium speed, wrist-action shaking at high speed, and end-over-end shaking. Four different soils were shaken with the resin for 1 hour. Results in Table 7 indicate that no consistent difference is introduced by using different shaking methods. In subsequent work, wrist-action shaking at medium speed was generally used.

Rate of phosphorus removal. The rate of removal of phosphorus released from soil by the resin was measured for four soils having different levels of phosphate fertility. One-gm. soil samples were added to 1 gm. samples of resin. Reaction was initiated by addition of 100 ml. of distilled water and shaking on a wrist-action shaker at medium speed. After various elapsed times of shaking, the resin was separated from soil and analyzed for phosphorus by the leaching procedure.

Results obtained are shown in Table 8 and Figure 2. It can be seen that all four soils are characterized by a continuous decrease in

Table 6. Phosphorus adsorbed from soils by Dowex 2 at different ratios of resin to soil

Ratio of resin to soil	Soil phosphorus adsorbed by resin, p.p.m. of soil	
	Langdon loam	Fargo clay
0.2	10.4	20.8
0.33	10.6	22.6
0.5	10.9	23.6
1.0	14.1	28.3
2.0	13.8	28.6

Table 7. Phosphorus adsorbed from soils by Dowex 2 with different methods of shaking

Soil	Soil phosphorus adsorbed by resin, p.p.m. of soil		
	Wrist-action, medium speed	Wrist-action high speed	End over end
"Marshall-like" silt loam	7.4	4.9	5.4
Langdon loam	12.8	11.6	11.6
Fargo clay	23.6	24.2	24.7
Waukegan silt loam	38.7	38.7	40.5

Table 8. Phosphorus adsorbed from soils by Dowex 2 as a function of time

Time, hours	Soil phosphorus adsorbed by resin, p.p.m. of soil			
	"Marshall-like" silt loam	Langdon loam	Fargo clay	Waukegan silt loam
1/4	5.0	7.9	14.0	25.0
1/2	6.2	9.9	18.4	31.0
1	7.4	12.8	23.6	38.7
2	8.6	14.1	28.3	46.5
4	9.2	14.9	30.5	52.8
8	9.6	16.6	36.6	59.2
12	9.3	17.1	38.4	63.3
24	9.9	19.6	43.6	73.6
72	11.5	22.8	50.7	90.7

