SOME FACTORS TO CONSIDER IN STUDYING THE FIXATION OF PHOSPHOROUS BY SOILS

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INTRODUCTION

The fixation phenomenon of soils is by no means new to soil investigators, altho like many other phenomena there are, no doubt, many things yet to be learned about it. As early as 1850 Way (48) expressed very definite ideas concerning the fixation of various substances by soils. Fixation may be either chemical or physical and is usually referred to as absorption. There is another term, "adsorption" which is sometimes used and is defined by Patten (39) as "a difference between the concentration or density of a film adjacent to a bounding solid and that of the mass of liquid or gas that bathes the solid", or "a specific attraction between a solid and absorbed material". There is a feeling on the part of some investigators that the term "adsorption" might well be dropped. In this work the writer has chosen to dispense with both of the above mentioned terms and use only the term "fixation".

The power which soils have for fixing substances from solution is far from being the least important factor in soil fertility. It is the belief of a large number of present day investigators that nearly all, if not all, of the material fixed by soils is fixed by the colloidal portion of the soil. Fixation by the soil plays a very important part in preventing soluble plant food elements from being lost thru leaching. Applied fertilizers and materials made soluble in the soil are prevented in this way from being lost while at the same time they are fairly easily accessible to the plants. As a rule when salts, the anions of which form soluble compounds with soil cations, are applied to soils the cations are fixed, while the anions are free to leach out or unite with other bases that have been liberated. This rule does not hold true, however, in the case of a phosphorous salt when applied to soils. In this case the phosphate radical is itself fixed.

The object of this work is not to determine whether or not phosphorous is fixed by soils, but rather to point out some of the things that must be considered in studying the fixation of phosphorous and some of the effects, on the soil, of an application of a phosphorous salt.

HISTORICAL

According to Prescott (40) it was known to Aristotle, the Greek philosopher, that sea water lost some of its taste when filtered thru sand. He states further that LeComte de Marselle in 1725 filtered sea water thru garden soil and then found by evaporation that a considerable amount of salt had been lost. Prescott (40) quotes Gazzero as stating in 1819 in a text book on manuring that he observed that soils take up soluble substances, a phenomenon which he considered an advantage to agriculture inasmuch as this fixed material may become available later as the plants need it.

Thompson (47) made quantitative determinations of absorption in 1845. He added solutions of ammonium sulphate to soils and then washed them out with water. Analysis showed that quite a lot of ammonia had been lost from solution and calcium and magnesium were found in the solution with the sulphate radical. Way (48) repeated the above experiments with other bases and obtained about the same results. He considered the fixation due to a chemical reaction. He reasoned that a physically absorbed substance could be washed out with water while a chemically absorbed substance was completely insoluble. In 1852 Way published another article (49) in which he registered his belief that the fixation of bases was due to the formation of aluminum silicates with the bases used, this, of course, being a chemical reaction again. Prescott (40) states that in 1858 J.V. Liebig took exception to Way's chemical theory and declared that, in his belief, the attraction of a soil for salts was of a purely physical nature.

Gordon (24), in an article published in 1923 described four different types of fixation from solution. 1. Chemical fixation which follows the mass law, 2. exchange adsorption (one ion adsorbed in place of one released), 3. partition ratio adsorption, and 4. electronic adsorption.

Cameron and Bell (7) expressed their belief that fixation was both physical and chemical. They report that when free P_2O_5 is added to a soil containing ferric hydroxide it is absorbed in such a way that the more P_2O_5 there is in solution the more there will be found in the solid ferric hydroxide; that is, the P_2O_5 forms a solid solution with the ferric hydroxide and the composition of the solid solution changes with that of the solution above it. When P_2O_5 is added to a soil containing CaO a solid solution is formed also. The per cent of P_2O_5 in the solid phase increases with increased percentage of P_2O_5 in the solution until a certain concentration is reached, and further increase of P_2O_5 in the solution does not increase the per cent of P_2O_5 in the solid phase. A definite chemical compound has been formed.

Prescott (40) found that, in his work, the concentration of P_2O_5 in the solution added to humus had no effect on the amount of P_2O_5 fixed. It is the opinion of the writer that the above mentioned conclusions could not have been drawn if a much greater range of concentrations of P_2O_5 had been used.

Schreiner and Failyer (44) found, in their work, that soils which give up phosphorous when leached with water also fix large quantities of this element when solutions of $CaH_4(PO_4)_2$ are passed thru them. This is evidence, in the writer's opinion, that the more concentrated the phosphorous solution added to a soil the more phosphorous it will fix. There is, of course, a limit to the amount of phosphorous that can be fixed by certain material. These investigators also find that if water is passed thru a soil highly saturated with phosphorous large quantities of the latter will be removed immediately, but a very large quantity will remain quite securely fixed by the soil. Subsequent leachings will contain only small quantities of phosphorous, indicating that altho the absorbed phosphorous content of the soil is great the soil solution is about normal so far as phosphorous content is concerned.

Parker (37) in studying the selective absorption of soils found that the total quantity of Ca, Mg, and Al in a solution of KCl after treating the solution with a soil was not quite equivalent to the K absorbed, but the difference was practically equivalent to the amount of free acid in the solution. He found that in all cases of base absorption the solution was left acid. He suggests that a small quantity of $NaNO_3$ added to the solution will prevent the liberation of other bases such as Ca and Mg.

Prescott (40) quotes König as saying that peat that is almost entirely free from calcium and other bases still absorbs phosphoric acid. Also that he observed negative absorption. That is, the absorption of water instead of salts from solution. A peat treated with N/10 KCl absorbed water and left the supernatent liquid more concentrated than the original solution.

According to statements made by Patten (39) Lagergren found that either the solute or the solvent could be absorbed and the solution could become either more concentrated or less concentrated on being added to the soil. Solutions of NaCl, KCl, NH_4CL and NH_4Br become more concentrated when added to charcoal while those of $NaNo_3$, KNO_3, Na_2SO_4, K_2SO_4 and NH_4NO_3 become less concentrated. This investigator found no change in the acidity of the solution when bases were absorbed. That is not in accord with the findings of most other investigators working along this line.

Patten and Waggeman (39) found that when soil high in organic matter was treated with a manure extract low in organic matter the extract finally became more concentrated with organic matter. This more nearly approaches the writer's idea of a case of true negative fixation, when a solution actually becomes more concentrated as a result of some substance being given up by the solid, whether it be soil or some other absorbing material.

EXPERIMENTAL

In some preliminary work it was found that by treating some muck soils with a 0.1 N solution of $CaH_4(PO_4)_2$ and then analyzing the supernatent liquid approximately six times as much phosphorous was fixed as when the same soils were treated with a 0.02 N solution. It is evident from the above mentioned results that if a more dilute solution had been used there would have been indications of a still smaller amount of phosphorous fixed. We might reason further that if a very dilute phosphorous solution were added to a soil containing a large quantity of phosphorous the soil would give up some of this element which would go to concentrate the remaining solution. This, again, would be an example of the writer's idea of true negative fixation. It was also found (33) that when either 0.10 N or 0.033 N solutions of KCl were kept in contact with muck soils for a period of about 10 hours the solutions became less concentrated than it was before being added to the soil, while a 1.0 N solution of the same salt kept in contact with the same soils for the same length of time was found to be more concentrated with potassium than it was before being added to the soil. This is a case of what is commonly called negative absorption, but what is, in reality, a case of the soil being unable to hold as much potassium as was contained in the water fixed by the soil.

With these thoughts in mind the writer attempted to find out, if possible, more about the phenomenon of the fixation of phosphorous especially by muck soils. Four samples of muck were chosen with care from as many different muck deposits in the vicinity of the college. These deposits have become fairly well known by the following names which will be used throughout this paper: 1. Woodworth muck which is well drained and supports vegetation although it is very acid. 2. Trowbridge muck which is very poorly drained and exceedingly acid, too acid to support plant growth. 3. Town Line muck, which is fairly well drained and underlain with marl at a shallow depth although it has a pH value of less than 7. 4. College muck, which is fairly well drained and only slightly acid in reaction. All samples were taken from the surface six inches. They were brought from the deposits, sifted thru a 3/16 inch sieve, air dried and thoroughly mixed.

In studying the fixation of phosphorous by these mucks the following method was adopted which is very similar to that used by other investigators: - Five grams of the air dried material were placed in Erlynmeyer flasks in duplicate and fifty c.c. of the desired phosphorous solution added. The flasks were stoppered, shaken and allowed to stand for twenty-four hours, after which the liquid was filtered off and a phosphorous determination made on an aliquot part of the filtrate. At the same time a phosphorous determination was made on the original solution. It was found that on passing a 0.10 N solution of $CaH_4(PO_4)_2$ thru a filter paper no change in phosphorous content could be detected by analysis, although G.K. Hardin and F.W. Zirban (23) found that a sugar solution was made more concentrated by passing it thru a dry filter paper and less concentrated by passing it thru a wet paper. To eliminate the possibility of a change in concentration due to passing the solution thru a filter paper the first few c.c. of filtrate in each case were discarded. The phosphorous determinations were made by the usual volumetric method.

One of the objects in mind was to study the effect, on fixation, of adding solutions of different concentrations. In making up these solutions of different concentration a stock solution was first prepared by dissolving $CaH_4(PO_4)_2$ in water at the rate of 84 grams per liter. The salt did not all dissolve, and, no doubt, a portion of it was converted into other phosphorous compounds. The residue was filtered off and from the filtrate a series of dilutions was made by use of carefully calibrated pipettes. The soils were treated in duplicate, as already described, with the above mentioned solutions. After filtering the soil out it was found necessary to further dilute the filtrate before analysis. This, also, was done with carefully calibrated pipettes. The results of the analysis were calculated on the basis of the total volume of solution added, and are shown in table 1 and figs. 1 to 4 inclusive. The pH values of the original mucks are also shown in table 1. The results of the analyses are the averages of two determinations which, in most cases checked very well. The " " signs in the table indicate positive fixation, while the " " signs indicate that the final solution was more concentrated than the original, which is commonly spoken of as negative fixation.

Table 1. - The mgs. of Phosphorous Fixed by Four Different Mucks Treated with Phosphorous Solutions of Different Concentrations.

Name of Muck	Trowbridge			Woodworth			Town Line			College Farm		
	mgs. P added	mgs. P recovered	mgs. P fixed	mgs. P added	mgs. P recovered	mgs. P fixed	mgs. P added	mgs. P recovered	mgs. P fixed	mgs. P added	mgs. P recovered	mgs. P fixed
	109.27	104.55	+4.72	109.27	91.05	+18.22	109.94	78.24	31.70	109.27	97.79	11.48
	211.10	208.40	+2.80	211.11	188.20	+22.91	214.15	168.62	45.53	211.25	186.82	24.43
	313.00	308.90	+4.10	313.00	294.70	+18.30	318.35	266.42	51.93	313.22	288.00	25.22
	414.80	418.80	-4.00	414.80	402.00	+12.80	422.60	371.00	51.60	414.94	383.78	31.16
	516.60	511.90	+4.70	516.60	503.20	+13.40	526.80	470.10	56.70	517.31	481.58	35.73
	614.80	616.45	-1.65	614.80	609.10	+5.70	633.80	574.00	59.80	620.64	590.80	29.84
	713.05	720.30	-7.25	713.10	709.60	+3.50	740.70	685.30	55.40	723.98	691.30	32.68
	811.20	820.80	-9.60	811.20	814.70	-3.50	847.70	779.00	68.70	827.25	792.50	34.75
	909.40	926.00	-16.90	909.40	923.30	-13.90	954.70	886.30	68.40	930.60	898.40	32.20
	1007.60	1021.80	-14.20	1007.60	1035.30	-27.70	1061.70	991.50	70.20	1033.95	1013.10	20.85
Original pH value		3.21			3.70			5.63			5.51	

Graph showing { I fixation of phosphorous by Trowbridge muck.
II fixation of phosphorous by the same muck with enough water added to approximately account for that held unfree.

