FACTORS AFFECTING PHOSPHORUS

FIXATION IN SOILS

By

Winnard Bo McAlister

Bachelor of Science.

Oklahoma Agricultural and Mechanical College

1937

Submitted to the Department of Agronomy

Oklahoma Agricultural and Mechanical College

In partial fulfillment of the requirements

for the Degree of

MASTER OF SCIENCE

1938

Approved:

Horace J. Harper
In charge of Thesis

Horace J. Harper
Head of Department of Agronomy

D. C. McIntosh
Dean of Graduate School

ACKNOWLEDGMENTS

CONTENTS

FACTORS AFFECTING PHOSPHORUS
FIXATION IN SOILS

INTRODUCTION

Phosphorus fixation in soil is of considerable agronomic importance because it affects the utilization of soluble phosphorus fertilizers by plants. The determination of the readily available phosphorus in soil has been investigated by many soil chemists. It is a well known fact that soluble phosphates in fertilizers, when added to the soil, become relatively insoluble and only very small quantities are lost in drainage water. Soils may show a deficiency in soluble phosphorus although the total phosphorus in the soil is very high. On some soils phosphorus fertilizers are applied each year in amounts which are greater than the crop will remove from the soil that year. The residual effect on the following crop will depend upon the degree of fixation by the soil. There are many factors which affect the fixation of the phosphorus such as calcium, iron, and aluminum minerals; kind and amount of phosphorus applied; time, temperature, and concentration of solution; ratio of soil to solvent; the reaction of the soil, the organic matter content, the silicasesquioxide ratio and the exchange capacity.

The experiment was undertaken to develop a simple method for the determination of phosphorus fixation and to study some of the factors effecting the absorption of phosphorus by soil since a knowledge of fixation is necessary in the intelligent use of fertilizers with respect to amount, kind and most effective placement of the phosphate.

REVIEW OF LITERATURE

The form in which phosphates are fixed in the soil depends much upon the abundance of the different materials in that soil capable of fixing phosphorus. Heck (15) pointed out the fact that phosphate fixation in soils may be purely chemical, the phosphorus taking the form of slightly soluble mineral phosphates or it may be of a biological nature in which the phosphorus exists, first as living and later in the organic matter resulting from the death and partial decay of micro-organisms.

Phosphorus is fixed in the soil through reactions with active calcium, iron, or aluminum and these elements may be regarded as active when they unite chemically with the phosphorus. Active calcium may be present in the soil in the exchangeable form as calcium carbonate, or any soluble calcium salt. Active iron and aluminum are believed to exist in the soil largely in the forms of the hydrated oxides.

Heck (12, 14, and 15) further states that the fixation of phosphorus as iron or aluminum phosphates does not necessarily depend upon iron or aluminum in the soil solution, but rather upon the state of hydration of the oxides. If the iron oxide is fully hydrated the normal phosphate may be formed.

$$2\ Fe\ (OH)_3 + 2\ H_3PO_4 \rightleftharpoons 2\ FePO_4 + 6\ H_2O$$
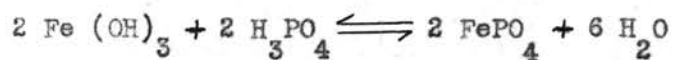
Ford (8) states that the dehydration of limonite by heating produced hematite, and this destroyed its fixing power, but limonite fixes phosphorus in a very stable form and is very reactive. The amount of limonite present in different soils is believed to vary greatly and it will persist in soils if it is once formed because soil temperatures are not high enough to dehydrate the limonite. Hibbard (16) also confirms the statement that

the fixing power of soils for phosphate correlates with the amount of hydrated iron oxide.

If the ratio of active calcium to active iron and aluminum is high the fixation will be more in the calcium form, but if the ratio of active iron and aluminum to calcium is high the fixation will be more in the iron and aluminum form. The calcium form is more soluble than those of iron or aluminum, and in general, the more soluble the phosphate used the more rapid is its rate of fixation.

Fraps (10) found that fixation occurs in the presence of 0.2 normal nitric acid, that this fixation is roughly proportional to the total iron and aluminum oxides, and that soils containing over ten per cent of these oxides absorbed over fifty per cent of the phosphorus added. He states that probably only a small percentage of the oxides of iron and aluminum in the soil have high fixing power.

Truog (27) states that, since phosphorus is fixed in soils to some extent in forms very difficultly available to plants and at least a portion of the phosphorus in the precipitated ferric and aluminum phosphates is available to plants, it seems that phosphorus must be fixed in the soil in forms less available than ordinary precipitated ferric and aluminum phosphates. Doughty (6 and 7) has shown that tri-calcium phosphate is formed at pH 7.0 and does not hydrolyze at a higher pH, but ferric and aluminum phosphates hydrolyze at a reaction range of pH 6.0 to 7.0, re-leasing phosphorus to the soil solution.

THE EFFECT OF HYDROGEN ION CONCENTRATION

The concentration of hydrogen ions in soil exerts a strong influence on phosphorus fixation since phosphates of calcium and magnesium are easily soluble below pH 7.0 but iron and aluminum phosphates are not

appreciably soluble above pH of 3.0. Hibbard (16) states that the iron and aluminum in soil colloids may fix phosphorus at pH values ranging from 3.0 to 8.0, but above pH 8.0 they may hydrolyze to form the soluble phosphate salt.

