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THE FIXATION OF PHOSPHORIC ACID BY THE SOIL



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THE FIXATION OF PHOSPHORIC ACID BY THE SOIL

BY

G. S. FRAPS

It has been known for a long time that soils have the power of removing phosphoric acid, potash, and some other substances from solution. This property, which is called fixation, was studied by soil chemists over fifty years ago, and is shown by the work of Way, Bretchneider, Peters, and others from 1861 to 1865, and is discussed on page 235 of Fraps' Principles of Agricultural Chemistry.

Fixation tends to prevent the potash, phosphoric acid, and ammonia of the soil from being washed out, thereby helping the soil to retain these valuable forms of plant food. If fixation did not occur, in the course of geological ages soils would no doubt become highly impoverished in plant food. Fixation hinders weathering agencies, including water, from removing plant food such as phosphoric acid or potash from the soil, but instead allows less important materials, such as soda and chlorine, to pass off into drainage water. This is an exceedingly interesting and wise provision of nature.

Fixation also tends to prevent loss of potash and phosphoric acid added to the soil in the form of fertilizers, but on the other hand, it tends to make phosphoric acid of fertilizers less available for plants. Fixation also interferes with the chemical analysis of the soil, in that the soil holds back and absorbs part of the plant food which would otherwise go into solution in the acids used by chemists.

This Bulletin is a study of the relation of fixation to properties of typical Texas soils, especially as related to the loss of phosphoric acid of fertilizers or to the estimation of active plant food in the soil.

METHOD OF DETERMINATION

As was shown by previous studies of other workers, the amount of fixation varies with time, temperature, concentration of solution, ratio of soil to solvent, and other factors. For the purpose of estimating the fixing power of Texas soils for phosphoric acid the following method was used:

METHOD FOR ABSORPTION OF PHOSPHORIC ACID BY SOILS

Strong Phosphate Solution.—Make up a solution of dibasic potassium phosphate, and determine phosphoric acid (P_2O_5) in 10 c.c. Dilute so that 20 c.c.=.0200 grams phosphoric acid.

Weak Phosphate Solution.—Place 200 c.c. of strong phosphate solution in a 2-liter graduated flask and make up to volume.

DETERMINATION

Bring 50 grams of the soil in contact with 200 c.c. weak phosphate solution in a dry bottle, well stoppered. Shake every half hour during the working day, and filter at the end of 24 hours. Measure off 100 c.c., add 8 c.c. nitric acid, neutralize with ammonia, acidify with nitric acid, evaporate to about 75 c.c., filter and wash if necessary, and determine phosphoric acid by the volumetric method. Run at least eleven soils and one blank on the solution at the same time. The blank should be run just as if it were a soil. If the solution is made up so that 10 c.c.=10 mg., and if a is the number of milligrams phosphoric acid found, then 10-a multiplied by 10 is the absorption in per cent. Otherwise it is necessary to divide by the quantity of phosphoric acid in the 10 c.c. of solution. Report results to nearest tenths per cent.

EFFECT OF TEMPERATURE

Effect of temperature on the absorption of phosphoric acid was studied by the method described above, the only variation being in the temperature. The solution in contact with the soil was kept five hours in ice water, or five hours at room temperature, or five hours in a water bath at 40 degrees, or for one hour in a boiling water bath. The results are given in Table 1.

The temperature had little effect upon the absorption by some soils, but it had a very decided effect upon absorption by others. With soil 1595 there is little effect, but with soils 1577 and 1581 considerable increases of fixation take place when the temperature rises.

Lab. No.			In ice water	Room temper- ature 31 degrees	Water bath 40 degrees	One hour in boiling water
1577	San Antonio Clav Loam,	1''- 6''	50.4	57.2	66.9	85.5
1581	Houston Black Clay Loam	6"-12"	34.6	40.9	48.4	. 60.5
1584	Willis Sand	1"- 6"	9.6	16.9	20.1	15.3
1585	Willis Sand	6"-12"	9.2	15.3	16.1	16.9
1591	Lufkin Sand	1"- 8"	1.6	2.8	3.6	4.8
1595	Austin Clay	1"- 6"	63.7	65.7	66.1	67.7

Table 1.-Effect of temperature on percentage of phosphoric acid absorbed.

EFFECT OF TIME

The effect of time upon the absorption of phosphoric acid by soils was studied, using the method given above, but allowing the solution to stand at room temperature for 5 hours, 24 hours, 48 hours, 5 days, and 10 days. The only variable condition was the time. The results of this experiment are given in Table 2. The absorption of phosphoric acid increases with the time of contact. Greater differences appear in the soils after five hours' contact than after ten days' contact. There is a tendency towards more complete absorption as the time of contact increases. This is not surprising, for the amount of phosphoric acid added to the soil is small, and there should be an abundance of fixing material to completely take up all this phosphoric acid, if sufficient time is allowed.

Lab. No.	5 Hours	24 Hours	48 Hours	5 Days	10 Days
1577	55.6	56.3	59.5	72.2	75.4
1586	21.5	30.2	39.6	55.6	65.9
1588	10.3		23.0	42.1	42.9
1593	53.1	55.6	64.6	80.1	80.9
595	15.1	22.2	29.6	60.3	72.2
597	29.3	34.9	40.0	60.3	61.1

Table 2.-Effect of time on percentage of phosphoric acid absorbed.

EFFECT OF SALT

Table 3 shows the effect of two grams salt used to coagulate the clay. The salt had little effect upon fixation but its use was not adopted for the work described in this Bulletin. The use of the salt aided in clarifying the solution for analytical work and it would probably be well to use a coagulant like this.

Table 3.-Effect of salt upon the percentage of phosphoric acid absorbed.

