

# Phosphate Retention By Muck Soils<sup>1</sup>

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## INTRODUCTION

The subject of phosphate retention, meaning the removal of phosphate from a solution by a soil or by a soil constituent, has been widely studied in soil science. Logically, much of the emphasis has been placed on mineral soils, for they make up the majority of the soils on earth. By comparison, therefore, the work done on phosphate retention by an organic soil seems to be very slight.

## LITERATURE REVIEW

Doughty (4)<sup>3</sup>, determining the retention capacity of peat soils for phosphorus at various pH levels, found that retention was at maximum at pH 2.0. A gradual decrease in retention occurred as the pH was increased. In determining the effect of leaching peat with acid on phosphate retention the data obtained showed that it decreased as compared with a water-leached peat, when fixation was measured at the same pH value in both cases.

To test the effect of iron absorption on phosphate retention he saturated the peat with iron; an increase in its phosphate-retention capacity was observed. Retention was a maximum at pH 2.5. A decrease was observed with a change of pH in either direction. The data were similar for an aluminum-saturated peat, but the maximum phosphate retention was at pH 4.5.

Evidence was obtained showing that water-soluble salts had considerable effects between pH's 6 and 8. Doughty finally reached the conclusion that the formation of iron, aluminum, and calcium phosphates would account for the retention of phosphate under field conditions.

Further studies carried on by Doughty (5) confirmed his previous findings, in that leaching with hydrochloric acid reduced the retention capacity of the peat, the extent being dependent on the normality of the acid used.

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<sup>3</sup> *Italic numbers in parentheses refer to Literature Cited, p. 193.*

Weidemann (12) found that the very acid mucks he studied showed negative retention of phosphorus, but the less acid mucks showed positive retention. Dunton (6), in phosphate-retention studies, proved that the addition of humus was effective in decreasing the fixation of the applied phosphorus. Burd (1), working with displaced soil solutions, suggested that organic matter does not adsorb phosphate, or if it does, the phosphate is held by such weak linkages that it is readily released to the soil solution or plant.

Dalton, *et al.* (2) stated that the principal products of phosphate fixation in acid soils formed by the reactions of soluble phosphates with iron and aluminum are relatively insoluble. Wild (13), in his review of phosphate retention by soils, asserted that phosphate ions may be retained by an exchange reaction with the hydroxyl ions that are normally linked with the iron and aluminum ions. Miller (10), through his work on phosphate retention by hydrated alumina, came to the conclusion that the mechanism by means of which hydrated ferric oxide retains phosphate is similar to that for hydrated aluminum oxide. Moser (11) found that there is a maximum phosphate fixation between pH 4.5 and 6.0. Ghosh and Bhattacharyya (7), working with hydrous gels of alumina and silica, demonstrated that phosphate ions are removed from solutions by forces of electrical attraction. Davis (3) reported that the degree of retention was dependent upon the pH of the applied solution.

Haseman, Brown, and Whitt (8) ascribed phosphorus retention in soils to certain calcium phosphate-exchange combinations with clay and hydrous oxides of iron and aluminum, and to phosphates of iron and aluminum. However, they emphasized that the exact nature of the reactions of phosphorus with the soil constituents was poorly understood because of the difficulty with which the products of the fixation reactions are detected and identified in soil systems.

## PHOSPHATE-RETENTION STUDIES

### PREPARATION OF SAMPLES

A peat-soil sample derived from low-ash vegetation was obtained from Orange County, N. Y. This soil had an original pH of 3.8. After the peat was limed a 1:2 soil-water suspension gave a pH of 5.15. The exchange capacity of the peat soil was 196 m.e. per 100 gm. of soil. At a pH of 5.15 the base saturation was 26 percent.

An air-dried sample of the peat was ground in a hammer-mill and part of it was used for the phosphate-retention studies on the untreated peat.