The condition of acidity or alkalinity of the soil is influenced by the nature of the reaction equilibrium that takes place between the phosphate ions and the soil bases. Beater (2) states that the effect of pH may not be looked upon as a dominant factor. A large excess of active iron and aluminum is believed to overshadow the influence of other factors in determining the products of the chemical action. Soils high in alkalinity usually contain calcium which reacts with the soluble phosphates. In acid soils calcium is low and the phosphorus combines with iron or aluminum. In general it may be said then that fixation in acid soils is of a more permanent nature than that in alkaline soils. The order of stability of the three compounds, $Ca_3(PO_4)_2$, $FePO_4$, and $AlPO_4$ varies directly with the pH value.

Pugh (20) states that calcium phosphate is insoluble within a pH range from neutral to strongly alkaline, while Brown (3) found that there was a far greater amount of available phosphorus at pH 7.9 than at any other reaction and explains this by the low solubility of iron and aluminum and the little free calcium at this reaction. Heck (12) quotes Gaarder's finding that calcium phosphate is least soluble at pH 6.5. Daughty (6) states that although the formation of iron, aluminum, and calcium phosphates will account for the fixation of phosphorus above pH 2.0 there is considerable fixation below this point. However, he does not explain the mechanism of this fixation.

Ravikovich (21 and 22) in comparing the fixing power of hydrogen soils and calcium soils found that, in all the established forms of ad-

sorption for hydrogen soils, the amount of adsorbed phosphorus changes as the pH value of the solution changes but the changes in pH between slight acidity and high alkalinity exerts no influence on the phosphorus adsorbed by soils saturated or unsaturated with calcium, to a certain degree; or by soils in which the amount of exchangeable calcium exceeds the exchange capacity of the soil established at pH 7.0.

Organic matter in soil as shown by Oberhalzer (19), and Gile (11) does not affect the availability of phosphates to any appreciable extent over and above its own phosphorus content. Daughty (7) concludes that soil organic matter as such has only a minor role, if any, in the fixation of phosphorus in difficultly available form when soluble phosphate fertilizers are applied to the soil. Bauer (1) on the other hand found that decaying organic matter produced a solvent action upon rock phosphate and this he believed was due to the action of the organic acids produced in the decomposition of organic matter. Ravikovich (21) states that the hydrogen and calcium organic exchange complexes possess practically no properties of phosphate fixation.

Soil colloids, according to Gile (11), cause phosphorus fixation. The effects of soil colloid on superphosphates seems to depend on several factors, namely the degree to which the colloidal material is staurated with phosphoric acid, the silica-sesquioxide ratio of the colloid; the effect of the colloid on the hydrogen-ion concentration of the medium and the content of organic matter. The efficiency of phosphorus fixation may be somewhat imperfect in some soils due to the contamination of the non-colloidal fraction with copper or other heavy metals that might be in the soil. The effect of the phosphate fixation in surface and sub-surface soils correlates fairly well with the silica-sesquioxide ratio of the colloids present. Soils containing colloids with a high silica-

sesquioxide ratio have low fixing power while those soils containing colloids with low silica-sesquioxide ratios have high phosphorus fixation. Gile (11) also states that the precipitation of ions from solution may play a part in the depressing effect of some colloids. Probably most of the effect is due to combination of the PO_4 ions with the iron and aluminum in the exposed surface of the soil colloids.

Scarseth and Tidmore (24) also found that the fixing power of soil colloids varies inversely as the $\frac{SiO_2}{R_2O_3}$ ratio of the colloid. They state that the pH of colloids varies directly with the base exchange capacity of the colloid.

Ravikovitch (21 and 22) in his work deals with phosphorus fixation, not from the chemical side, but from the field of physico-chemical reactions. He has established that the adsorption of phosphate ions proceeds on the basis of an equivalent exchange with the exchangeable anions of the soil complex. The adsorbed phosphate ions may reappear in the solution when they come in contact with other anions, and the liberation of the phosphate ions should proceed on the same principal of anion exchange which took place when these ions entered the complex. The hydroxyl ions are the most effective anions in phosphate replacement. In his experiment the existence of the different forms of adsorption is connected with the phenomenon of adsorption of phosphate ions with other ions of equivalent valences. In other words the adsorption of phosphorus by the soil complex proceeds on the principle of an equivalent anion exchange. The amount of adsorption depends on the anion exchange capacity of the soil complex, which is equal to the base exchange capacity, and on the valence of the phosphate ions which take part in the adsorption.

Davis (5) states that the absorption of the phosphate by the soil minerals and the formation of equilibrium complexes take place in soils

artificially depleted of exchangeable bases, thus eliminating the possibility of cations of soluble salts present in the soil, or cations replaced from the soil by those present in the solution, forming precipitates with the phosphate ions.

Heck (13) states that soils from which exchangeable bases had been removed fixed more phosphates in the difficultly available form than did soils containing exchangeable bases and that the increase was somewhat proportional to the exchangeable bases removed. Conversely, increased exchange capacity tends to decrease phosphate fixation provided that the proper degree of base saturation is maintained.

Fraps (10) shows that temperature had little effect upon the fixation of phosphates in some soils, but it had a very decided effect upon the fixation of phosphorus in others. He also states that ignition of soil increases the fixing power in many cases. This, he explained, may be due to the heat converting part of the carbonate of lime to calcium oxide which would unite more readily with phosphoric acid, or it may be in part probably due to changes in the activity of the iron and aluminum compounds.