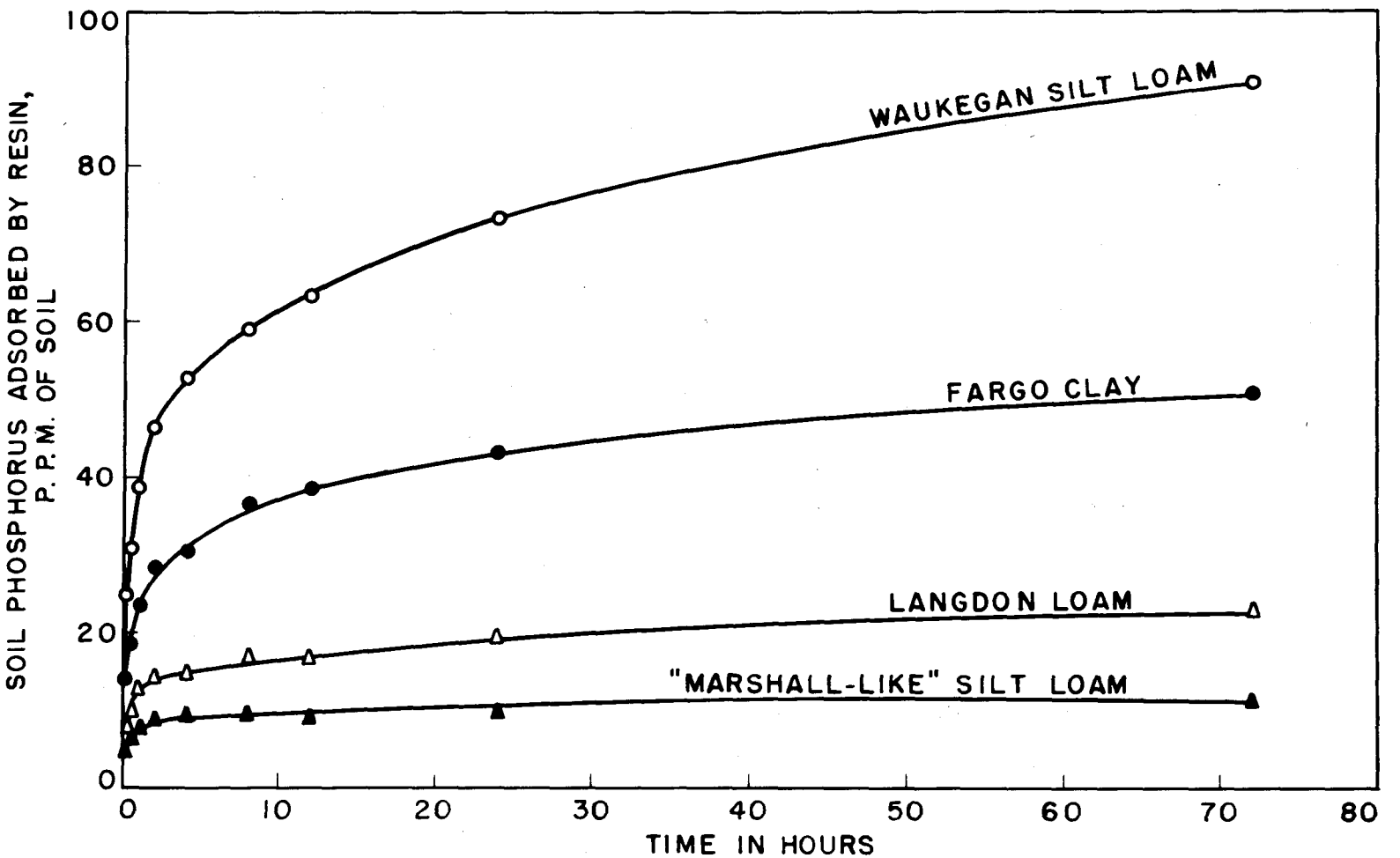

Fig. 2. Phosphorus adsorbed from soils by Dowex 2

the rate of phosphorus release. The part of the soil phosphorus that is easily released seems to have been removed by the resin within 2 hours. On the other hand, the slow release apparently extended beyond 72 hours.

Recovery of phosphorus added. Recovery of added phosphorus was checked with two soils, Langdon loam and Fargo clay. One-gm. samples of soil were shaken for 2 hours or 24 hours with 100 ml. of solutions containing 10 or 200 γ of phosphorus. One-gm. samples of resin were then added to the soil suspensions, and shaking was continued for 2 hours or 24 hours.

Results in Table 9 show the nonrecovered phosphorus for each treatment. This was calculated according to the following equation:

nonrecovered phosphorus = (phosphorus added in solution + phosphorus removed from the untreated soil) - phosphorus removed from the treated soil.

Values of phosphorus removed from the untreated soils were taken from Table 8.

The data show that with a given addition of phosphorus, the quantity of nonrecovered phosphorus was consistently lower with the 24-hour than with the 2-hour period of adsorption by the resin. With a given time of adsorption by the resin, the quantity of nonrecovered phosphorus usually increased with increasing rate of addition. Most of the added phosphorus was held in the easily-released form. Phosphorus retained in the slowly-released form seemed to be a function of both phosphorus added and time

Table 9. Recovery of added phosphorus from soil by resin adsorption

Length of resin adsorption period, hours	Added P not recovered by resin adsorption,			
	P added = 10 γ		P added = 200 γ	
	Reaction period = 2 hours	Reaction period = 24 hours	Reaction period = 2 hours	Reaction period = 24 hours
		- Langdon loam -		
2	2.7	2.2	11.8	19
24	1.5	1.3	5.4	3.5
		- Fargo clay -		
2	4.1	4.1	9.5	17.8
24	2.8	0.5	2.8	4.0

elapsed between the addition and extraction.