Laboratory No.	With NaCl	Without NaCl
1295	77.6	72.0
1296	94.4	91.2
1297	68.8	63.6
$\begin{array}{c} 1298 \dots \dots \\ 1301 \dots \dots \end{array}$	69.6	61.2
1301	12.4	11.2
1302	93.6	90.0

EFFECT OF ACID UPON FIXATION

It was shown in Bulletin 126 that treatment with acid may remove part but not all of the fixing power of the soil for phosphoric acid. In order to study this further, two portions of 50 grams of the soil each were weighed out, and one portion was treated with 50 c.c. water and 20 c.c. concentrated hydrochloric acid, stirred well and allowed to stand. The acid was decanted through a filter, and the treatment repeated until all of the calcium carbonate had been decomposed. The soil was then washed with water and allowed to dry. The original soil, and the soils treated with acid were tested at the same time and under the same conditions for absorption of phosphoric acid by the method previously described.

The results of this work are given in Table 4. The treatment with acid, which should remove all carbonate of lime, varies in its effect upon the different soils. It decreases the fixation of some soils decidedly, while it has little or no effect upon that of others. Soils with high fixation, such as numbers 823, 853, and 873, are especially liable to have their fixation little affected by washing with acid.

This fact was also pointed out in Bulletin 126, in connection with

the estimation of active phosphoric acid removed from the soil. As pointed out in that Bulletin, soils with a fixing power exceeding 80 per cent., by the method described above, may give up to the acid used for estimation of active phosphoric acid only a small proportion of the phosphoric acid really soluble in the solvent, on account of withdrawing by fixation. The treatment with the acid reduces the fixing power of some of the soils to a considerable extent, while the fixing power of others remains high, and phosphoric acid removed by fifthnormal acid may not represent the active phosphoric acid actually present in the soil. It is possible that a preliminary treatment with acid like that described above, before estimating the absorption of the soil for phosphoric acid, might be used in connection with the estimation of active phosphoric acid of the soil, for the purpose of attempting to judge of the effect of fixation upon the active phosphoric acid. and the amount which might be actually present in the soil. This matter requires further study, for so far the study has not led to any clarifying results.

Laboratory No.	Original soil	Acid treated	
823 827	91.2 34.5	91.2 31.5	
831	66.0	31.4	
851	52.1	21.7	
853	94.9	89.2	
873	94.8 67.7	$92.2 \\ 45.0$	
$\begin{array}{c}111\\325\\\ldots\end{array}$	60.2	45.0	
334	32.5	26.4	
338	71.1	76.6	
816	23.4	19.0	
880	46.3	12.2	
882	71.3	22.5	
838	62.9	10.7	
928	47.7	25.6	
932	50.3	18.5	
933 939	74.4	25.6 32.5	

Table 4.--Effect of extraction with acid upon percentage of phosphoric acid fixed.

EFFECT OF IGNITION

It was shown in Bulletin 135 of this Station that ignition affects some phosphates of iron which may occur in the soil, rendering their phosphoric acid decidedly more soluble in acid. It is a question if ignition would not render iron and aluminum compounds in soils more active as regards fixation.

Effect of ignition upon the phosphoric acid absorbed by the soil was studied by weighing out 50 grams of the soil, igniting in a platinum dish until all organic matter was destroyed, transferring to a bottle, and treating with potassium phosphate as described in the method for the absorptive power of soils. Another portion of the same soil without ignition was tested at the same time and under the same conditions.

The results of some of these experiments are given in Tables 5, 6, and 7. The effect of the ignition is to increase the absorption power

THE FIXATION OF PHOSPHORIC ACID BY THE SOIL.

of the soil in many cases. This may be due to the heat's converting part of the carbonate of lime to calcium oxide, which, of course, would unite more readily with phosphoric acid. It is also in part probably due to changes in the character of the iron and aluminum compounds in the soil, caused by the ignition. It has been shown in Bulletin 135 that ignition renders more soluble certain soil phosphates, and causes part of the iron and aluminum oxides to become more soluble in acids.

Laboratory No.	Original	Ignited
821	28.8	. 35.4
822	16.2	32.3
832	82.3	80.7
834	53.1	67.7
828	4.2	19.3
335	87.9	90.4
997	89.9	89.4
337		
341	98.5	91.0
309	78.3	97.0
333	94.5	98.5
823	98.4	93.2
831	67.2	99.0
851	41.5	68.7
348	6.7	5.6
818	21.7	43.7
932	46.8	98.5
933	67.0	98.6
940	58.6	69.5
	68.4	99.8
963	73.7	81.3
968		
992	62.7	64.6
078	31.1	73.7

Table 5.-Effect of ignition of soil upon percentage of phosphoric acid fixed.

Table 6.-Effect of treatment with acid and ignition upon percentage of phosphoric acid absorbed

Laboratory Number	Original	Ignited direct	Treated acid	Treated acid, then ignited
1593. 1594. 1597. 1590. 1931. 1586. 1587. 1588. 1589. 1580. 1580. 1582. 1582. 1582. 1925. 1927. 1932. 1933. 1934. 1935.	$\begin{array}{c} 56.4\\ 68.1\\ 31.9\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	$\begin{array}{c} 86.8\\ 99.0\\ 98.8\\ \hline \\ 23.8\\ 34.4\\ 73.4\\ 14.6\\ 51.8\\ 74.4\\ 99.0\\ 97.9\\ 28.7\\ 71.4\\ 86.0\\ 52.3\\ 69.8\\ 46.2\\ 85.9\\ 58.6\\ 77.3\\ \end{array}$	$\begin{array}{c} 32.8\\ 37.5\\ 6.9\\ 31.3\\ 1.5\\ 0\\ 26.1\\ 4.7\\ 3.5\\ \cdots\\ 24.7\\ 38.7\\ 6.7\\ 23.6\\ 0\\ 5.0\\ 35.7\\ 15.6\\ 52.5\\ 47.0\\ 38.4 \end{array}$	$\begin{array}{c} 81.9\\ 53.4\\ 16.2\\ 63.6\\ 11.8\\ 30.2\\ 68.7\\ 19.3\\ 41.5\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $

Laboratory Number.	Not treated	Treated 3 1/3N HCl	Ignited and then treated 3 1/3 N. acid
1585. 1588. 1579. 1583. 1933. 1934. 1935. 1936. 1927. 1930. 1594. 1927. 1930. 1594. 1925.	$18.5 \\ 10.7 \\ 7.8 \\ 53.7 \\ 62.5 \\ 51.5 \\ 52.0 \\ 59.5 \\ 44.0 \\ 5.3 \\ 66.0 \\ 35.0 \\$	$\begin{array}{r} 3.4\\ 0\\ 4.4\\ 19.0\\ 22.0\\ 17.5\\ 0\\ 17.5\\ 0\\ 0.5\\ 8.0\\ 15.0\\ 15.0\end{array}$	$\begin{array}{c} 7.3\\ 12.2\\ 6.3\\ 34.6\\ 40.0\\ 25.5\\ 45.0\\ 31.0\\ 27.0\\ 17.5\\ 36.0\\ 25.5 \end{array}$

Table 7.-Effect of treatment with acid and ignition upon percentage of phosphoric acid absorbed.

In order to test this matter further, samples of the soil were weighed out, treated with acid, and ignited. In experiment 762, the sample was first washed with acid, and then ignited, while in experiment 765 the sample was first ignited and then washed with the acid. The results of this work are given in Tables 6 and 7. The effect of the treatment with acid alone is to reduce the phosphoric acid absorbed. The phosphoric acid absorbed is greater for the soils ignited and treated with acid than for the soils treated with acid and not ignited. This increase occurs when the soil is first treated with the acid and then ignited, or when first ignited and then treated with acid. This shows that the effect of the ignition is to change the iron and aluminum compounds so that they absorb the phosphoric acid to a greater extent.

FIXATION BY MINERALS

A study of the fixation of phosphoric acid by minerals which might occur in the soil should throw some light upon the part which such minerals take in the process. Accordingly, a number of minerals were secured, ground finely, and treated with phosphate by the method already described for soils, with the exception that 20 grams of minerals were used in place of 50 grams of soil. Two or more samples of some minerals were secured of different origin. The results are given in Table 8. Table 8.—Percentage of added phosphoric acid fixed by minerals (20 grams to 20mg.).

	Sample No. 1	Sample No. 2	Sample No. 3
Prehenite	12.1	24.2	-
Siderite	$77.8 \\ 22.6$	45.6	37.7
Haematite	32.2	39.9	45.5
Natrolite	10.9	12.1	
Goethite	19.8	27.6	
Chrysolite	$\begin{array}{c} 17.8 \\ 7.0 \end{array}$		
Wernerite	10.1	25.7	
Stilbite	10.2		
Labradorite	$35.8 \\ 60.3$	16.4	41.7
Wollastonite.	39.5	47.1	
Serpentine	85.3		
Epidote	$4.7 \\ 36.6$	31.1	35.0
Xaolinite	28.8		
Falc	6.8		
erpentine	$ 48.8 \\ 36.8 $		
Carbonate of Lime	66.0	48.5	
Prochlorite	8.2		and the second se
Amphibole	$19.9 \\ 20.6$		

None of the minerals examined showed as high a fixing power as some of the soils. The highest is 77.8 per cent. with one sample of siderite. While 20 grams of the mineral were used, and 50 grams soil, yet none of the soils would hardly be likely to contain more than this quantity of the mineral.

It would appear that some soils contain mineral of much higher fixing power than any of the minerals examined. This difference may be due in large part to the physical character of the mineral in the soil; the soil minerals may be more hydrated, and less compact, than the minerals found in deposits.

All the minerals examined showed some fixation, but the fixation with some is slight and may be due to physical causes.

FIXATION OF PHOSPHORIC ACID OF FERTILIZERS

The available phosphoric acid of fertilizers is considered to be present as mono-calcium phosphate, which is soluble in water, and as dicalcium phosphate, which is only slightly soluble in water, but readily taken up by plant roots. When the fertilizer is placed in the soil the mono-calcium phosphate is slowly dissolved by the soil moisture, and partly taken up by plant roots and partly fixed by the soil. This process does not take place rapidly.

Let us leave out the action of the plant roots, and consider what occurs in the soil alone. Each lump of fertilizer becomes a center from which the soil moisture dissolves the phosphate. When the solution leaves the lumps of fertilizer, it comes in contact with soil particles, and part of the phosphoric acid is fixed. The amount which is fixed depends upon the strength of the solution, and on the fixing power of the soil particles. The fixing power of the soil particles nearest the lump of phosphate may become completely saturated, while the particles further away fix less and less, because the strength of the solution decreases, by fixation, the further it passes from the phosphate. Finally no further fixation occurs, and the solution represents the original soil moisture. Under these conditions there is a lump of acid phosphate, surrounded by a comparatively strong solution of phosphate, which decreases in strength as the distance from the phosphate increases. The size of the area of strong phosphate solution depends greatly upon the fixing power of the soil and the amount of moisture present. Surrounding the lump of acid phosphate would be soil particles whose fixing power for phosphoric acid is completely saturated, and around this a zone of gradually decreased fixation.

This condition would not be permanent but might be slow to disappear entirely. The lump of phosphate would finally lose all its soluble material, and finally the remaining rock phosphate might become less soluble than the fixed phosphate surrounding it. The fixed phosphate nearest the fertilizer would probably be more soluble in soil moisture than that in the remainder of the soil. It therefore would again dissolve slowly, and pass on to zones of greater fixation, and this process would continue until the solubility of the soil phosphates would become nearly uniform, and the added phosphate distributed through the soil.