PEAT TREATED WITH  $\text{Ca}(\text{OH})_2$ 

One hundred grams of the untreated peat were diluted with 300 ml. of distilled water. To this soil-water suspension 2.2 gm. of powdered  $\text{Ca}(\text{OH})_2$  were added, and the resulting mixture was stirred continuously for 12 hours. At the end of this time the pH of the suspension was taken, using a Beckman pH-meter, and was 6.15. The corresponding base saturation at this pH was 55 percent.

The soil-water mixture was placed on a Büchner funnel and filtered using suction. The soil was then washed several times with distilled water. After this the soil was air-dried and stored for future use.

## COLUMN PACKING

To 10 gm. of the air-dried peat soil 40 ml. of 95-percent ethyl alcohol were added. The mixture was boiled under reduced pressure so as to remove air from the peat.

A short chromatographic column (13 mm.  $\times$  460 mm.) was then filled with the peat-alcohol suspension, applying 10 pounds of air pressure. On top of the level peat, a layer of 0.2 gm. of cellulose powder was placed. This cellulose powder was Whatman chromatography-grade ashless cellulose powder.

After the column was packed it was washed with distilled water to rid it of alcohol. Finally, the column was eluted, using a 0.001-M solution of  $\text{CaCl}_2$ , the concentration most likely to occur in the soil solution.

## APPARATUS

An automatic drop-count fraction collector was used for taking the different fractions that were to be analyzed. With it small fractions of the liquid passing through the column were collected in a large number of test tubes fixed in a horizontal wheel. This wheel rotated sufficiently to move a new test tube under the outlet of the column as soon as a predetermined number of drops have been collected.

## FRONTAL ANALYSIS

The behavior of a substance which travels through a chromatographic column in a given medium depends upon the affinity of the substance for the column material in the medium. If we allow a solution containing one component to pass through a column packed with an adsorbing medium, we can determine by analysis the position and concentration of that component in the effluent liquid. This is frontal analysis.

## OPERATION

After the column was eluted for a reasonable time with the 0.001-M  $\text{CaCl}_2$  solution it was removed from its position. The liquid on top of the

cellulose layer was removed carefully and, without allowing any air to enter the column, a 300  $\gamma$ P/ml. phosphate solution was placed in a fixed vertical position on top of the automatic fraction collector and the column liquid was displaced at the rate of 3 ml./hr. The flow of liquid was maintained constant by the use of a Mariotte bottle filled with the phosphate solution on top of the column and this, in turn, was connected to the column headpiece by means of Tygon tubing.

Fractions of 16 drops, or approximately 1 ml., were collected in 18  $\times$  150-mm. test tubes and diluted to 3 ml. with distilled water before analyzing for phosphorus.

The exact weight of liquid that was analyzed was determined by weighing five empty test tubes and then reweighing them after the 16 drops were collected so as to obtain the volume of liquid per tube.

#### METHOD OF ANALYSIS

A modified procedure of the method developed by Kitson and Mellon (9) for the determination of phosphorus as molybdivanadophosphoric acid was used.

In the procedure 1-ml. aliquots of the solutions to be analyzed were taken. The aliquots were diluted with 1 ml. of distilled water and to each of them 1 ml. of 2.5-N HNO<sub>3</sub> was added. One milliliter of 0.125-percent ammonium vanadate and 1 ml. of 2.5-percent ammonium molybdate were then added. The solution was mixed well after each addition. Optical densities were read after 15 minutes at 470  $\mu$  using a Junior Coleman Spectrophotometer.

#### REAGENTS

Ammonium molybdate, 2.5 percent: Dissolve 12.5 gm. of (NH<sub>4</sub>)<sub>7</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O in distilled water and dilute to 500 ml.

Ammonium vanadate, 0.12 percent: Dissolve 1.25 gm. of NH<sub>4</sub>VO<sub>3</sub> in 500 ml. of boiling water (use a 1-l. Pyrex volumetric flask), cool the solution somewhat, add 20 ml. of concentrated HNO<sub>3</sub>, cool and dilute to 1 l.