Comparison of P^{32} Equilibration and Resin Adsorption

In preceding sections, data were given on soil phosphorus exchanging with P^{32} or removed by resin adsorption at different time intervals for Fargo clay and Waukegan silt loam. These data, together with water-soluble phosphorus, are shown in Table 10. It will be noted that the numerical values for solid phase exchangeable phosphorus and phosphorus adsorbed on the resin are nearly the same, and that the values for solid phase plus water-soluble phosphorus exceed those for phosphorus adsorbed on the resin.

The close agreement between solid phase exchangeable phosphorus and phosphorus adsorbed on the resin is to some extent fortuitous, as becomes evident from a consideration of the processes involved with the respective procedures. Soil phosphorus exchangeable with P^{32} was calculated by multiplying the ratio of P^{32} in the soil solid phase to that in solution by the P^{31} in solution. Thus, the results represented solid-phase exchangeable phosphorus only, and did not include phosphorus in solution. In the resin adsorption procedure, however, the phosphorus in solution and that initially in the solid phase were removed together, with no distinction between the two forms. Another possible source of difference between the rate curves lies in the fact that the results obtained with the P^{32} equilibration procedure may vary somewhat with the length of time of equilibrating soil and

Table 10. Comparisons of values obtained by P^{32} equilibration and resin adsorption

	Soil phosphorus, p.p.m. of soil							
	Fargo clay				Waukegan silt loam			
	P^{32} equilibration			Resin	P^{32} equilibration			Resin
Time, hours	Solid phase	Water-soluble	Sum	adsorption	Solid phase	Water-soluble	Sum	adsorption
1/4	18.3	2.0	20.3	14.0	26.1	9.1	35.2	25.0
1/2	19.5	1.1	20.6	18.4	31.3	7.4	38.7	31.0
1	24.2	2.0	26.2	23.6	36.4	9.5	45.9	38.7
2	29.1	2.4	31.5	28.3	43.5	9.5	53.0	46.5
4	35.2	2.4	37.6	30.5	50.3	9.6	59.9	52.8
8	36.4	1.8	38.2	36.6	54.8	8.8	63.6	59.2
12	38.4	1.9	40.3	38.4	58.9	8.8	67.7	63.3
24	44.6	1.9	46.5	43.6	69.7	8.7	78.4	73.6

solution before the addition of P^{32}. The cause of this behavior has not been determined.

Another cause of difference between the rate curves lies in the time scale. With both P^{32} equilibration and resin extraction, the time of reaction was taken as that of shaking. In the P^{32} equilibration procedure, the effective time was somewhat longer than that stated because of the time required for centrifugation. Some exchange undoubtedly occurred during centrifugation, which would lead to high results. This source of error would have the greatest effect on the results obtained during the shorter time intervals. In the resin procedure, it was possible to separate the resin from soil almost instantly after shaking. In this procedure, however, there is some time lag between release of phosphorus from soil and its adsorption by the resin. At any given time, therefore, the phosphorus released from the soil is somewhat in excess of that adsorbed by the resin. Existence of such a time lag was verified by determining the phosphorus remaining in solution when 1 gm. of soil and 1 gm. of resin were shaken with 100 ml. of water for 2 hours and then removed by centrifuging. The phosphorus remaining in solution was on the order of 1 to 2 γ in the case of Langdon loam, Fargo clay, and Waukegan silt loam.

Finally, the quantity of water-soluble phosphorus in equilibrium with soil increases with the quantity of solution present. It is probable that the increase in water-soluble phosphorus is mainly at the expense of solid-phase exchangeable phosphorus. The sum of solid phase and water-soluble phosphorus is probably relatively constant

with change in ratio of solution to soil. It is this value with which the resin adsorption data are more properly compared.