The nature of the fixing substances in the soil would have an effect upon the soil fertility. Some fixing particles no doubt hold the phosphoric acid more loosely than do others, so that some give up their phosphoric acid more readily to plant roots than others. The relative predominance of these two classes of fixing particles would affect the rapidity with which the fertilizer phosphate becomes unavailable to plants. This would be one explanation why acid phosphate is more available in some soils than in others. It might be found, for example, that a soil with high fixing power for phosphoric acid but low in carbonate of lime might receive benefit from lime on account of its helping to hold the phosphoric acid in more available forms. The carbonate of lime particles might change the phosphates to phosphate of lime, and influence the soil favorably in this respect.

PERCOLATION AND FIXATION

In order to test further the effect of the soil upon acid phosphate, 850 grams of soil were placed in galvanized iron tubes about 14 inches long and 2 inches in inside diameter, having a piece of cloth tied over the lower end. One gram acid phosphate was mixed with the top three inches of the soil, and 100 c.c. water added. The mixture was allowed to stand 24 hours, and then percolated with water until 1000 c.c. had collected. The time required for this varied considerably from 3 hours to 4 days. With some of the soils, successive percolations were made.

Table 9 contains the results of this experiment on soils having an absorptive power for phosphoric acid, by the method already described, of more than 50 per cent. The amount of phosphoric acid in the first percolate averaged 0.4 mg. in 1000 c.c., or 0.4 parts per

THE FIXATION OF PHOSPHORIC ACID BY THE SOIL.

million. The fixation of phosphoric acid by the column of soil was thus almost complete.

Table 9.-Milligrams of phosphoric acid in 1000 c.c percolate from soils plus acid phosphate

Laboratory Number	Mg. phosphoric acid in percolate	Absorption power for phosphoric per cent
855	0.2	80
1067		92
1122		97
1124		75
1126		78
1138		98
932		64
960	0.3	67
1140	1.2	51
1145	0.3	54
1136	0.2	52
Average	0.4	

A series of experiments with soils having an absorptive power less than 50 is given in Table 10. As the untreated soils in these experiments gave up more phosphoric acid to water than the soils listed in Table 9, experiments were made on these soils both with and without additions of acid phosphate. It is seen from the table that considerable amounts of phosphoric acid were dissolved by the percolating water and carried down through the soil.

19 (19 (19 (19 (19 (19 (19 (19 (19 (19 (No additi	ion	Aci	id phosph	ate	Total three	Phos- phoric
Laboratory Number	First perco- late	Second perco- late	Third perco- late	First perco- late	Second perco- late	Third perco- late	perco- lations	acid absorbed
318	$2.4 \\ 19.8 \\ 3.4 \\ 3.5 \\ 1.7 \\ 3.9 \\ 1.1 \\ \dots \\ 7.6$	$1.3 \\ 5.9 \\ 1.3 \\ 0.7 \\ 2.9 \\ 1.1 \\ \dots \\ 3.5$	$0.9 \\ 3.1 \\ 1.3 \\ 1.1 \\ 0.9 \\ 1.7 \\ 0.9 \\ \dots \\ 2.5$	$\begin{array}{r} 46.2\\ 93.1\\ 50.4\\ 77.6\\ 82.2\\ 42.6\\ 39.5\\ 29.0\\ 99.1 \end{array}$	$7.6 \\ 12.0 \\ 17.1 \\ 21.0 \\ 19.3 \\ \dots \\ 16.1 \\ 16.8 \\ 5.2 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	$6.9 \\ 10.3 \\ 5.2 \\ 9.4 \\ 8.4 \\ \\ 9.4 \\ 13.2 \\ 4.8 \\ 4.8 \\ $	$\begin{array}{c} 60.7\\ 115.4\\ 72.7\\ 108.0\\ 109.9\\ 42.6\\ 65.0\\ 59.0\\ 109.1 \end{array}$	
Average A	5.7	2.3	1.5	62.2	14.8	8.5	82.5	7.5
314 913 174 895	2.1 1.1 1.4 2.0	$0.5 \\ 0.7 \\ 0.5 \\ 1.9$	$0.8 \\ 0.4 \\ 0.6 \\ 1.4$	50.7 48.2 53.7 21.2	$12.8 \\ 14.6 \\ 14.4 \\ 24.1$	$4.6 \\ 6.6 \\ 7.1 \\ 0.1$	$68.1 \\ 69.4 \\ 75.2 \\ 45.4$	$14.6 \\ 14.9 \\ 10.4 \\ 18.0$
Average B	1.6	0.9	0.8	43.5	16.5	4.6	64.5	14.2
	$1.0 \\ 1.3 \\ 1.0 \\ 5.2 \\ 3.3 \\ 0.7 \\ 3.6 \\ \cdots \cdots$	$\begin{array}{c} 0.4 \\ 1.0 \\ 0.3 \\ 3.0 \\ 0.3 \\ 0.5 \\ 2.6 \\ \cdots \cdots \end{array}$	$\begin{array}{c} 0.1 \\ 0.9 \\ 0.3 \\ 1.8 \\ 0.3 \\ 0.4 \\ 2.0 \\ \cdots \cdots \\ \cdots \cdots \end{array}$	$\begin{array}{c} 25.0 \\ 13.0 \\ 22.5 \\ 38.7 \\ 52.4 \\ 21.4 \\ 16.1 \\ 4.1 \\ 3.3 \end{array}$	$5.8 \\ 7.0 \\ 11.9 \\ 23.2 \\ 20.5 \\ 7.3 \\ 12.5 \\ 10.6 \\ 6.7 \\ \end{cases}$	$3.8 \\ 7.6 \\ 1.8 \\ 9.8 \\ 5.4 \\ 4.3 \\ 10.1 \\ 8.8 \\ 8.3$	$\begin{array}{r} 34.6\\ 27.6\\ 36.2\\ 71.7\\ 78.3\\ 33.0\\ 38.7\\ 23.5\\ 18.3\\ \end{array}$	$\begin{array}{c} 22.5\\ 27.3\\ 28.9\\ 29.2\\ 21.1\\ 25.8\\ 21.0\\ 28.0\\ 30.0\\ \end{array}$
Average C	2.3	1.2	0.7	21.7	11.7	6.7	40.2	25.9
826	$0.6 \\ 1.0$	0.3 0.8	$0.3 \\ 0.3$	$\begin{array}{c} 22.2\\10.4\end{array}$	6.0 8.8	$4.3 \\ 6.2$	$32.5 \\ 25.4$	$37.4 \\ 42.4$
Average D	0.8	0.6	0.3	16.3	7.4	5.3	29.0	39.9

Table 10,-Mg. phosphoric acid percolated from soils with and without acid phosphate.

