

THESIS

**FIXATION OF PHOSPHORUS IN COLORADO SOILS AND ITS
RELATION TO PHOSPHATE AVAILABILITY TO PLANTS**

Submitted by

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In partial fulfillment of the requirements

for the Degree of Master of Science

Colorado State College

of Agriculture and Mechanic Arts

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***FIXATION OF PHOSPHORUS IN COLORADO SOILS AND ITS
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Introduction

Chemical Properties of Phosphorus.--Phosphorus is one of the most active elements and exists in nature in a large number of chemical combinations. Under suitable conditions it may have a valence range from a negative 3, as in phosphine gas (PH_3), to a positive valence of 5, as in phosphoric anhydrid (P_2O_5). However, it is so readily oxidised that in soils or other systems where there is an abundance of oxygen or other oxidising materials it usually has the highest positive valence. In an aqueous solution, P_2O_5 takes up three molecules of water to form ortho-phosphoric acid (H_3PO_4) in which phosphorus is a constituent of the acid radicle. Ortho-phosphoric acid, being comparatively strong, reacts readily with basic material to form phosphates. Since, in any normal soil, bases constitute a considerable portion of the soil material, phosphorus is normally found with some base replacing one or more of the hydrogen atoms, the degree of replacement depending upon the bases present and the reaction of the solution.

Phosphorus Compounds in Soil.--The predominating bases found in soils are Ca, Mg, Al, Fe, K, Na, NH_4 , and Ti. The phos-

*The term "fixation" as used in this paper includes precipitation, adsorption or any other process which changes the phosphorus in readily soluble compounds to a condition more resistant to leaching by water passing through the soil.

phates of NH_4 , K, and Na are relatively soluble. Mn and Ti tend to form slightly soluble phosphates, but little study has been made of the phosphates of these elements in the soil. When several salts are placed together the ones that are least soluble will precipitate first. Therefore, because of their low solubilities, the phosphates of calcium, magnesium, iron, or aluminum will be the first precipitated. Which one of these precipitated salts will be the most stable will depend upon several factors. One of the most important of these factors is the soil reaction. The phosphates of calcium and magnesium are soluble in acid solutions, increasing with acidity from a pH of 7, where they are only slightly soluble, to strongly acid, where they are extremely soluble. If the reaction is extremely acid the phosphates of iron and aluminum are very soluble, but as the pH rises toward a slightly acid reaction they become relatively insoluble. Iron phosphate has its least solubility at a pH of about 3 or 4 and aluminum phosphate has its least solubility at a pH of about 6 to 6.5 (15). As the pH increases above these points the phosphates of iron and aluminum become more soluble.

Iron and Aluminum Phosphates.--It follows from the above facts that the retention of phosphates over a pH range of approximately 2 to 6.5 is due, in a measure, to the precipitation with iron and aluminum, but part of the retention may also be due to combinations with the iron aluminum colloidal silicate complex. This soil colloidal complex is primarily an aluminum silicate with varying amounts of iron, calcium, magnesium, and other bases. Since phosphate and other acids may also become constituents of the colloidal

silicate, phosphate retention increases with an increase in the ratio of aluminum and iron to silica. At a pH of 6, calcium, iron, and aluminum phosphates have about equal solubilities; consequently, at this pH each of these bases, if in equal concentrations, has an equal chance in competition for any soluble phosphate present (4). At pH 6 the divalent cations begin to play a role in fixation of phosphorus and their role increases with alkalinity. As the pH gets higher, the phosphate ions attached to the colloidal silicate micelle are replaced by OH^- ions and precipitated by calcium and magnesium ions if these are present. At a pH above 8 the divalent cations are the major factor in phosphate fixation.

Calcium and Magnesium Phosphates.---Because of the high pH in alkaline calcareous soils it is generally assumed that most of the phosphate retention is due to precipitation by divalent cations, but because of the fact that some of these soils may at times be neutral or slightly acid, fixation on the surface of the soil colloids or fixation to some extent by iron or aluminum cannot be considered as improbable. Magnesium phosphates react about the same as those of calcium, but are somewhat more soluble (37). Furthermore, in alkaline calcareous soils there usually is considerably more active calcium than magnesium. For these reasons, it is evident that calcium is the most important cation in retaining phosphorus in alkaline calcareous soils.

Calcium phosphate may occur in the soil as simple mono-calcium, dicalcium, and tricalcium salts, or in the form of more com-

plex compounds such as chlor-, fluor-, hydroxy-, or carbonate-apatite. It is also possible that calcium with one of its valences in electrostatic equilibrium with the micelle of the colloidal silicate might connect with a phosphate, such as H_2PO_4^- , with its other valence and retain it there in this manner.

Though in general there is a similarity in the types of phosphates in a region where the soils are predominantly calcareous and tend to be alkaline, there are many differences between various soils of such a region which greatly affect the solubility and availability of these compounds to plants. Among these differences are variations in reaction, amount and kind of salts, and the amount and nature of the organic matter.

Soil reaction is one of the most variable as well as one of the most important factors determining the solubility and type of calcium phosphate. If the pH is around 6 or lower, monocalcium phosphate ($\text{Ca}_3(\text{H}_2\text{PO}_4)_2$) and dicalcium phosphate (CaHPO_4) will predominate (1). The monocalcium phosphate is very soluble. The dicalcium phosphate is relatively soluble, but less so than the monocalcium form. As the alkalinity increases, slightly soluble tribasic phosphates in the form of hydroxy- and carbonate-apatite are likely to become important (29).

Other factors which influence phosphate solubility are the various electrolytes commonly present including the chlorides, sulfates, and carbonates of calcium, magnesium, sodium and ammonium. Calcium, due to its common ion effect, tends to reduce the amount of

phosphorus in solution. Calcium also may replace another cation in a soluble phosphate, such as an ammonium or sodium phosphate, and render it less soluble. The basic salts of calcium may raise the pH so as to render the phosphate less soluble. With a high pH and an excess of calcium carbonate, conditions would favor the formation of carbonato-apatite (9), which is presumably less soluble than the tricalcium phosphate (29).

In the presence of calcium carbonate, if there were an excess of sodium salt present (for example, sodium chloride), it would have a tendency not only to increase temporarily the phosphate in solution but also to increase the amount of calcium in solution. The soluble calcium would react with the phosphorus to render it less soluble. So, in reality, the total effect would be to reduce the amount of soluble phosphate rather than to increase it. In the absence of an excess of calcium the tendency would be to increase the solubility of the phosphate. Ammonium and potassium salts would tend to react in a manner very much similar to salts of sodium.

Organic matter affects the solubility of phosphorus to a considerable degree, primarily through the activity of its decomposition products. The organic phosphates in the organic matter are only slightly soluble, but become readily available to plants when broken down by the micro-organisms of the soil. In this decomposition carbon dioxide is given off, which tends to lower the pH and makes some of the inorganic calcium phosphate more soluble. In addition to the carbon dioxide from decomposing organic matter, there

is a considerable amount of carbon dioxide given off by the living plant roots. Because of the concentration of the carbon dioxide in the immediate zone of the roots there probably is a considerable localized reduction in pH. Thus, an intensive local solvent action on the soil phosphate seems probable. But the problem of solubility is not the only factor in phosphate availability to plants. Some of the more important of the other factors are the degree of phosphate saturation of the adsorbing clay minerals and the reaction of the soil aside from the solubility effect.

Phosphates Available to Plants.---It has been generally assumed that the plants depend upon the phosphate ion in true solution for their supply of phosphorus. Recently, however, considerable evidence has been found (10, 31) to indicate that ions adsorbed by the colloidal silicate may be taken into plants through a process of ionic exchange. For this reason, the degree of phosphate saturation of the adsorbing clay minerals may be an important factor in phosphate availability aside from the effect of silicate adsorption on solubility. The amount of phosphate that a clay will adsorb will depend upon the type of clay. The degree of "tightness" with which a phosphate is held to the clay mineral will be determined to a large extent by the percentage of saturation of that clay. So a knowledge of the saturation capacity is important. For example, if a clay has a very high saturation capacity and only a small amount of phosphorus is present, the phosphorus that is present will be held so "tightly" that plants probably will not be able to get it. Not only this, but if more phosphates are added to the soil they will immediately be

"tied up" with the clay mineral. The amount of phosphorus that will need to be added to a soil in order that the clay will have its saturation capacity satisfied to a certain extent and at the same time leave some for the plant is a function of the saturation capacity.

It has already been stated that carbon dioxide affects the solubility of phosphates in alkaline calcareous soils, but it may affect availability to plants in other ways than just by changing the solubility. Since the adsorption of anions by plants is greatly restricted at high pH values, the addition of carbon dioxide would tend to increase phosphate adsorption by lowering the concentration of OH^- ions. There is evidence that the H_2PO_4^- ion is preferable (31) in plant adsorption to HPO_4^{--} and that PO_4^{---} ions are very slightly adsorbed. The carbon dioxide would tend to increase the availability of phosphorus because it would increase the acidity, and this would increase the ratio of $\frac{\text{H}_2\text{PO}_4^-}{\text{HPO}_4^{--}}$.

From these facts it may be concluded that a diagnosis of the soil conditions in a region where calcareous soils predominate involves an answer to the following questions:

1. In combination with what elements do the phosphates occur?
2. What is the pH of the soil under the conditions which prevail in the field?
3. What is the solubility of the phosphates over this pH range?
4. What is the "maximum fixing capacity" of the soil?

5. How much of this "fixed" phosphate is likely to be available for plant use when phosphate fertilizer is added?

Despite the extensive research on the soil phosphate problem, these questions still remain largely unanswered for the soils of Colorado and other parts of the arid West. This study is directed toward an answer to these questions for some typical Colorado soils, with the hope of arriving at generalizations applicable to general conditions prevalent in the state.

Review of Literature

The literature covering a report of the extensive studies made of soil phosphates contributes much toward answering the questions just stated. Many suggestions have been made regarding the form of soil phosphates and their solubilities.

Phosphate Minerals in Soil.--There are a great number of phosphate minerals which exist in nature. It is possible that some of these well-known minerals constitute the supply of natural phosphate in the soil. If this is true, then a study of the solubilities of these natural minerals compared with the solubility of soil phosphates should give a clue as to what phosphates are present in the soil. Dahlberg and Brown (8) have studied a number of these minerals in acetic acid sodium acetate solutions (pH 5) and potassium carbonate solutions (pH above 12) and found the following solubilities using 0.10 grams of mineral per 150 cc. of solution.

Mineral	Formula	Pct. P in Com- pound	p.p.m. in Acetate Buffer	p.p.m. in K ₂ CO ₃ Solu- tion
Apatite	Ca ₃ (PO ₄)F	16.4	2077	1202
Chlorapatite	Ca ₃ (PO ₄) ₂ Cl	15.6	4264	696
Collensite	(Ca ₂ (MgFe))(PO ₄) ₂ ·2.5H ₂ O	13.9	3521	1012
Quercyte	Ca ₃ (PO ₄) ₂ ·H ₂ O	14.3	3337	1049
Tripillite	(MnFe)PO ₄ ·F	11.3	603	3917
Griphite	(MnCa,Mg ₂)O·Al ₂ (PO ₄) ₂ ·H ₂ O	14.4	1344	11451
Dufrenite	FePO ₄ ·Fe(OH) ₃	2.5	200	2069
Vivianite	Fe ₂ (PO ₄) ₃ ·8H ₂ O	12.3	98	66423
Variscite	AlPO ₄ ·2H ₂ O	14.6	1071	86631
Wavellite	Al(OH) ₃ (PO ₄) ₂ ·5H ₂ O	9.4	125	35095
Tricalcium phos- phate reagent	Ca ₃ (PO ₄) ₂	20.0	37335	10000
Aluminum phos- phate reagent	AlPO ₄	25.4	1863	169341
Phosphate rock		10.0	13333	8000

Hester, Carolus and Blume (24) found close agreement with Dahlberg and Brown in a study of some similar compounds chemically prepared. Their results are shown below:

Compound	Percent P in Compound	p.p.m. P ₂ O ₅ in Solution*	
		Water	Sodium Acetate
Fe ₃ (PO ₄) ₂ ·8H ₂ O	12.4	0	0
FePO ₄ ·4H ₂ O	13.9	11	12
AlPO ₄	25.4	24	34
Mn ₃ (PO ₄) ₂ ·7H ₂ O	12.9	27	109
Ca ₃ (PO ₄) ₂	20.0	27	414
Mg ₃ (PO ₄) ₂ ·8H ₂ O	15.2	58	1187
CaHPO ₄ ·2H ₂ O	18.0	133	742
MgHPO ₄ ·3H ₂ O	17.8	167	1292
Rock Phosphate	14.7	2	10

* Obtained by putting the minimum amount of solid soluble in contact with solvent.

Teakle (43) found that the phosphates of iron, aluminum, manganese and calcium are soluble in strong acid solutions, and that the solubility decreases with increasing pH until a minimum characteristic of each compound is reached with the exception of the calcium salt. These minima were: Iron, pH 3; aluminum, pH 6; manganese, pH 6.4; calcium phosphate in the presence of excess calcium continued to decrease to a very low value, and then ran asymptotically to the origin. Doughty (15) found iron phosphates to reach a minimum solubility at a pH of about 4.0 and aluminum phosphate at a pH of about 6.5. The results of Dahlberg and Brown (8) show, with the minerals they studied, that the aluminum and iron phosphates were soluble at a high pH and considerably less soluble at a pH of 5.0. Their results also show that the phosphates of calcium and magnesium tend to be soluble in an acid reaction and slightly soluble at a high pH. The results of Hester, Carolus and Brown, Teakle, and Doughty (24, 43, 15) indicate that iron and aluminum phosphates are less soluble in an acid reaction (pH 5) and more soluble in an alkaline reaction (pH 12) than are the phosphates of calcium and magnesium.

Doughty (15) inferred that when both iron and aluminum are present a soil should possess high "fixing" powers over a wide range of reaction. Davis (13) found extensive fixation occurring at pH values from pH 0.25 to 7. Brown (7), working with acid soils, found that he could obtain a greater amount of soluble phosphorus at a pH 7.5 to 8 than at any other reaction, and explained this by the low solubilities of iron and aluminum hydroxide at this reaction, and the small amount of free calcium in the soils studied. Heck (20), also

working with acid soils, states that phosphates fixed by iron are less soluble than those fixed by aluminum, and that those fixed by calcium are the most soluble. Ford (16) states that calcium and magnesium phosphates are readily available in acid soils, but that iron fixes phosphates in large amounts. Ford, Heck, and Truog and Ford (16, 21, 46) found that the hydrated iron as goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) fixed phosphates to a larger extent than did the unhydrated iron as hematite (Fe_2O_3). This explains why the yellow soils fixed more phosphates than the red soils, the yellow color being due to the hydrated iron. Teth (44) indicates that phosphorus combines not only with the iron and aluminum, in an acid soil, but that it may also be retained by replacing silica and OH^- groups on the mineral colloid. The soil colloid is a salt composed of an acidoid and a basoid part. The basoid part consists mostly of aluminum with varying amounts of iron and other bases. Gile, Hibbard, Mattson, and Scarseth and Tidmore (18, 25, 27, 41) found that the fixing power of the soil colloid varies with the amount of basoid present, and hence is inversely proportional to the silica-sesquioxide ratio. Heck (22) cites evidence to show that the removal of exchangeable bases from soils cause more fixation in a difficultly available form than in soils containing exchangeable bases. Cook (12) also found that a decrease in base saturation tended to lower the solubility of "soluble" and "native" phosphates. Davis (13) tentatively concludes that phosphate fixation in soils artificially depleted of replaceable bases, which can precipitate phosphate, is due to the absorption of the phosphate by the soil mineral and the formation of equilibrium silicate complexes.

Hibbard (25) suggests that in alkaline solutions iron is hydrolysed, liberating phosphate which combines with calcium, the hydrolysed iron remaining insoluble. He states that this may happen at a pH above 8. Searseth (40) states that the phosphate ion is replaceable by OH^- ions, so as the pH rises the phosphate retained by the colloidal silicate is replaced with OH^- ions. Ravikovitch (39) presents evidence that around the neutral point retention on the surface of the soil colloid is very important. He suggests that it may be retained there by calcium, with one of the valences of calcium in electrostatic equilibrium with the colloidal silicate and the other valence combined with a phosphate such as H_2PO_4^- . At neutral reaction he suggests that the amount of phosphate retention depends upon the exchange capacity of the soil complex and upon the valence of the phosphoric acid ion which takes part in the retention. Bradfield, Searseth, and Steele (6) state that at a pH of from 6 to 10 the divalent cations are responsible for most of the fixation of phosphorus.

From the above studies it is evident that as the pH rises iron and aluminum become less important in phosphate "retention" and magnesium and calcium become more important. Naftel, Pugh, and Ravikovitch (34, 37, 38) found magnesium phosphates to react about the same as calcium phosphates, except that they were more soluble. It is also true that there is usually a small amount of active magnesium compared to calcium in alkaline calcareous soils. Therefore, calcium can be considered the most important cation in retention of phosphates in alkaline calcareous soils.

Calcium Phosphates.---The type of calcium phosphates that are formed in calcareous soils and their solubilities depend upon several factors. The soil reaction is one of the most important of these factors. Benne, Perkins and King (5) show that calcium ions do not precipitate phosphorus from H_3PO_4 solutions until the pH approaches 5.5. The formation of dicalcium phosphate ($CaHPO_4$) was found by Austin (1) to be at a pH of about 6. As the alkalinity increases, the solubility decreases. Bassett (2) found that as the alkalinity increased to a high value, hydroxy-apatite ($Ca_3(PO_4)_2 \cdot Ca(OH)_2$), which has a low solubility, is formed. He suggests that this may be the phosphate usually found under normal soil conditions. However, McGeorge and Breeseale (29) state that in alkaline calcareous soils where there is an excess of calcium carbonate hydroxy-apatite is changed to carbonato-apatite, $(Ca_3(PO_4)_2)_3CaCO_3$, which they claim is still less soluble.

Another factor affecting the solubility of calcium phosphate is the amount and kind of electrolytes present. McGeorge and Breeseale (29) found $NaCl$ and Na_2SO_4 reduced the solubility of phosphates in alkaline calcareous soils. If common ions are present in sufficient concentrations according to the law of mass action they should decrease the solubility. However, Buehrer (9) found that $CaSO_4$ did not affect the amount of phosphorus going into solution from monocalcium phosphate. McGeorge and Breeseale, and Buehrer (30, 29, 9) state that the presence of calcium as the carbonate decreases solubility.