The effect of time upon the absorption of phosphates increases with the duration of contact, but generally, the greatest percentage of phosphorus is fixed in twenty-four hours after it is placed in the soil. There is a tendency toward more complete fixation in the soil as the time of contact increases. All of the phosphorus should be fixed if given sufficient time, provided there is enough fixing material in the soil to react with all of the phosphorus. Hibbard (16) states that clay soils fix within a year all of the phosphorus added, whereas in a 1:1 soil-water mixture most of the fixation takes place in one hour. Scarseth and Tidmore (23) state that when very soluble phosphates, such as mono-ammonium or mono-calcium phosphates, are added to an acid soil, the fixation of

phosphate ions takes place as rapidly as the phosphate is diffused throughout the soil and comes in contact with the colloids. The rate of fixation is considerably influenced by the ratio of soil to solution. Brown (3) showed that biennial surface applications of superphosphate penetrate not more than two or three inches and perhaps much less in sixteen years. Phosphate fixation under natural conditions is a time reaction and may proceed rapidly in some soils and slowly in others, but generally under normal field conditions equilibrium is established in one to twelve months.

A review of the procedures for studying phosphorus fixation in soil as suggested by Gile (11) in which he compares the growth made by millet in pure quartz sand to the growth made in sand to which sufficient soil was added to supply 1 per cent of colloidal material; the method suggested by Fraps (9 and 10) in which he uses 50 grams of soil in contact with 200 cc. weak phosphate solution in a dry bottle which was well stoppered. The suspension was shaken every half hour during the working day and filtered at the end of 24 hours. The method of analysis was as follows: add 8 cc. of nitric acid to 100 cc. of filtrate; neutralize with ammonia, acidify slightly with nitric acid, evaporate to about 75 cc., filter and wash if necessary and determine phosphoric acid by the volumetric method. Heck (15) leached small amounts of soil with .002 normal sulfuric acid at the rate of 25 cc. an hour. Beaters (2) treated the soil with citric acid and evaporated the solution to dryness in order to destroy the citric acid before the phosphorus can be determined in the residue. These methods are all empirical and no one method has been generally or officially accepted as the best method to use in determining degree of phosphorus fixation in soil. What is wanted is a method that will give reliable and reproducible results with least expense of time, labor, money, and

equipment, and a method that will correlate as closely as possible with the extraction of phosphorus by plants. Laboratory procedures treat the soil in a manner not possible in nature consequently such factors as availability can only be determined by the analysis of soils taken from areas where fertilizer tests have been conducted and a known response has been secured.

EXPERIMENTAL RESULTS

The procedure worked out for this study is simple, convenient, and rapid. It consists of adding 0.1 mgm. of P. as di ammonium phosphate to ten grams of soil and allowing the liquid to evaporate at room temperature. The temperature should range between 27 - 30 degrees centigrade to secure rapid evaporation of the water. The rate of evaporation can also be hastened by passing an air current over the soil by means of an electric fan. In this experiment the time of drying 10 ml. of water from 10 grams of soil varied from twenty four to forty eight hours. The texture of the soil also is a factor in determining the time of evaporation. After the soil is dry it is pulverized and placed in a leaching tube and leached with 200 ml. of 0.1 normal acetic acid. The phosphorus in the filtrate is determined by the Deniges molybdenum blue method and the quanity fixed is determined by substracting the amount in the filtrate from the total amount of phosphorus present in the solution which was added to the soil.

Soils differ greatly in their fixing power. High fixation may be expected in clay soils whereas in sandy soils the fixation is usually somewhat limited.

The soils used in the present experiment were taken from official soil survey samples selected from different parts of the state of Oklahoma. Table 1 gives the general character of the soils used in the fixation experiments. Most of these soils are deficient in available phosphorus as determined by the 0.2 normal sulfuric acid method and the total phosphorus content was also relatively low.

These samples were treated by the following method to study phosphorus fixation. Ten grams of air dry soil was placed in a 100 cc. beaker and

Table 1. Physical and chemical characteristics of soils used in the phosphorus fixation experiment.

Soil No.	Counties where samples were collected	Depth samples were taken	pH of soil	per cent sand	per cent silt	per cent clay	per cent organic matter	Total P. lbs. per acre	Available Phosphorus P. P. M.*
1721	Murray	Surface	7.10	29.84	45.00	25.16	3.22	405	18
1722	Murray	Subsurface	6.73	18.20	49.36	32.44	2.48	325	0
1723	Murray	Surface	6.58	50.00	31.56	18.44	1.37	285	2
1724	Murray	Subsurface	6.11	37.56	32.60	29.84	2.10	320	0
1725	Murray	Surface	7.52	17.84	68.18	20.62	1.73	295	18
1726	Murray	Subsurface	5.90	22.20	47.60	31.20	1.32	270	0
1727	Murray	Surface	6.86	29.20	53.40	17.40	3.08	275	7
1728	Murray	Subsurface	7.20	28.80	46.20	25.00	1.32	260	3
1641	Choctaw	Surface	6.21	19.35	59.25	21.40	2.47	375	6
1642	Choctaw	Subsurface	5.33	19.35	54.25	26.40	1.21	265	2
1643	Choctaw	Surface	7.95	21.20	37.12	41.60	.81	130	6
1644	Choctaw	Subsurface	6.49	24.20	44.40	31.40	.31	95	1
1645	Choctaw	Surface	8.31	11.96	49.12	38.92	3.40	715	36
1646	Choctaw	Subsurface	8.12	7.96	33.12	58.92	3.57	595	18
1647	Choctaw	Surface	7.72	33.96	49.12	16.92	1.38	245	10
1648	Choctaw	Subsurface	5.83	41.96	39.72	18.32	.39	150	6
1649	Choctaw	Surface	6.77	41.32	35.36	23.32	2.37	395	22
1650	Choctaw	Subsurface	6.37	54.96	22.72	22.32	1.70	260	6
2693	Greer	1½" - 10"	7.45	23.32	55.76	20.92	2.32	620	48
2695	Greer	22" - 36"	8.02	19.32	53.64	27.04	1.34	580	36
2696	Greer	36"	8.56	21.24	47.36	31.40	1.18	480	32
2710	Greer	0" - 12"	7.16	71.46	15.50	13.04	0.83	300	8
2711	Greer	12" - 22"	7.40	66.96	13.40	19.90	1.92	340	0
2714	Greer	0" - 12"	7.45	75.96	11.00	13.04	1.00	160	20
2719	Greer	12" - 28"	7.44	75.24	9.56	15.40	0.53	160	4