This experiment showed the possibility of the loss of phosphoric acid from the soils having low fixing power, when heavy rains follow applications of fertilizer. On the other hand, it must be remembered that the subsoil usually has a higher fixing power than the surface soils, so that the phosphoric acid carried down from the surface soil may be held by the subsoil. But the possibility of the loss of phosphoric acid from fertilizers must be considered in connection with the composition and characteristics of soils.

That a greater loss of soil phosphoric acid by percolating water takes place from soils of low fixing power, is also shown in this table. The loss from a soil with low fixing power may be six times that from a soil with a high fixing power. As stated above, when the possibility of loss in this way is considered both the surface and the subsoil must be taken into consideration.

Table 11 shows the effect of several percolations upon soils with low fixing power. The time during which the acid phosphate is in contact with moist soil has an effect upon the possibility of loss. This was studied with two soils. The results are given in Table 12. In this experiment the acid phosphate was mixed with the soil as described above, 100 c.c. water added, and then the percolation was begun after 24 hours with one set, after 48 hours with the second set. and five days with the third set, and ten days with the fourth. The amount of phosphoric acid extracted decreased decidedly with the time of contact before the percolation took place. There are still considerable amounts of water-soluble phosphoric acid in the soil.evidence that the phosphoric acid is soluble, and further evidence of the possibility of its being taken up easily by plants. It appears probable that the phosphoric acid of fertilizers applied in water-soluble form upon soils with low fixing power, may be easily taken up by plants, and may be partly washed from soils by rain.

	896 No addition	896 Acid phosphate	1120 Acid phosphate	1134 Acid phosphate	1283 Acid phosphate
First percolate 1000 c.c Second percolate Fourth percolate Fourth percolate Sixth percolate Seventh percolate Lighth percolate Ninth percolate Tenth percolate Twelfth percolate Twelfth percolate	· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·	3.4 3.7	3.3 6.7 8.3 3.7 4.3 2.3 2.0 1.8 1.8
Total	11.2	49.5	30.5	96.2	36.5
Absorption power for phosphoric acid, per cent	21.0		28.0	5.6	30.0

Table 11.-Milligrams phosphoric acid in successive percolates.

THE FIXATION OF PHOSPHORIC ACID BY THE SOIL.

1998		113	4	1	896										
First percolation after 24 hours First percolation after 48 hours First percolation after 5 days First percolation after 10 days Second percolation Third percolation Fifth percolation Fifth percolation Sixth percolation Seventh percolation Highth percolation Ninth percolation Tenth percolation	15.8 10.8 10.2 6.3 6.1		$ 10.8 \\ 11.6 \\ 8.0 \\ 6.0 $	$7.9 \\ 6.4$		$\begin{array}{c} 15.4 \\ 11.6 \\ 9.6 \\ 6.9 \\ 5.6 \\ 4.8 \end{array}$	$ \begin{array}{r} 8.4 \\ 12.2 \\ 8.3 \\ 7.5 \\ 6.5 \\ 6.1 \\ 5.5 \\ 4.7 \\ 4.8 \\ \end{array} $	$\begin{array}{c} 12.0\\ 5.1\\ 4.6\\ 4.4\\ 5.6\\ 5.1\\ 4.6\end{array}$							
Total	77.2	82.9	68.3	53.8	88.5	89.0	67.8	41.4							
Fixing power of salt	5.6				21.1										

Table 12.-Milligrams phosphoric acid in percolates-effect of time.

It is possible that it would be best to supply phosphoric acid to soils with low fixing power in forms that are not readily soluble in water, but easily taken up by plants. This is especially to be considered when heavy rains are liable to occur, which would cause considerable amounts of water to pass through the soil. With moderate amounts of rain, the phosphoric acid would be dissolved, but it would remain in the soil. There is also a possibility that it would be best to apply available phosphates in forms not readily soluble in water to soils with a very high fixing power, especially if there are indications that the phosphoric acid fixed by such soils is not available to plants. If applied in a form not soluble in water, it would remain for a longer time in a condition available to plants, provided that it is available in the first place. The question of the effects of fixation upon the availability of acid phosphate and other fertilizers requires further study.

The fixation of the water-soluble phosphoric acid of the acid phosphate takes place partly in the soil immediately in contact with the phosphates, and partly from the solution as it passes through the soil. As explained above, the solution should be more concentrated next to the particles of soluble phosphate, and should become less concentrated as it passes away from these particles and comes in contact with the fixing particles of the soil. The solution would decrease progressively in concentration as it passes down through the soil, until the condition of equilibrium is reached between the solubility of the phosphate of the soil and the fixing power of the soil.

In order to study this phase of the matter, three percolators were prepared for each soil, the first containing 850 grams of soil but no addition, the second containing 850 grams soil, with one gram acid phosphate mixed with the top 150 grams, and the third containing a mixture of one gram acid phosphate and 150 grams soil. The difference between the phosphoric acid in the percolate from the first and the second percolations represents the effect of the acid phosphate on the entire soil column, while the difference between the phosphoric acid in the percolations represents the phosphoric acid withdrawn by the column of 700 grams of soil. These results are given in Table 13.