It is evident from the data in Table 10 that the soil phosphorus found by resin adsorption is not identical with the sum of the solid phase and water-soluble phosphorus for the corresponding time interval. On the other hand, the agreement is remarkably good in comparison with the wide differences in absolute values obtained by conventional tests for soil phosphorus availability. Values obtained by both P^{32} and resin measurements involve phosphate exchange. The exchanging ion is tagged orthophosphate in the former case, and hydroxyl or some other ion in the latter. It appears that with both methods the values obtained depend primarily on a combination of two fundamental properties of the soil phosphorus, namely, the extent of the dissociation of orthophosphate groups from the soil and the accessibility of the various phosphate groups to the solution.

Resin-Adsorbed Phosphorus and "A" Values

The ultimate objective of the resin-adsorption technique described in the foregoing pages is the estimation of availability of soil phosphorus to plants. The present section reports the results of a preliminary investigation of this problem.

As shown in Table 8 and Figure 2, the value obtained for resin-adsorbed phosphorus increases with time, rapidly at first and then more slowly, indicating the existence of a complex reaction. When the

same data are plotted on a log-log scale (Fig. 3), the rate curve for each soil becomes two straight lines. This behavior suggests the existence of two distinctive reactions differing in rate.

By means of the method of least squares, empirical equations were calculated for the two linear segments of the log-log curve. The two equations for each soil were solved simultaneously for the time at which the change occurred from one reaction to the other. This procedure affords one means of selecting a particular time interval in preference to another. The time at which the lines intersected was found to range from 56 to 90 minutes (Table 11).

To test the resin-adsorbed phosphorus as a measure of phosphorus fertility, 16 different soils were extracted for 2 hours by the resin. The values for phosphorus adsorbed in 2 hours gave a correlation of 0.94 with "A" values (20) in comparison with a correlation of 0.87 between the Bray test (6) and "A" values (Table 12, Figures 4 and 5). The high correlation between resin-adsorbed phosphorus and "A" values suggests that the phosphorus measured by this technique provides a good estimate of availability of soil phosphorus to plants.