* Phosphorus soluble in a 1 to 10 extract of 0.2 normal sulfuric acid.

Table 1
(Continued)

Soil No.	Counties where samples were collected	Depth samples were taken	pH of soil	per cent sand	per cent silt	per cent clay	per cent organic matter	Total P. lbs. per acre	Available Phosphorus P. P. M. *
2720	Greer	28" - 50"	7.03	69	2.0	29.00	0.40	200	0
2446	Craig	0 - 1	8.02	49	32.0	19.00	4.18	1028	20
2448	Craig	6 - 13	6.67	22.5	49.0	28.50	0.80	732	0
2452	Craig	0 - 11	5.46	52.4	28.36	19.24	4.08	892	2

* Phosphorus soluble in a 1 to 10 extract of 0.2 normal sulfuric acid.

10 cc. of solution containing 0.1 mgm. of P. as di ammonium phosphate per cc. was added to each soil. At the same time 10 grams of each soil was treated with 10 cc. of distilled water. These soils were dried at different temperatures as follows: room temperature, which ranged from 27 - 30 degrees C., 45, 80 and 110 degrees centigrade for a period of 24 and 48 hours. The phosphorus was extracted from these soils with 100 ml. of 0.01 normal sulfuric acid which was agitating about every 5 minutes for 1 hour. The soil suspension was filtered and an aliquot of the clear solution was taken and phosphorus determined by Deniges molybdenum blue method as modified by Truog (26).

In order to compare the extraction method with the leaching method, 5 grams of soil were placed in leaching tubes and leached with 200 ml. of 0.01 normal sulfuric acid solution. A similiar quantity of soil was extracted for one hour with frequent agitation and the results of leaching and shaking on the removal of easily soluble phosphorus from surface and subsurface soils are given in table 2. These results agree with those obtained by Fraps (9) which show that phosphorus fixation occurs in the presence of 0.01 normal sulfuric acid. They also show that the shaking method does not remove as much of the added phosphorus as the leaching method. When a soil is leached a fresh solution is constantly coming in contact with the soil and the soluble phosphorus is carried away thus preventing reprecipitation. It is usually true that the readily available phosphates go into solution rapidly. At the end of one hour all of the readily available phosphorus has been dissolved except in those soils high in this nutrient.

The effect of temperature on the absorption of phosphorus was studied by the leaching method as described above. A solution of di ammonium phosphate was added to each sample and the soils were subjected

Table 2. Efficiency of shaking as compared with leaching on the removal of available phosphorus from soil. The results are given in parts per million.

Soil No.	Treatment	Method of Treatment					
		Shaking			Leaching		
		Incubation Temperatures					
		45°C.	80°C.	110°C.	45°C.	80°C.	110°C.
1	1 hour	32.0	34.0	40.0	38.05	40.7	48.1
1	24 hours	23.1	30.40	64.95	58.95	62.65	86.65
1	48 hours	25.2	26.25	27.95	60.0	64.1	93.40
2	1 hour	36.0	37.3	42.6	43.25	45.4	49.8
2	24 hours	49.8	51.5	53.6	60.0	46.66	72.6
2	48 hours	51.8	55.9	58.8	66.6	70.83	81.45
3	1 hour	4.4	4.6	4.4	4.4	4.8	6.8
3	24 hours	8	9.6	11.8	6.7	6.85	7.0
3	48 hours	5.6	6.0	8.0	6.8	6.4	10.6

Table 3. Effect of Temperature on the Percentage of Phosphorus Adsorbed from a Solution of Di Ammonium Phosphate. The results are given in parts per million.

| Soil No. | Treatment | Incubation Temperatures | | | |
		27°C	45°C	80°C	110°C
1	Surface heated 1 hr.	32.0	32.0	34.0	40.0
1	Surface heated 24 hrs.	20.0	23.1	30.4	64.95
1	Surface heated 48 hrs.	24.0	25.2	26.25	27.95
2	Surface heated 1 hr.	35.2	36.0	37.3	42.6
2	Surface heated 24 hrs.	48.2	49.8	51.5	53.6
2	Surface heated 48 hrs.	50.0	51.8	55.9	58.8
3	Subsurface heated 1 hr.	4.4	4.4	4.6	4.4
3	Subsurface heated 24 hrs.	8	8	9.6	11.8
3	Subsurface heated 48 hrs.	5.6	5.6	6.0	8.0

to the various temperatures, 27, 45, 80, and 110 degrees centigrade.
The results are given in Table 3. It was found that heating does not
uniformly affect phosphorus fixation in soil. An increase in temperature
from 45 to 80 to 110 degrees centigrade affects the percent fixed in each
case. The number of samples studies was too limited to draw any definite
conclusions, however it would appear that heating is not important as far
as fixation is concerned under field conditions.