Phosphate solution 300  $\gamma$ P/ml.: Dissolve 2.6409 gm. of KH<sub>2</sub>PO<sub>4</sub> in 0.001-M CaCl<sub>2</sub> solution. Dilute to a volume of 2 l. with additional 0.001-M CaCl<sub>2</sub> solution.

#### DISCUSSION OF RESULTS

##### PHOSPHATE RETENTION BY UNTREATED PEAT

Triplicate runs were made for the studies on phosphate retention by the untreated peat. Values for phosphorus concentration expressed as  $\gamma$ P/ml., are given for each tube analyzed in each run. See table 1.

TABLE 1.—*Frontal-analysis chromatography data for the untreated peat as  $\gamma$ P/ml.*

Tube No.	Replication 1	Replication 2	Replication 3
2	7		4
5	7		4
10	7	7	4
15	13	7	4
20	13	7	4
25	13	7	4
27	13	7	4
28	13	7	4
29	13	7	18
30	13	7	68
31	34	7	117
32	88	7	157
33	133	18	178
34	162	58	196
35	184	113	209
36	203	144	221
37	214	178	227
38	227	191	227
39	239	203	232
40	245	221	239
41	245	227	245
42	245	239	245
43	250	239	250
44	250	245	250
45	257	250	250
46	263	257	257
47	263	257	257
48	263	257	257
49	263	257	257
50	270	257	263
51	270	263	263
52	270	263	270
53	270	263	270
54	270	270	270
55	270	270	270
56	277	277	270
57	277	277	270
58	277	283	270
59	277	283	270
60	283	283	270
61	283	283	270
62	283	283	270
63	283	283	270
64	283	283	270
65	283	283	277
66	283	283	277
67	292	292	277
68	292	300	277
69	292	300	277

TABLE 1.—(Continued)

Tube No.	Replication 1	Replication 2	Replication 3
70	292	300	277
71	300	300	277
72	300	300	277
73	300	300	277
74	300	300	277
75	300	300	277
76	300	300	277
77		300	277
78		300	277
79		300	277
80			277
81			277
82			277
83			277
84			277
85			277
86			277
87			277
88			277
89			277
90			283
91			283
92			292
93			292
94			292
95			300
96			300
97			300
98			300
99			300
100			300

The curve shown in figure 1 represents a typical curve obtained by plotting optical density against fraction number. Data essential for the calculation of amount of phosphorus retained are given in table 2.

The mean amount of phosphorus retained by the acid peat was  $636 \pm 3.5$  pounds per acre. Table 3 shows a summary of the amount of phosphorus retained by the untreated peat.

#### PHOSPHATE RETENTION BY PEAT TREATED WITH $\text{Ca}(\text{OH})_2$

An increase in phosphorus retention was observed when the peat was treated with  $\text{Ca}(\text{OH})_2$ . Data necessary for calculating the amount of phosphorus retained by the peat are given in table 4. Results of analyses on the