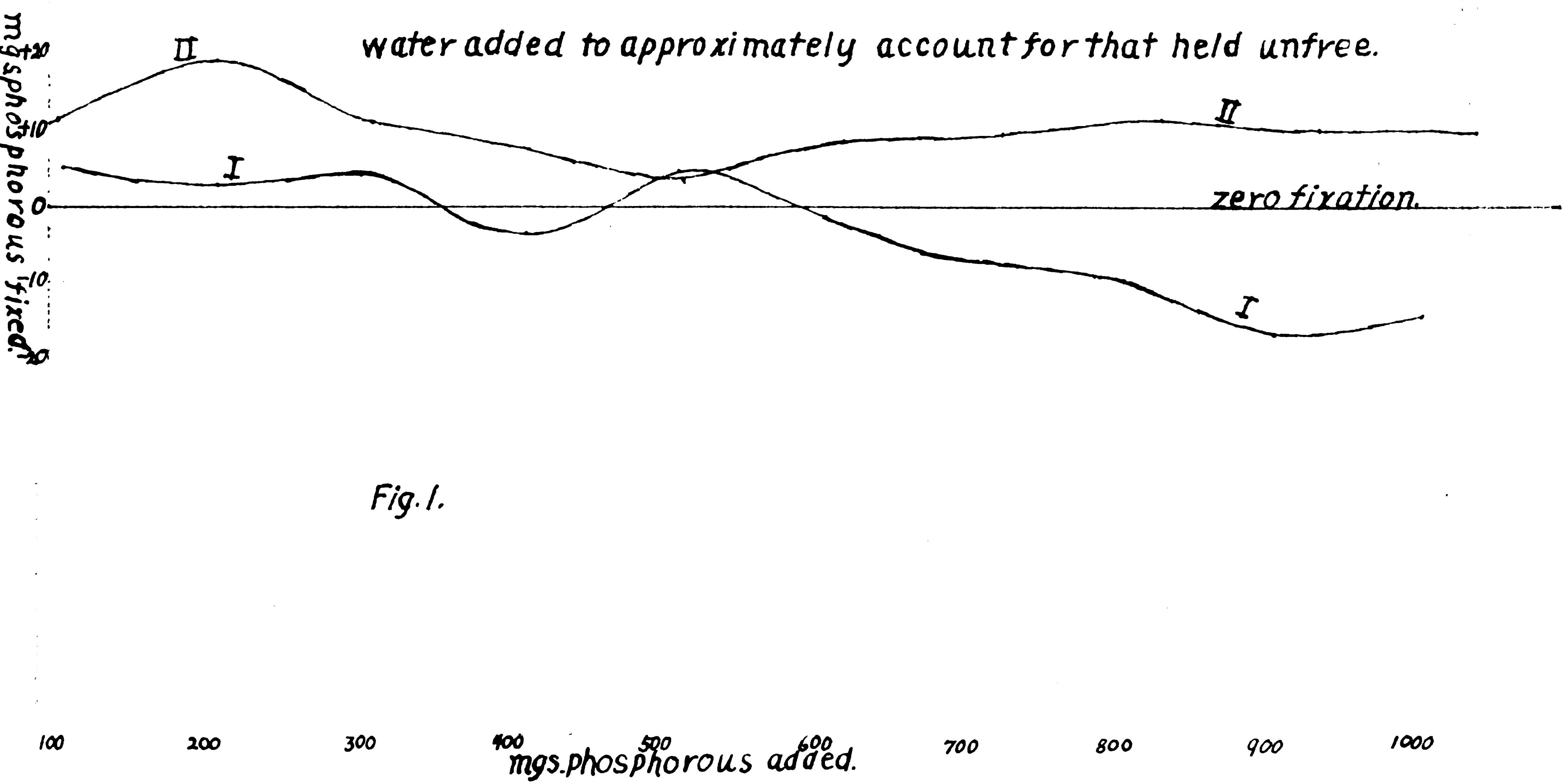


Fig. 1.

Graph showing { I fixation of phosphorous by Woodworth muck.
II fixation of phosphorous by same muck with enough water added to approximately account for that held unfree.

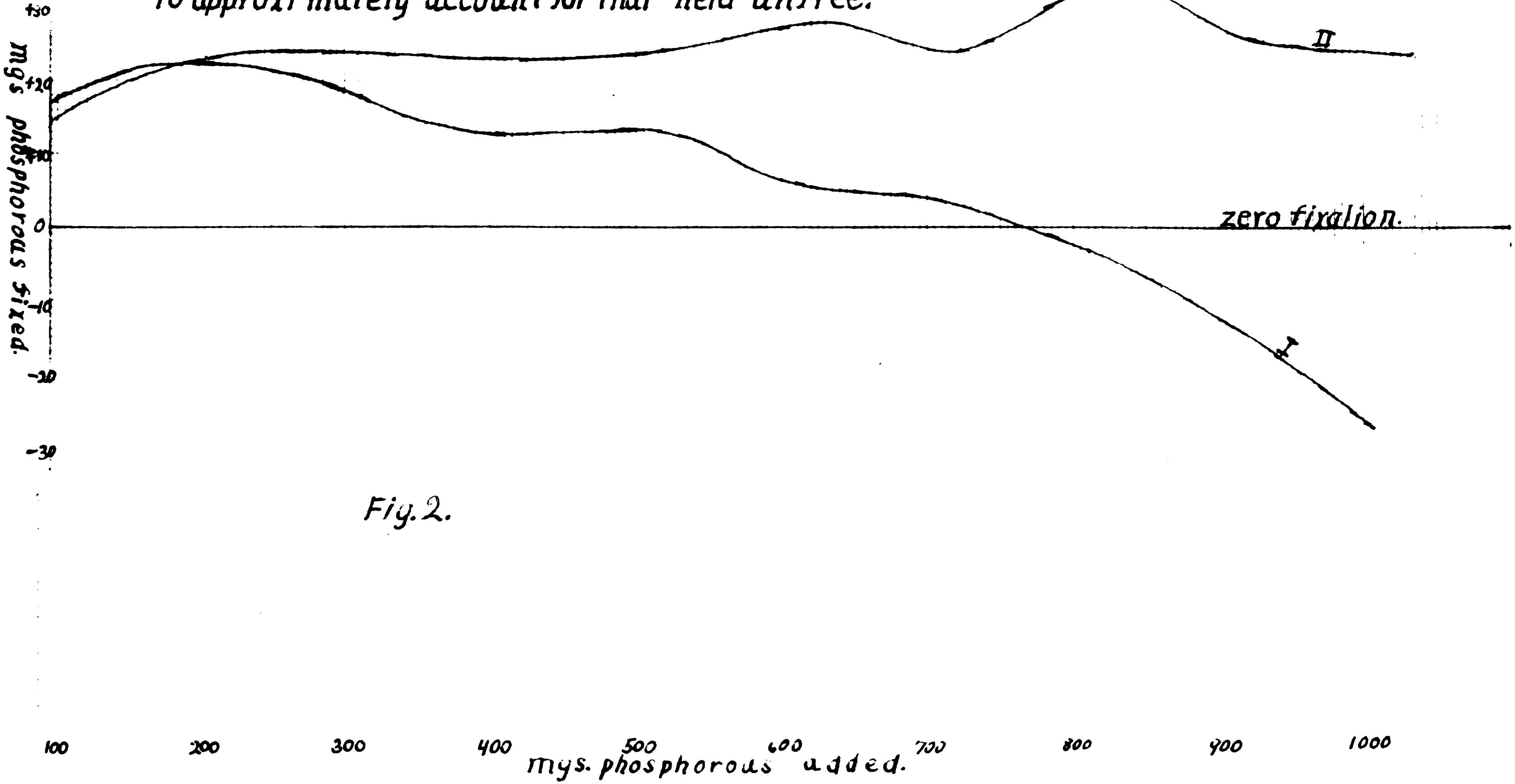


Fig. 2.

I Graph showing fixation of phosphorous by Town Line muck.

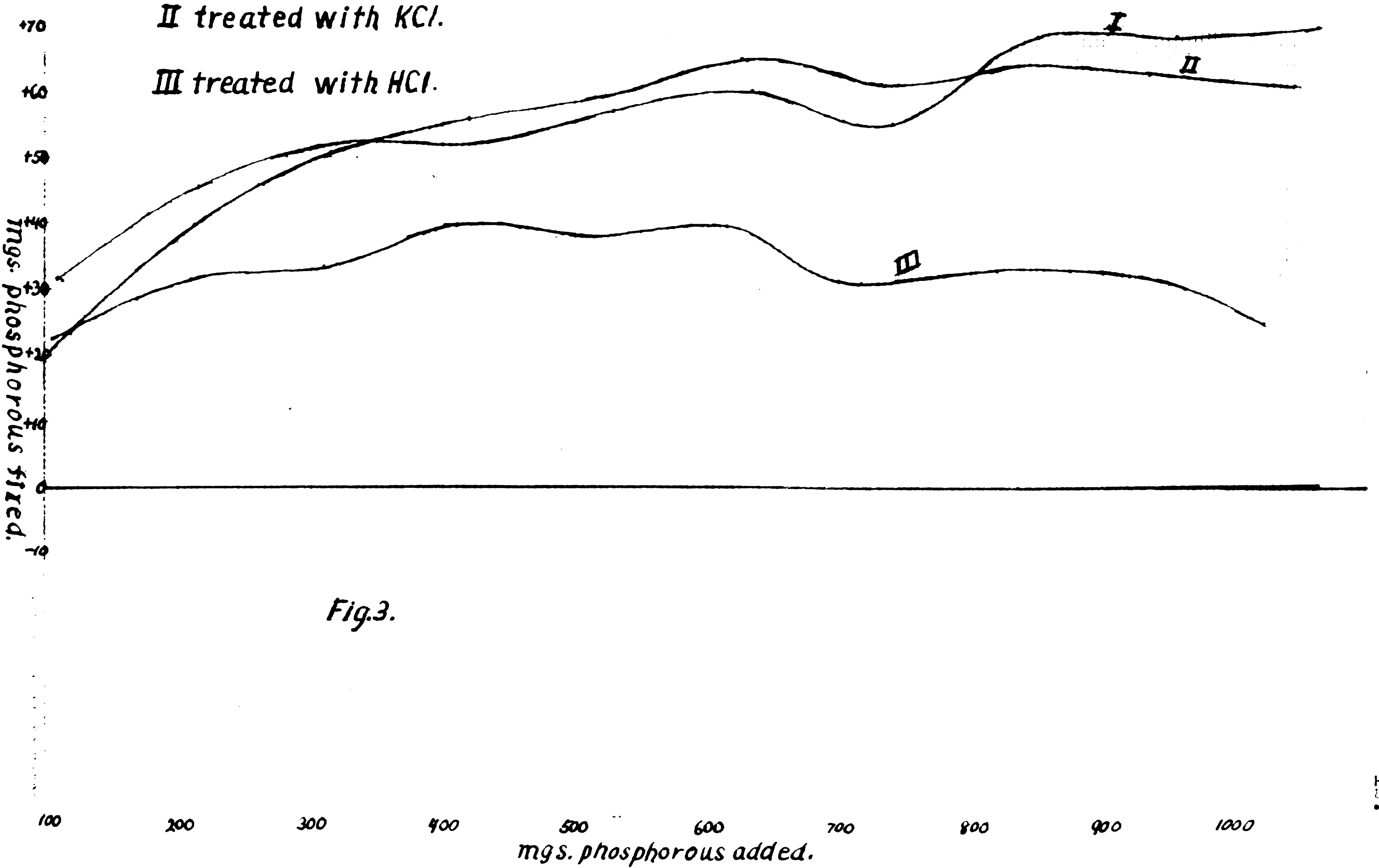


Fig.3.