Solubility is not the only factor affecting availability.

Some of the more important of these are: Movement of phosphates in soil, the degree of phosphate saturation of the absorbing clay mineral, and the soil reaction aside from solubility effect. The importance of the movement of phosphates in affecting their availability arises from the fact that fertilisers are applied to the soil surface. Hockensmith, et al., Metzger, Heck and Truog, Heck, and Beater (26, 32, 23, 20, 19, 3) found that phosphates did not move appreciably in soils. For this reason, when a soluble phosphate is added to a soil it should be placed so that it will be where the plant roots can reach it readily. Heck (19) found that when soluble phosphates were added to a wet soil most of the fixation took place within a few hours.

Adsorption by Clay Colloid.--Another factor which affects the availability of phosphates is the phenomenon of adsorption by the clay colloid. The saturation capacity of the clay mineral and the degree to which it is satisfied determines the magnitude of this factor. This has been recognised as important in phosphate availability by Snider, Gile, Mattson, Parker, Burd and Murphy, Conrad, Gardner and Kelley, and others (42, 18, 27, 35, 10, 11, 17).

Soil Reaction and Availability.--Probably the most important factor of all in determining the amount of phosphorus available to plants is the soil reaction. The soil reaction of calcareous soils is affected to a large extent by the carbon dioxide given off by the roots of plants. Truog (45) states that rock phosphorus is available to plants that have an extensive root system and give off

a considerable amount of carbon dioxide. The principal effect that carbon dioxide has in alkaline calcareous soils is to lower the pH. This increases the solubility of the phosphates. McGeorge and Breeseale (29) state that the reaction is reduced considerably in the immediate zone of the root hairs. McGeorge and Breeseale (31) also suggest that the carbon dioxide, by reducing the OH^- ion concentration, increases plant absorption of phosphates. The carbon dioxide reduces the pH and, therefore, increases the ratio of $\frac{\text{H}_2\text{PO}_4^-}{\text{H}_2\text{PO}_4^{--}}$.

Buehrer (9) points out that H_2PO_4^- is taken up by plants more readily than HPO_4^{--} or PO_4^{---} .

Since the type of phosphate and its availability is affected so much by pH, it is natural that the pH would be an important factor in determining the type and amount of phosphate present in a soil. Dean (14) has devised a method by which he attempts to fractionate the soil phosphates. The soil is first treated with NaOH. The soluble phosphates are, as he terms them, alkali soluble inorganic phosphates (mostly iron and aluminum) and some organic phosphates. He treats the residue with H_2SO_4 and calls this the inorganic acid soluble, but alkali insoluble (mostly calcium and magnesium). The residue which is left is simply termed insoluble phosphates. The phosphates soluble in NaOH would consist not only of those adsorbed to the colloidal silicate, but also the iron and aluminum and some organic phosphates. The H_2SO_4 extraction would contain the calcium and magnesium phosphates. This method provides no means for further separating the different kinds of phosphates, which is important in

determining phosphate availability. Gardner and Kelley (17) in studying the effect of pH on the solubility of phosphorus in a number of Colorado soils have shown considerable variation between the curves of various soils of this area. They have also shown that there is a close relationship between the solubility at the pH at normal field moisture and availability of phosphorus to plants.

Methods and Materials

The investigations made in the solution of this problem were studies of:

1. The solubility curves of phosphates as a function of the pH.
2. The pH at moisture equivalent under carbon dioxide pressure of the air, and the pH at moisture equivalent under 0.83 atmospheres pressure of carbon dioxide.
3. The "maximum fixing capacity" of the soil.
4. The rate of extraction by successive leachings of the added phosphate.

1. Solubility Curves.--In determining the solubility curves as a function of the pH, the varying pH values were produced by using different concentrations of H_2SO_4 and K_2CO_3 . One part of soil to ten parts of solution was used. The suspensions were shaken for one hour and then centrifuged. The pH was determined by use of the glass electrode. The phosphate analyses were made by a modification of the Deniges Method as described by Whitney and Gardner (47). In some cases where the solution remained cloudy after centrifuging it was necessary to filter it through an alundum filter. When this was necessary 5 to 10 ml. were filtered through and discarded, so

there would be a minimum error due to sorption of phosphates by the filter. The next fraction filtered through was used for analysis. As a check, some of the clear solutions were filtered in the same manner and phosphate determined before and after filtering. No differences in phosphate concentrations were noticed as a result of filtering. A graphical study of the data was made by plotting the p.p.m. of phosphorus in solution against the pH of the solution.

2. The pH at Moisture Equivalent.--The pH values at the moisture equivalent under carbon dioxide pressure of laboratory air and under 0.83 atmospheres pressure of carbon dioxide were determined and superimposed on the solubility graphs. The pH at the moisture equivalent was measured by making the soils up to the desired moisture content and allowing them to stand in a saturated atmosphere for 24 hours and then reading the pH with the glass electrode. The pH under 0.83 atmospheres pressure of carbon dioxide was determined by making the soil up to moisture equivalent and placing in a container over water. This container was evacuated and filled with carbon dioxide. This was repeated twice. It was then allowed to stand for 24 hours when the samples were removed one at a time and the pH determined immediately.

3. Fixing Capacity.--The "maximum fixing capacity" of a soil, as used here, will refer to the amount of phosphate that is held back by a soil when a solution of phosphate is passed through it. This obviously varies with the concentration of the phosphate, the pH, and the type of phosphate used. But if these factors are

held constant, a maximum fixing capacity can be determined that will depend upon the properties of the soil. This function was determined by placing varying amounts of soil in a 30 ml. test tube with a small hole in the bottom. The lower end of the tube was placed in a solution of known concentration of either KH_2PO_4 or K_3PO_4 . The solution was allowed to rise by sapillary flow until the soil was saturated. The tube was then centrifuged and the amount of phosphorus was determined in the liquid that rose to the top due to the compaction of the soil. By knowing the amount of phosphorus that was taken up by various amounts of soil and the amount of phosphorus that was in the solution after the solution had passed through the soil, the maximum fixing capacity was calculated.

4. Rate of Extraction.--The rate of extraction of the added phosphate by successive leachings was determined by placing soil in a tube and allowing a solution of known concentration of KH_2PO_4 to rise by capillarity. The soil in the tube was divided into layers and when phosphorus was carried up past the lower layer, the lower two layers were analysed for phosphorus in successive extracts with one percent potassium carbonate. If no phosphorus passed the lower layer, the experiment was repeated with a higher concentration. The soil was placed in 50 ml. tubes, diluted to 1-5, and shaken for 30 minutes, and then centrifuged. This was repeated until the extracts gave little or no test for phosphorus. The amount of phosphorus recovered by these extractions and the percent recovery were then calculated. From these data and the shape of the curves the rate of extraction was studied.

It was thought that the phosphate might be fixed in a less available form if the treated soils were allowed to stand over a longer period of time. Samples of these soils were taken and treated. They were then made up to the moisture equivalent point and allowed to stand for 24 hours, dried in an oven at 110° C. for 12 hours, and allowed to stand dry for another 12 hours. After this, the process was repeated ten times and then the phosphate was determined.

Eighteen soils were used in the investigation. Some of the properties of the soils studied are listed in table 1.

The soils listed in table 1 are all calcareous, with the exceptions of Nos. 10, 11, 12, 13, and 17. The soils were selected so that the calcareous and non-calcareous soils of the state would be represented. Soil No. 10 is a soil from the foothills and is very slightly acid. Soils Nos. 12 and 13 are soils from the mountains and are distinctly acid having pH values of 5.0 and 5.6, respectively. Soil No. 9 is a subsoil from Baca County.

Table 1. Properties of the Soils Used in the Investigation*

Soil No.	Type	Lime		Total P ₂ O ₅	Available P		pH Field Conditions	pH-O.83 Atmospheres Pressure of CO ₂	Moisture Equivalent
		Pct.	Pct.		Alkalil Extract	Acid ² Extract			
					p.p.m.	p.p.m.			
1	Fort Collins Loam	4.8	.21	1.12	2.24		7.1	6.2	24.98
2	Fort Collins Loam	6.9	.19	0.53	0.58		7.2	6.7	26.47
3	---- Clay Loam	9.2	.26	1.79	2.27		7.7	7.0	11.71
4	Subsoil to 3 Clay Loam	26.7	.20	0.45	0.56		7.6	6.9	22.73
5	Billings Clay Loam	9.7	.28	1.12	1.11		8.9	7.3	26.29
6	Weld Fine Sandy Loam	4.5	.18	0.56	0.76		8.1	6.6	18.94
7	Larimer Clay Loam	4.5	.14	0.45	0.56		7.7	6.8	18.75
8	Weld Clay Loam	5.8	.16	0.42	0.58		7.4	6.6	22.63
9	Cass Fine Sandy Loam	2.8	.19	0.62	2.23		7.2	6.5	24.72
10	Neville Fine Sandy Loam	Less .1	.12	1.72	2.22		6.8	6.5	11.98
11	---- Sandy Loam	Less .1	.14	0.45	0.22		7.0	6.1	14.74
12	---- Sandy Loam	Less .1	.19	1.053	0.13		5.0	4.6	21.58
13	---- Sandy Loam	Less .1	.11	0.903	0.273		5.6	5.3	12.79
14	Weld Clay Loam	1.2	.17	0.90	0.98		7.8	7.1	18.96
15	Fort Collins Clay Loam	4.4	.22	1.12	0.71		7.1	6.4	24.39
16	Subsoil to 2 Clay	9.5	.23	0.45	0.51		7.4	6.2	21.33
17	Dunkirk Silt Loam	---	.20	2.19	0.22		6.4	5.6	26.64
18	Weld Fine Sandy Loam	5.9	.12	0.33	0.71		7.2	6.3	18.00

¹Method by Whitney and Gardner (47).²Method by Dahlberg and Brown (8).³Solution slightly cloudy due to organic matter.

*Part of these data and part of the figures from 1 to 12 were taken from a paper by Gardner and Kelley (17).

Experimental Results

Solubility Curves.--The phosphate solubilities as affected by pH of soils Nos. 1 to 18 are shown in figures 1 to 10. The buffering capacities of these soils are also shown. In addition to showing the effect of pH on solubility, and the various amounts of acid or bases on the pH of the various soils studied, the curves throw considerable light on the nature of the phosphate compounds in the soil and their probable availability to plants. All of these curves tend to have the same general shape, reaching a minimum at a pH of a little above 7, and rising rapidly with increasing acidity and less rapidly on the more basic side. The fact that the solubility curves rise rapidly on the acid side and are low at a pH of around 7 indicates that the phosphates present are principally in the form of calcium phosphates with not more than traces of iron or aluminum phosphates. Iron and aluminum phosphates would be less soluble in the acid region and more soluble in the basic region. The rise in the curves at the higher pH values indicate that there are some phosphates adsorbed to the colloidal micelle or present in a less basic form of calcium salt than the tricalcium phosphate, or both. The solubility of these soil phosphates under normal field conditions should be indicated by the portion of the curve between the two dotted vertical lines intersecting the curves in figures 1, 2, 3, and 4 and the two heavy lines in figures 5, 6, 7, 8, 9, and 10. The line to the left is the pH value at moisture equivalent under 0.83 atmospheres pressure of carbon dioxide and the line to the right is the

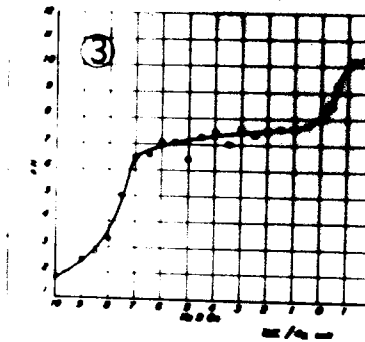
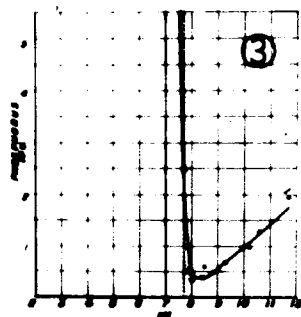
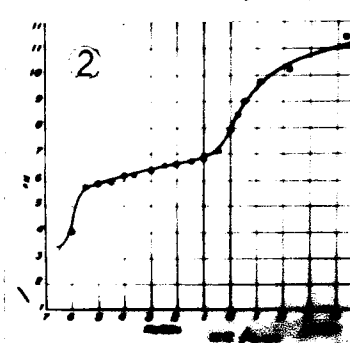
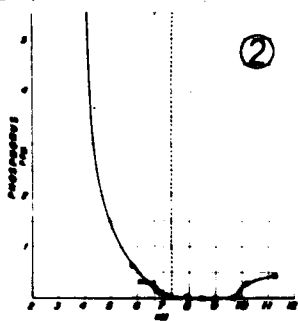
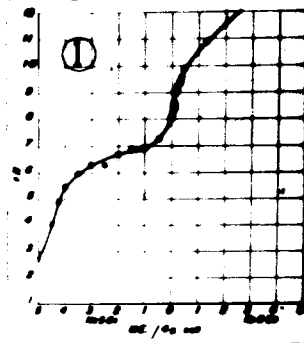
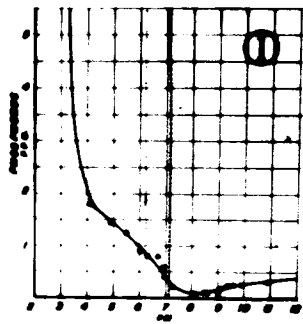


Figure 1 Phosphate solubility and buffer capacity

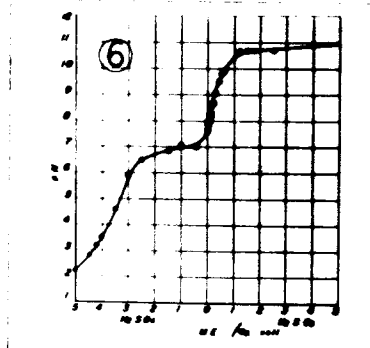
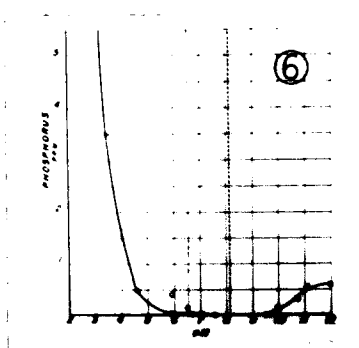
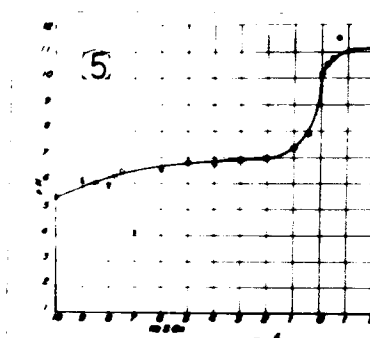
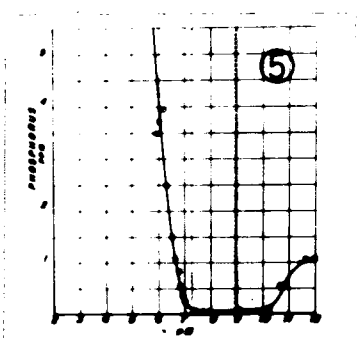
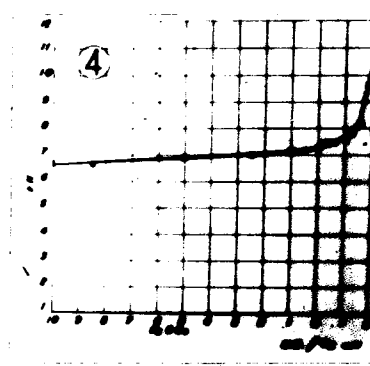
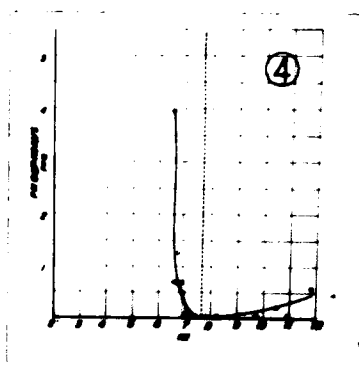


Figure 2 Phosphate solubility and buffer capacity

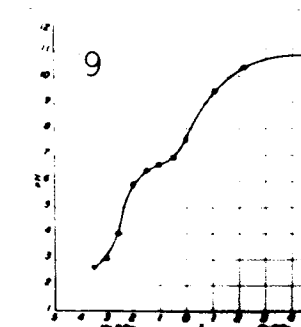
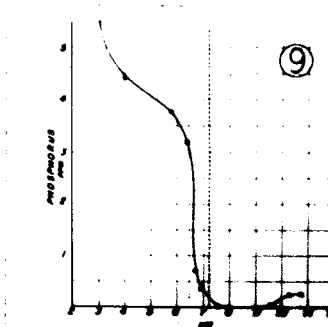
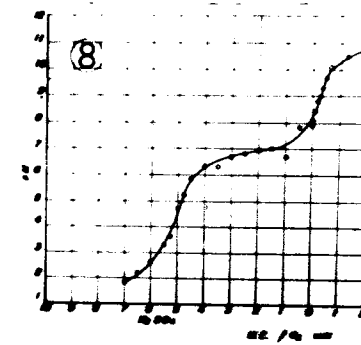
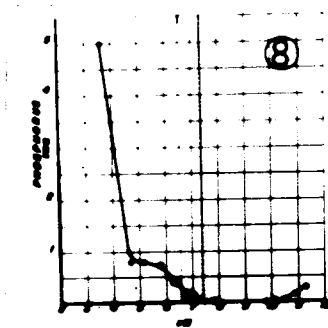
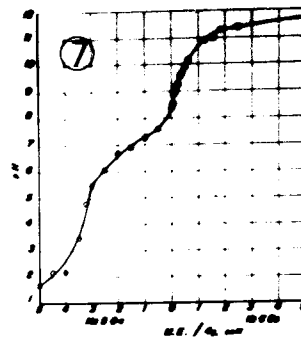
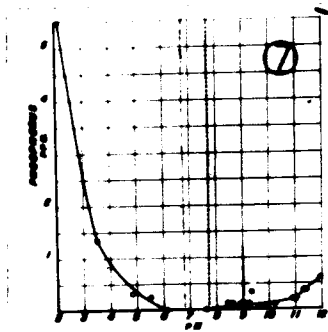