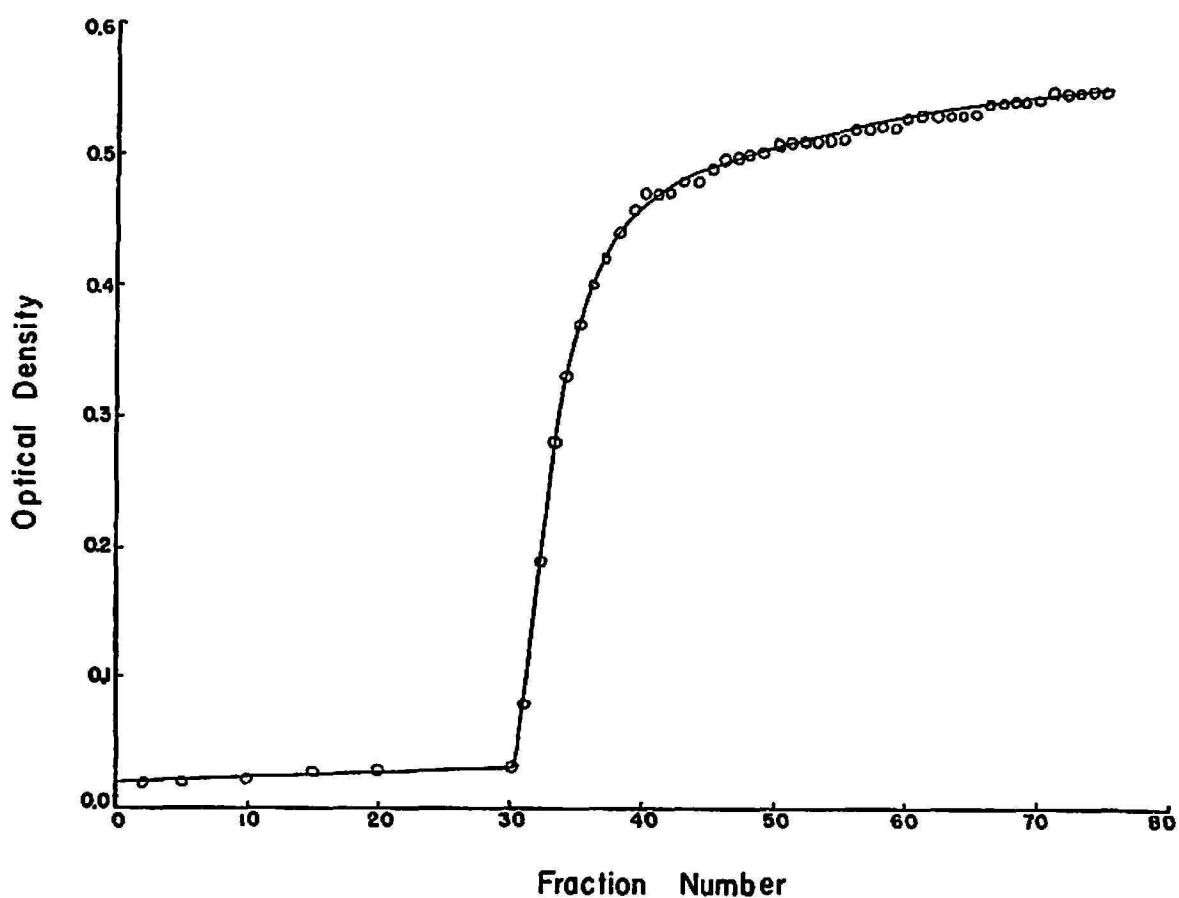


FIG. 1.—Optical densities of samples obtained in the study on phosphorus retention by an acid peat.

TABLE 2.—Data for calculating the phosphorus retained by untreated peat

Item	Run No. 1	Run No. 2	Run No. 3
Weight of peat..... grams	10	10	10
Weight of cellulose..... do.	.2	.2	.2
Weight of empty column..... do.	49.96	49.96	49.22
Weight of column + peat + cellulose + liquid..... do.	82.0	83.18	79.88
Fraction volume..... do.	.981	.949	.998
$V_0$ = column volume..... do.	21.8	23.02	20.5
$V_2$ ..... do.	32.3	33.7	31.1
$V_2 - V_0$ , volume of solution from which P was removed..... do.	10.5	10.7	10.6
Phosphorus concentration..... $\gamma$ P/ml.	300	300	300
Amount of P retained..... lb./A.	630	642	636

different fractions are seen in table 5. A typical curve obtained by plotting optical density versus fraction number is shown in figure 2.

When the untreated peat was eluted with the phosphate solution a point was reached at which the analyses of the fractions were the same as those



for the original solution. This point was never reached for peat treated with  $\text{Ca}(\text{OH})_2$ . The shape of the curve obtained indicates that a very slow process by which phosphorus had been retained by the peat was occurring in the column behind the phosphate front. The phosphorus retained by the peat treated with  $\text{Ca}(\text{OH})_2$  was  $1,094 \pm 37.7$  pounds of P/A. of soil. Table 6 shows a summary of the amount of phosphorus retained by the peat treated with  $\text{Ca}(\text{OH})_2$ .