Graph showing fixation of phosphorous by College muck.

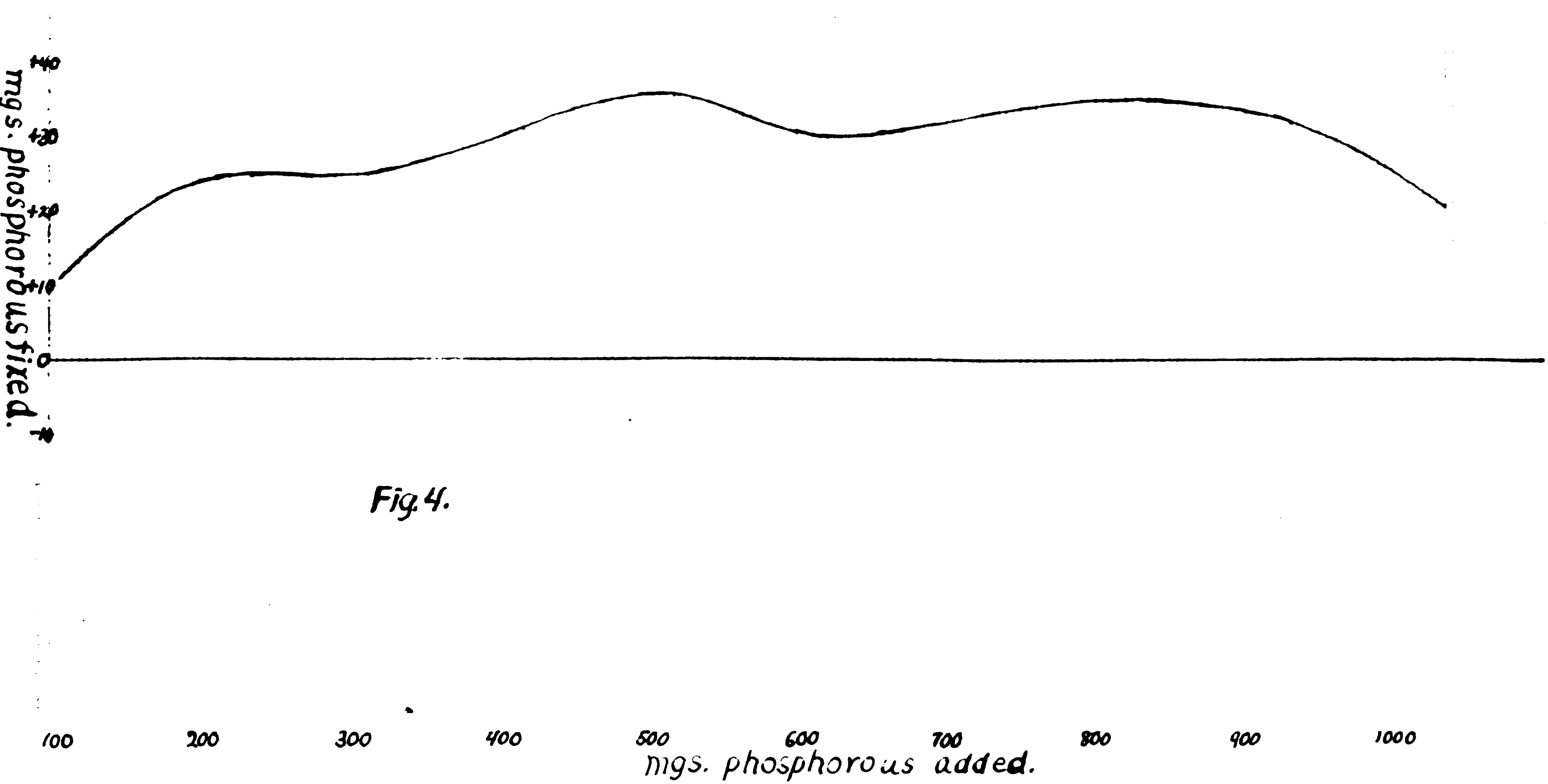


Fig. 4.

We see from these figures that the two mucks which were described as being very acid both showed negative fixation of phosphorous from the more concentrated solutions, while the other two showed positive fixation from all concentrations of solution used. There is no doubt in the writer's mind but that in all four soils there was more phosphorous fixed from the more concentrated solutionsthan from the more dilute solutions, but the indications of negative fixation by two of the mucks was brought about by the fact that they could not fix as much phosphorous as there was in the water than was rendered unfree, hence some phosphorous was left to concentrate the remaining solution. In the case of the other two mucks the phosphorous was fixed by combining chemically with calcium which accounts for the greater quantity fixed, thus leaving the final solution somewhat diluted. These statements will be substanciated by work reported further on in this paper.

In as much as the two mucks with the higher pH value showed no negative fixation and the two very acid ones did show negative fixation the next step was to study the effect of added lime on the fixation of phosphorous by the very sour mucks. Eleven samples of one hundred grams each were weighed out of each batch of very sour muck and mixed thoroughly with varying quantities of calcium oxide. The following treatments were made per acre, considering an acre six inches of muck soil to weigh 1,000,000#: - No treatment, 1 ton, 3 tons, 5 tons, 7 tons, 9 tons, 11 tons, 13 tons, 16 tons, 20 tons and 25 tons. These quantities of calcium oxide were weighed out and mixed thoroughly in a mortar with a small portion of the 100 gram sample of muck and then added to the remainder of the muck sample and mixed thoroughly with it. This provided for a uniform distribution of the calcium oxide throughout the muck. Ordinarily the oxide tends to remain in little balls. When these mixtures were made they were placed in jars and one liter of water added. They were shaken occasionally for a week and then filtered and dried and fixations studies made on them. The check sample was treated with water the same as the rest, but it received no calcium oxide. In making these studies the concentrations of phosphorous were used that gave approximately no fixation with the untreated muck. The results of these treatments are shown in table 2 and figs. 5 and 6.

Table 2. - The mgs. of Phosphorous Fixed by Trowbridge and Woodworth muck Treated with Calcium Oxide.

CaO Treatment	Trowbridge			Woodworth		
	mgs. P added	mgs. P recovered	mgs. P fixed	mgs. P added	mgs. P recovered	mgs. P fixed
none	636.10	640.10	4.00	657.60	648.80	8.80
1 ton	"	639.40	3.30	"	645.50	12.10
3 tons	"	534.00	2.10	"	538.10	19.50
5 "	"	631.30	4.80	"	627.30	30.30
7 "	"	629.30	6.80	"	629.30	28.30
9 "	"	627.25	8.85	"	623.20	34.40
11 "	"	619.85	16.25	"	621.90	35.70
13 "	"	613.75	22.35	"	599.60	58.00
16 "	"	586.10	50.00	"	573.30	84.30
20 "	"	551.70	84.40	"	540.30	117.30
25 "	"	508.50	127.60	"	505.90	151.70

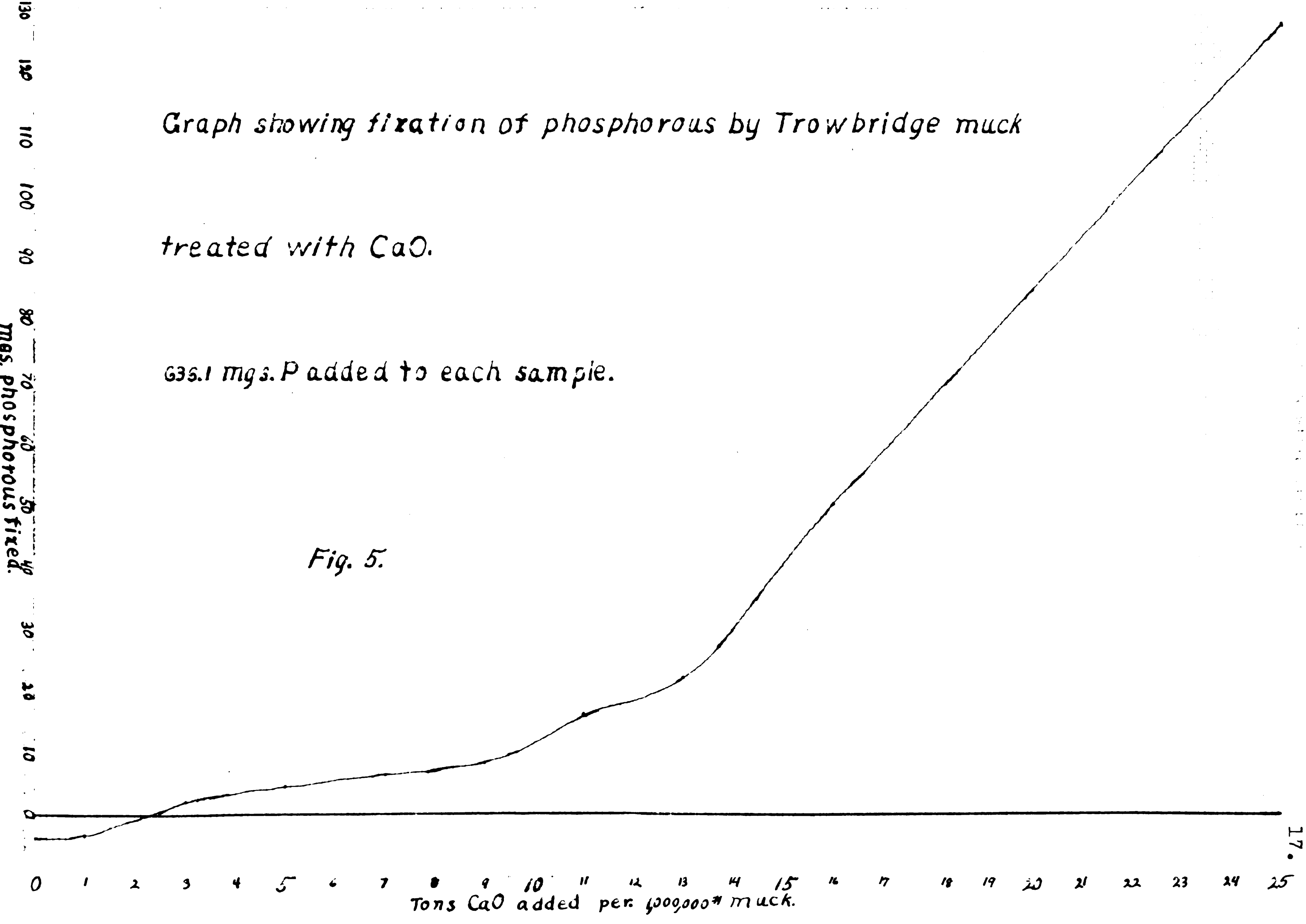
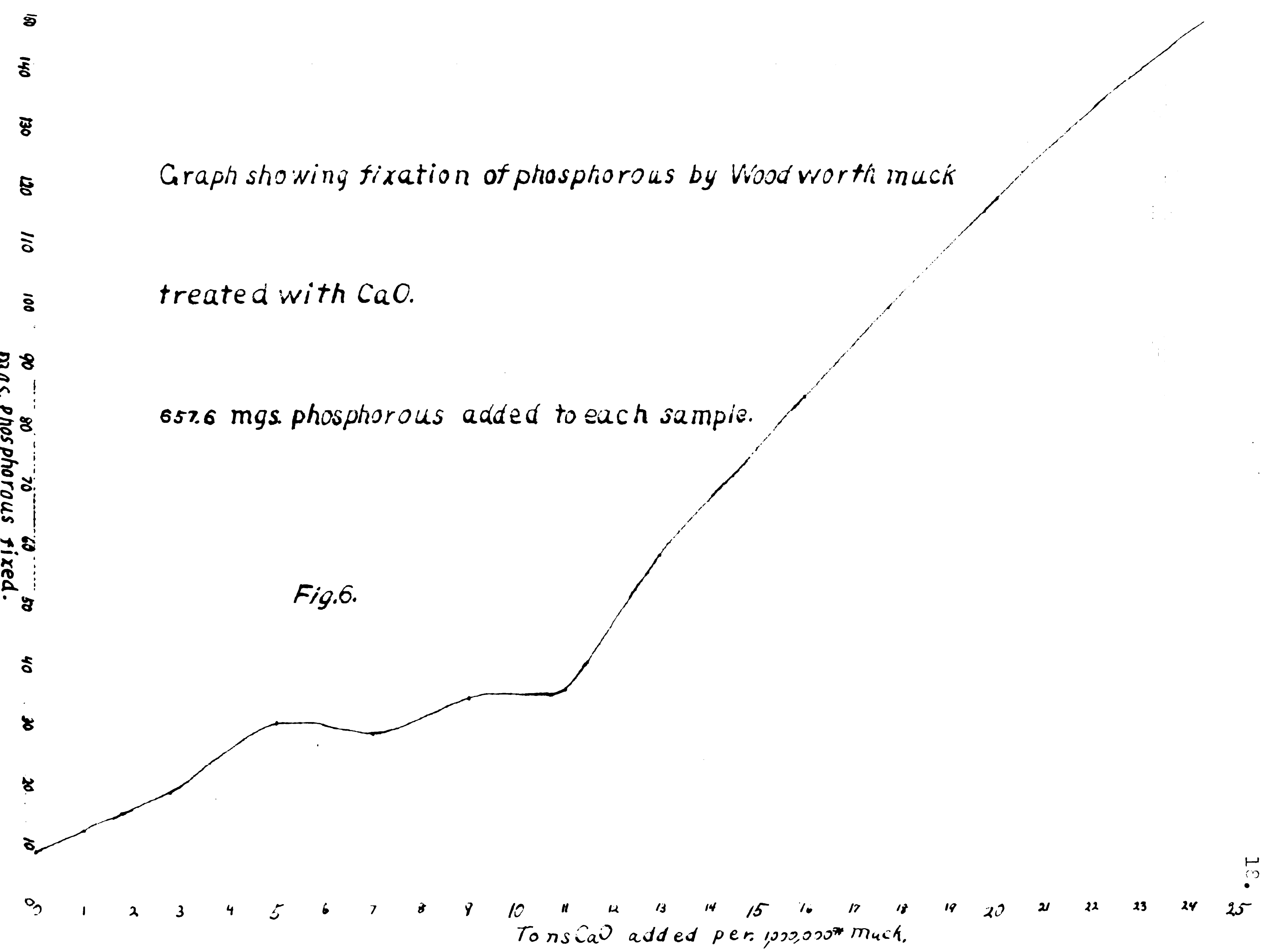