Figure 3 Phosphate solubility and buffer capacity

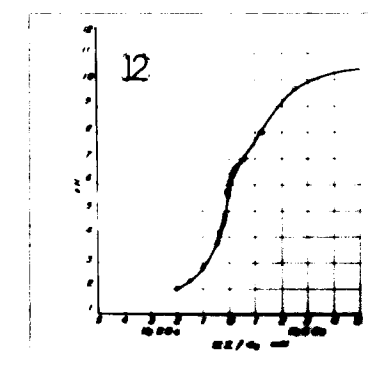
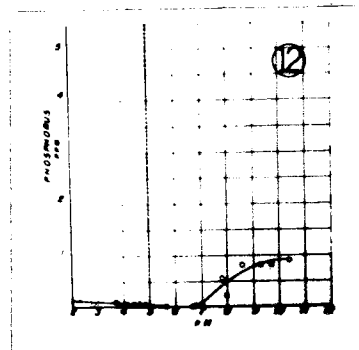
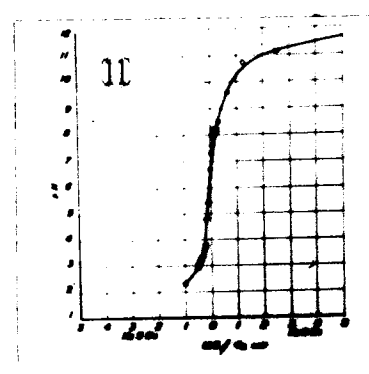
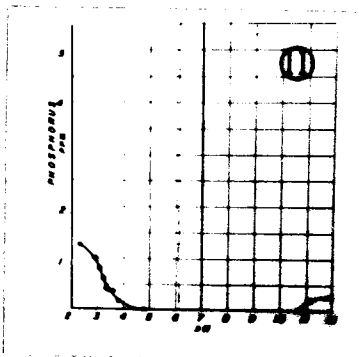
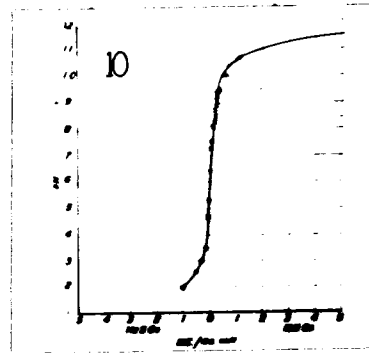
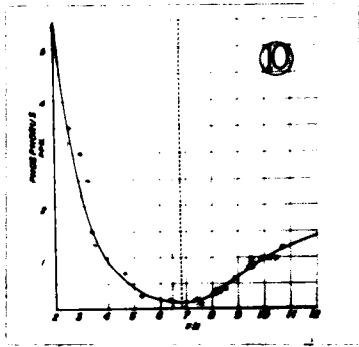


Figure 4 Phosphate solubility and buffer capacity

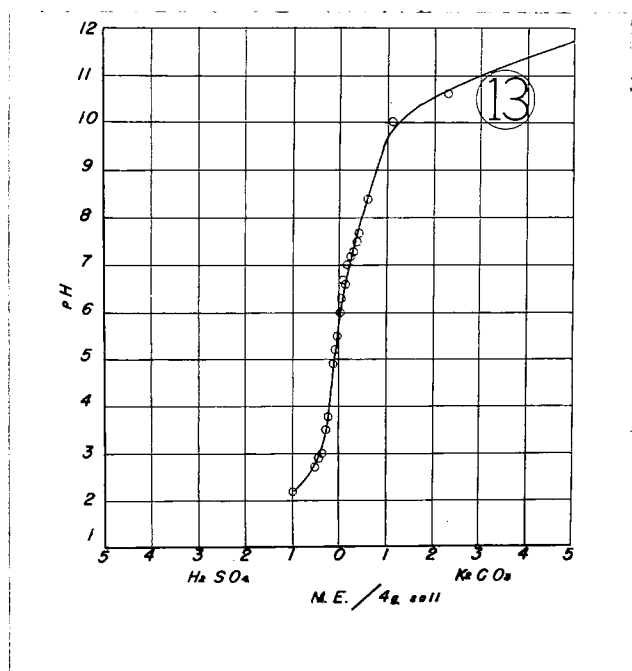
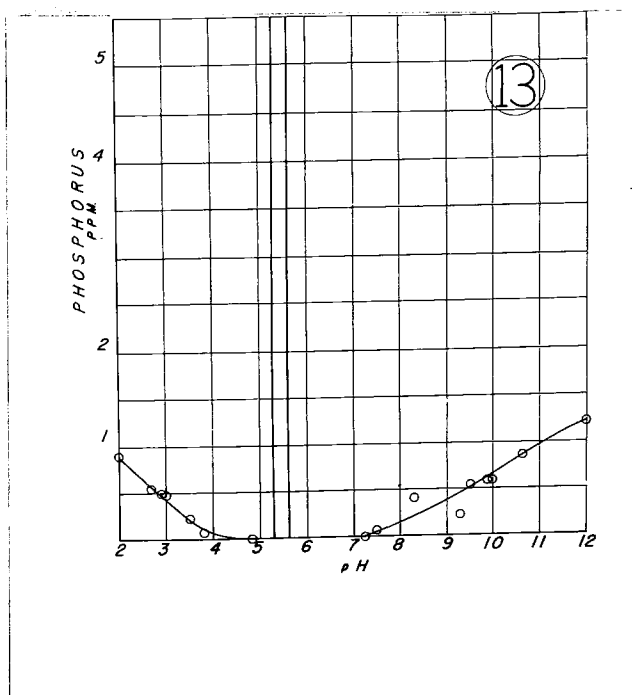


Figure 5 Phosphate solubility and buffer capacity

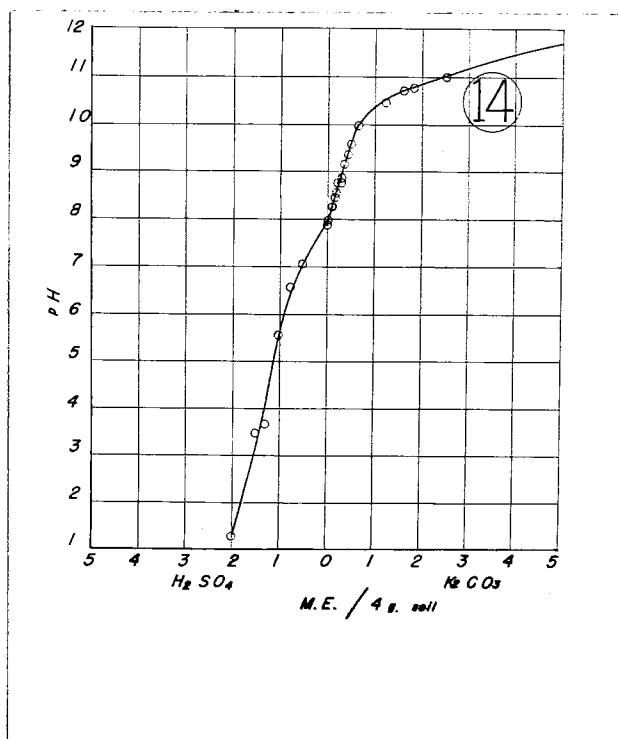
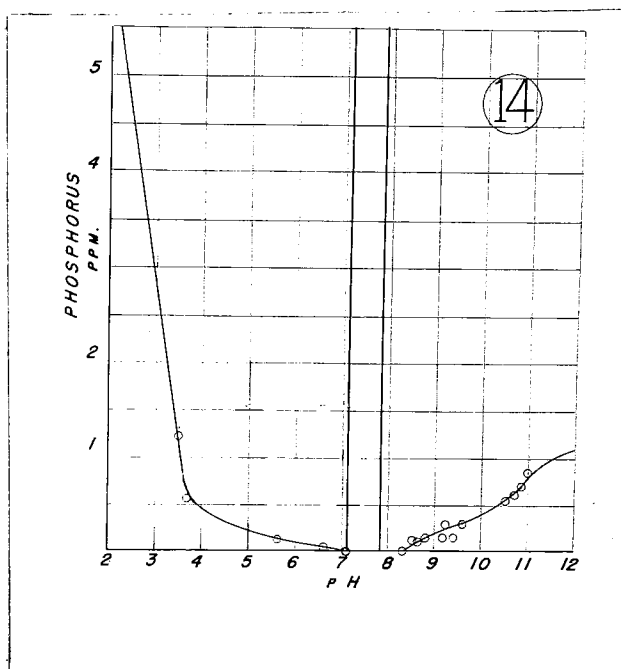


Figure 6 **Phosphate solubility and buffer capacity**

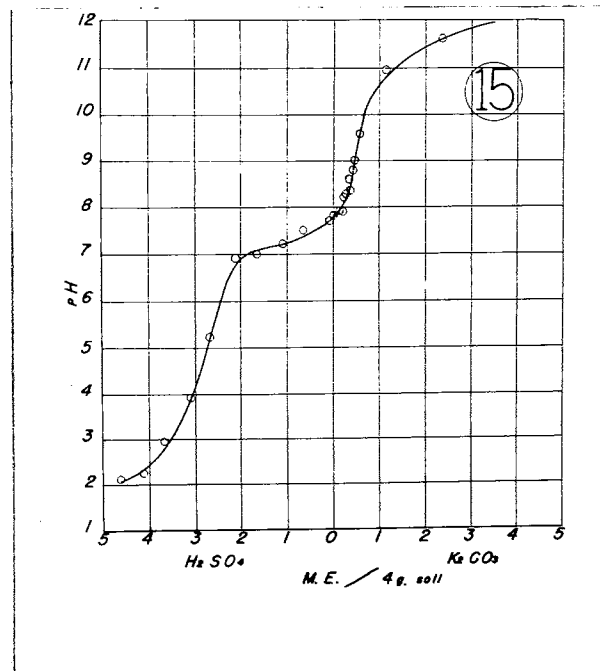
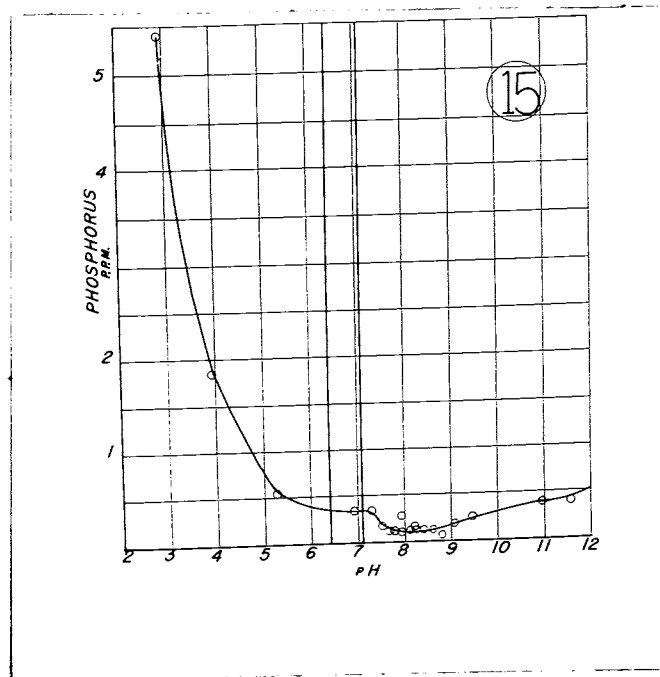


Figure 7 Phosphate solubility and buffer capacity

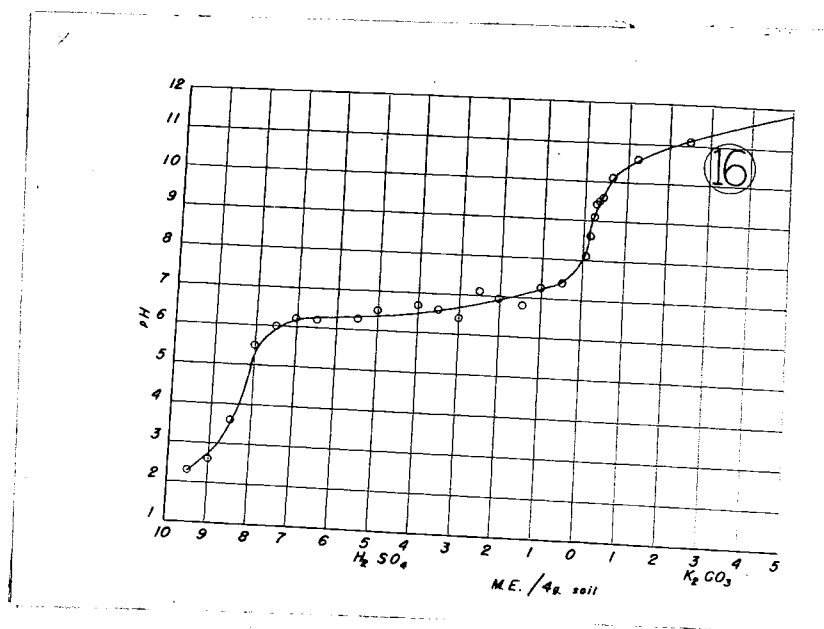
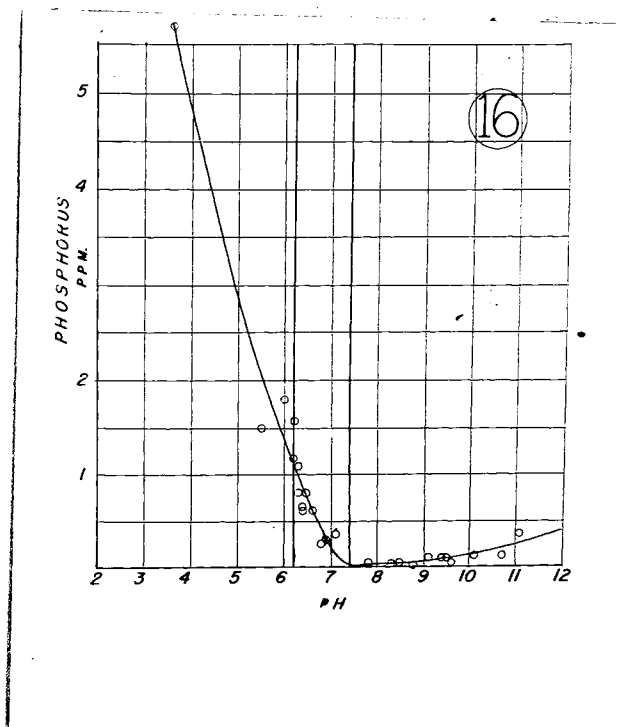


Figure 8. Phosphate solubility and buffer capacity

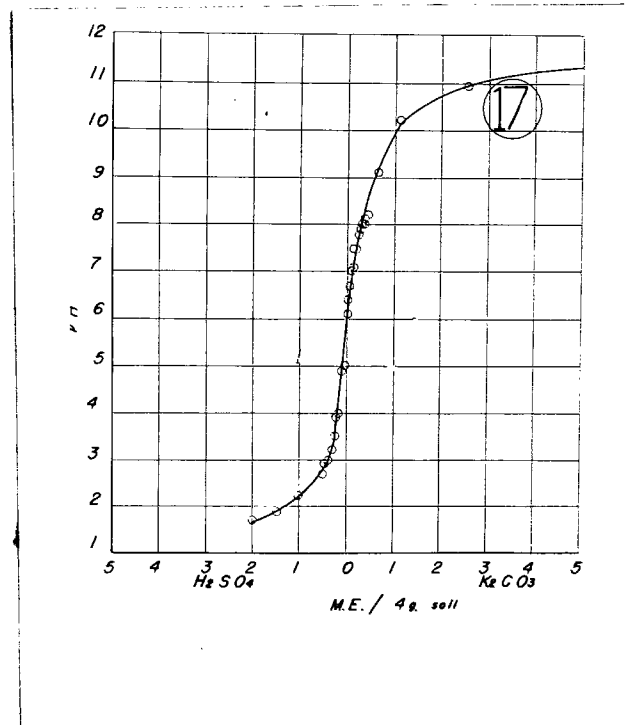
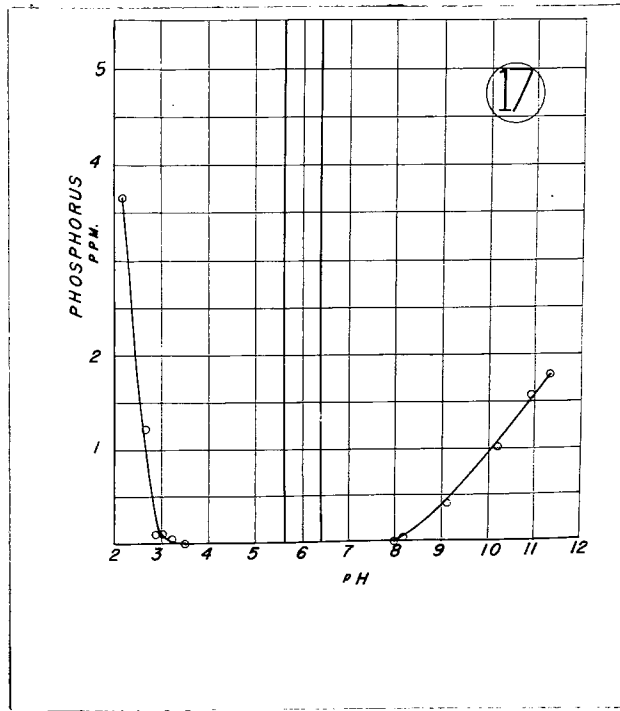


Figure 9 Phosphate solubility and buffer capacity

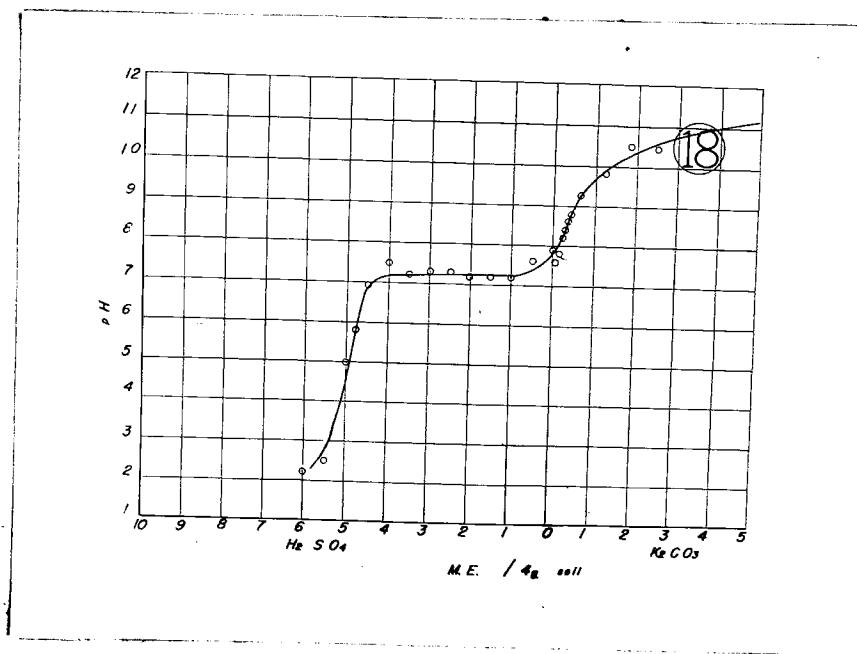
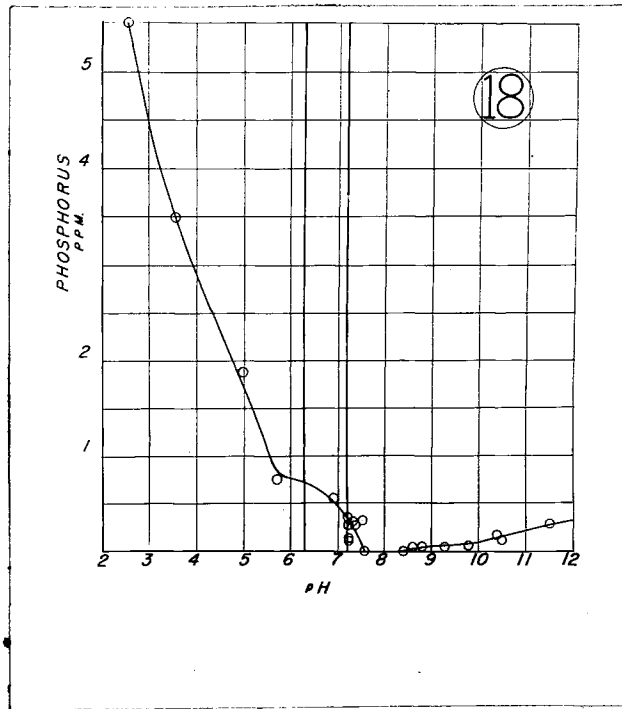


Figure 10 Phosphate solubility and buffer capacity

pH value at the same moisture, but with only the carbon dioxide pressure present in the laboratory air. The two lines should indicate the range between the minimum and maximum pH values of the soil under normal field conditions.