The percentage of absorption of phosphorus by soil was increased
with the time of contact and there is a tendency towards more complete
absorption as the time of contact increases as shown in Table 3. The
greatest percentage of soluble phosphorus in most cases is fixed in the
first twenty four hours after it is placed in the soil. This is in
accordance with the findings of Fraps (9), Scarseth and Tidmore (23)
and Hibbard (16).

Repeated wetting followed by drying is thought to render soil
phosphates more insoluble. Results of an experiment to test this theory
are given in Table 4. Duplicate samples of soil No. 1 and 4 were dried
in an oven at 45, 80, and 110 degrees centigrade for a period of 48 and
168 hours. Di ammonium phosphate was added in solution to these soils
before placing them in the oven. One of the samples remained in a dry
condition after the liquid evaporated and distilled water was added to
the duplicate sample every day. An increase in the fixing power of these
soils for phosphate occurred in all comparisons except one when the samples
which were moistened each day were composed with the dry samples.

Ford (8) and Heck (12, 14 and 15) find that phosphates are fixed as
iron and aluminum phosphates. A study was made of the soluble iron in
the soil by the KSCN method (31) to find if there were any correlation

Table 4. Effect of Repeated Wetting and Drying on Fixation of Phosphorus Added to Soil.

Soil No.	Treatment of soil samples.	Incubation	Temperatures	
		45°C	80°C	110°C
		Parts per million of P. recovered.		
1	Dry soil heated 48 hrs.	103.3	116.4	104.6
1	Dry soil heated 168 hrs.	119.23	100.0	109.9
1	Wet soil heated 48 hrs.	82.7	87.3	97.1
1	Wet soil heated 168 hrs.	116.4	80.0	123.3
4	Dry soil heated 48 hrs.	59.1	54.0	80.0
4	Dry soil heated 168 hrs.	64.0	56.4	68.6
4	Wet soil heated 48 hrs.	51.1	35.7	65.5
4	Wet soil heated 168 hrs.	53.3	51.7	62.6

between soluble iron in 0.05 normal HCl and the percentage of phosphorus fixed. The SiO_2 was determined by the molybdenum method (32) to see if phosphorus has been displaced by silica. There is a correlation between the low silica and high fixing power of the soils but there are other factors which fix phosphorus besides the displacement by silica. The fixing capacity of these soils, the parts per million of silica displaced and the parts per million of iron soluble in 0.05 HCl are recorded in Table 5.

It will be seen from these data that there is no correlation between the percentage of phosphorus fixed and the solubility of iron in 0.05 normal HCl. Where the percent of soluble iron was high the quantity of soluble silica was low. On the other hand where the easily soluble iron was low silica was high. It seems probable, therefore that there might be a relation between the fixing capacity of the soil and the ratio between soluble iron and silica.

The effect of pH is thought to have a great influence on phosphorus fixation and pH determines the form phosphorus will be fixed in the soil. Figure No. 1 is a comparison between the pH of the soil and phosphorus

Table 5. The Relation Between Easily Soluble Iron, Soluble Silica in
Surface, and Surface Soils as Compared with Phosphorus Fixed.

Soil No.	% P. Fixed	P. P. M. of Silica Displaced	P. P. M. of Iron Soluble in 0.05 N. Hcl.
1721	41	50	15
1722	57	40	10
1723	42	50	10
1724	45	45	10
1725	36	110	10
1726	25	65	10
1727	65	0	25
1728	70	10	25
1641	45	85	15
1642	70	55	15
1643	75	30	25
1644	90	30	17.5
1645	46	50	10
1646	67	75	10
1647	100	13	105
1648	100	10	70
1649	39	50	50
1650	24	40	30
2693	23	15	10
2695	72	50	25
2696	78	30	40
2710	100	24	220
2711	98	10	280
2714	90	-20*	225
2719	90	20	225
2720	86	60	170
2446	90	40	195
2448	98	-22	220
2452	54.5	80	7

* The negative value occurs because more silica was obtained from the
untreated soil than from the soil to which phosphorus was added.