Graph showing fixation of phosphorous by Trowbridge muck
treated with CaO.
635.1 mgs. P added to each sample.
130
120
110
100
90
80
70
60
50
40
30
20
10
0
mgs. phosphorous fixed.
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
Tons CaO added per 1,000,000# muck.

Fig. 5.



Graph showing fixation of phosphorous by Woodworth muck treated with CaO.

657.6 mgs. phosphorous added to each sample.

Fig.6.

In preparing the phosphorous solutions with which to treat these soils concentrations were not secured that gave exactly zero fixation. They were near enough the right concentration, however, to serve the purpose very well. We see that by adding to five grams of the Trowbridge muck fifty c.c. of solution containing 036.1 mgs. of phosphorous there was a negative fixation of 4.00 mgs. If several samples of muck not treated with CaO had received the same treatment of phosphorous solution the fixation in each case should have been the same, but when the muck receiving twenty-five tons of calcium oxide was subsequently treated with the above mentioned phosphorous solution it fixed 127.6 mgs. of phosphorous. This difference in the amount of phosphorous fixed was due to the calcium present. The increase in phosphorous fixation due to the lime treatment was not directly proportional to the magnitude of the amount of lime added. The curves in figs. 5 and 6 show that there was a slight increased fixation with increase in lime treatment up to a certain point and from there on the increase in fixation was much greater than the increase in amount of lime added. Such variations are in all probability due to formation of different compounds of phosphorous and calcium. These same results in general hold true with the Woodworth muck. It will be interesting to note at this time that the twenty-five tons of calcium oxide per 1,000,000# of muck did not neutralize the Trowbridge muck and it raised the pH value of the Woodworth muck only slightly above 7. That gives one an idea of the extreme acidity of these materials.

Since fixation of phosphorous could be so markedly increased in sour mucks by the addition of lime it was thought well to study the effect on phosphorous fixation by high lime mucks by removing the lime with acid or substituting for calcium a base that forms a more soluble compound with phosphorous. Accordingly two 200-gram samples of the Town Line muck were weighed into jars. To one was added a liter of 3 N KCl and to the other was added a liter of 0.1N HCl solution. The mucks were allowed to remain in contact with these solutions for twenty-four hours and then they were thrown on filter papers in large funnels and allowed to drain. The necks of the funnels were then stoppered and another liter of solution added to each one. These solutions were allowed to drain off after 24 hours and each sample washed with three liters of water. The 3 N solution of KCl was recommended by Gedroiz (16) for substitution of bases in mineral soils. He reports that the major portion of the calcium is usually removed from mineral soils by the first few leachings. Gedroiz also used 10% HCl solution for removing bases from mineral soils. It was thought that a 10% solution of HCl would be too strong to add to an organic soil, hence the weaker solution was used. The washing was perhaps insufficient to remove the excess of HCl and KCl from these materials. Further washing was avoided because washing removed such a large amount of the colloidal portion of the organic material, especially when treated with KCl. In this case the leachings were almost black with organic colloids. After these soils were treated with $CaH_4(PO_4)_2$ and then leached with water the first leachings came thru fairly clear, but with continued leaching the flocculating material was removed and the leachings again contained large quantities of colloids. The fixation studies were made on these soils by the method already described and the results are shown in table 3 and fig. 3.

Table 3. - The mgs. of Phosphorous Fixed by Town Line Muck Treated with HCl and with KCl and Subsequently Treated with Phosphorous Solutions of Different Concentration.

Treatment	HCl			KCl		
	mgs. P added	mgs. P recovered	mgs. P fixed	mgs. P added	mgs. P recovered	mgs. P fixed
	104.14	81.61	22.53	106.6	85.0	21.6
	206.39	174.69	31.70	210.4	170.6	39.8
	308.64	275.19	33.45	314.3	263.0	51.3
	410.90	370.30	40.60	418.2	362.2	56.0
	513.28	475.50	37.78	522.0	462.7	59.3
	615.00	575.30	39.70	625.9	561.2	64.7
	717.00	685.95	31.05	729.8	669.1	60.7
	818.40	785.75	32.65	833.6	769.6	64.0
	920.60	888.30	32.30	937.5	874.8	62.7
	1022.30	996.90	25.40	1041.4	980.7	60.7

The treatment of this muck with KCl solution increased its alkalinity considerably which is in accord with the findings of other investigators, but the figures do not show that it decreased, to any extent, its power to fix phosphorous. The HCl treatment, however, did cause a considerable decrease in phosphorous fixation altho there was no negative fixation manifested. Had this muck been treated with a stronger solution of HCl it is quite likely that it would have shown negative fixation of phosphorous from a concentrated solution. The writer has found (unpublished results) that when high lime mucks were treated with HCl solutions of different concentrations and then treated with uniform treatments of phosphorous solutions the sample which received more concentrated solutions of HCl fixed correspondingly smaller quantities of phosphorous.

We have seen that very acid mucks fix phosphorous negatively from concentrated solutions, that high lime mucks do not fix phosphorous negatively from solutions of any concentrations, that very acid mucks when treated with lime do not fix phosphorous negatively, and that high lime mucks tend to fix less phosphorous from concentrated solutions after they are treated with acid. It remains now to show an explanation for the so-called negative fixation of phosphorous which the writer believes to be due to the irregular ratio between the amounts of phosphorous and water fixed from solutions of different concentrations.

The unfree water held by these mucks was determined by the dilatometer method as devised by Bouyoucos (5), and the hygroscopic coefficient was determined in the usual way by allowing them to remain for a week in a saturated atmosphere in a dessicator over a dilute solution of H_2SO_4. The results of these determinations are given in table 4.

Table 4. - The Hygroscopic Coefficient and the Unfree Water, as Determined by the Dilatometer Method, of the Mucks used in this Work.

Name of Muck	Hygroscopic Coefficient	Unfree water %
Trowbridge	15.08	45.0
Woodworth	15.44	50.8
Town Line	18.37	58.6
College	25.00	66.7

There is a tremendous difference between the unfree water and the hygroscopic coefficient of these mucks as shown in table 4. It is quite possible that neither set of figures represent the amount of water that the soils will take out of the role as a solvent. In view of this fact the writer attempted, by using the figures obtained in making fixation studies, to arrive at some conclusion as to how much water was taken out of the role as a solvent by some of these mucks. The following is an example of the method used. The figures were obtained by a study of the phosphorous fixation by Woodworth muck and are found in table 1.

1. 50 cc = solution added in each case.

2. 765 = mgs. phosphorous in 50 cc of solution used when no fixation, neither negative nor positive, was evidenced.

3. $\frac{765}{50} = 15.3$ = mgs. phosphorous in 1 cc of above mentioned solution.

4. Let X = cc H_2O held unfree by five grams air dry muck used.

5. 91.05 = mgs. phosphorous recovered after treating soil with most dilute solution used.

6. $\frac{91.05}{50} = 1.821$ = mgs. phosphorous in 1 cc of above mentioned filtrate.

7. $50 - X$ = cc of free solution in all cases.

8. $15.3X$ = mgs. phosphorous in water held unfree by soils when no fixation was evidenced.

9. Now if we assume that soils will fix the same amount of phosphorous regardless of the concentration of the solution added, then
$15.3X$ = mgs. phosphorous fixed by soil from most dilute solution used.

10. Then $15.3X + 1.821(50 - X)$ = mgs. phosphorous in 50 cc of the most dilute solution used which was found to be 109.27

11. $15.3X + 91.05 - 1.821X = 109.27$

12. $13.479X = 18.22$

13. $X = \frac{18.22}{13.479} = 1.35$ = cc H_2O made unfree by 5 grams air dried muck.

14. This muck was found to hold 8% water when air dried. Then 5 grams of air dried muck consisted of 4.6 grams muck and .4 grams of water.

15. $1.35 + .4 = 1.75$ cc held unfree = 38%.

The same method was used in determining the amount of water held unfree by Trowbridge muck. In making these determinations it was necessary to assume that soils fixed the same amounts of both water and phosphorous from solutions of any concentration which, of course, is not exactly true. Although the figures obtained in this way are not exactly correct they will serve in the attempt to show the cause of negative fixation.