From the solubility curves, figures 1 to 10, it can be inferred that soil No. 3 should not respond to phosphorus fertilization, since the curve remains above 0.50 p.p.m. throughout the region between the two dotted lines. The work of Parker (35) and others show that plants do well in this concentration. Soils Nos. 2, 4, 5, 6, 7, 8, 10, 11, 12, 13, 14, and 17 are low in phosphorus at a pH corresponding to field conditions and should respond to phosphate fertilization in the field. The response of Soils Nos. 1, 9, 15, 16, and 18 would appear to be questionable from the solubility curves, since at the pH reached by the use of 0.83 atmospheres of carbon dioxide there appears to be sufficient available phosphate, but at the pH obtained with only the carbon dioxide pressure of the laboratory air there is low available phosphate. Soils Nos. 1 and 2, figure 1, are highly buffered. One atmosphere of carbon dioxide did not lower the pH enough to raise the phosphate concentration above 0.50 p.p.m. in these soils. Soil No. 3 is highly buffered, but it has a sufficiently high phosphate concentration for plant growth below pH of 8. Soil No. 4 is the subsoil of No. 3, is very high in lime, and has a high buffering capacity as is indicated by the buffer curve. Soil No. 5 is a highly alkaline soil from a slick spot on the Western Slope. The curve indicates it should respond to phosphorus. Soil Nos. 6, 7, and 8, which are very deficient in phosphate, are soils which produce

blackheart beets, and are found to respond to phosphate fertilization. From the solubility curve of soil No. 9 it appears that if the plant can give off enough carbon dioxide to get a concentration of one atmosphere, there would be an ample supply of available phosphorus. If, however, the plant cannot give off enough carbon dioxide to reduce the pH below 6.8, the curve indicates a phosphate deficiency. Evidently the latter is the case as plants grown on this soil respond to phosphate treatment. Soils Nos. 10, 11, 12, 13, and 14, figures 4, 5, and 6, are only slightly buffered and are deficient in available phosphorus. Soil No. 11 responds very well to phosphate fertilization. The curves for soils Nos. 15 and 16, figures 7 and 8, indicate a response would be expected, but with less certainty than for soils Nos. 10, 11, and 12. Soil No. 17, figure 9, is an acid soil from New York state and is very deficient in soluble phosphorus and is only slightly buffered. Soil No. 18, figure 10, is another soil which produces blackheart beets, yet from the solubility curve alone it would be questionable as to whether this soil would respond to phosphate treatment.

It is clear from the solubility and buffer curves that phosphate fertilization is necessary on many of the above soils. However, they do not show the amount of phosphate necessary. It is important to know how much phosphorus should be added and what happens to the phosphorus after it is incorporated in the soil. In order to obtain some data that will help to answer these questions, the maximum fixing capacity and the resistance to leaching of the added phosphate were studied.

Fixing Capacity.---The maximum fixing capacity (the power of a soil to take phosphorus out of a phosphate solution) was determined for soils Nos. 1, 7, 9, and 10. The results are listed in table 2.

Table 2. "Maximum Fixing Capacity"

Soil No.	Mgm. P per 10 g. Soil	Pounds of P per Acre 6 Inches	Pounds Treble Superphosphate per Acre 6 Inches
Using KH_2PO_4			
1	59.76	11,952	60,800
7	66.12	13,224	67,270
9	76.32	15,264	77,648
10	39.00	7,800	39,678
Using K_3PO_4			
1	50.88	10,176	51,765
7	51.48	10,296	52,376
9	75.12	15,024	76,427
10	36.96	7,392	37,603

Soils Nos. 1, 7, and 9 are calcareous, but soil No. 10 contains no lime. The maximum fixing capacity was approximately the same when determined by the use of K_3PO_4 , containing 1.2 percent phosphorus, as it was when determined by the use of KH_2PO_4 of the same phosphate concentration. It was expected that in calcareous soils more phosphate be fixed from an acid phosphate than from a basic salt due to the difference in effect on the solubility of calcium carbonate. However, it was found, as the table shows, that the fixation was about the same regardless of whether K_3PO_4 or KH_2PO_4 was used. The reason for this probably can be explained by the fact that the soil contains soluble calcium as calcium sulfate.

From the table, it is evident that all these soils are capable of taking an extremely large amount of phosphorus out of the solution and that phosphate movement in the soil would be extremely small. Most of the phosphorus fixed in this manner is not unavailable to plants, and is relatively soluble in water, which is evident from a study of soils Nos. 1 to 12, figures 12 to 23. However, some phosphorus is adsorbed or fixed by the colloid that does not readily go into solution. In order to find this latter amount, the soils were treated with KH_2PO_4 and then washed with 2 percent KCl solution until the phosphate content of the extract approached the solubility of normal soil phosphates. The 2 percent KCl solution was used instead of water in order to obtain solutions that were not turbid. It was assumed that the phosphate solubility in 2 percent KCl would not be greater than in water (29, 36). Figure 11 shows a calculated curve for the washing of a phosphate treated soil assuming that all the phosphate applied stayed in solution. Figures 12 to 23 show the actual amount of phosphates in solution after successive washings with 2 percent KCl. The phosphorus in solution was plotted against the number of washings. The experimental curves for the various soils are of the same general nature and indicate that the amount of phosphate in these successive washings is not merely a function of dilution, but also of precipitation and adsorption. The curve for soil No. 4, figure 15, has a definite hump that may be attributed to the high amount of calcium carbonate and calcium sulfate present in this soil. Soils Nos. 10, 11, and 12, figures 21, 22, and 23, tend more to follow the calculated curve based on complete solubility.

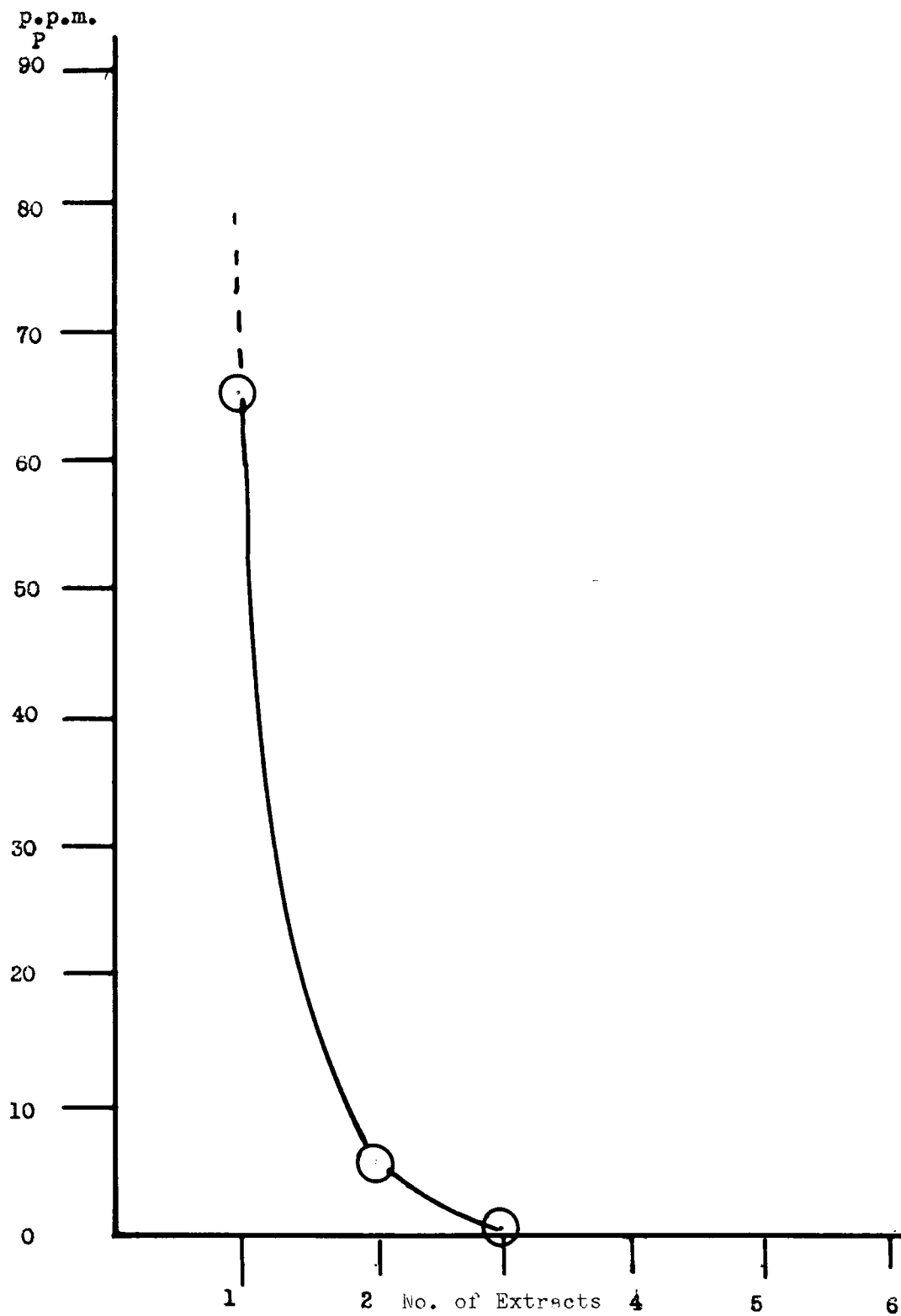


Figure 11 Calculated curve for a soil treated with KH_2PO_4 and extracted successively with 2 percent KCl