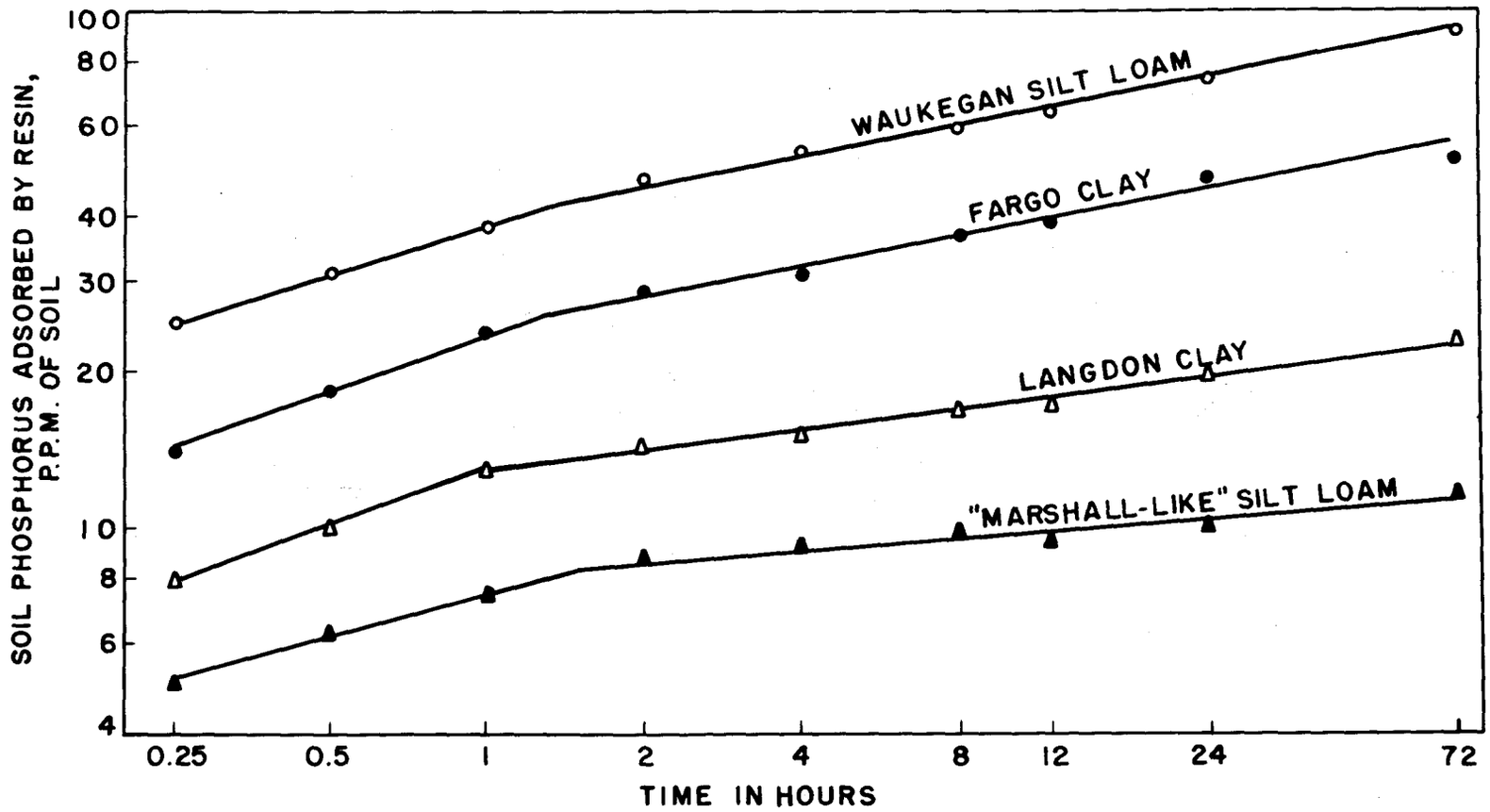

Fig. 3. Soil phosphorus adsorbed by resin vs. time, log-log scale

Table 11. Equation expressing resin-adsorbed phosphorus as a function of time, and estimated duration of the rapid reaction

Soil	Equation expressing		Length of rapid reaction, minutes
	Rapid reaction	Slow reaction	
"Marshall-like" silt loam	$y^* = 7.45\ t^{0.283}$	$y = 8.12\ t^{0.075}$	90
Langdon loam	$y = 12.74\ t^{0.348}$	$y = 12.49\ t^{0.138}$	56
Fargo clay	$y = 23.90\ t^{0.377}$	$y = 25.06\ t^{0.169}$	76
Waukegan silt loam	$y = 38.67\ t^{0.315}$	$y = 40.58\ t^{0.186}$	88

*y = phosphorus adsorbed on the resin at time t.

Table 12. Resin-adsorbed phosphorus, "A" values and other data (10) for 16 soils

Soil type	U.S.D.A. No.	State	pH	Per cent* yield	Bray** phosphorus, lb. P_2O_5/A	"A" value‡** lb. P_2O_5/A	Soil P adsorbed by resin in 2 hours p.p.m.
Edgeley silt loam	51631	N.D.	5.6		28	162	15.3
Fargo clay	51629	"	5.9		62	237	28.3
Langdon loam	51630	"	6.5	69.8	18	97	14.1
Cheyenne fine sandy loam	51568	"	6.4	70.8	9.2	125	5.9
Barnes silt loam	51619	Minn	6.2	75.4	46	197	17.1
Fargo silty clay loam	51617	"	7.5	29.9	23	113	10.3
Waukegan silt loam	51616	"	5.5		112	676	46.5
"Marshall-like" silt loam	51618	"	6.6	19.7	9.2	91	8.6
Barnes loam	51626	S.D.	6.2		44	267	26.0

* Per cent yield = $\frac{\text{Yield without phosphate fertilizer}}{\text{Yield with adequate phosphate fertilizer}} \times 100$.