For this work samples of Trowbridge muck and Woodworth muck were weighed into Erlynmeyer flasks as already explained and as much water added to each sample as it would hold unfree. They were then treated with phosphorous solutions of different concentrations as already explained and the fixation determinations made. The results are shown in table 5, and figs. 1 and 2.

Table 5. - The mgs. of Phosphorous Fixed by Very Acid Mucks with as Much Pure Water Added as They Would Hold Unfree.

Trowbridge Muck, 5 grams 1.0 cc water			Woodworth Muck, 5 grams 1.4 cc water		
mgs. P added	mgs. P recovered	mgs. P fixed	mgs. P added	mgs. P recovered	mgs. P fixed
105.62	94.41	11.21	103.06	87.68	15.38
209.09	190.20	18.89	206.39	183.46	22.93
312.54	302.16	10.38	309.86	286.00	23.86
416.00	408.73	7.27	413.05	389.85	23.20
519.17	515.30	3.87	516.63	492.35	24.28
624.65	615.76	8.89	619.82	592.19	27.63
730.00	720.32	9.68	723.00	698.75	24.25
835.35	824.14	11.21	826.20	793.20	33.00
940.80	930.72	10.08	929.38	903.80	25.58
1046.20	1035.30	10.10	1032.70	1009.00	23.70

The 1 cc of water added to five grams of Trowbridge muck air dried was sufficient, with what water was already in it, to make 28%. Likewise the 1.4 cc added to Woodworth muck was sufficient to make 38%. Table 5 and Figs. 1 and 2 show that when as much water is added to a muck as it will hold unfree there is not much variation in the amount of phosphorous fixed by the muck from solutions of different concentrations. There is no indication at all of negative fixation.

It is evident from the results of this work that if there were some method of determining accurately the amount of water that a soil will hold unfree it would be more nearly possible to determine the exact amount of material that the soil would fix from solution.

Effect of Phosphorous Treatment on Acidity.

We have seen that the acidity of muck soils has a tremendous influence on their ability to fix phosphorous. It is interesting now to note the effects of a treatment of $CaH_4(PO_4)_2$ on the acidity of the soil. There is quite a difference of opinion among investigators as to whether acid phosphate will make soil sour. Burgess (6) found that the application of acid phosphate in varying amounts caused a slight decrease in acidity. Conner (10) obtained about the same results. Morse (35) found that very little change took place in the H-ion concentration of soils that had been treated with acid phosphate for a period of years. Skinner and Beattie (45) reported a slight increase in soil acidity due to the addition of acid phosphate to some of their field plots. Coe (9) found that Ammo-phos effected the reaction of soil two to three inches away from where the fertilizer was applied in the hill, the change in reaction depending on the amount of fertilizer applied.

The increase in acidity found by Coe was due to excessive applications of the Ammo-phos.

Harper (26) found that acid phosphate applied on the basis of hill fertilization caused an immediate increase in acidity. In case of soils which are poorly buffered with basic material, such as $CaCo_3$ or easily hydrolyzable silicates and do not contain a very large amount of iron and aluminum the acidity of the soil solution produced by the hill application of acid phosphate was very slowly neutralized. In case of neutral or basic soils, or soils containing large amounts of iron and aluminum the acidity caused by the acid phosphate was rapidly neutralized. These results seem to indicate that the acidity or lack of acidity produced by applying acid phosphate to soils depend upon the amount of acid phosphate added and the nature of the soil.

After the phosphorous solutions were removed, by filtering from the various samples of muck used in this work the pH determinations were made on the residue by the electrometric method described by Spurway (46). In all cases the phosphorous treatments were made in duplicate. Therefore, there were , in all cases, duplicate samples of residue for pH determinations. One of each set of duplicates throughout the work was leached with 400 cc of distilled water before the pH determination was made, while on the other the determination was made without leaching. Table 6 shows the pH value of the materials untreated, after treatment with phosphorous solutions of different concentration, and after subsequent washing with 400 cc of water. The phosphorous treatments referred to are those given in table 1. The effect of the $CaH_4(PO_4)_2$ on the acidity of these soils can be seen much more clearly in figs. 7, 8, 9, and 10.

Table 6. - The pH Value of Four Mucks Untreated, after Treatment with Phosphorous Solutions of Different Concentrations, and after Subsequent Washing with 400 cc of water.

Mgs. P added (Approximately)	Trowbridge			Woodworth			Town Line			College		
	Original	Treated	Treated and Washed	Original	Treated	Treated and Washed	Original	Treated	Treated and Washed	Original	Treated	Treated and Washed
109.27	5.21	3.09	3.38	5.70	3.45	3.67	5.63	4.94	5.14	5.51	4.78	5.24
211.10			3.40		3.35	3.70						
313.00		3.04			3.30			4.46	4.77		4.11	4.87
414.80			3.48		3.20							
516.60		3.00			3.20			4.13	4.56		3.84	4.63
614.80			3.48		3.14							
713.05		2.98						3.92	4.43		3.58	4.45
811.20			3.48		3.13							
909.40		2.94			3.06	3.65		3.75	4.31		3.47	4.45
1007.60		2.92	3.55		3.04	3.67		3.72			3.35	4.23

Graph showing the pH value of Trowbridge muck treated with $CaH_4(PO_4)_2$ with and without subsequent washing.

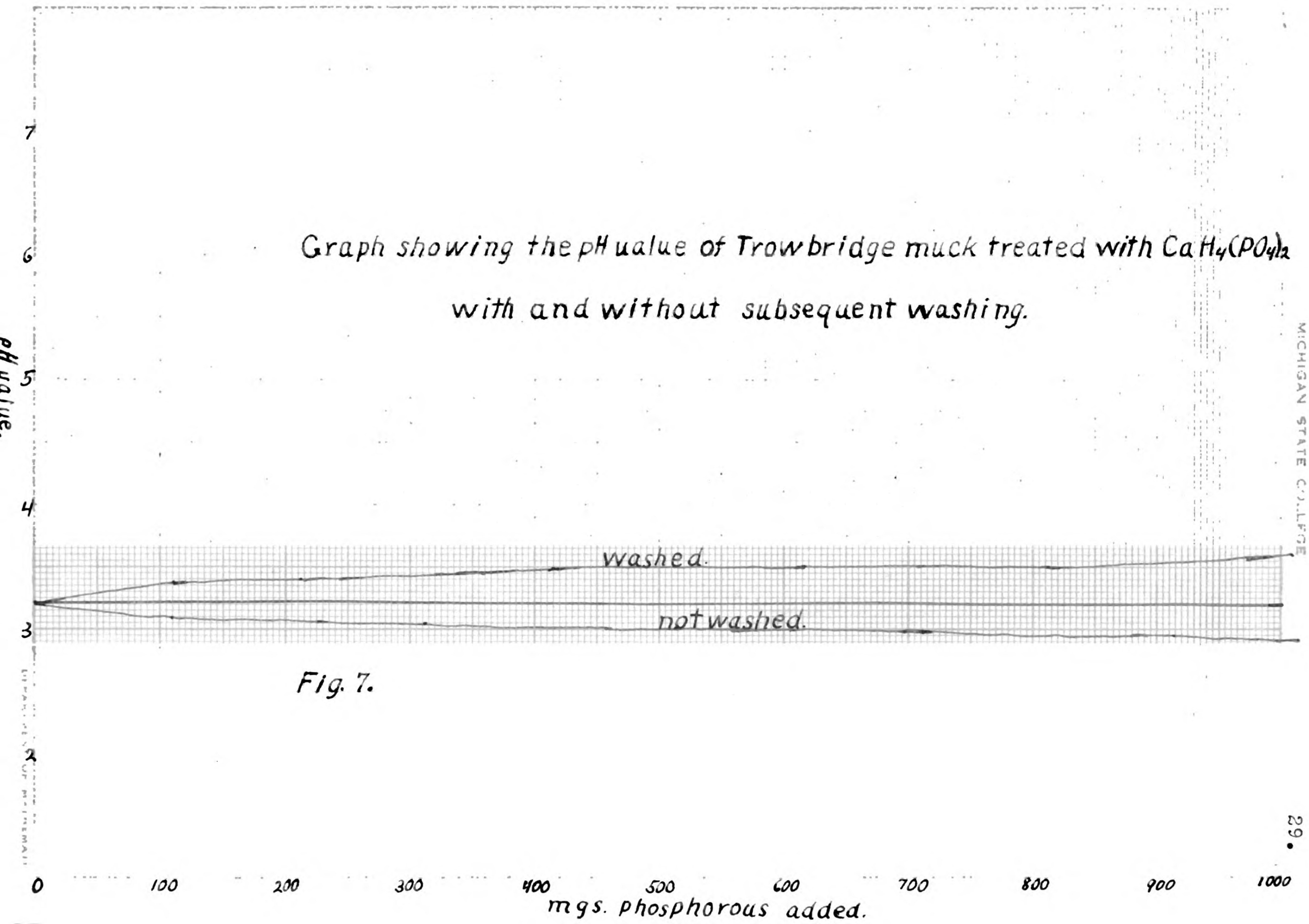


Fig. 7.

Graph showing the pH value of Woodworth muck treated with $CaH_4(PO_4)_2$ with and without subsequent washing.

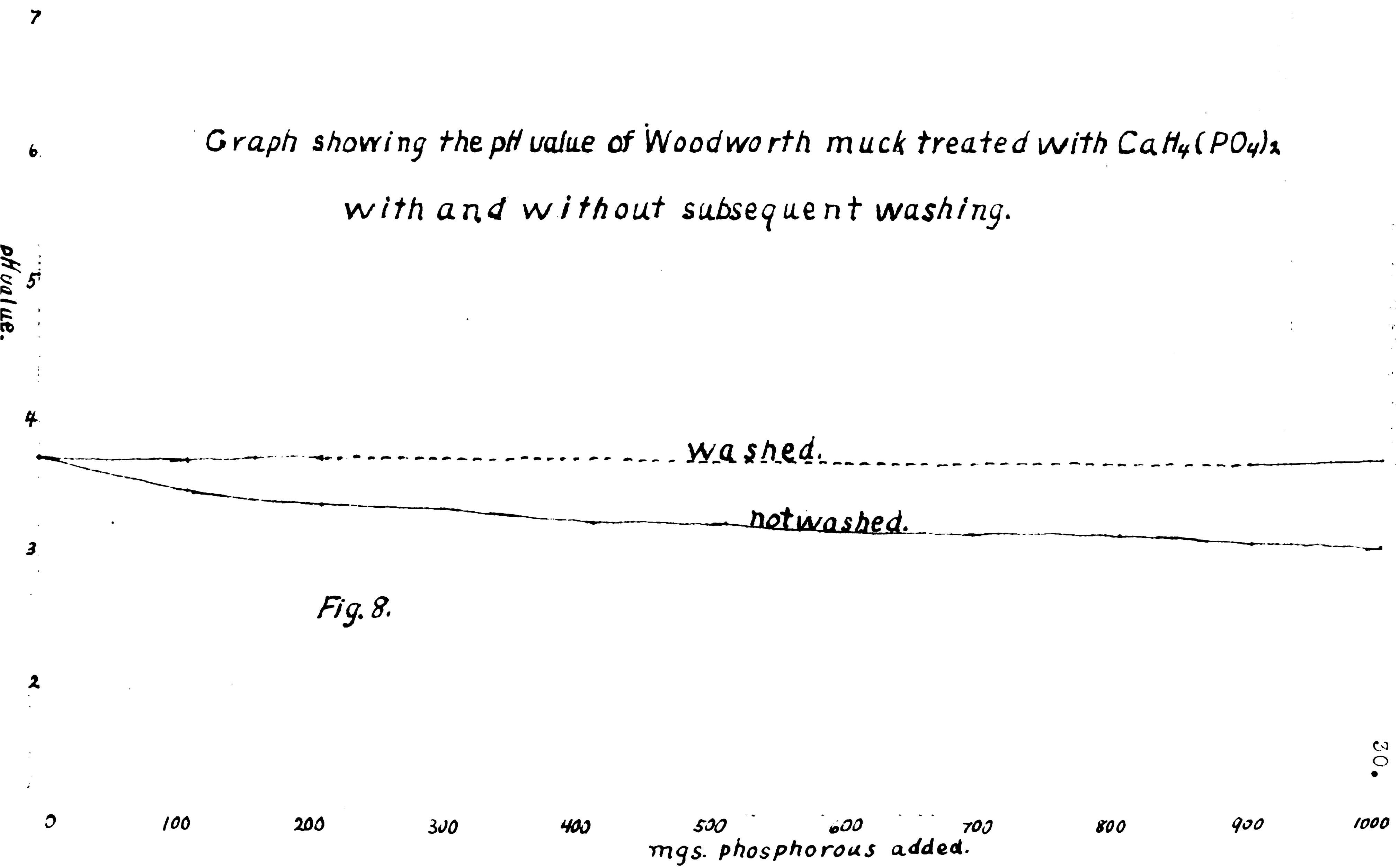


Fig. 8.