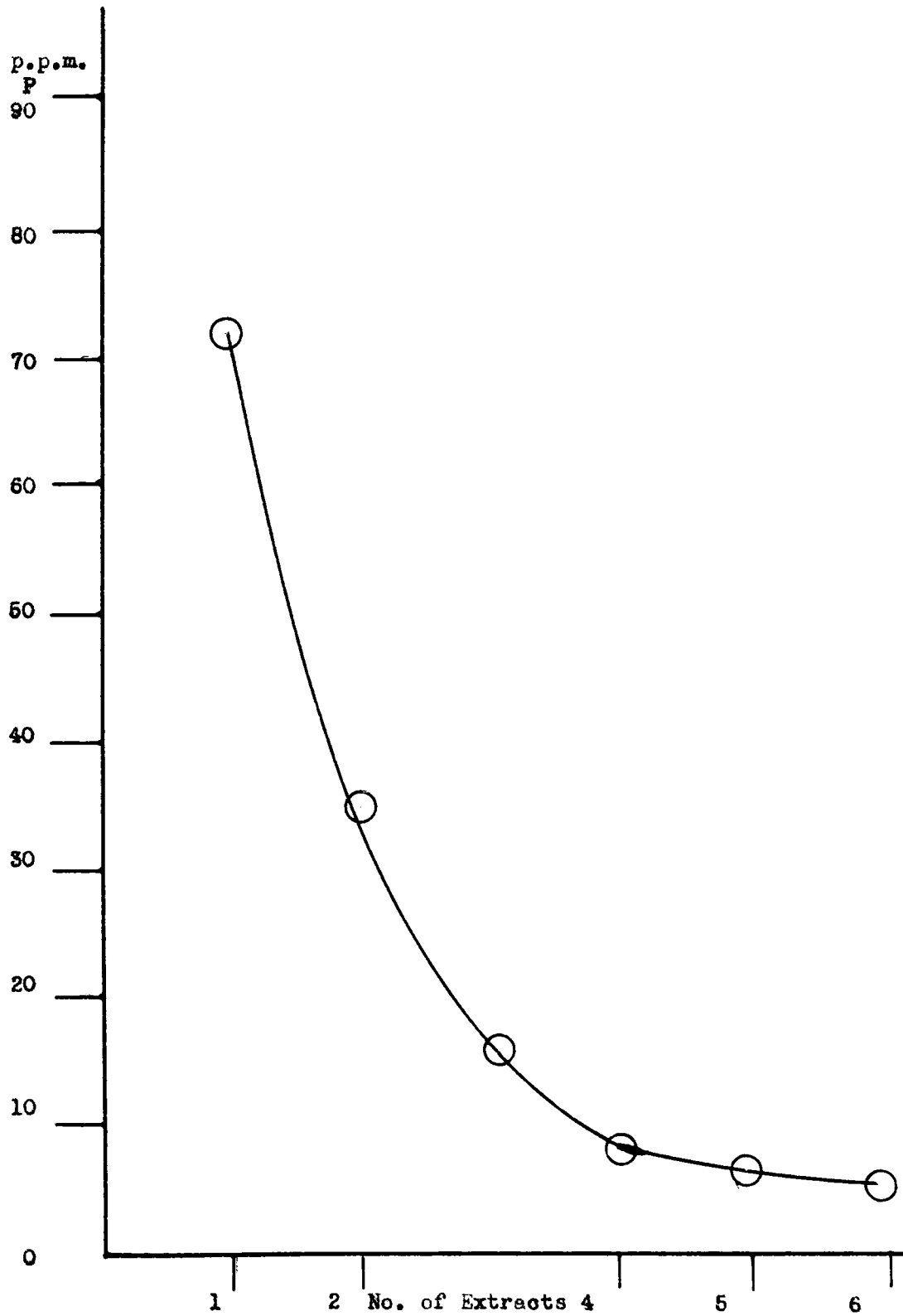


Figure 12 Soil # 1 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

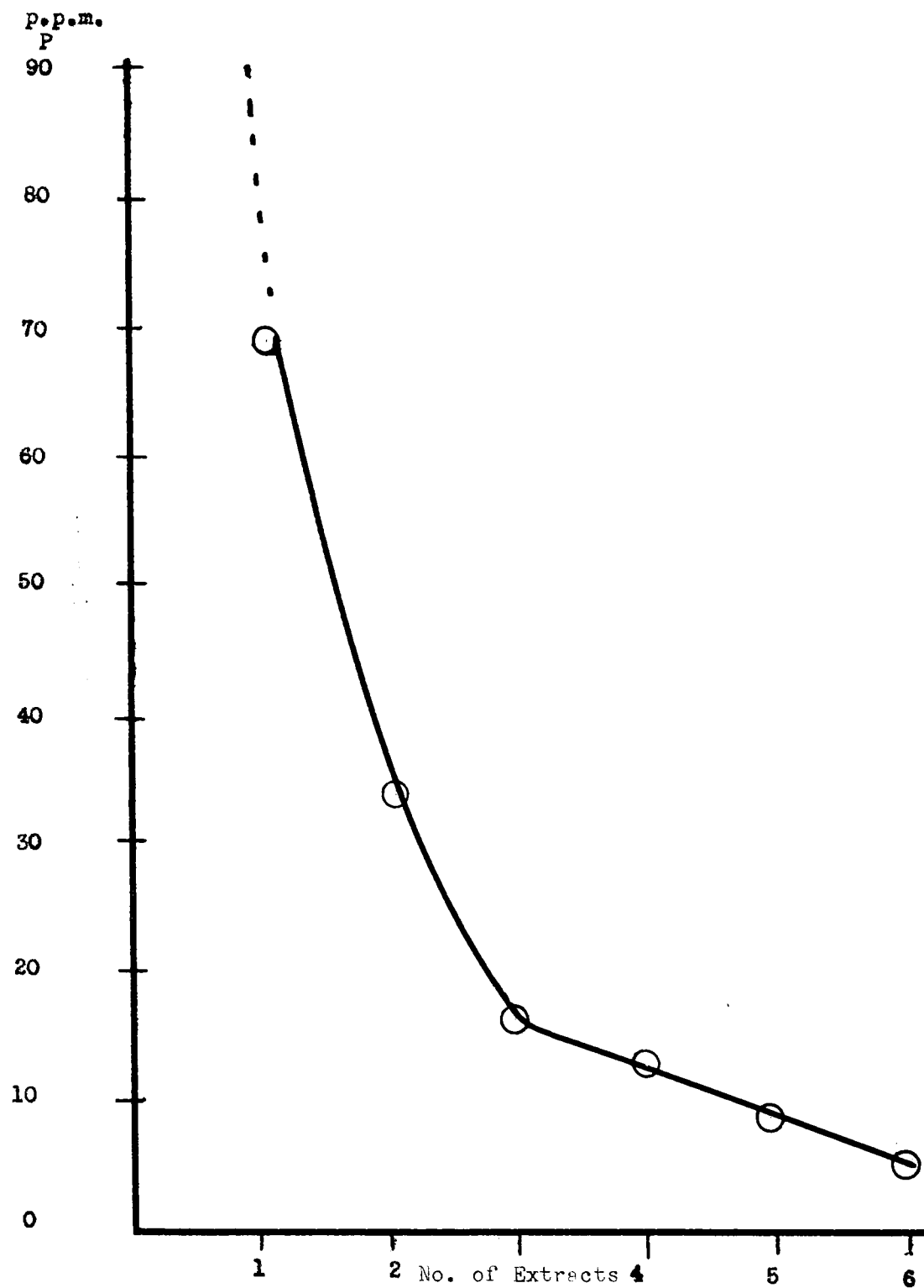


Figure 13 Soil # 2 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

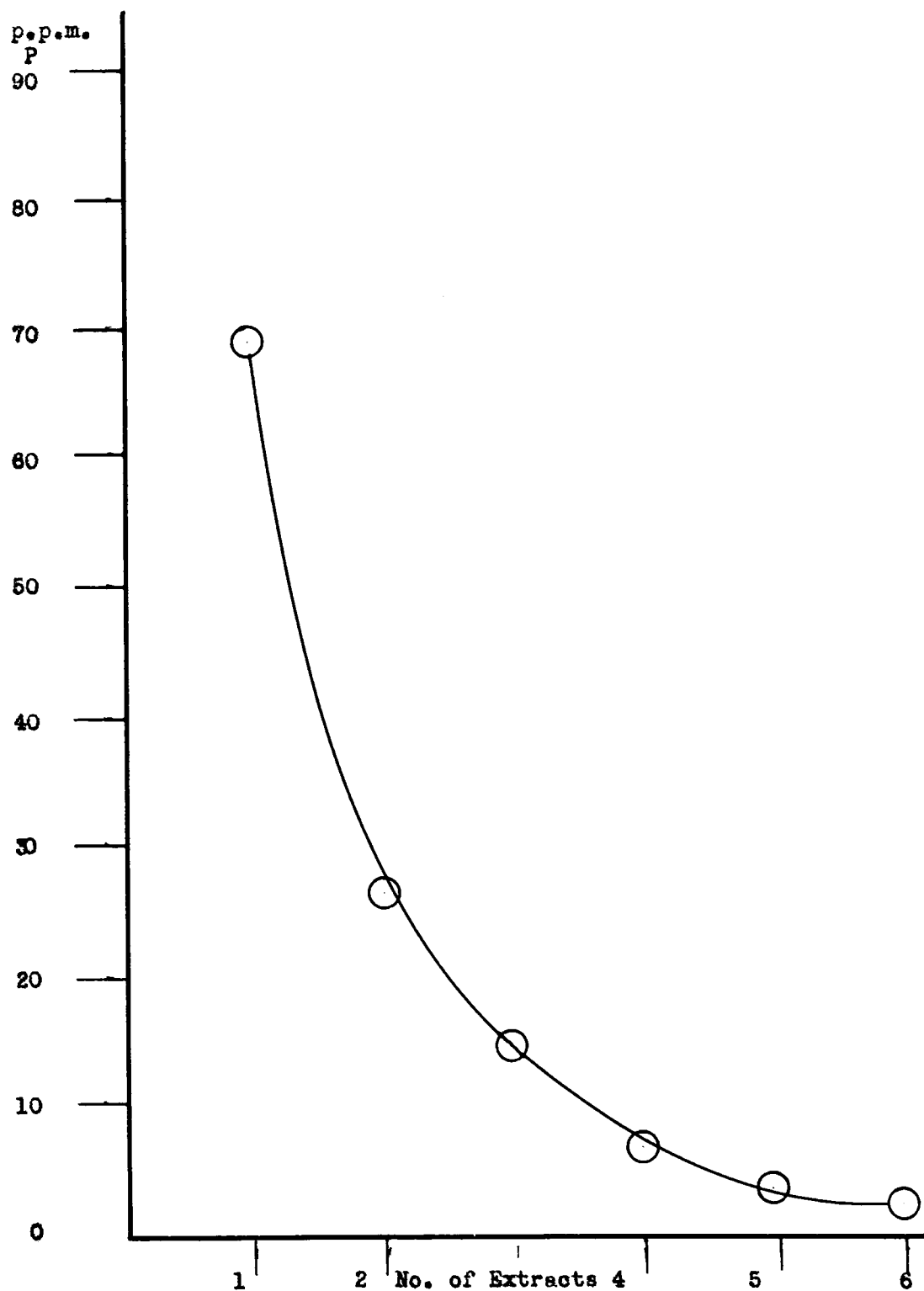


Figure 14 Soil # 3 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

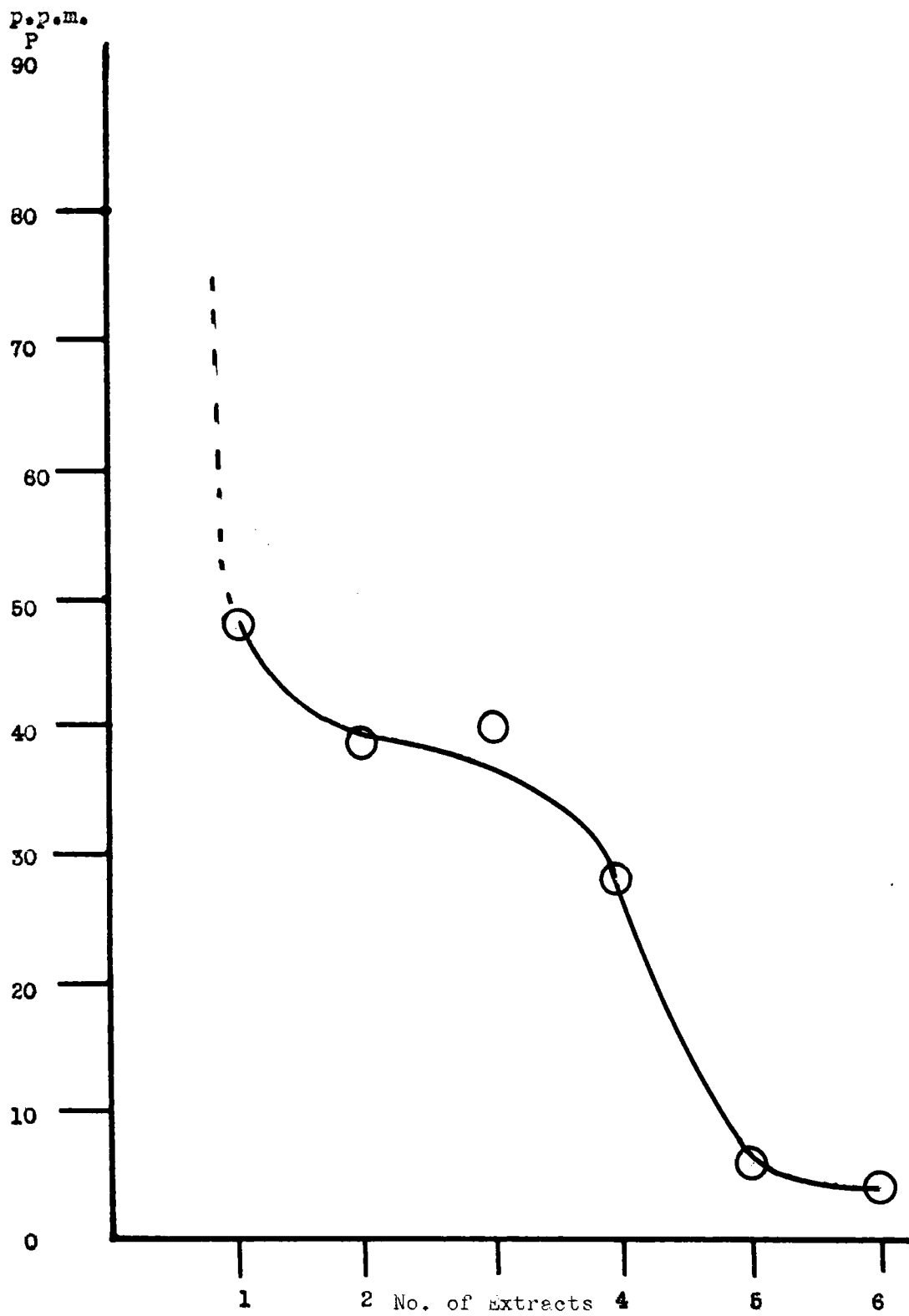


Figure 15 Soil # 4 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

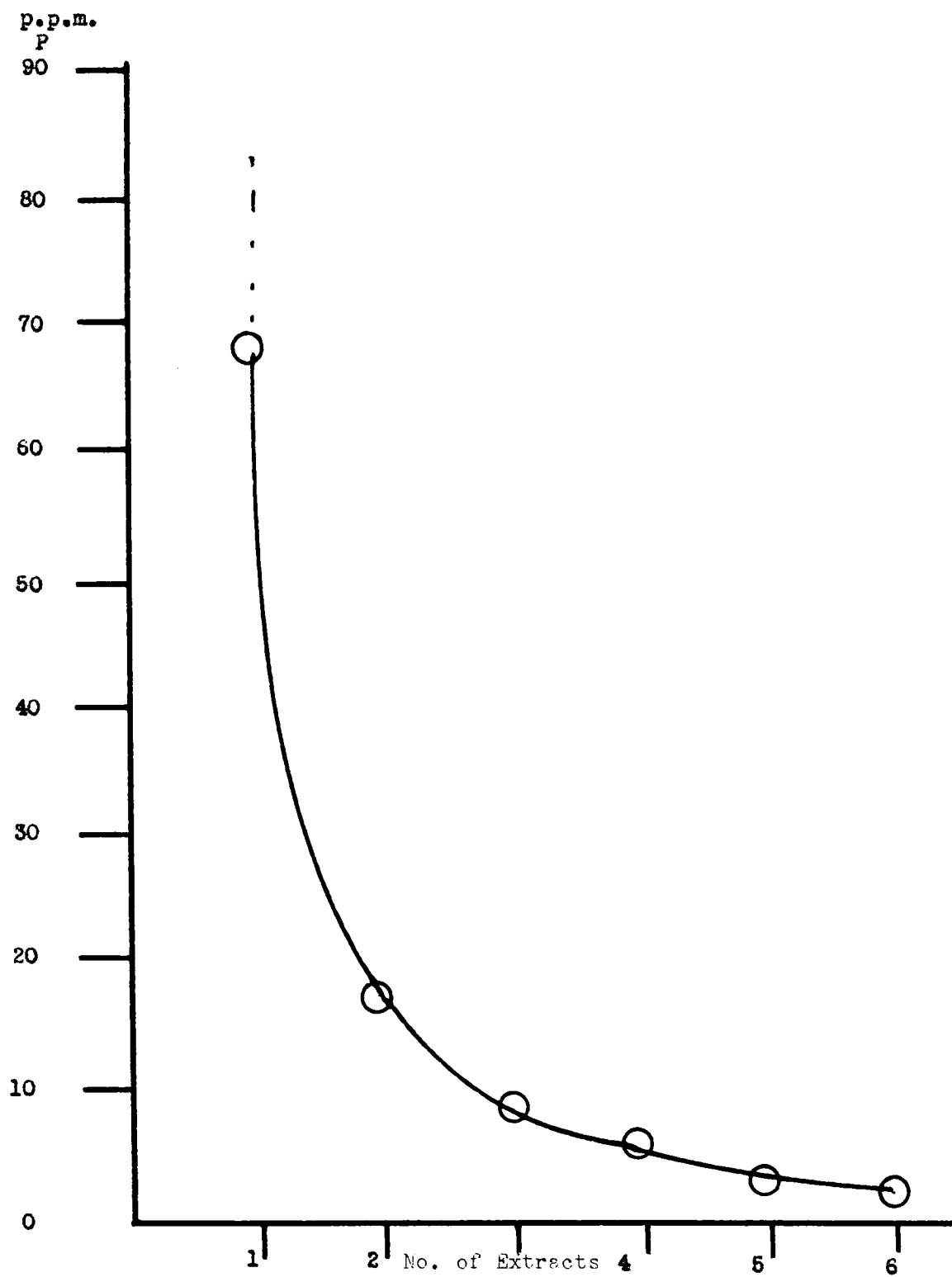


Figure 16 Soil # 5 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

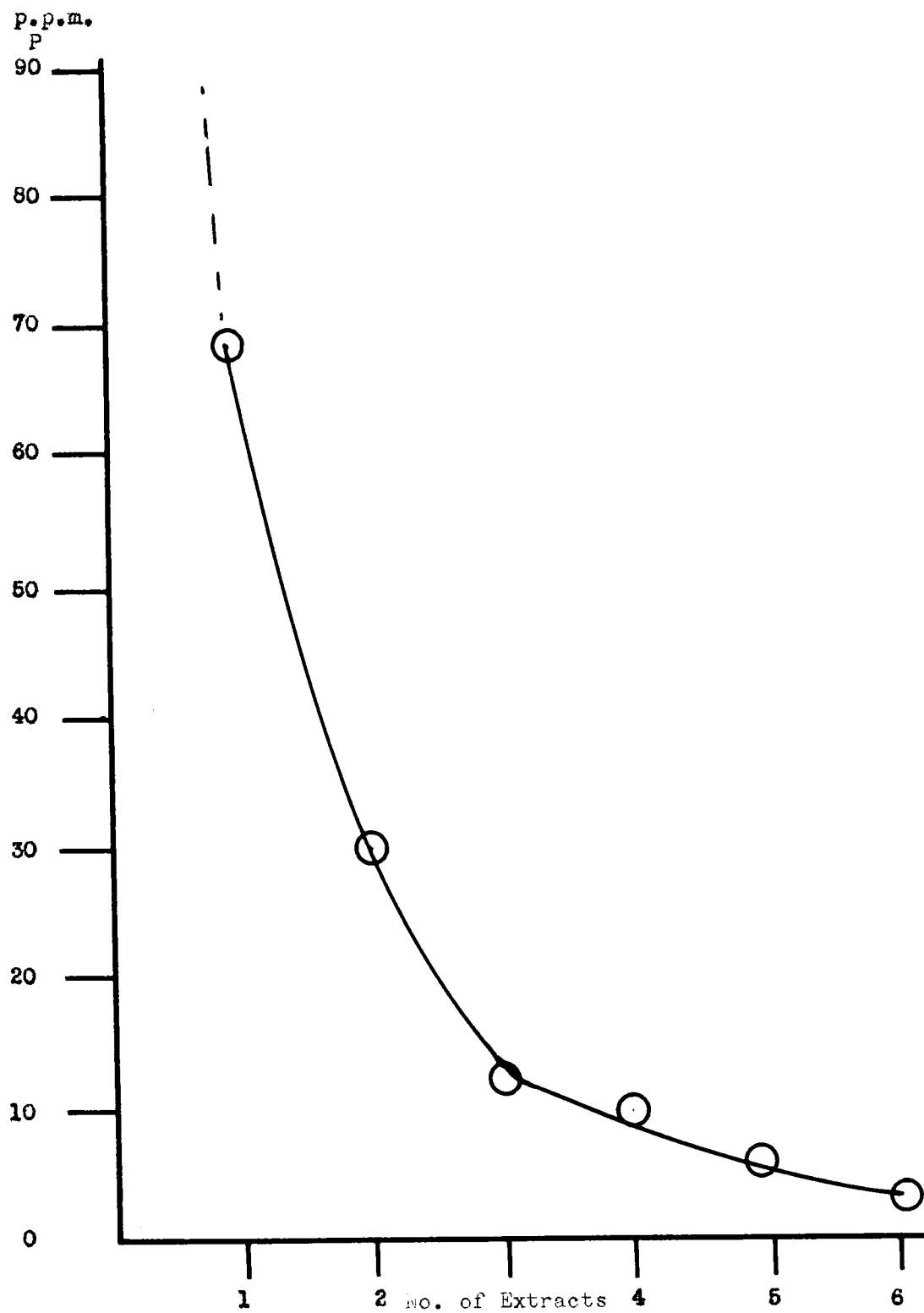


Figure 17 Soil # 6 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