** 0.03 N NH_4F - 0.025 N Hcl extractant.

*** Average value of 40, 80, 160 P_2O_5 applications.

Table 12 (continued)

Soil type	U.S.D.A. No.	State	pH	Per cent yield	Bray phosphorus, lb. P_2O_5/A	"A" value, lb. P_2O_5/A	Soil P adsorbed by resin in 2 hours p.p.m.
Hastings silt loam	51587	Nebr.	5.3	86.5	53	173	12.8
Carrington clay loam	51588	"	6.0	7.9	4.6	57	3.8
Holdrege silt loam	51570	"	6.0		69	241	22.7
Miami loam	51628	Mich.	6.4	12.2	8	94	8.6
Muscatine silt loam	51622	Ill.	4.9	27.1	13	78	5.3
Elliott silt loam	51623	"	4.7	29.4	10	61	4.7
Munjor silty clay loam	51585	Kans.	5.9	84.9	101	285	28.9

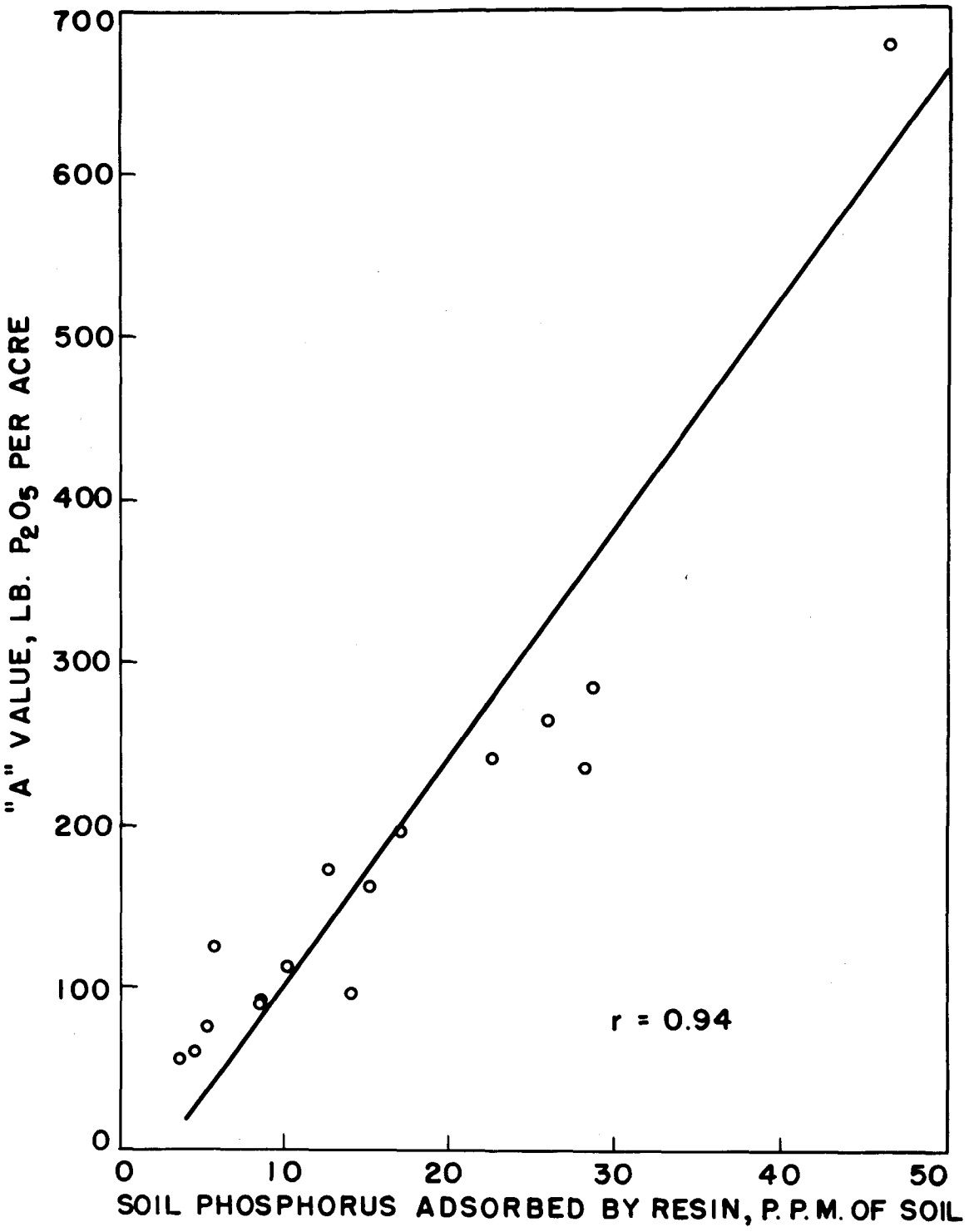

Fig. 4. "A" values vs. soil phosphorus adsorbed by resin in 2 hours

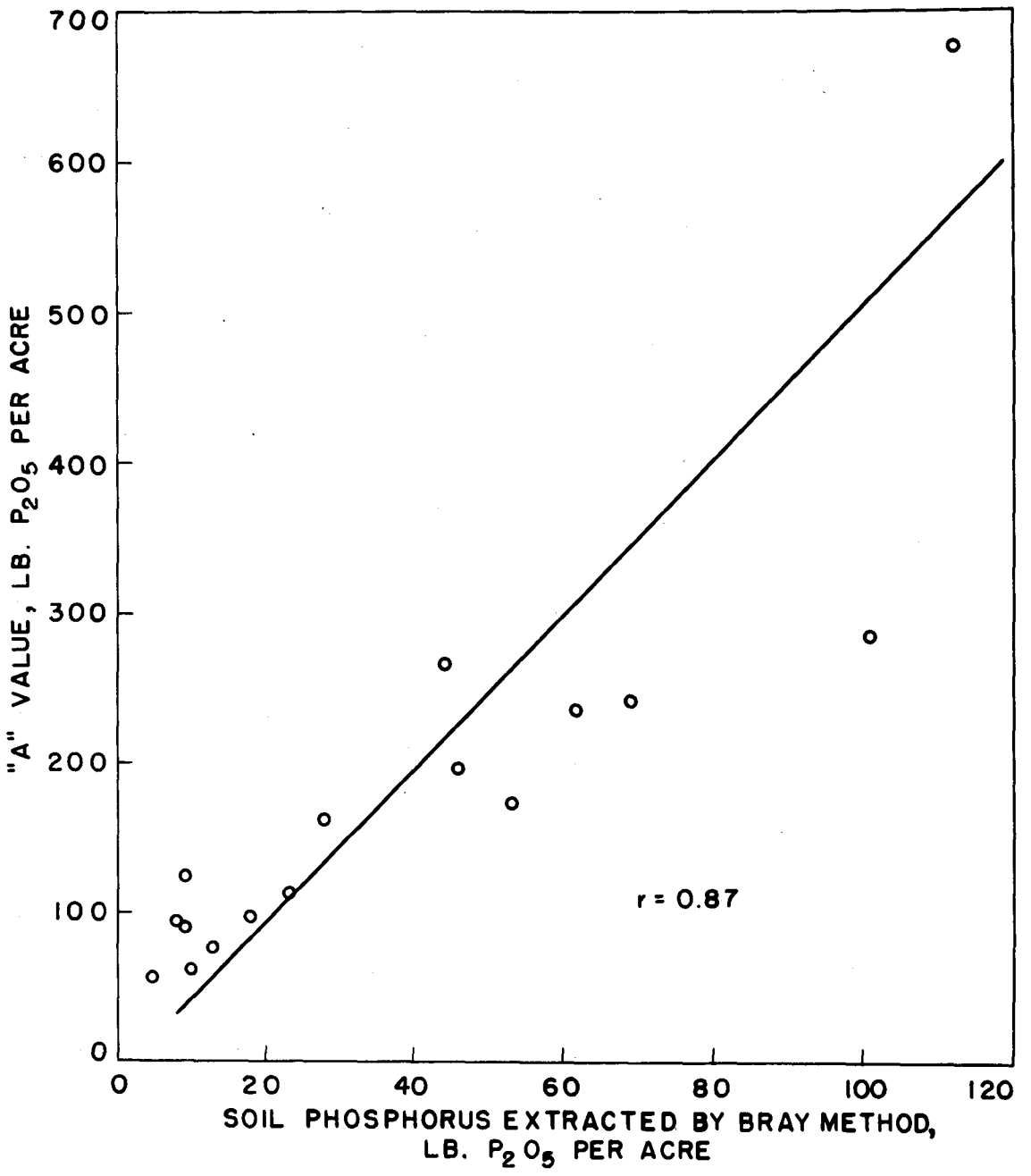

Fig. 5. "A" values vs. soil phosphorus extracted by Bray method

SUMMARY AND CONCLUSIONS

The ultimate objective of this investigation was to develop a method for estimating the availability of soil inorganic phosphorus to plants through the use of an anion exchange resin. An investigation of phosphorus adsorption from solutions by the resin Dowex 2 showed that small quantities of phosphorus were adsorbed almost quantitatively over a pH range covering that encountered in agricultural soils. Where complete removal was not attained a percentage of the added phosphorus was removed. Further, the rate of phosphorus removal by the resin was found to be controlled by the concentration of phosphorus at surface of the resin particles, and not by a resin characteristic such as internal