Graph showing the pH value of Town Line muck treated with $CaH_4(PO_4)_2$ with and without subsequent washing.

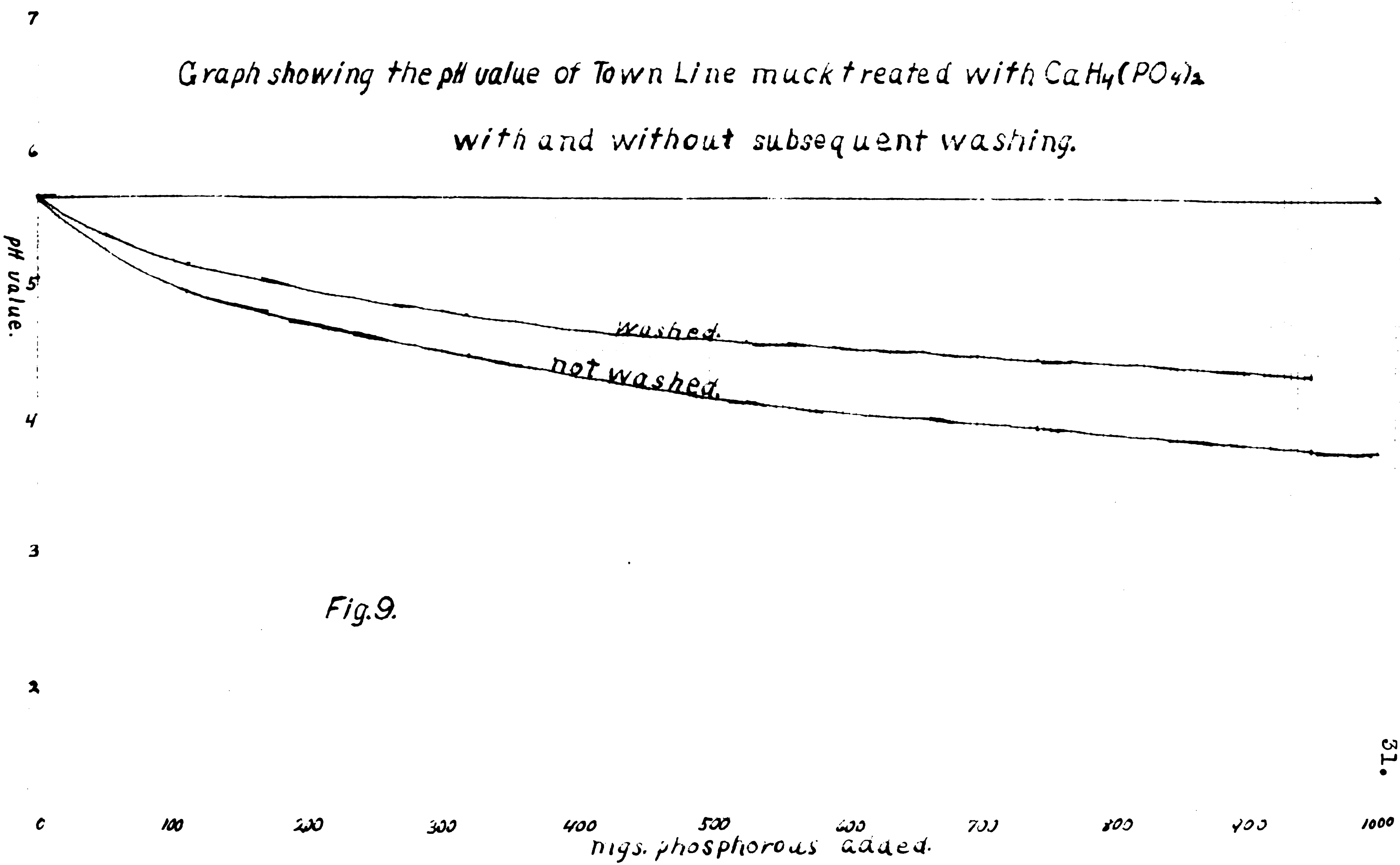


Fig.9.

Graph showing the pH value of College muck treated with $CaH_4(PO_4)_2$ with and without subsequent washing.

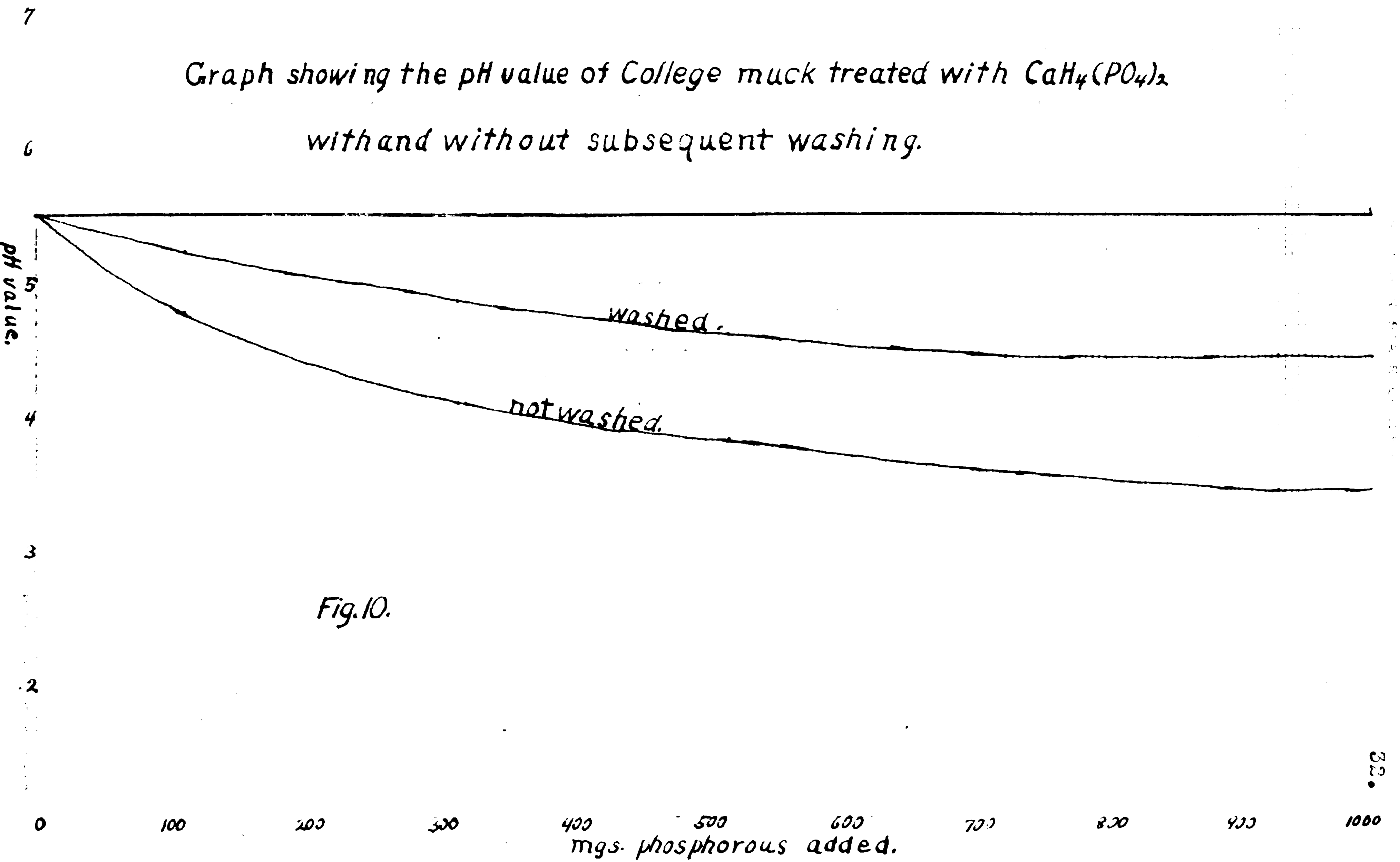


Fig. 10.

The treatment invariably causes an increase in acidity, and the greater the concentration of the phosphorous solution, the greater is this increase. That is not at all strange when we consider the fact that the pH values of the phosphorous solutions used ranged from 2.80 in the most dilute solution down to 2.54 in the most concentrated solution. The change in the pH value of the soils due to the addition of the phosphorous solution was proportional to the difference between the original pH values of the soils and that of the solutions added. That is; the change in pH value was greatest in the soils that were more nearly alkaline in reaction.

When these soils were leached after treatment with phosphorous solution the acidity in all cases was deminished. In the case of the Trowbridge muck the acidity after leaching was less than that of the original soil. The acidity of the Woodworth muck was the same after leaching as that of the original soil. While in the case of the Town Line and College mucks the increased acidity due to the phosphorous treatment was not removed by leaching with 400 cc of water.

Since the acidity of the Trowbridge muck was less after treatment with phosphorous solution and subsequent washing than it was originally it was thought that it might be possible to change the acidity of the original mucks by washing them with water. Accordingly 5 gm. samples were weighed into Erlynmeyer flasks, 50 cc of water added and allowed to stand one day. They were then filtered and washed with 400 cc of water each. The pH determinations were then made and the values are given in table 7 along with those of the original materials.

Table 7. - The pH Values of Four Muck Soils Before and After Leaching with 400 cc of water.

Name of Muck	Original pH Value	pH Value after Leaching
Trowbridge	3.21	3.25
Woodworth	3.70	3.79
Town Line	5.63	5.58
College	5.51	5.48

The figures in table 7 do not show any consistent change in the pH value of these mucks due to washing them with water. We must conclude then that the higher pH value of the Trowbridge muck after treatment with phosphorous solution and subsequent leaching was due to the fact that the phosphorous treatment changed the acid properties of the soil in such a way that they could be removed by leaching with water.