18

Per cent
Phosphorus
Fixed

100
90
80
70
60
50
40
30
20
10
0

5   5.5   6   6.5   7   7.5   8   8.5   9

pH

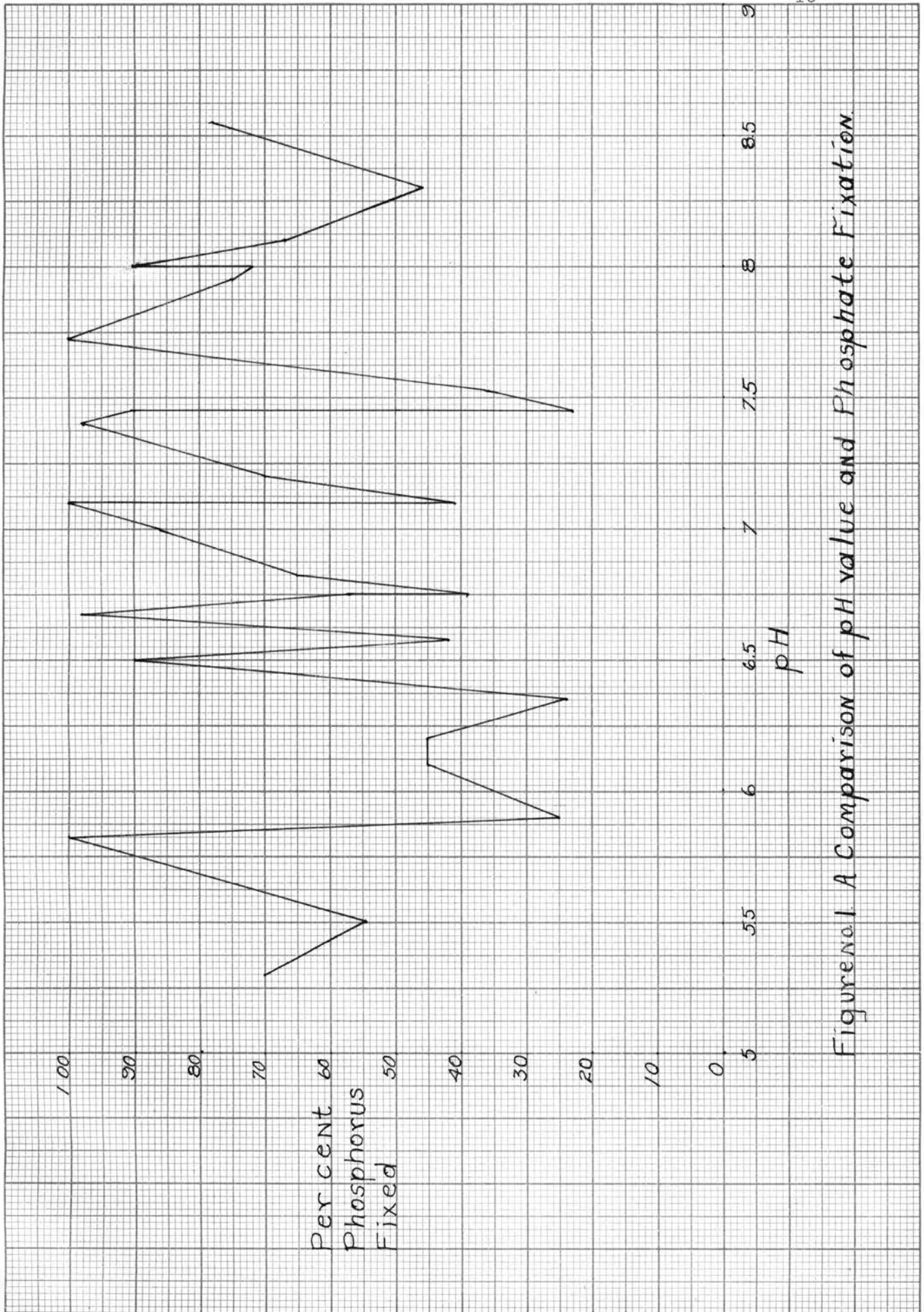Figure no.1 A Comparison of pH value and Phosphate Fixation.

absorbed. No correlation occured between the pH of the soil and the percentage of phosphorus fixed.

The amount of phosphorus absorbed depends on the anion exchange capacity of the soil complex and on the valence of the phosphoric acid ions which take part in the absorption. The PO_4 combines with the soil colloids to form compounds or complexes which results in a change in the composition and structure of the colloidal alumino silicate. A colloid was prepared by dispersing a clay soil in water then centrifuging to get the colloidal material. This colloidal material was treated with hydrogen peroxide (30) to get rid of organic matter and then with soidum sulfide and oxalic acid to reduce and dissolve the iron. The base exchange material was washed with distilled water dried and the fixing capacity determined as previously described and seventy-two per cent of the phosphorus was fixed by this material which did not contain any iron. The fixing capacity of this colloid is recorded in Table 6. It thus seems evident that there are agencies in the soil which fix phosphorus other than hydrated forms of iron oxide.

Table 6. Effect of Purified Base Exchange Material on Phosphorus Fixation.

P. P. M. of P. Added	P.P.M. of P. Recovered	P.P.M. of P. in Blank	P. P. M. of P. Fixed.
100	30	2	72
100	30	2	72

A study of the percentage of clay in the soil and the phosphorus fixed is shown in figure 2. It is quite evident that no correlation occurs. But from the study of Table 5 there is more fixation in the subsurface soils than in the surface soils. There is a larger percentage of clay in the subsurface soils. To study this Kirkland fine sandy loam surface and subsurface soil samples, which contained 2.6% total iron in the surface and 3.8% in the subsurface was treated for seven days at temperature $27^{o} - 30^{o}$, 70 and 100 degrees centigrade. In Table 8 these results are recorded. It is quite evident that there is more phosphorus fixed in the subsurface soils than in the suface soils in all cases.

Marshall (29) finds that clay minerals can be classified according to lattice type. There may be a 1:1 or a 2:1 fixed lattice type in the different minerals which may be found in soils. Some investigations indicate that the $SiO_2 - R_2O_3$ ratio is an important factor in phosphorus fixation. In some of these clays this ratio does not satisfactorily define the layer replacements and shows no simple relationship to the base exchange capacity.