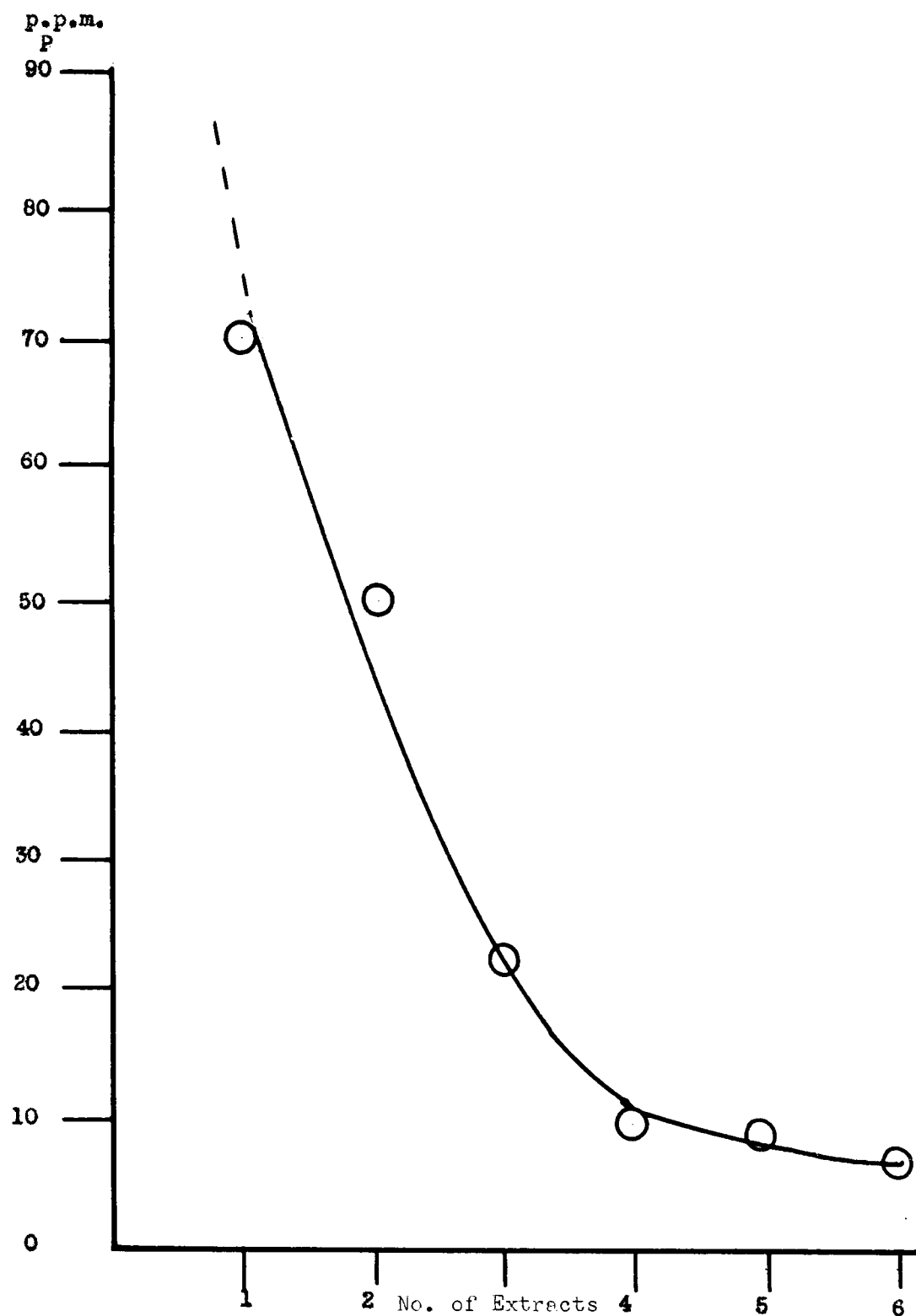


Figure 18 Soil # 7 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

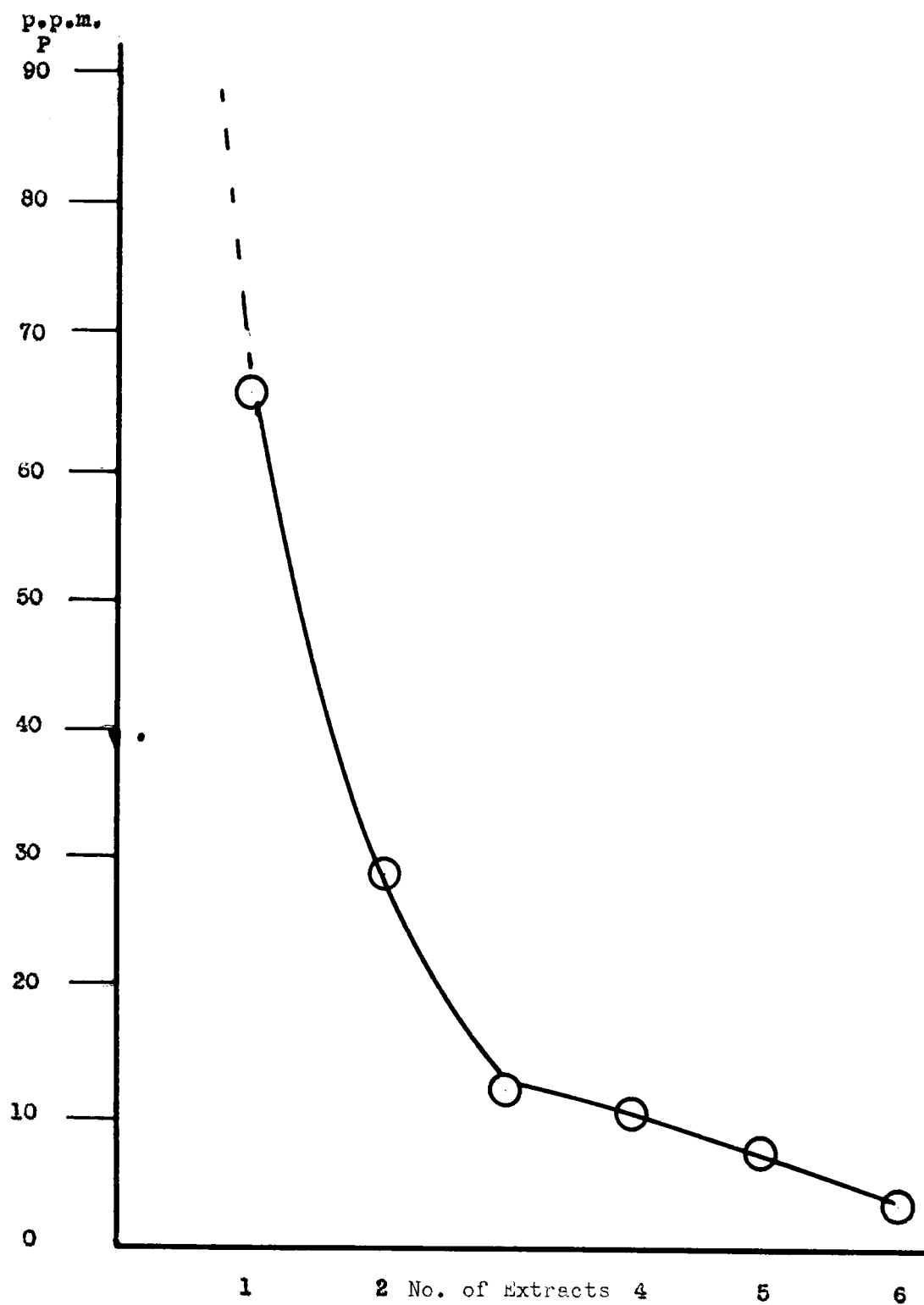


Figure 19 Soil # 8 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

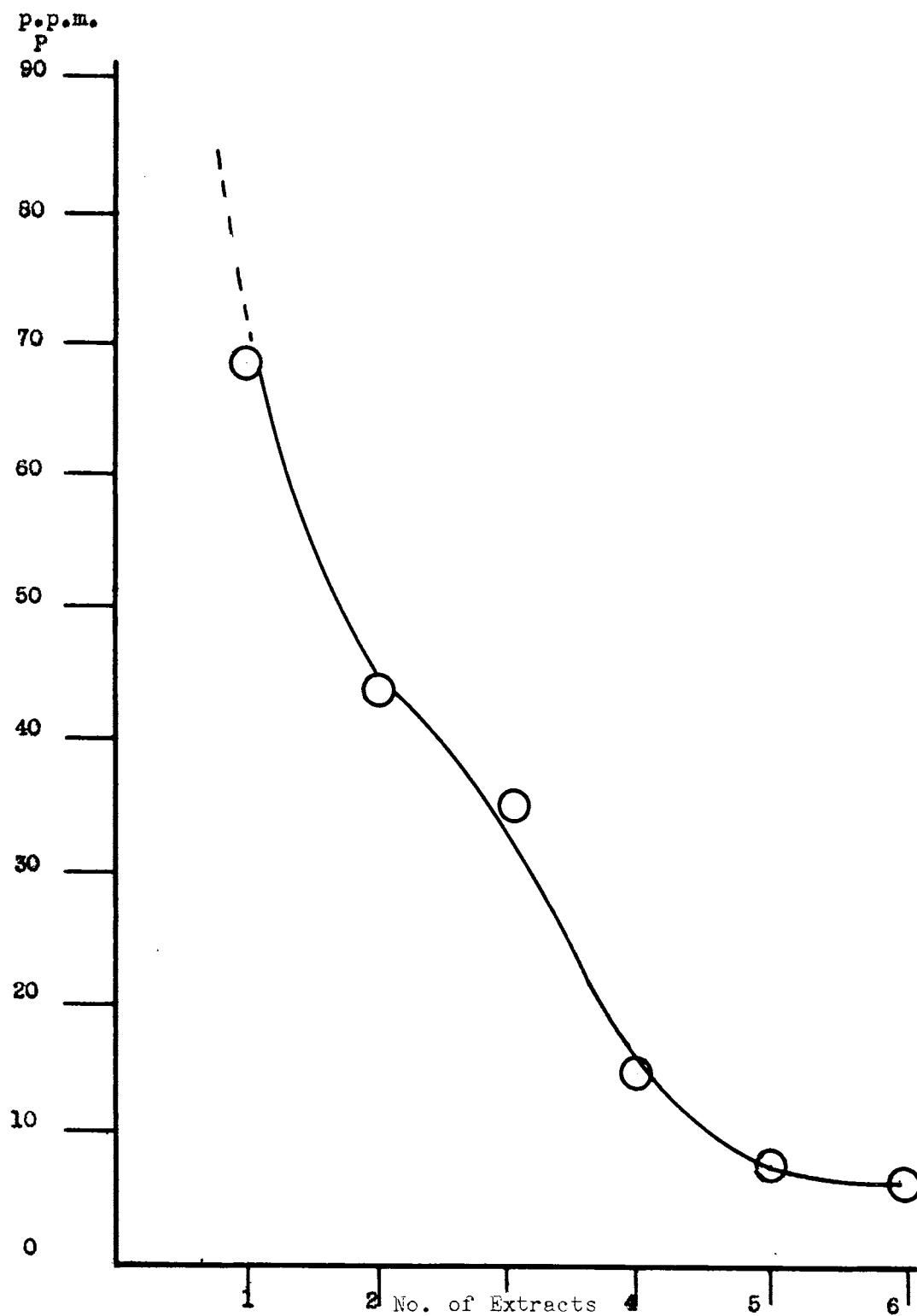


Figure 20 Soil # 9 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

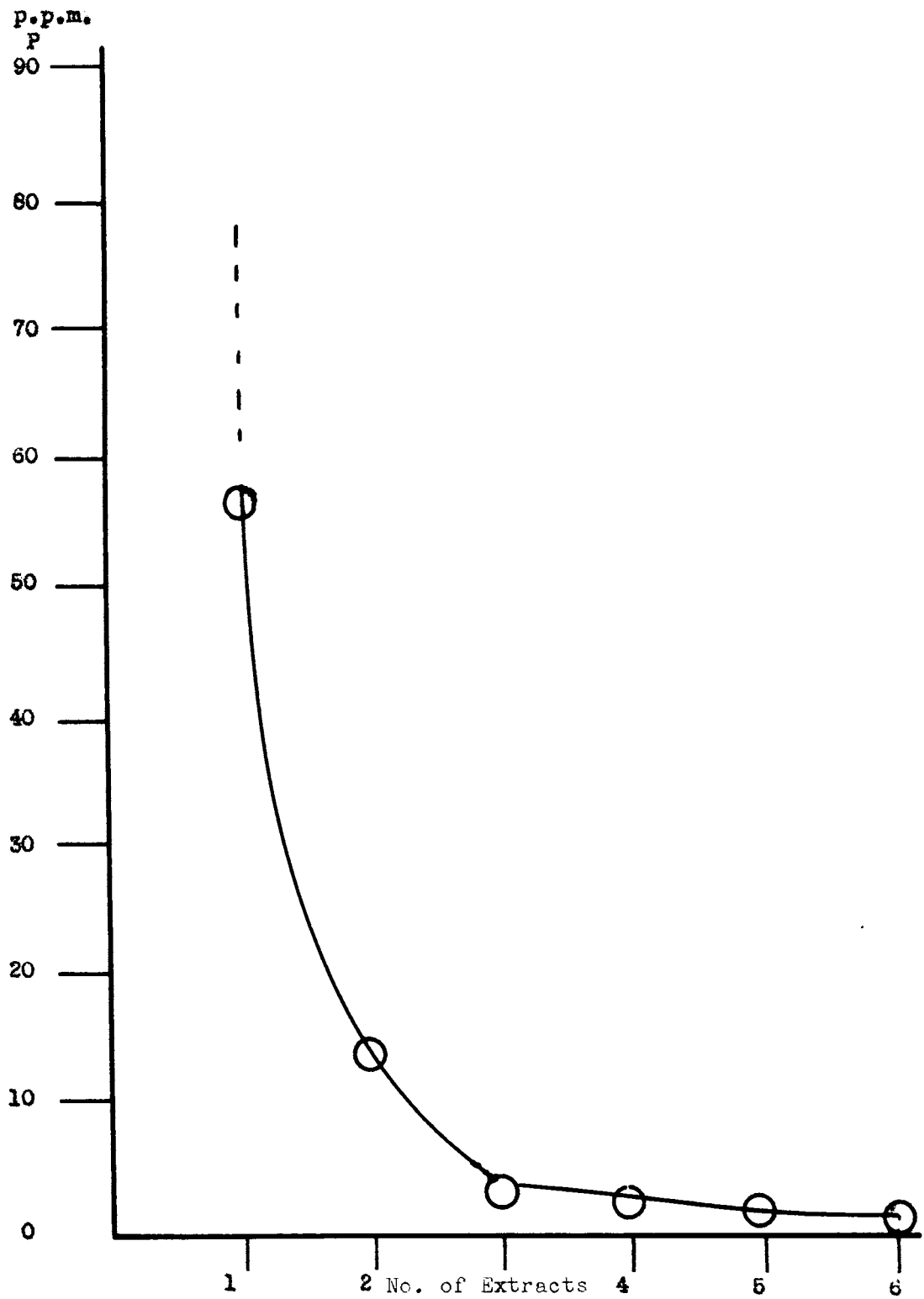


Figure 21 Soil # 10 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

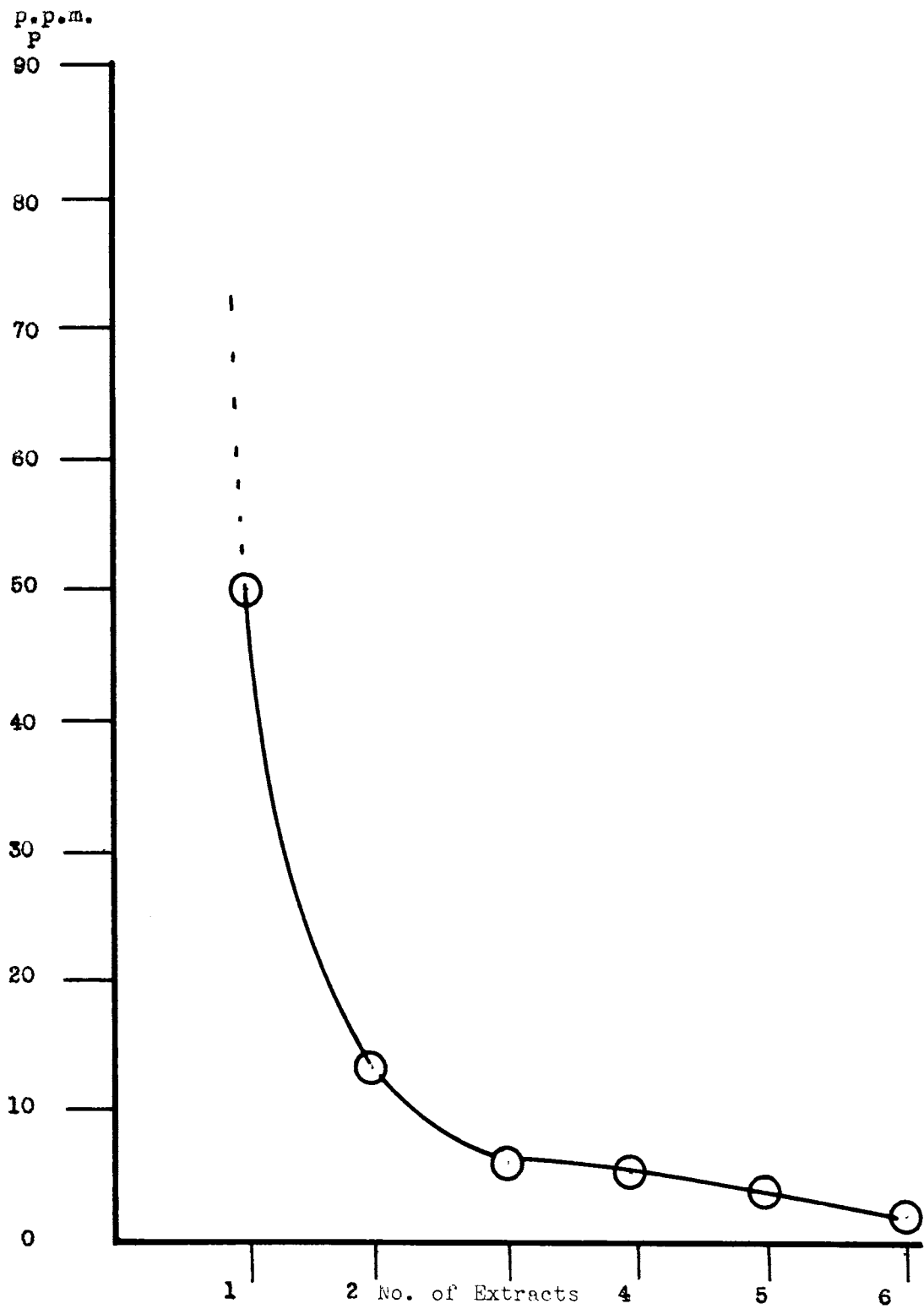


Figure 22 Soil # 11 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

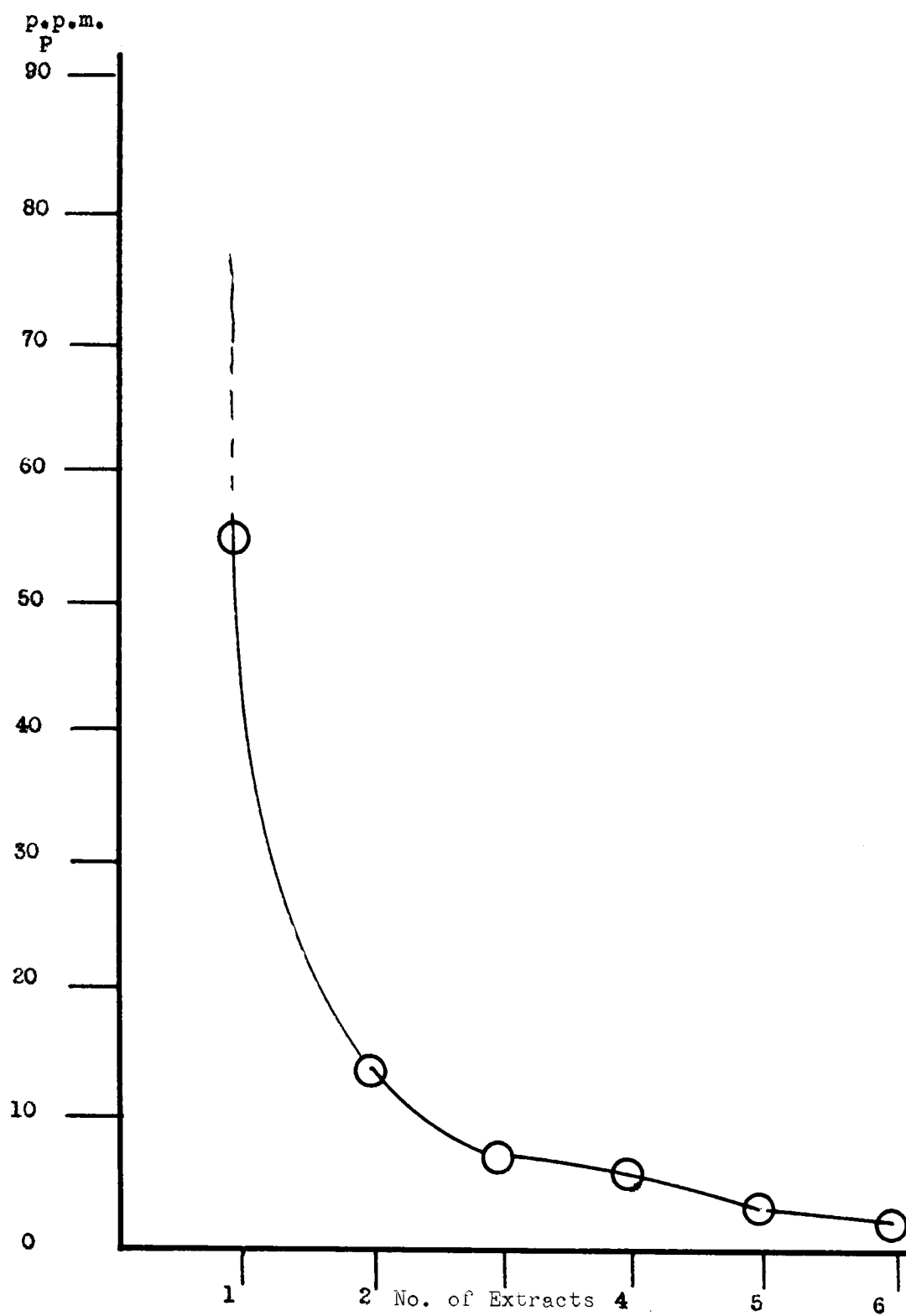


Figure 23 Soil # 12 Treated with KH_2PO_4 and extracted successively with 2 percent KCl