Lab. No.		850 gm. soil	850 gm. soil and phosphate	150 gm. soil and phosphate	Fixing power of soil
1809	First 1000 c.c., mg Second 1000 c.c.	0.6 0.4	0.5 1.3	39.5 18.3	53.1
	Total	1.0	1.8	57.8	
	Caught by 700 grams of soil			56.0	
1931	First 1000 c.c., mg Second 1000 c.c.	$2.0 \\ 0.7$	22.7 9.1	$\substack{64.7\\11.7}$	27.5
	Total	2.7	31.8	76.4	
	Caught by 700 grams soil			44.6	
1577	First 1000 c.c., mg Second 1000 c.c.	$\substack{0.5\\0.2}$	$\begin{array}{c} 0.4 \\ 0.9 \end{array}$	$\begin{array}{c} 13.5\\12.7\end{array}$	56.7
	Total	0.7	1.3	26.2	
	Caught by 700 grams soil			24.9	
1932	First 1000 c.c., mg Second 1000 c.c., mg	$\substack{0.8\\0.3}$	19.2 8.7	$\substack{60.5\\12.4}$	29.2
	Total	1.1	27.9	72.9	
	Caught by 700 grams soil			45.0	
1592	First 1000 c.c., mg Second 1000 c.c., mg	$\substack{0.0\\0.3}$	$\begin{array}{c} 17.4\\ 12.9\end{array}$	$\begin{smallmatrix} 55.8\\ 0.0 \end{smallmatrix}$	2.9
	Total Caught by 700 grams soil	0.3	30.3	$\begin{array}{c} 55.8\\25.5\end{array}$	
1586	First 1000 c.c., mg Second 1000 c.c., mg	x x	14.4 x	$\substack{51.1\\10.3}$	
	Total		14.4	61.4	
	Caught by 700 grams soil			47.0	

Table 13.-Effect of column of soil on mg. phosphoric acid in percolate.

x-Evaporated as fast as it came through.

It is plain from the results given in the table that the column of 700 grams of soil has a great effect upon the amount of phosphoric acid taken from the soil. 'These results should be expected. Soil 1592 has a very low fixing power, but it still withholds a considerable proportion of the acid phosphate added.

It is evident from these figures that a large part of the absorption occurs in the column of soil below the fertilizer, and that the fertilizer passes into solution and then is taken up when this solution comes in contact with the soil particles. The rate of this change depends upon the water present in the soil, the fixing power of the soil, the amount of rainfall after the fertilizer is applied, and other conditions. There is likely to be little loss when the soil has a fixing power of more than 50 per cent.

If acid phosphate is applied at the rate of 1 gram to 850 grams of soil, as in these experiments, it would require an application of 2300 pounds to the acre, to equal the amount used in the experiments,

THE FIXATION OF PHOSPHORIC ACID BY THE SOIL.

if mixed with *all* the surface soil to a depth of 7 inches, but since the acid phosphate could not be mixed with the entire top inch of the soil, but would be either put in the furrow or applied more or less lumpily, a much smaller application would correspond to this proportion. The conditions of the experiment might be paralleled by the application of 100 to 200 pounds acid phosphate applied in a furrow.

The amount of rainfall required to duplicate the conditions of the experiment would be very large. Calculated on the area of the tubes used, a percolation of 20 inches rainfall through 12 inches soil would approximately equal the percolation of 1000 c.c. water under the conditions of the experiment. This would remove on an average about 60 per cent. of the water-soluble phosphoric acid, if all the rain should fall within 24 hours of the application. A percolation of 20 inches is out of the question. Rain sufficient to cause a percolation of 4 inches might occur; this would mean a total rainfall of much more than 4 inches, since the ground must become saturated before any percolation takes place.

A sandy soil about 14 inches deep with a saturation capacity of 30 per cent. would require about 5 inches of water to saturate it to the depth of $13\frac{1}{3}$ inches, if the soil were dry to begin with. Some rain would run off on the surface. If the soil were half saturated, rain of $3\frac{1}{2}$ inches would be needed for 1 inch percolation if no run-off occurred.

A heavy rain of 3 or 4 inches within ten days of the application might cause some percolation, and a loss of 3 or 4 per cent. of the water-soluble phosphoric acid added to light sandy soils with sandy subsoils. There is likely to be little loss when the fixing power exceeds 50 per cent.

RELATION OF FIXING POWER TO COMPOSITION

The fixing power of 761 surface soils and 651 subsoils for phosphoric acid was determined by the method already described.

The soils studied were divided into surface soils and subsoils, and the analyses arranged into groups according to the percentage of phosphoric acid fixed by the soil. The average results of these tabulations are given in Tables 14 and 15. An examination of these tables shows that the active phosphoric acid in both surface and subsoils increases until the absorption is 40 to 60 per cent., and then decreases. The acid consumed increases until the absorption is 60 to 80 per cent. in both tables, and then decreases. The lime increases in the same way as the acid consumed.

	P ₂ O ₅ absorbed	$\begin{array}{c} {\rm Active} \\ {\rm P}_{2}{\rm O}_{5} \\ {\rm per \ millon} \end{array}$	Acid consumed per cent	Per cent CaO	Per cent MgO	Per cent Fe ₂ O ₃ and AlsO ₃	Number averaged	Per cent of number in groups.
Group 0- 20 P ₂ O ₅ absorbed Group 20- 40 P ₂ O ₅ absorbed Group 40- 60 P ₂ O ₅ absorbed Group 60- 80 P ₂ O ₅ absorbed Group 80-100 P ₂ O ₅ absorbed	$\begin{array}{c} 12.92 \\ 30.85 \\ 50.11 \\ 69.41 \\ 88.15 \end{array}$	$75.4 \\ 100.7 \\ 84.9$	$3.33 \\ 11.36 \\ 22.35 \\ 48.07 \\ 32.64$	$\begin{array}{r} .21\\ .93\\ 1.81\\ 5.34\\ 2.62\end{array}$.11 .23 .43 .71 .72	$ \begin{array}{c} 1.66\\ 3.86\\ 6.96\\ 9.82\\ 13.24 \end{array} $	$151 \\ 212 \\ 189 \\ 136 \\ 78$	$19.8 \\ 27.6 \\ 24.7 \\ 17.8 \\ 10.1$
	Contraction of the second			100	16.5		766	

Table 14.-Surface soils-table of averages-fixation phosphoric acid.