The fixing power of a number of materials other than soil is recorded in Table 7. Permutite, kaolin and muscovite fixed a high percentage of the soluble phosphorus which was not removed by leaching with 0.1 normal acetic acid. Results indicate that phosphorus may be fixed by substances other than iron. Anion exchange has been used to explain the results which were secured.
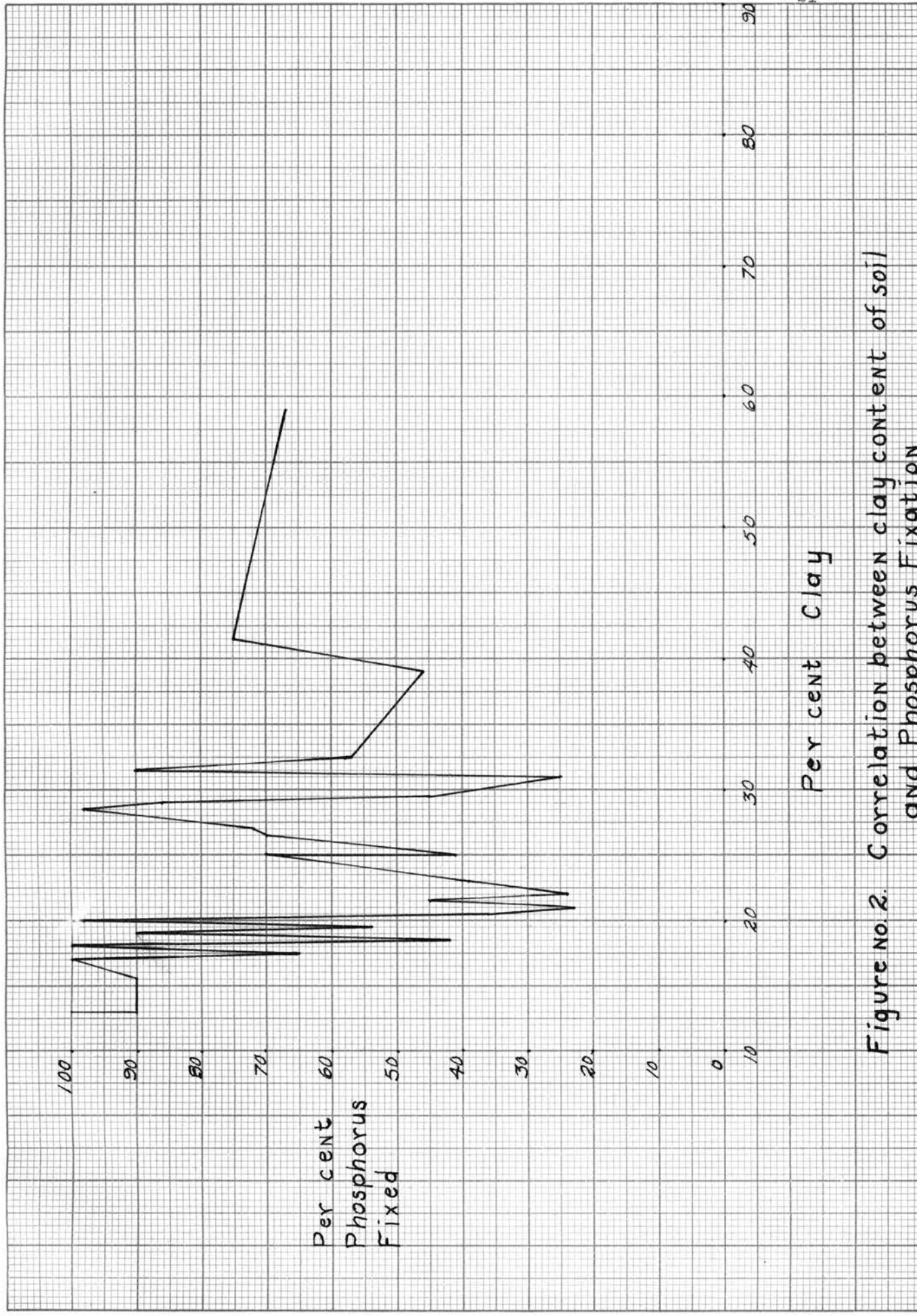
Figure no. 2.   Correlation between clay content of soil and Phosphorus Fixation

Table 7. Fixation of Phosphorus Added as Di Ammonium Phosphate by
          Various Substances.

Substance	Amount in Grams	Po_4 in P. P. M.	
		Added	Fixed
Permutite	20	100	97
Kaolin	20	100	80
Feldspar	20*	100	0
Pumice	20*	100	35
Muscovite	20*	100	80

* Through 100 mesh sieve.

Table 8. The Relation Between Fixation of Phosphorus by Surface and Subsurface Soil.

Days Treated	Incubation Temperature of Soils					
	100°C		70°C		27° - 30° C.	
	Surface	Subsurface	Surface	Subsurface	Surface	Subsurface
	% of P.	Fixed	% of P.	Fixed	% of P.	Fixed
1	76	94	73	95	70	96
2	75	95	70	94	68	91
3	49	95	54	93	66	85
5	44	94	49	93	59	93
7	48	93	51	91	51	90

SUMMARY

A study was made of different procedures for fixing phosphorus and the factors affecting phosphorus fixation. It was found that leaching removes more soluble phosphorus from a soil than extraction by shaking. The method used in this experiment of determining phosphorus fixation is rapid, convenient, and very simple.

It was found that heating does not effect the phosphorus fixed in soils uniformly, but an increase in temperature increases the per cent of phosphorus fixed. The absorption of phosphorus by soil increased with time of contact. Repeated wetting and drying makes phosphorus more insoluble.

No correlation was found between the pH of the soil or the percentage of clay and phosphorus fixed. But there is a tendency for subsurface soils to fix more phosphorus than surface soils. As seen from Table 8 the surface soil fixed only 76 per cent of the phosphorus added while the subsurface soil fixed 94 per cent of the phorphorus added.