The phosphate was washed out rather quickly from these non-calcareous soils. This is probably due to the small amount of lime present. After most of the soluble phosphate has been removed by the successive washings the soils were extracted with 0.1 N NaOH, and the amount of phosphate present in the extract determined. This, according to Burd and Murphy (10), is the amount that is adsorbed or fixed by the colloidal particles, and corresponds to Burd and Murphy's "adsorption capacity". This adsorption capacity, along with the percent phosphate saturation of the original soil, is shown in table 3.

Table 3. Adsorption Capacity and Percent Saturation

Soil No.	Adsorption Capacity			Initial Percent Phosphate Saturated
	Mgm. P per 100 g. Soil	Pounds P per Acre 6 Inches	Pounds Treble Superphosphate per Acre 6 Inches	
1	15.0	300	1,526	7.5
2	20.0	400	2,035	2.6
3	8.8	176	897	20.3
4	50.5	1,000	5,087	0.8
5	11.5	230	1,170	9.7
6	14.4	288	1,424	3.9
7	16.4	328	1,668	2.7
8	14.4	288	1,456	2.9
9	15.0	300	1,526	4.1
10	14.0	280	1,424	12.2
11	48.6	972	4,945	0.9
12	70.7	1,414	7,193	1.5

Table 3 shows the maximum amount of phosphorus that would be adsorbed by the soil colloid that could not readily be washed out with water. However, most of this probably is available to plants (10), and is a very small amount in comparison with the maximum fixing capacity, table 2. According to Bradfield, Scarseth, and Steele (6)

the phosphorus adsorbed by a soil is small at a pH of 7.5 or above as compared to the amount that will be adsorbed at lower pH values, such as around a pH of 4 to 5. This is due to the fact that hydroxyl ions are highly adsorbed, so as the pH increases the phosphate ions adsorbed by the colloid are replaced by hydroxyl ions. Soils Nos. 11 and 12 are more acid than the others, and from table 3 it is seen that they have higher adsorption capacities than the other soils, except soil No. 4. The behavior of soil No. 4 is rather contradictory to Bard and Murphy's theory, and also to the theory of Bradfield, Searseath and Steele if we accept the idea that the phosphorus extracted by the alkaline solution comes from the soil colloid. Soil No. 4 is very high in both calcium carbonate and calcium sulfate and a better explanation of the large value for the alkaline extracted phosphate from this soil seems to be that considerable phosphate was present in a monocalcium or dicalcium precipitate.

Rate of Extraction.---The curves, figures 24 to 30, soil Nos. 1, 2, 3, 7, 9, 10, and 11, show the amount of phosphorus extracted from the phosphate-treated soils by successive leachings with K_2CO_3 . In preparing these curves it was assumed that tricalcium phosphate would be relatively insoluble in K_2CO_3 and that the phosphate extracted would consist of either the less basic calcium phosphates or of phosphates adsorbed by the colloid and, therefore, should give a measure of the sum of these two fractions. If the fixation is an adsorption phenomenon, the amount of phosphorus in solution should be proportional to the amount adsorbed and a smooth curve should result. On the other hand, if the fixation is a case of precipitation as a

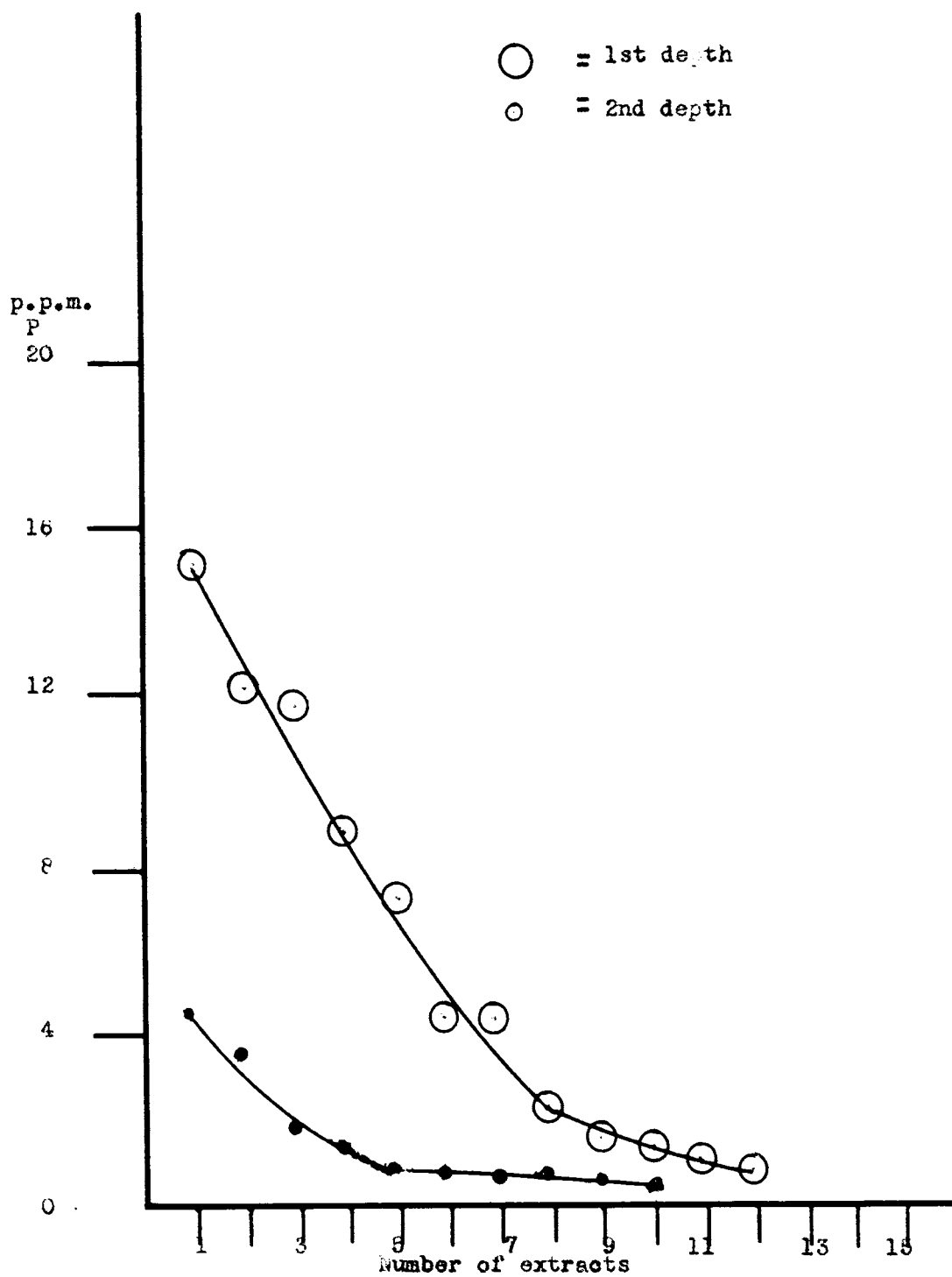


Fig. 24 Solubility of phosphates in successive extracts (K_2CO_3) of soil # 1 treated with KH_2PO_4

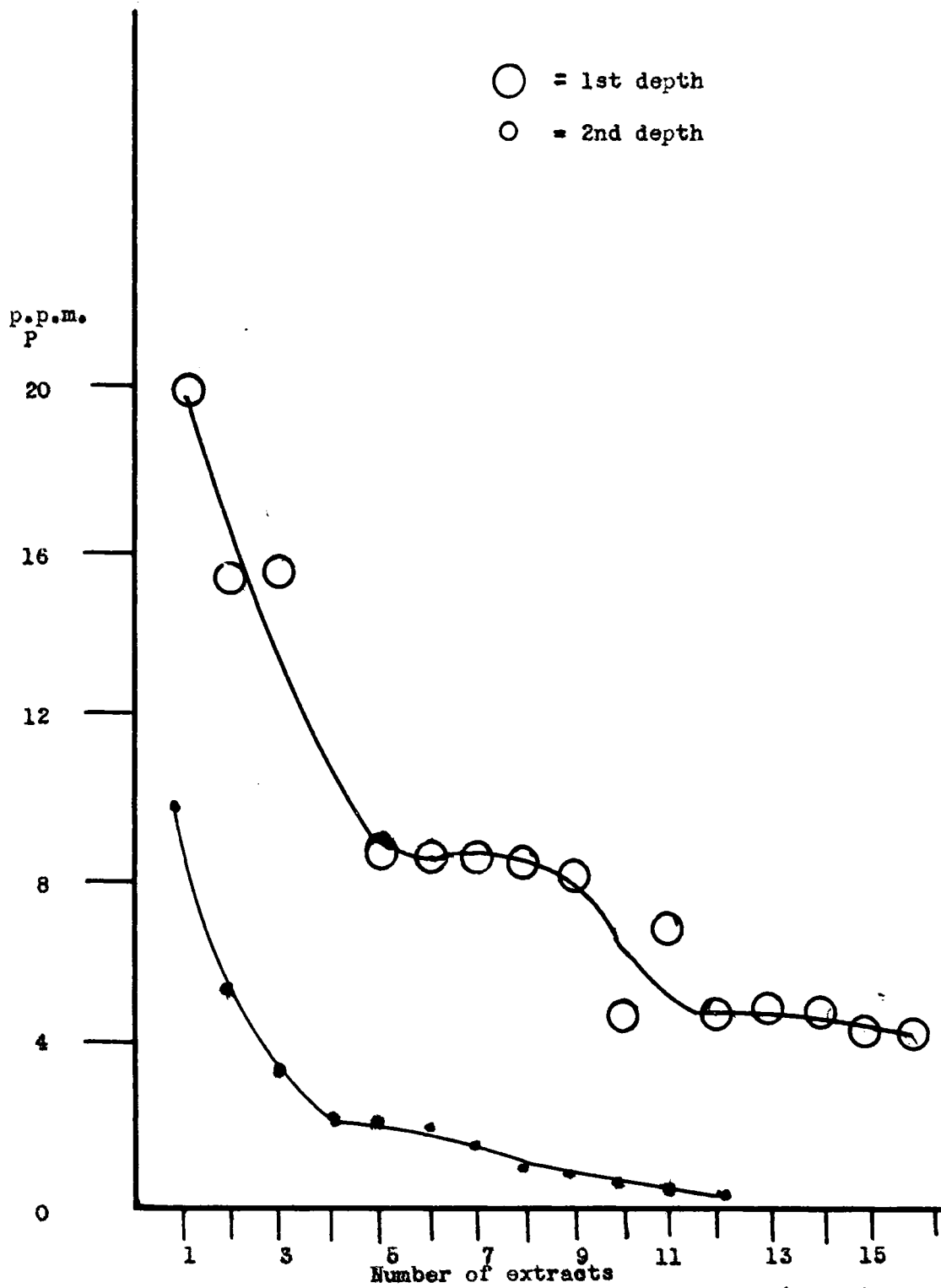


Fig. 25 Solubility of phosphates in successive extracts (K_2CO_3) of soil # 2 treated with KH_2PO_4

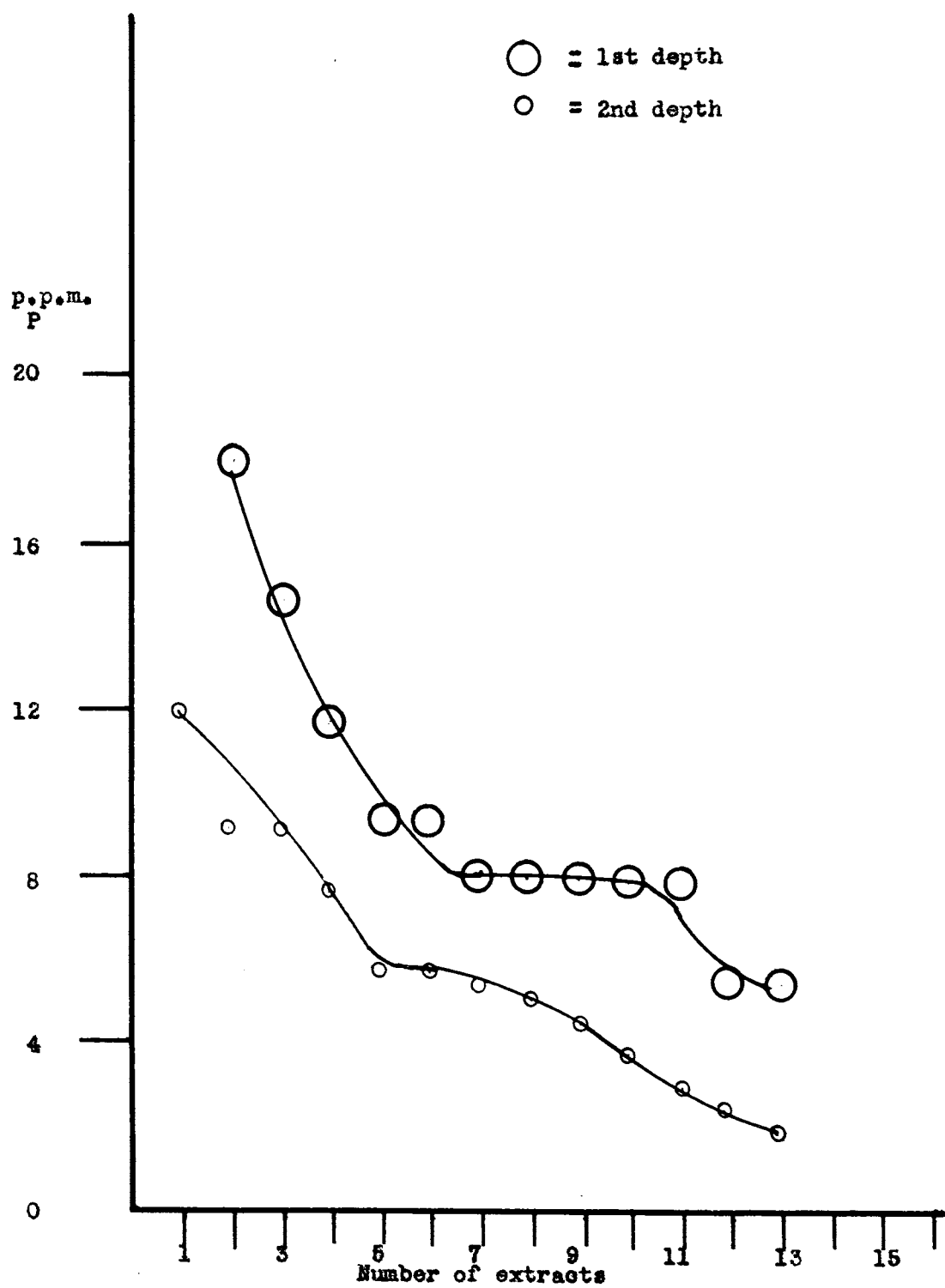


Fig. 26 Solubility of phosphates in successive extracts (K_2CO_3) of soil # 3 treated with KH_2PO_4

