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AVAILABILITY OF PHOSPHATES AND
THE FEEDING POWER OF
PLANTS

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The use of commercial phosphate fertilizers began in Europe about the middle of the nineteenth century. From that time to the present the use of these fertilizers has increased throughout the world that their economic use is a problem of vast importance. The relative values of the many different types of these fertilizers on their availability to plants and the profits to be gained from their use are all questions of the greatest interest to the farmer and also questions which from the present conflicting data are often extremely difficult of answer.

The extensive growth of legumes has done much to avert the necessity for the purchase of commercial nitrogen, but the supply of soil phosphorus, once depleted, can be replaced in no such simple manner. There is but one way to increase the amount of phosphorus in a soil and that is by the application of a fertilizer. When it is remembered that the supply of phosphorus in most soils is extremely low, ranging from a few hundred to three thousand pounds per acre eight inches, and that the demands of crops upon this element are by no means small, it becomes evident that after years of continuous cropping the phosphorus content may be so lowered as to become the limiting factor in crop production.

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Introduction of the soil is made by The use of commercial phosphate fertilizers began in Europe about the middle of the nineteenth century. From that time to the present the use of these fertilizers has so increased throughout the world that their economic use is a problem of vast importance. The relative values of the many different phosphates, the effect of liming on their availability to plants and the profits to be gained from their use on different soil types are all questions of the greatest interest to the farmer and also questions which from the present conflicting data are often extremely difficult of answer.

The extensive growth of legumes has done much to avert the necessity for the purchase of commercial nitrogen, but the supply of soil phosphorous, once depleted, can be renewed in no such simple manner. There is but one way to increase the amount of phosphorous in a soil and that is by the application of a fertilizer. When it is remembered that the supply of phosphorous in most soils is extremely low, ranging from a few hundred to three thousand pounds per acre eight inches, and that the demands of crops upon this element are by no means small, it becomes evident that after years of continuous cropping the phosphorous content may be so lowered as to become the limiting factor in crop production.

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Only a small amount of any element of the soil is made available to the plant at any one time. This is a wise provision of nature for were large amounts of soluble salts formed in the soil at any time, leaching would soon cause the loss of such quantities of these essential plant foods as to be ruinous to agriculture. Fertility has been defined as the rate at which plant food is being made available. It is necessary in applying phosphates as well as any other fertilizers to a soil to consider not only the amount of potential plant food in the fertilizer but also the factors which will directly or indirectly affect its availability to the plant. The nature of the soil, whether light or heavy, its reaction, and the crops to be grown upon it are primary considerations. Maximum crop production may cease while chemical analysis still shows a considerable amount of the element to be present in the soil. We are, in fact, immediately much more concerned with the availability of the soil phosphorous than with the total amount present and it is with this question that the present investigation deals.

The experimentation has been along two lines; first, an attempt to ascertain by means of sand cultures the effect of soluble calcium in the nutrient solution upon the availability of raw rock phosphate to several different plants and to reach a solution as to the causes of this effect; second, to determine the effect of leaching upon the availability to different plants of iron, aluminum and calcium phosphates. The latter work is largely a continuation of

work done in this laboratory by Buser, Noer and Tang.

Historical Review

Research as to the effect of the addition of lime upon the availability of raw rock phosphate has been largely confined to field experiments on soils of widely varying types and as might be expected there is a marked lack of agreement in results and conclusions.

Prianishnikov,⁽¹⁾ working with sand cultures, found that the addition of calcium carbonate decreased the availability of insoluble phosphates. With both bone meal and raw rock phosphate the effect was very detrimental. The addition of ammonium salts, however, increased the availability of these substances. At the conclusion of extended research, he emphasizes that the ability of different plants to assimilate phosphorous varies more widely than the properties of the phosphates. He also concludes the character of the soil as a medium and the interaction of accompanying fertilizers to be of prime importance.

Field investigations as to the influence of liming on the availability of phosphates, carried on at the Rhode Island Experiment Station,⁽²⁾ show widely varying results with different plants. On the plots fertilized with raw rock phosphate, lime was found to have a depressing effect on corn, millet and potatoes, and a beneficial effect on

(1). Landw. Versuch. Sta. vol. 65 pp. 23

(2). Rhode Island Exp. Sta. Bul. 58, 114, 118, 151.

mixed hay, turnips, squash, cabbage, clover, beets, barley, mangelwurzel, tomato and lettuce. Oats and peas seemed to be very slightly affected. Floats were not found to be as efficient as the other phosphates used, and also decreased the beneficial effect of liming so marked with the other phosphates. They conclude that the points to be observed in phosphate fertilization are the kind of soil, the kind of crop, the possibility of adding floats to manure, the source of the phosphate and its solubility as well as its other characteristics.

M. Maercher⁽³⁾ found that the application of lime with superphosphate was valuable in ferruginous soils in preventing the soluble phosphates from being converted into the more insoluble iron phosphates.

F. C. Chirikov⁽⁴⁾ concluded as a result of experiments carried out with barley and buckwheat in nutritive media that the excretion of acids by roots is inadequate to explain a number of facts in connection with the nutrition of higher green plants. Roots of different plants disturb the equilibrium in the medium in very unlike ways, absorbing predominately CaO or P_2O_5 as the case may be, and the relation of these plants to P_2O_5 must differ considerably. Barley does not take up P_2O_5 from phosphorite in the presence of calcium nitrate or any other calcium salt, but from phosphorite alone

(3). Zeitch. d. Landw. Central-Vereins d. prov. Sachsen
(1891) pp. 105-114.