When the per cent of soluble iron, was compared with silica displaced and the fixing capacity of the soil it was found that the amount of iron was low when the amount of silica was high and if the phosphorus is not fixed as iron phosphates the phosphates are displaced by the silica. Other inorganic substances fix phosphorus, such as kaolin, muscovite, and permutite. These results may be explained by anion exchange.

REFERENCES

1. Bauer, F. C., 1921.
The relation of organic matter and the feeding power of plants to the utilization of rock phosphate.
Soil Science 12: 21-41.

2. Beater, B. E., 1938.
The Measurement of phosphate Fixation in Soils.
Soil Science 44: p. 277.

3. Brown, L. A., 1935.
A study of phosphorus penetration and availability in soils.
Soil Science 39: 277-287.

4. Daughty, 1931.
Phosphorus studies on Alberta soils.
Scientific Agri. 12: 44-51.

5. Davis, L. E., 1935.
Sorption of phosphates by monocalcaveous Hawaiiaw soils.
Soil Science 40: 129-158.

6. Doughty, J. L., 1930.
The fixation of a phosphate by a peat soil.
Soil Science 29: 23-25.

7. Doughty, J. L., 1935.
Phosphate fixation in soils, particularly as influenced by organic matter.
Soil Science 40: 191-202.

8. Ford, M. C., 1933.
The nature of phosphate fixation in soils.
Jour. of American Society of Agronomy 25: 134-144.

9. Fraps, G. S., 1912.
Active Phosphoric acid and the needs of the soil for phosphoric acid in pot experiments.
Tex. Agr. Exp. Sta. Bul. 200.

10. Fraps, G. S., 1922.
The Fixation of phosphoric acid by the soil.
Tex. Agr. Exp. Sta. Bul. 304.

11. Gile, Philip, L., 1933.
The effect of different collodial soil materials on the efficiency of super phosphate.
U. S. D. A. Tech. Bul. No. 371.

12. Heck, A. F., 1935.
Availability of fixation of phosphorus in Hawaiian soils.
Jour. Amer. Soc. Agron. 27: 874-884.

13. Heck, A. F., 1934.
    Effect of the degree of base saturation of a soil on its capacity
    to fix phosphorus in difficultly available form.
        Soil Science 38: 463-470.

14. Heck, A. F., 1934.
    A method for determining the capacity of a soil to fix phosphorus
    in difficulty available form.
        Soil Science 37: 477-482.

15. Heck, A. F., 1934.
    Phosphate fixation and Penetration in Soils.
        Soil Science 37 p. 343.

16. Hibbard, P. L., 1935.
    Factors influencing phosphate fixation in soils.
        Soil Science 39: 337-358.

17. McGeorge, W. T., 1934.
    The determination of phosphate availability in caleareaus soils
    by electrodialysis.
        Soil Science 38: 347-353.

18. McGeorge, W. T., and Breazeale, J. T., 1932.
    Studies on iron, aluminum, and organic phosphates and phosphate
    fixation in caleareous soils.
        Ariz. Agr. Exp. Sta. Tech. Bul. 40.

19. Oberholzer, Petrus C. J., 1936.
    The decomposition of organic matter in relation to soil fertility
    in acid and semiarid regions.
        Soil Science 42: 359-376.

20. Pugh, A. J., 1934.
    Laws of soil colloidal behavior; III colloidal phosphates.
        Soil Science 38: 219-239.

21. Ravikovitch, S., 1934.
    Anian Exchange: I. Adsorption of the phosphoric acid ions by soils.
        Soil Science 38: 219.

22. Ravikovitch, S., 1934.
    Anion Exchange; II. Liberation of the phosphoric acid ions adsorbed
    by soils.
        Soil Science 38: 279.

23. Scarseth, G. D., and Tidmore, J. W., 1934.
    The fixation of phosphates by clay soils.
        Jour. of American Soc. Agron. 26: 152-162.

24. Scarseth, G. D., and Tidmore, J. W., 1934.
     Fixation of phosphates by soil colloids.
          Jour. Amer. Soc. Agron. 26: 138-151.

25. Scarseth, G. D., and Tidmore, J. W., 1935.
     The mechanism of phosphate retention by natural alumino silicate
     colloids.
          Jour. Amer. Soc. Agron. 27: 596-616.

26. Truog, Emil, 1930.
     Determination of readity available phosphorus.
          Jour. Amer. Soc. Agron. 22: 874-882.

27. Truog, Emil, 1916.
     The utilization of phosphates by agricultural crops, including a
     new theory regarding the feeding power of plants.
          Wisconsin Agri. Exp. Sta. Rev. Bul. 41.

28. Wrenshall, C. L., and McRibber, R. R., 1935.
     A comparison of some methods used in extracting soil phosphates,
     with a proposed new method.
          Jour. Amer. Soc. Agron. 27: 511-518.

29. Marshall, E. C., 1936.
     Soil Science and Mineralogy.
          Proceedings Soil Science Society of America Vol. 1: p. 23.

30. Truog, E. Et al, 1936.
     Procedure for special type of mechanical and mineralogical soil
     analysis.
          Proceedings Soil Science Society of America Vol. 1: 101-112.

31. Daniel, H. A., and Harper, H. J., 1934.
     An accurate method for the determination of small amounts of iron.
          Jour. of Assoc. of Official Agri. Chemists. Vol. 17: 286-290.

32. Port, Eugene Baker, 1933.
     The colormetric determination of silica.
          Unpublished Thesis, Okla. A. & M. Col.

Berniece L. Black, typist.