Table 15.-Table of averages-subsoils-fixation phosphoric acid.

	P ₂ O ₅ absorbed	$\begin{array}{c} Active \\ P_2O_5 \\ per million \end{array}$	Acid consumed per cent	Per cent CaO	Per cent MgO	$\begin{array}{c} \operatorname{Per \ cent} \\ \operatorname{Fe2O_3 \ and} \\ \operatorname{Al_2O_3} \end{array}$	Number averaged	Per cent of number in groups
Group 0- 20 P ₂ O ₅ absorbed Group 20- 40 P ₂ O ₅ absorbed Group 40- 60 P ₂ O ₅ absorbed Group 60- 80 P ₂ O ₅ absorbed Group 80-100 P ₂ O ₅ absorbed	$11.97 \\ 29.87 \\ 50.75 \\ 70.22 \\ 88.21$	$\begin{array}{r} 43.45\\38.74\\74.19\\53.49\\19.61\end{array}$	$2.83 \\ 9.53 \\ 24.32 \\ 31.72 \\ 23.78$	$.15\\.62\\2.34\\3.55\\3.21$.13 .20 .41 .70 .53	$1.98 \\ 4.16 \\ 7.24 \\ 9.97 \\ 12.73$	$\begin{array}{r} 63 \\ 88 \\ 126 \\ 190 \\ 180 \end{array}$	9.7 13.6 19.4 29.7 27.6
							647	

The percentage of iron and aluminum oxides increases with the percentage of phosphoric acid fixed, in both surface and subsoils. There is an average relation between the iron and aluminum compounds in the soil, and the amount of phosphoric acid fixed. The iron and aluminum compounds mentioned are those dissolved by strong hydrochloric acid, according to Hilgard's method, that is, by heating the soil in a boiling water bath 16 hours with hydrochloric acid 1.115 specific gravity.

STATISTICAL RELATIONS

The relation between the phosphoric acid absorbed and the amount of iron and aluminum oxides dissolved from the soil by strong acid, was studied by statistical methods. Surface soils and subsoils were studied separately. Table 16 is the correlation table for the surface soils. The correlation table for the subsoils is similar, and is not given.

The correlation factor R between the phosphoric acid absorbed and the percentages of iron and aluminum oxides in the surface soils is $.774 \pm .010$.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$		050	0.51-1.0	1.01-1.5	1.51-2.0	2.01-2.5	2.51-3.0	3.01-3.5	.51-	4.01-4.5	4.51-5.0	5.01-5.5	5.51-6.0	.01-6.	6.51-7.0	.01-7.	.51-8.	8.01-8.5	8.51-9.0	9.01-9.5	51-10.	10.01-10.5	.51-11.		51-12.	01-12.	.51-13.	.01-13.	.51-14.	.01-14.	14.51-15.0	.01-15.	15.51-16.0	16.01-16.5	16.51-17.0	17.01-17.5	17.51-18.0	18.01-18.5	18.51-19.0	19.01-19.5	19.51-20.0	20.01-20.5	20.51-21.1	Total
Total 852 79 54 42 43 36 33 26 23 29 22 24 22 20 24 17 19 18 16 8 15 14 21 11 6 6 14 8 6 3 9 6 4 6 7 2 2 1 1 2 2761	$\begin{array}{c} 5 & 1\!\!-\!10 \\ 10 & 1\!\!-\!15 \\ 15 & 1\!\!-\!20 \\ 20 & 1\!\!-\!25 \\ 25 & 1\!\!-\!30 \\ 30 & 1\!\!-\!35 \\ 35 & 1\!\!-\!40 \\ 40 & 1\!\!-\!45 \\ 45 & 1\!\!-\!50 \\ 55 & 1\!\!-\!55 \\ 55 & 1\!\!-\!60 \\ 60 & 1\!\!-\!65 \\ 55 & 1\!\!-\!60 \\ 60 & 1\!\!-\!75 \\ 70 & 1\!\!-\!75 \\ 75 & 1\!\!-\!80 \\ 80 & 1\!\!-\!85 \\ 85 & 1\!\!-\!90 \\ 90 & 1\!\!-\!95 \\ \end{array}$		15 13 10 4	$ \begin{array}{c} 12 \\ 19 \\ 8 \\ 7 \\ 32 \\ 1 \\ $	8 12 8 11 5	56710421	4556555 1	564 23 1	$ \begin{array}{c} 3 \\ 8 \\ 4 \\ 4 \\ 4 \\ 1 \\ 1 \end{array} $	$ \begin{array}{c} 2 \\ 6 \\ 2 \\ 3 \\ 3 \\ 1 \\ 2 \end{array} $	43333	226 335 4			an internal	1 1 4 5 1	52 3 1 1	111	$ \begin{array}{c} 4 \\ 4 \\ 1 \\ 1 \\ \cdot \\ \cdot \\ 2 \\ \cdot \\ \cdot$		222 2121 111 1	ī	$ \begin{array}{c} 1 \\ 1 \\ 1 \\ 2 \\ 1 \\ 2 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 1 \\ 1 \\ 2 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 2 \\ 1 \\ $	2 1 ··2	$\begin{array}{c}1\\ 1\\4\\2\\1\end{array}$	···· ··· ··· ··· ··· ··· ··· ··· ··· ·	i	1	⁴ 3 3 ··3 2 ··			··· ·· ·· ·· ·· ·· ·· ·· ·· ·· ·· ·· ··			22	3	111	···· ··· ··· ··· ··· ···	······································	•••••••••••••••••••••••••••••••••••••••	······································	······································	······································	443549 549 549 549 549 549 549 549 549 549

Table 16.-Correlation between percentages of iron and aluminum oxides and percentages of phosphoric acid absorbed.