Table 8 and figs. 11 and 12 shows the pH values of Trowbridge and Woodworth muck treated with varying quantities of CaO and subsequently treated with a uniform treatment of phosphorous solution with and without subsequent washing. We see from these figures that adding CaO to the Trowbridge muck at the rate of 25 tons to 1,000,000 pounds of muck did not neutralize it. That fact gives one an idea of the extreme acidity of the soil. The same treatment of CaO raised the pH value of the Woodworth muck to 7.31, somewhat above the neutral point. The phosphorous treatments increased the acidity of these soils considerably, but a large portion of the increased acidity was removed by leaching. The curves in figs. 11 and 12 show that the phosphorous treatments of these soils cause a gradual rise in their pH value with increased applications of lime until a certain point is reached after which increased lime applications do not change the acidity. This change takes place at a pH value of approximately 4 in both soils and is, in all probability, due to the formation of an insoluble phosphate. Usually the break in such curves occurs higher on the pH scale.

Table 8. - The pH Values of Trowbridge and Woodworth Muck Treated with Different Quantities of CaO and Subsequently Treated with a Uniform Amount of $CaH_4(PO_4)_2$ with and without Subsequent Washing with 400 cc water.

CaO Treatment	Trowbridge muck			Woodworth muck		
	CaO Alone	+ $CaH_4(PO_4)_2$		CaO Alone	+ $CaH_4(PO_4)_2$	
		Washed	Not Washed		Washed	Not Washed
None	3.23	3.57	3.04	3.82	3.64	3.11
1 ton	3.50	3.74	3.16	3.90	3.74	3.23
3 tons	3.87	3.75	3.21	4.28	3.84	3.35
5 "	4.18	3.75	3.36	4.43	4.00	3.50
7 "	4.46	3.96	3.45	4.95	4.18	3.69
9 "	4.80	4.13	3.60	5.34	4.33	3.82
11 "	4.95	4.35	3.77	5.65	4.53	3.97
13 "	5.24	4.46	3.92	6.09	4.68	4.09
16 "	5.58	4.82	4.02	6.49	4.94	4.02
20 "	6.05	5.16	4.06	6.93	5.11	4.02
25 "	6.78	5.16	4.09	7.51	5.21	4.09

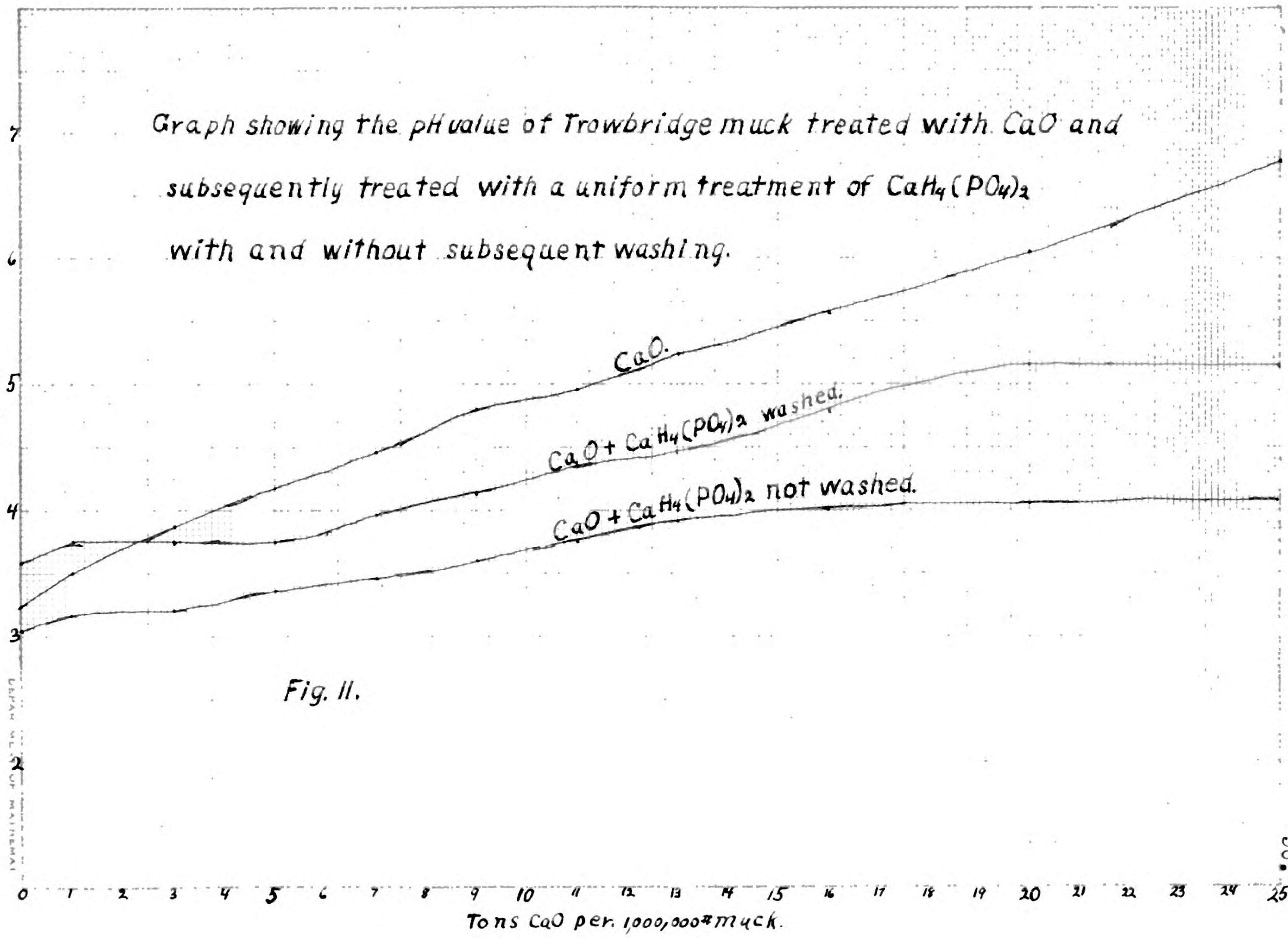

Graph showing the pH value of Trowbridge muck treated with CaO and subsequently treated with a uniform treatment of $CaH_4(PO_4)_2$ with and without subsequent washing.
CaO.
CaO + $CaH_4(PO_4)_2$ washed.
CaO + $CaH_4(PO_4)_2$ not washed.
2
3
4
5
6
7
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
Tons CaO per 1,000,000# muck.

Fig. 11.

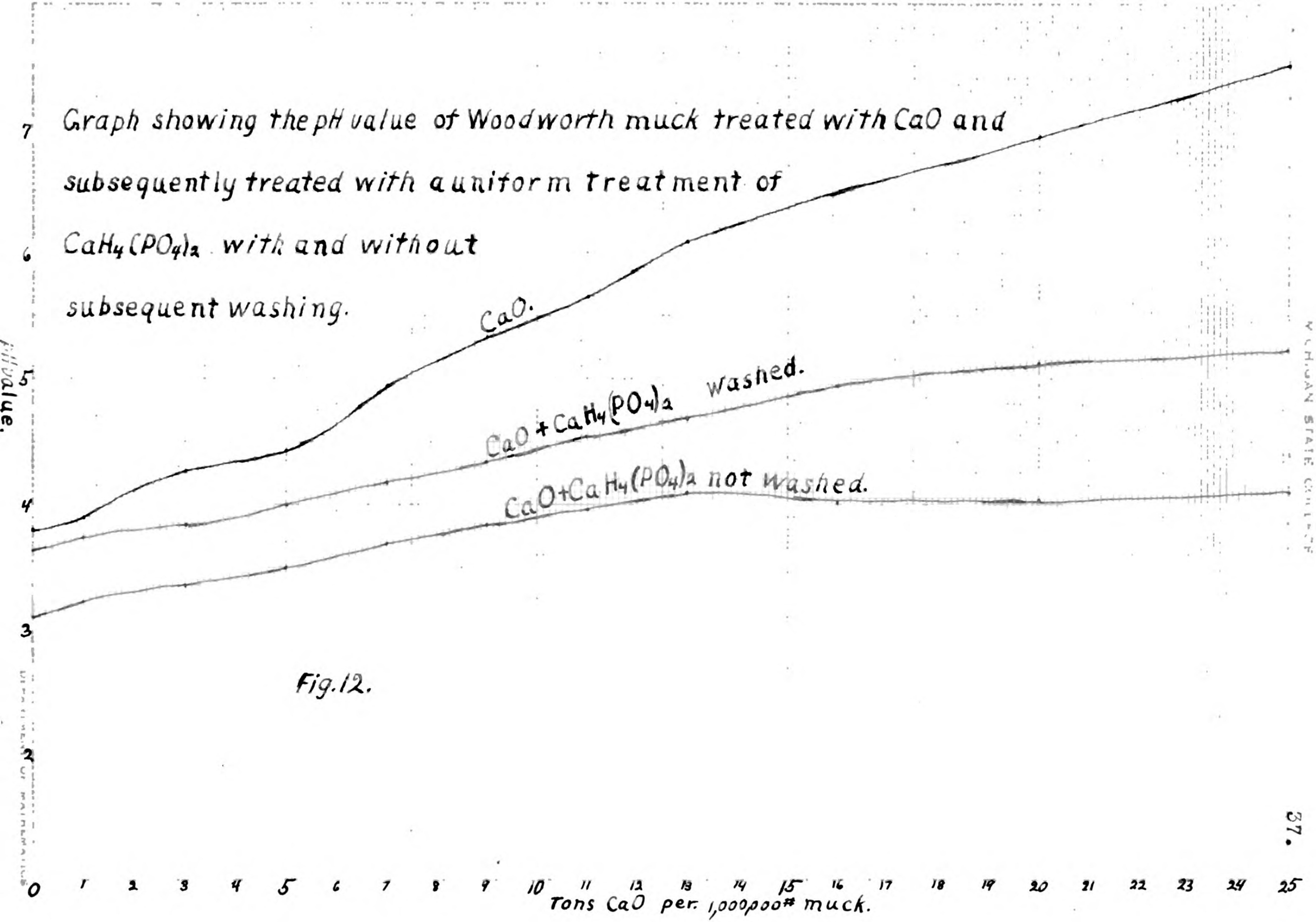

Graph showing the pH value of Woodworth muck treated with CaO and subsequently treated with a uniform treatment of CaH4(PO4)2 with and without subsequent washing.
CaO.
CaO + CaH4(PO4)2 washed.
CaO+CaH4(PO4)2 not washed.
pH value.
Tons CaO per 1,000,000# muck.
7
6
5
4
3
2
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

Fig.12.

The break in the curve at a pH of 4 in this particular case is due to the high concentration of phosphorous solution used. Austin (2) found that in titrating solutions of $CaH_4(PO_4)_2$ with alkali similar breaks in the curves were produced which varied with the concentration of phosphorous solution used. The higher the concentration of the phosphorous solution used, the lower on the pH scale was the break in the curve.

Table 9 and figs. 13 and 14 show the pH value of Town Line muck treated with HCl and with KCl and in each case treated with phosphorous solutions of different concentrations with and without subsequent washing with 400 cc of water. The KCl treatment left the soil much more alkaline than it was before treatment, while the HCl treatment made it more acid. The treatment with Phosphorous solution increased the acidity in each case, but, as pointed out before, the increase in acidity varied with the difference between the acidity of the phosphorous solution and that of the soil. The increase in acidity due to the phosphorous treatment was entirely removed by washing in the case of the soil treated with HCl as shown in fig. 14. This was true also of Woodworth muck treated with phosphorous solution, as shown in fig. 8. The increase in acidity due to the phosphorous treatment of the muck already treated with KCl was not removed by washing. This is in accord with the results obtained with all mucks of high pH value used in this work.