TABLE 3.—A summary of the quantity of phosphorus retained (lb./A.) by the untreated peat

Replication run No.	P retained	Mean	Standard deviation
1	630	—	—
2	642	636	$\pm 3.5$
3	636	—	—

TABLE 4.—Data for calculating the phosphorus retained by peat treated with  $\text{Ca}(\text{OH})_2$

Item	Run No. 1	Run No. 2	Run No. 3
Weight of peat..... grams	10	10	10
Weight of cellulose..... do.	.2	.2	.2
Weight of empty column..... do.	50.0	49.22	50.0
Weight of column + peat + cellulose + liquid..... do.	82.51	81.42	82.76
Fraction volume..... do.	.952	.974	.982
$V_0$ = column volume..... do.	22.3	22.0	22.6
$V_2$ ..... do.	40.7	41.6	39.3
$V_2 - V_0$ , volume of solution from which P was removed..... do.	18.4	19.6	16.7
Phosphorus concentration..... $\gamma\text{P/ml.}$	300	300	300
Amount of P retained..... lb./A.	1,104	1,176	1,002

As the treated peat was 55-percent base-saturated, but only 26-percent base-saturated when untreated, this means that an increase of 29 percent in base saturation caused a net increase of 458 pounds of phosphorus retained by the peat. In other words, the calcium treatment was responsible for the retention of that amount of phosphorus.

The increase in retained phosphorus possibly could be ascribed to three different forms of calcium phosphates in the peat: Tricalcium phosphate, dicalcium phosphate, and monocalcium phosphate. These forms of phosphates have different solubilities and, to a great extent, their presence is determined by the pH of the soils in which they occur. Tricalcium phos-



TABLE 5.—*Frontal-analysis chromatography data for peat treated with Ca(OH)<sub>2</sub> as  $\gamma$ P/ml.*

Tube No.	Replication 1	Replication 2	Replication 3
2	2	4	4
5	2	4	4
10	2	4	4
15	2	4	4
20	2	4	4
25	2	4	4
26	2	4	4
27	2	4	4
28	2	4	4
29	2	4	4
30	2	4	4
31	2	4	4
32	2	4	4
33	2	4	4
34	2	4	4
35	2	4	4
36	2	4	4
37	2	4	4
38	2	4	4
39	2	4	54
40	22	4	117
41	68	25	144
42	113	68	167
43	117	117	184
44	139	133	191
45	154	149	203
46	162	157	209
47	167	162	214
48	178	184	214
49	178	196	214
50	191	196	214
51	191	196	214
52	191	232	221
53	203	232	227
54	203	232	221
55	203	239	232
56	214	239	232
57	221	239	227
58	221	239	227
59	227	239	232
60	227	239	232
61	227	239	232
62	227	239	232
63	227	239	232
64	239	239	232
65	239	239	239
66	239	239	239
67	239	239	245
68	239	239	245
69	239	239	245

TABLE 5.—(Continued)

Tube No.	Replication 1	Replication 2	Replication 3
70	239	245	250
71	245	245	245
72	245	250	250
73	250	250	245
74	250	250	250
75	250	250	250
76	257	250	250
77	257	250	263
78	257	250	245
79	257	257	257
80	257	257	263
81	257	257	257
82	263	257	263
83	270	257	263
84	270	257	263
85	270	257	263
86	270	257	263
87	270	257	263
88	270	257	263
89	270	257	263
90	270	257	263
91	270	257	263
92	270	257	263
93	270	257	263
94	270	257	263
95	270	257	263
96	270	257	263
97	270	257	263
98	270	257	263
99	270	257	263
100		257	263
101			263
102			270
103			263
104			270
105			270
106			270
107			270
108			270
109			270
110			270
111			277
112			277
113			270
114			270
115			270
116			270
117			270
118			270
119			270
120			270

phate would be the least available of the three forms present, followed by the dicalcium phosphate and the monocalcium phosphate.