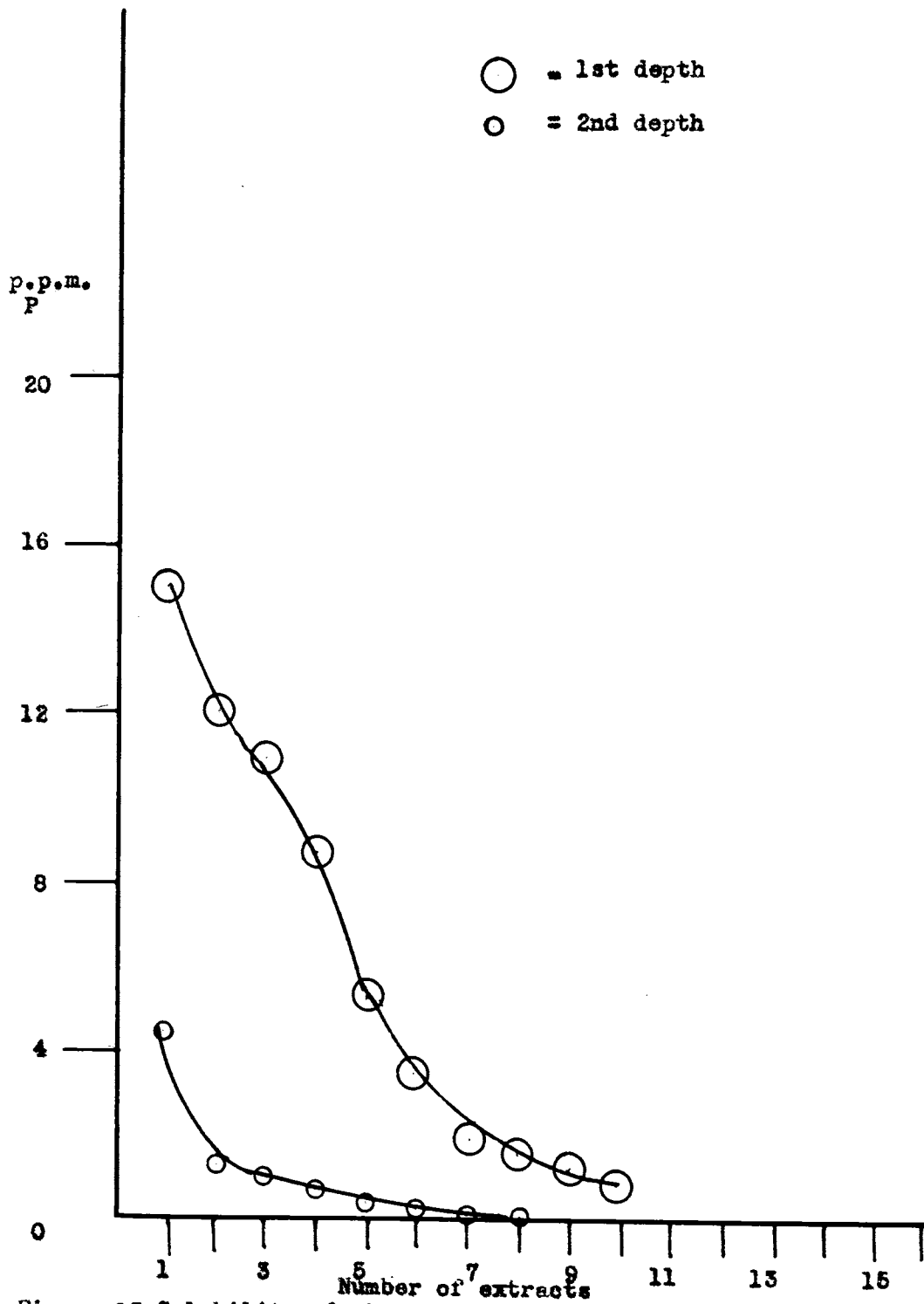


Figure 27 Solubility of phosphates in successive extracts (K_2CO_3) of soil # 7 treated with KH_2PO_4

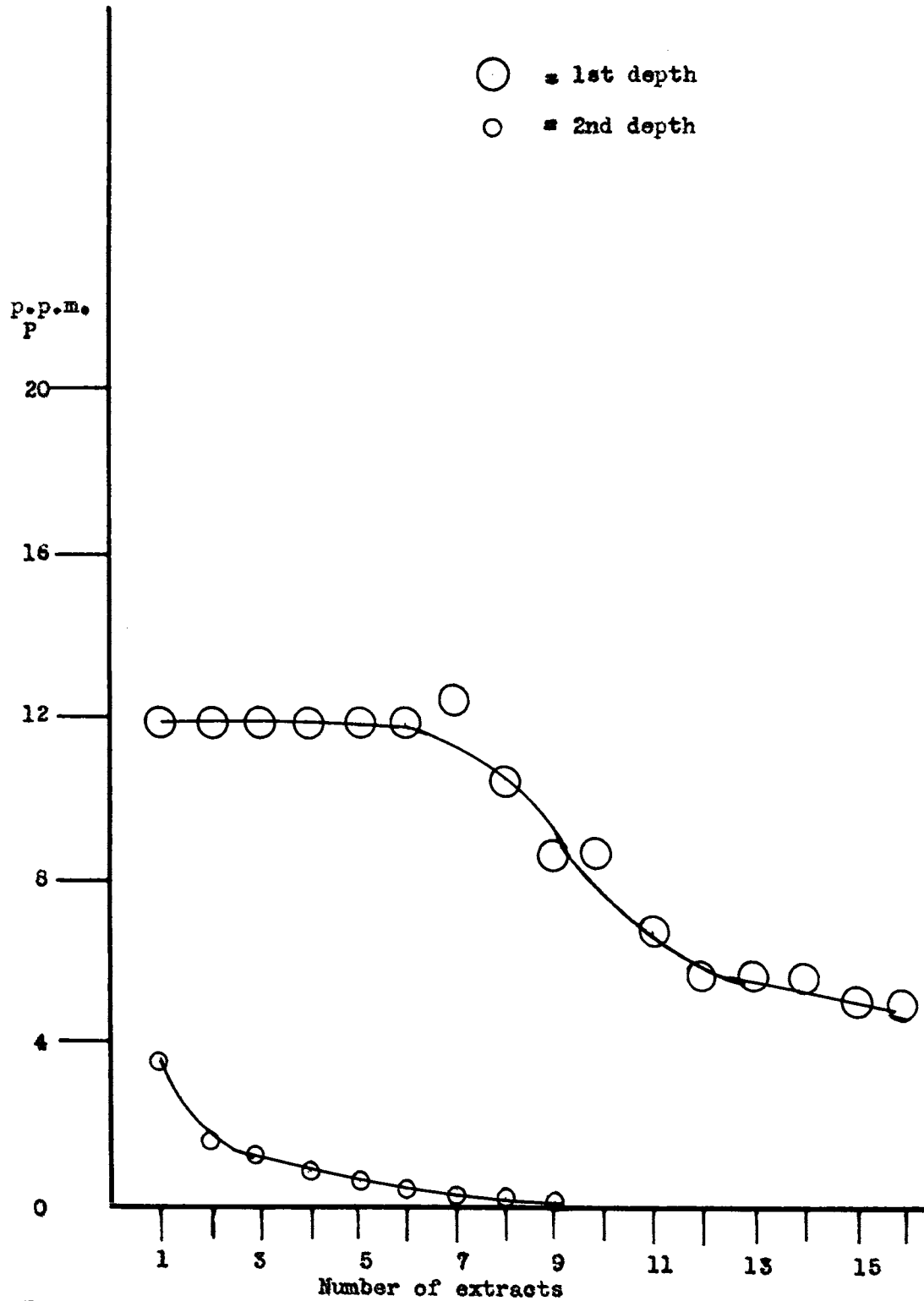


Figure 28 Solubility of phosphates in successive extracts (K_2CO_3) of soil # 9 treated with KH_2PO_4

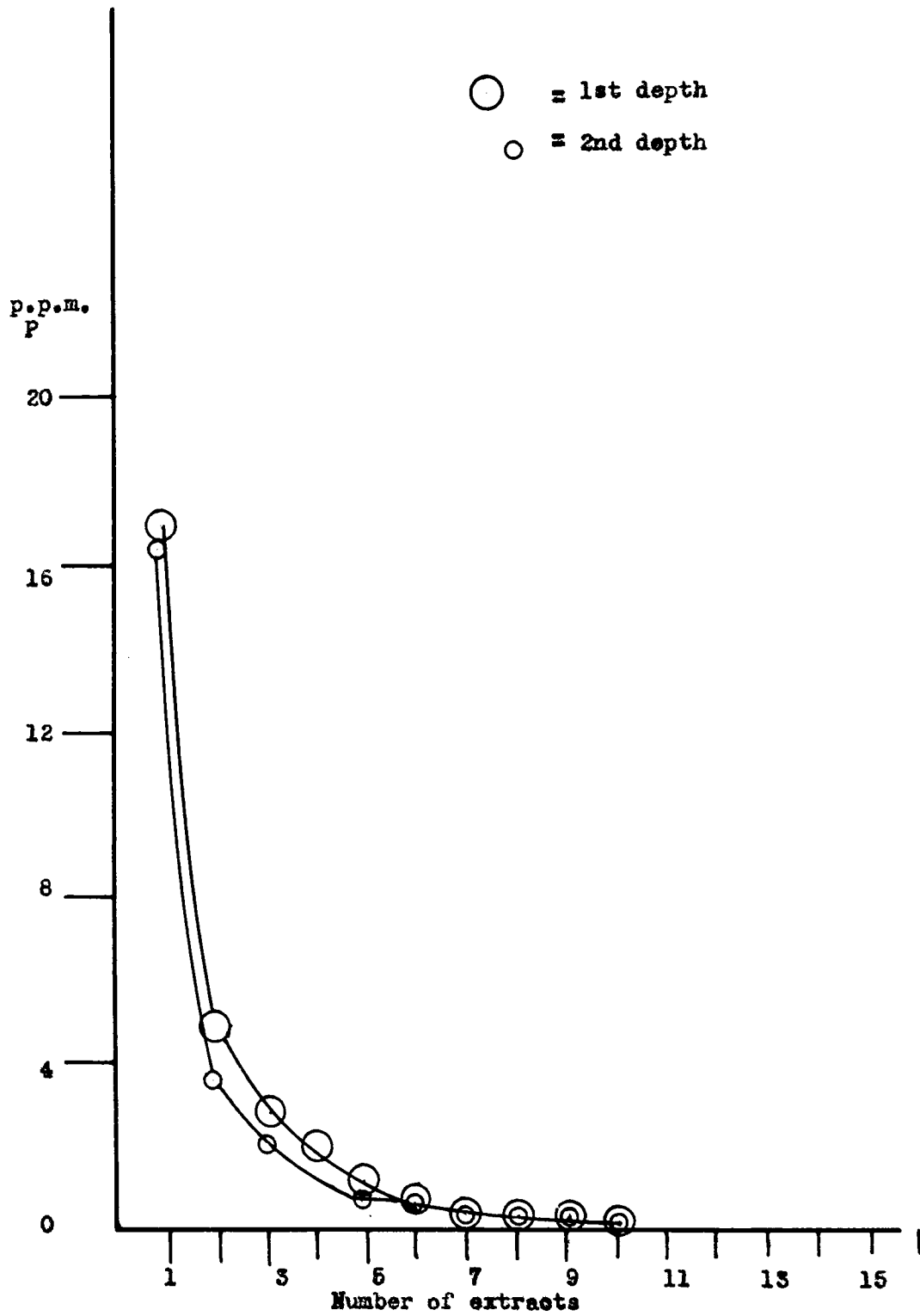


Figure 29 Solubility of Phosphates in successive extracts (K_2CO_3) of soil # 10 treated with KH_2PO_4

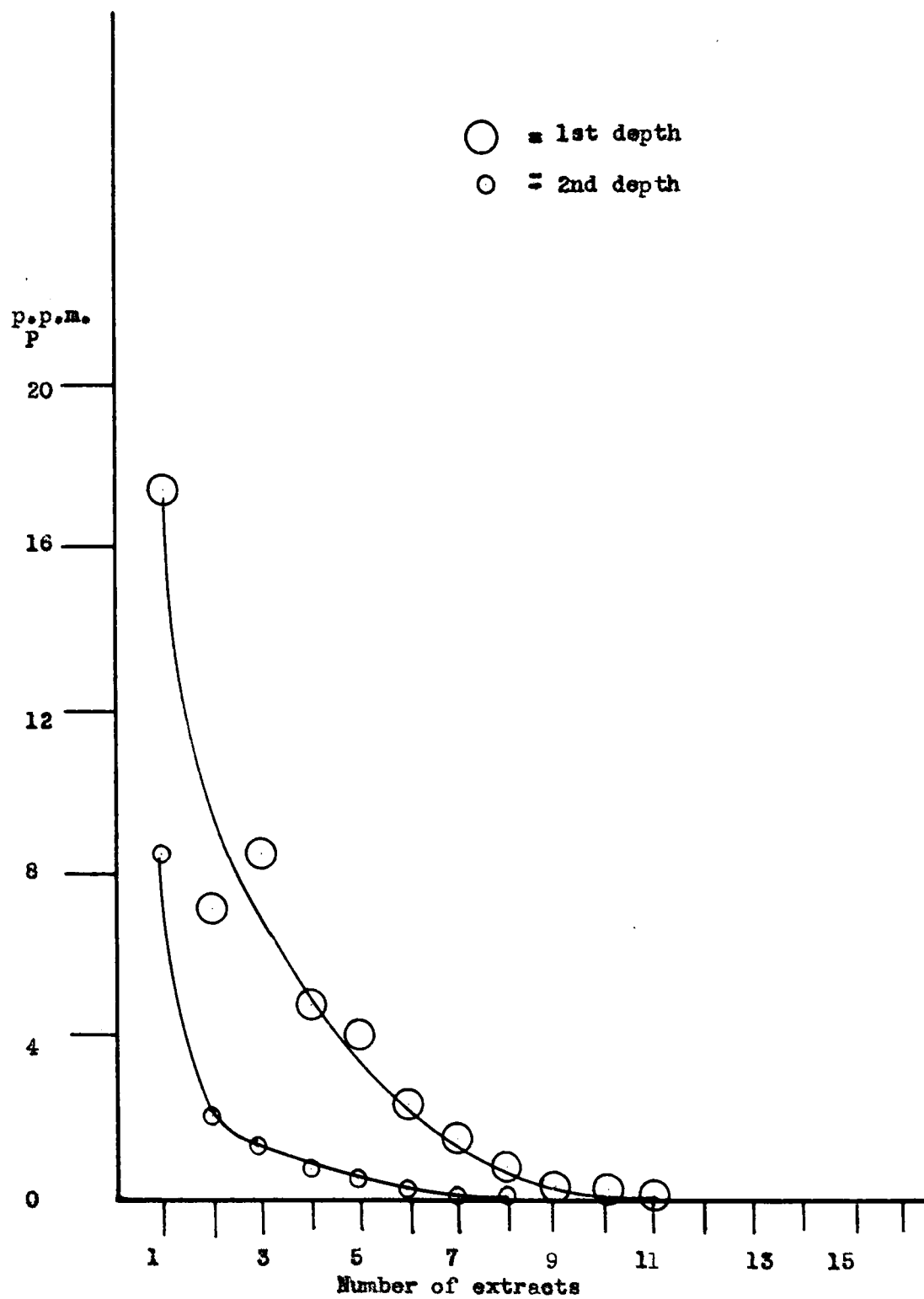


Figure 30 Solubility of Phosphates in successive extracts (K_2CO_3) of soil # 11 Treated with KH_2PO_4

slightly soluble compound or compounds, the amount in solution should depend upon the solubility of these compounds rather than upon the amount fixed and the resulting curve should show definite steps as each compound disappears.

The solubility of the phosphates in successive extracts of one percent K_2CO_3 are shown in figures 24 to 30. Table 4 shows the amount of phosphorus taken up by the soil, the amount recovered by all the extracts, and the percent recovery.

Table 4. Percent Recovery of Added Phosphate

Soil No.	Amount of P Taken Up mgm.	Amount of P Recovered mgm.	Percent Recovery	Percent $CaCO_3$
1	4.266	4.686	109.0	4.8
2	11.677	8.254	70.7	6.9
3	10.725	12.675	118.2	9.2
7	3.996	3.520	88.1	4.5
9	10.845	8.690	80.1	2.8
10	3.266	3.401	104.3	Less .1
11	3.480	3.680	105.7	Less .1

Figure 24, soil No. 1, indicates an adsorption curve until about the eighth extract, from which it appears to be a solubility phenomenon. The curves for soils Nos. 2, 3, and 9, figures 25, 26, and 28, indicate solubility phenomena, although figures 25 and 26 tend toward an adsorption curve for the first three or four extracts. These curves indicate that two definite compounds of different solubilities are formed, the more soluble compound being washed out in about nine to eleven extracts, some of the less soluble compound still being present after the last washing. The curve for soil No.

7, figure 27, tends to follow an adsorption curve, but not so close to one as Nos. 10 and 11, figures 29 and 30. Since these two soils are non-calcareous, it is not surprising that they tend to follow an adsorption curve. In all of these soils most of the added phosphate was recovered, as is indicated in table 4. In soils Nos. 10 and 11 the added phosphate was recovered rapidly, requiring only four to six washings.

It was thought that the fixed phosphate might be less available if the treated soils were allowed to stand longer or alternatively wet and dried. There was no difference noticed between the soils which were wet and dried and the soils that were kept at the moisture equivalent.

Conclusions

The results of these investigations lead to the following generalisations:

1. That most of the phosphates present in the calcareous soils are in the form of calcium phosphates with only negligible amounts of phosphorus present in combination with iron or aluminum, and a comparatively small amount adsorbed to the colloidal silicate. The predominating part of the calcium phosphate is evidently present in a slightly soluble tribasic form, with small amounts in the dibasic or monobasic form. The readily available portion evidently is from the phosphorus adsorbed to the colloid or from the phosphates less basic than in calcium phosphate. The non-calcareous soils studied also contain negligible quantities of iron and aluminum phos-

phates, but they contain appreciably higher quantities of adsorbed phosphates than the calcareous soils.

2. That when phosphates are added to the soil comparatively large quantities are fixed, i.e., taken out of solution. However, most of this can be removed by washing before the solubility becomes so low that plant growth would be restricted. As the added phosphate is leached a smooth curve is obtained for the non-calcareous soils, indicating that the fixation is largely a sorption phenomenon. In the calcareous soils the leaching of the added phosphate gives curves which follow solubility steps. This indicates that the phosphorus is largely in the form of relatively soluble precipitates.

Summary

In a study of the fixation of phosphorus and its availability to plants, the following investigations were made:

1. The solubility of phosphorus as a function of pH.
2. The pH at moisture equivalent under a carbon dioxide pressure of the laboratory air and the pH at moisture equivalent under 0.83 atmospheres of carbon dioxide.
3. The maximum phosphate fixing capacity of the soils.
4. The rate of extraction by successive leachings of the added phosphate.

From the above studies the following conclusions were drawn:

1. That calcium phosphates predominate in calcareous soils.

2. That in calcareous soils there is a very small amount of phosphorus adsorbed to the colloidal silicate, and that iron and aluminum phosphates are negligible.
3. That these soils fix large amounts of phosphorus but that it is readily available to plants.
4. That adsorption by the colloid apparently is much more important in non-calcareous soils.

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