Table 9. - The pH value of Town Line Muck Treated with KCl and with HCl and subsequently Treated in Each Case with Phosphorous Solutions of Different Concentrations with and without Subsequent Washing with 400 cc water.

*Phosphorous Treatment	Treated with KCl			Treated with HCl		
	Original	Treated with Phos.	Treated and Washed	Original	Treated with Phos.	Treated and Washed
	7.03	6.09	6.05	3.64	3.52	3.72
	—	—	—	—	—	—
		4.70	4.92		3.33	3.67
		—	—		—	—
		4.26	4.67		3.23	3.64
		—	—		—	—
		3.94	4.50		3.14	3.62
		—	—		—	—
		3.72	4.31		3.09	3.55
		3.69	4.19		3.04	3.53

*Phosphorous treatment shown in table 3.

Graph showing pH value of Town Line muck treated with KCl and subsequently treated with $CaH_4(PO_4)_2$ with and without subsequent washing.

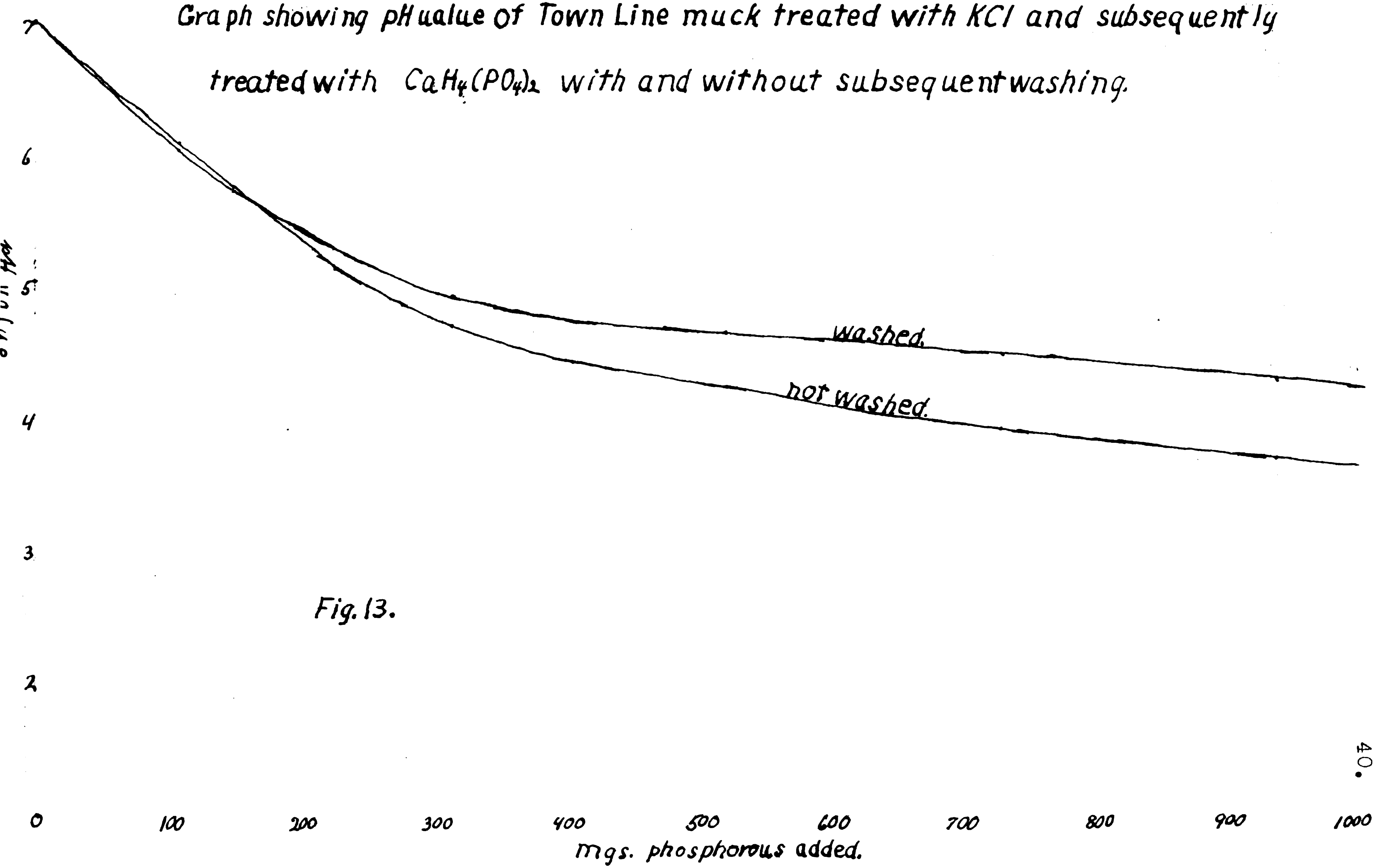


Fig. 13.

Graph showing pH value of Town Line muck treated with HCl subsequently treated with $CaH_4(PO_4)_2$ with and without subsequent washing.

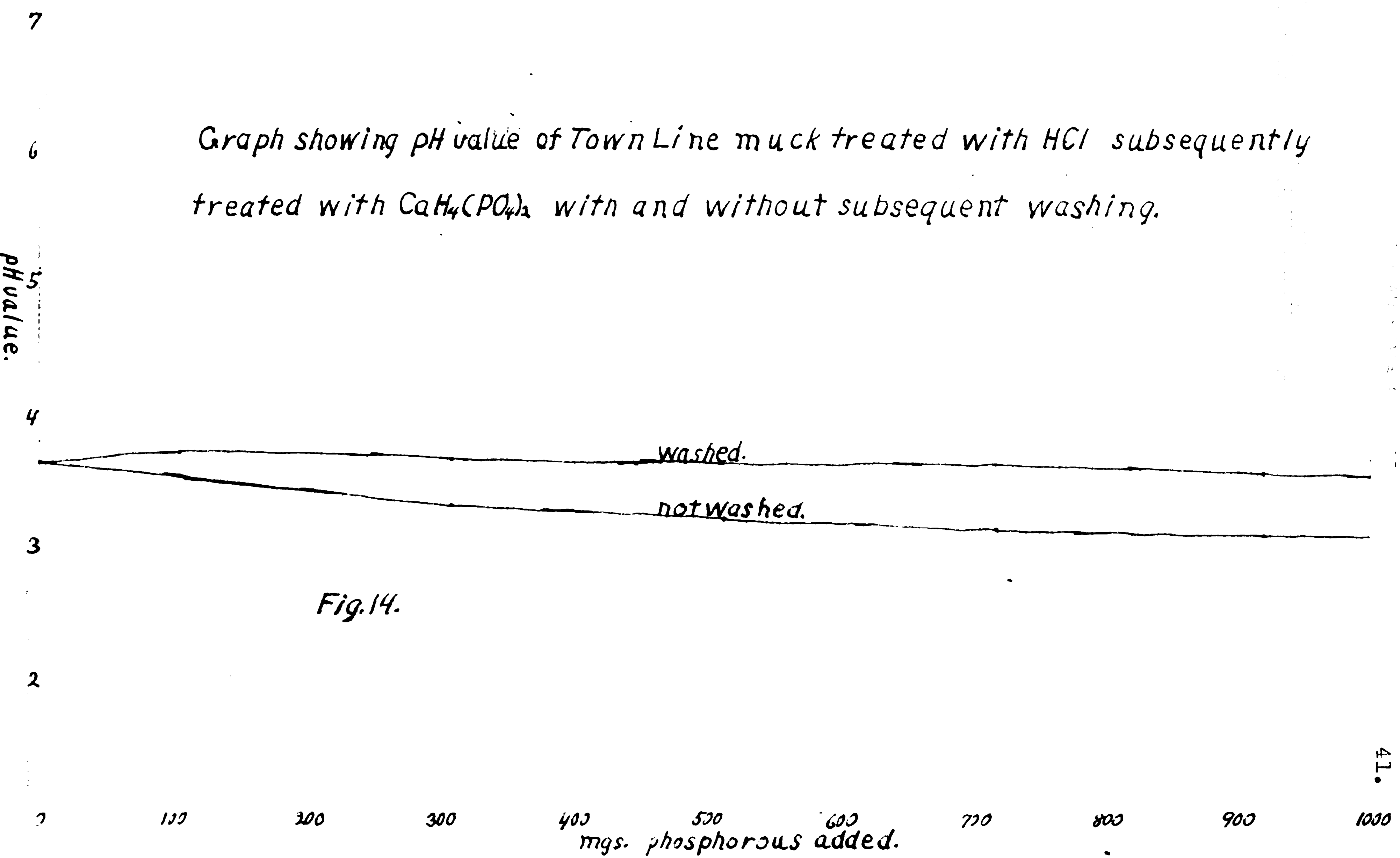


Fig. 14.

Every sample of muck treated with phosphorous solution throughout this work was made distinctly more acid and only in a few cases was this acidity removed by leaching. It must be remembered that these results are not comparable with those obtained in agricultural practice and these facts do not necessarily dispute the statements of investigators who say that applications of acid phosphate do not make soil sour, for the rate of application of phosphorous in this work is far in excess of any ever used in agricultural practice. The only cases in which investigators report any considerable degree of increased acidity due to acid phosphate treatment is in case of an unusually large application.

SUMMARY

1. Phosphorous fixation studies were made on two very acid mucks and two more nearly neutral by treating them with solutions of $CaH_4(PO_4)_2$ of different concentrations.

2. These studies were repeated on one of the latter after treating one sample with KCl and one with HCl.

3. Phosphorous fixation studies were made on the two very acid mucks by treating them with phosphorous solutions of uniform concentration after they had been treated with varying amounts of calcium oxide.

4. Phosphorous fixation studies were made on the two very acid mucks after as much distilled water had been added as they would hold unfree.

5. pH determinations were made on 1, all of the mucks untreated, 2 those treated with HCl, 3 those treated with HCl, 4 those treated with varying quantities of CaO, and 5 on all of the mucks after treatment with $CaH_4(PO_4)_2$ with and without subsequent leaching with 400 cc of water.

CONCLUSION

1. Very acid mucks show an indication of negative fixation of phosphorous when treated with a highly concentrated solution of $CaH_4(PO_4)_2$. This phenomenon is due to the fact that the mucks cannot fix as much phosphorous from a concentrated solution as there is in the water that is rendered unfree and some of this phosphorous is liberated to concentrate the remaining solution.

2. Mucks with a relatively high pH value do not show any indications of negative fixation of phosphorous regardless of the concentration of the solution with which they are treated. This is, no doubt, due to the fact that the phosphorous reacts chemically with the lime to form an insoluble compound.

3. When high lime mucks are treated with acid their ability to fix phosphorous from solution is considerably lessened.

4. When mucks that show an indication of so-called negative fixation are treated with as much water as they can render unfree the phosphorous fixation results will be positive regardless of the concentration of phosphorous solution with which they are treated.

5. Large applications of phosphorous such as were used in this work increase the acidity of soils considerably, the change in pH value being proportional to the difference be-

tween that of the soil and that of the solution used. That is; the pH value of a soil that is nearly alkaline will change much more than that of one with a low pH value.

6. It is apparent that exceedingly large volumns of water would be required to remove this increased acidity in some cases.

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* The original articles were not reviewed by the writer. The writer, however, reviewed a resume of this work by Page, H.J. of the Rothamsted Experiment Station, Harpenden, England, which is published in the Transactions of the Second commission of the international society of soil science by D.J. Hissink, Groingen, Holland. The work was translated from the Russian by Dr. S.A. Waksman.