The correlation factor R between the phosphoric acid absorbed and the iron and aluminum oxides dissolved from the subsoil is $.701 \pm .013$.

These figures show a close correlation between the phosphoric acid absorbed from the soil and the quantity of iron and aluminum oxides dissolved by the strong acid referred to above. There is evidently a close relation between these two factors. The regression coefficient is 0.15 for surface soils and 0.14 for subsoils. The percentage of phosphoric acid absorbed multiplied by the regression coefficient gives approximately the average percentage of iron and aluminum oxides. The iron and aluminum oxides divided by this factor gives approximately the average absorption.

A study was also made of the correlation between the phosphoric acid absorbed and the quantity of lime dissolved by strong hydrochloric acid. The correlation factor R for the surface soils is .098 \pm .024.

The correlation factor R for the subsoils is $.060 \pm .026$.

The correlation factor between the phosphoric acid absorbed by the soil and the amount of lime present is, therefore, very low indeed. The percentage of iron and aluminum compounds in the soil is of much greater influence upon the amount of phosphoric acid absorbed than the percentage of lime compounds.

RELATIVE FIXATION BY TEXAS SOILS

Tables 14 and 15 also show the numbers of surface and subsoils in each group with different fixation powers. Since 1413 soils were examined, these results should represent fairly well the relative fixing powers of Texas soils. About 10 per cent. of the surface soils, and 28 per cent. of the subsoils, have a fixing power of over 80 per cent. The subsoils have a higher fixing power than the surface soils.

RELATION OF FIXATION OF PHOSPHORIC ACID TO ACTIVE PHOSPHORIC ACID.

The fact was brought out in Bulletin 126 of this Station that the phosphoric acid dissolved from soils by N/5 nitric acid did not necessarily represent all the phosphoric acid which could be dissolved from the soil by this reagent, but represented the equilibrium between the phosphoric acid dissolved and the phosphoric acid fixed from the solution. Known amounts of phosphoric acid added to the soil were not entirely recovered but the amount recovered depended upon the fixing power of the soil for phosphoric acid. This fixation would interfere with the interpretation of the analysis of soils with high fixing power, since the actual amount of phosphoric acid present would remain uncertain. The uncertainty would be in the direction of the soil's appearing poorer than it really is.

Further work with pot experiments has so far not permitted a demonstration of the effect of fixation upon the results, chiefly for the reason that the number of soils with high fixing power included in the pot experiments is comparatively small. Soils having a fixing power of more than 80 per cent. would be chiefly affected, and as shown in

tables these would be about 10 per cent. of Texas surface soils and 27 per cent. of subsoils. Not all of these soils would be affected, since some soils of this group have much lower fixing power in acid solution than in neutral.

ACKNOWLEDGMENT

Mr. S. E. Asbury, J. B. Rather, Herman Lebeson, Charles Buchwald, and other members of the staff, took part in the laboratory and other work involved in this Bulletin.

SUMMARY AND CONCLUSIONS

This bulletin is the study of the relation of fixation to properties of typical Texas soils, especially as related to the loss of phosphoric acid from fertilizers, or the estimation of active plant food in the soil.

A comparison of fixation at different temperatures showed that with some soils considerable increases took place when the temperature increased.

The fixation of phosphoric acid by the soil increased with the time of contact.

The addition of two grams of salt added to precipitate the clay had little effect upon the amount of phosphoric acid fixed.

Treatment with acid, which would remove the carbonate of lime, had little effect upon fixation by some soils, while it decreased the fixation by other soils considerably.

Igniting the soil increased the power of the soil to fix phosphoric acid, even when the lime had been removed by previous treatments with acid.

A number of minerals examined for fixation did not have high enough fixing power to explain fixation by the soils. The soil minerals have a higher fixing power than the minerals found in deposits.

A lump of phosphate in the soil is probably surrounded by a solution decreasing in strength as the distance increases and by zones of soil particles which increase in fixing power, according to the more or less complete satisfaction of their fixing power by the soluble phosphoric acid.

Soils having a fixing power of more than 50 per cent. lost practically no phosphoric acid when treated with acid phosphate and subjected to percolation under the conditions described.

Soils having a fixing power of less than 50 per cent. lost considerable amounts of fertilizer phosphoric acid by percolation.

A large part of the fixation took place in the soil column below the mixture of soil and fertilizer.

The amount of phosphoric acid in the percolate decreased as the time of contact between the soil and fertilizer increased before water was applied.

Heavy rains would be required to cause loss of phosphoric acid even from soils of low fixing power, under natural conditions. A rain of 3 or 4 inches within ten days might cause a loss of 3 or 4 per cent. of the water-soluble phosphoric acid applied to light sandy soils with sandy subsoils, having a fixing power of less than 50 per cent. An examination of 761 surface soils and 651 subsoils showed that the percentages of iron and aluminum oxides increased as the percentages of phosphoric acid fixed increased.

The correlation factor R between the phosphoric acid absorbed and the percentages of iron and aluminum oxide dissolved from the surface soils was $.774 \pm .010$.

The correlation factor R for the subsoils was $.701 \pm .013$.

There was a close correlation between the phosphoric acid fixed by the soils and the quantities of iron and aluminum oxides dissolved by strong acid from the soils.

The correlation factor R between the quantity of lime dissolved by strong acid, and the phosphoric acid fixed was $.098 \pm .024$ and for the subsoils it was $.060 \pm .026$. There was little correlation between the phosphoric acid absorbed by the soil and the amount of lime present.

A table is given showing the relative fixation of 1413 Texas soils.

Further work is required on the relation between the fixation in the soil and the effect of fixation upon the active phosphoric acid recovered from the soil.