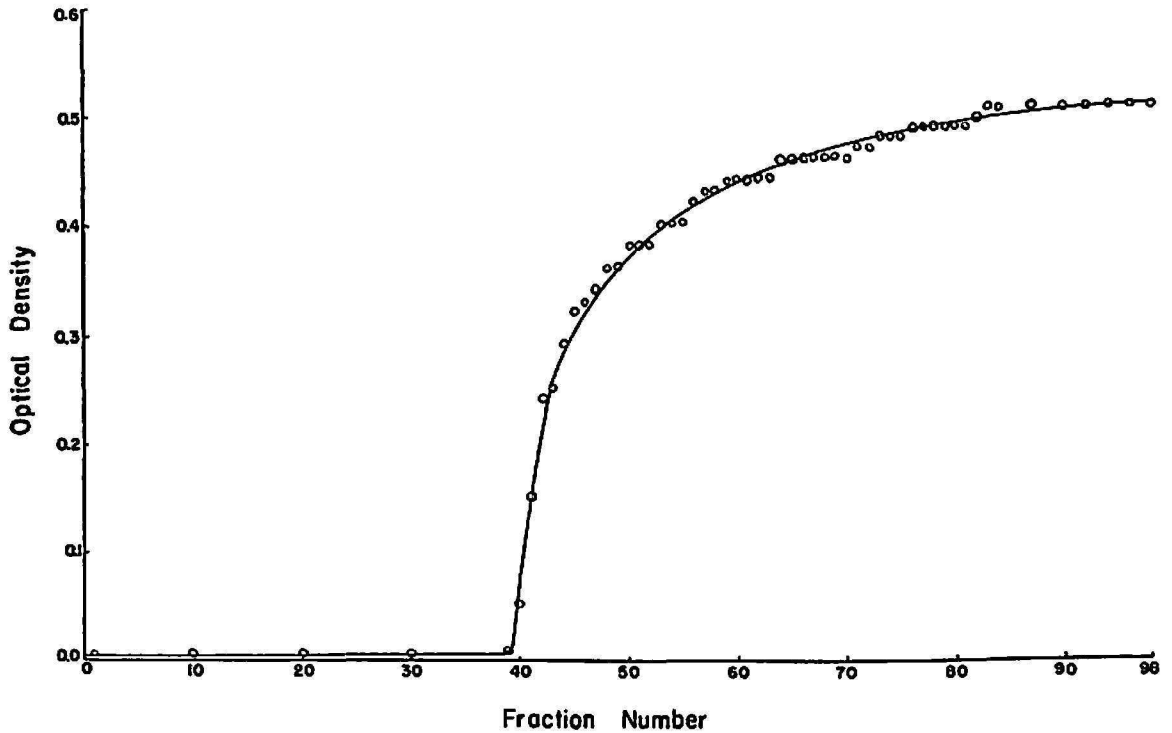


FIG. 2.—Optical densities of samples obtained in the study on phosphorus retention by a peat treated with  $\text{Ca}(\text{OH})_2$ .

TABLE 6.—A summary of the quantity of phosphorus retained (lb./A.) by peat treated with  $\text{Ca}(\text{OH})_2$

Replication run No.	P retained	Mean	Standard deviation
1	1,104	—	—
2	1,176	1,094	$\pm 37.7$
3	1,002	—	—

### SUMMARY AND CONCLUSIONS

A refined procedure for the determination of phosphorus retention by an organic soil by means of frontal-analysis chromatography has been used with success.

The following conclusions were drawn from the investigations:

1. Frontal-analysis chromatography can be used for the determination of phosphate fixation in soils.
2. Calcium has a role in phosphate fixation in organic as well as in mineral soils.

## RESUMEN

Se ha usado con éxito el análisis cromatográfico frontal para estimar la cantidad de fósforo retenido por un suelo orgánico.

Como resultado de esta investigación se ha llegado a la siguiente conclusión:

1. El análisis cromatográfico frontal puede usarse en investigaciones sobre la fijación de fósforo en suelos orgánicos.

2. En los suelos orgánicos, igual que en los suelos minerales, el calcio juega un importante papel en la fijación del fósforo.

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