diffusion. These results indicate that with a sufficient number of resin particles in an agitated aqueous suspension of soil and resin, the rate of phosphorus removed by the resin should be a measure of the rate of phosphorus release from soil.

In experiments with soil, the rate of phosphorus adsorption by the resin was measured by determining the phosphate content of the resin after wet sieving to eliminate the soil. It was found that phosphorus removal by resin adsorption increased with the ratio of resin to soil up to a value of 1 to 1 by weight. A further increase to a ratio of 2:1 resulted in no further increase in phosphorus

removal. Thus, beyond a ratio of 1 part of resin to 1 part of soil, the rate of phosphorus removal from the soil was presumably independent of the ratio and instead was a function of the rate of release from the soil.

Phosphorus removed from soil by the resin increased with time, rapidly at first and then more slowly. A similar behavior was obtained by measuring the rate of exchange between soil phosphorus and P^{32}. The quantities of soil phosphorus adsorbed by the resin during a given time were below the quantities equilibrated with P^{32} during the same interval of time. The numerical values are nevertheless remarkably similar in comparison with the wide differences in absolute values commonly obtained by conventional tests for soil phosphorus availability. It appears that the similarity in numerical value obtained by the two processes results from their similarity in action and their independence of the accessory characteristics of soils. Both methods involve exchange of soil phosphate and some other anion. It is presumed that with each method the rate of exchange in a function of degree of dissociation of the phosphate and accessibility to the solution.

When the data for the amount of soil phosphorus adsorbed by the resin after different intervals of time were plotted on a log-log scale, the rate curve for each soil became two straight lines. This behavior suggests the existence of two distinct reactions differing

in rate. The time at which the lines intersected was found to range from 56 to 90 minutes.

The values of resin-adsorbed phosphorus for estimating availability of soil inorganic phosphorus was investigated using a group of 16 soils. One gm. of Dowex 2 resin of > 32-mesh size was shaken 2 hours with 1 gm. of < 100-mesh soil and 100 ml. of water. The resin was then separated from the soil by pouring the suspension through 82-mesh sieve cloth. To extract the adsorbed phosphorus, the separated resin was leached with 10 per cent sodium chloride solution.

The values for phosphorus adsorbed in 2 hours gave a correlation of 0.94 with Fried and Dean "A" values obtained in a greenhouse experiment. The correlation between the Bray test and "A" values was 0.87. The high correlation between resin-adsorbed phosphorus and "A" values suggests that the phosphorus measured by this technique provides a good estimate of the availability of soil phosphorus to plants.

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