(4). Zhur. Opytn. Agron. (Russ. Jour. Exp. Landw) 15 (1914)
No. I pp. 54-65.

it may utilize P_2O_5 to a considerable degree. Buckwheat behaves differently taking up P_2O_5 in either the presence or absence of calcium nitrate. He explains this difference upon the supposition that buckwheat takes up from the nutrient solution CaO more energetically than P_2O_5 while in the case of the barley P_2O_5 is more energetically taken up than CaO.

D. A. Gilchrist⁽⁵⁾ summarizes results at Cockle Park and says that while these are somewhat contradictory, a high lime content in slags seems to be advantageous and a high iron content not disadvantageous.

A large amount of investigation as to the effect of liming upon soil fertility has been carried on, but little of this has had special reference to the availability of the soil phosphorous.

Extensive investigations have been made to determine the effect of leaching on insoluble phosphates by the U. S. Bureau of Soils.⁽⁶⁾ They found it impossible to prepare iron, aluminum and calcium phosphates to correspond exactly to their respective formulae. After leaching prepared phosphates of the metals mentioned with water, they found them to contain more base than the original salts. Neutral salts in solution were found to increase the amount of CaO and P_2O_5 going into solution but had little effect on the

(5). County Northumb. Ed. Com. Bul. 2I (1914) pp. 35-43.

(6). U. S. Bu. Soils Bul. 4I.

iron and aluminum phosphates. Acid salts increased the amount of CaO going into solution while calcium salts decreased it. Carbonated water had little effect on the solubility of iron and aluminum phosphates but increased the solubility of calcium phosphate materially above that in pure water. They state that the soil contains an excess of base over that which is required to unite with the phosphoric acid, and that therefore the least soluble phosphates are the ones that will be formed and control the soil concentration.

Baugley,⁽⁷⁾ of the University of North Wales, working with freshly prepared iron, aluminum and calcium phosphates found that ignition and subsequent extraction with boiling water has a very detrimental effect on the availability of the phosphates. When these salts were leached with boiling water and not previously ignited, peas used them as efficiently as superphosphate. In most cases the action of calcium phosphate was inferior to that of aluminum and iron phosphates.

Prianishnikov⁽⁸⁾ found that heating aluminum and iron phosphates decreased their availability. Bone meal also lost some of its availability, which fact he ascribes to the formation of calcium carbonate in the process of heating.

L. H. Merrill,⁽⁹⁾ studying the availability of calcium phosphate and redonda to different plants, found that in

(7). Jour. Agr. Sci. Vol. IV.

(8). Landw. Versuch. Sta. Vol. 65 pp. 23.

(9). Maine Exp. Sta. Rept. (1898)

most cases calcium phosphate gave better results than redonda, and that barley, corn and oats made no satisfactory growth on either. Turnips, rutabagas and kohlrabi were found to be very strong feeders on calcium phosphate. Redonda was found to be readily available to the Graminae.

In investigations at the Rhode Island Experiment Station (IO) it was found that raw redondite was of little value as a fertilizer, giving poorer results than raw rock phosphate with all crops except the turnips. Roasted redondite when applied with lime proved to be a much more efficient fertilizer than raw rock phosphate.

Buser, Noer and Tang, (II) working at this laboratory with several freshly precipitated phosphates in sand cultures found that there was much variation in plants with regard to their feeding power on iron, aluminum and calcium phosphates. The iron and aluminum phosphates were more available to most plants than the tri-calcium phosphate. There was some coordination between plants of the same families as to their behavior toward these phosphates; in general, the Graminae favored aluminum and iron phosphates while the Cruciferae and Leguminosae were indifferent or preferred the calcium phosphate.

(IO). Rhode Island Exp. Sta. Bul. II4.

(II). Bachelor's thesis- U. of W. Buser and Noer (1912)

Phosphate	Amount of Phosphate	Nutrient Sol.
" Acid phosphate "	"	No. 1
" Raw rock "	5.0 "	No. 1
" " "	5.0 "	No. 2

The phosphates were thoroughly mixed with the sand by

Experimental-Part I.

Plan of Investigation.

The object of this investigation was to determine the effect of soluble calcium salts in the nutrient solution upon the availability of raw rock phosphate. The following species of plants were used: buckwheat, oats, corn, millet, barley, rape, alfalfa, tobacco, sunflower and turnip. Two successive crops were grown in sand cultures. A series of seven jars was used for each species of plant, each jar containing twelve kg. of phosphorous free sand.

Two nutrient solutions were made up, one containing soluble calcium and the other containing no soluble calcium.

Nutrient Solutions.

<u>No. 1 (sol. Ca)</u>		<u>No. 2 (no Ca)</u>	
KNO ₃	200 gms.	KNO ₃	120 gms.
NaNO ₃	100 "	NaNO ₃	60 "
CaCl ₂	95 "	MgCl ₂	1 "
MgSO ₄	45 "	MgSO ₄	5 "
Water	5 liters	Water	3 liters

Table I Nutrient Solution, Kind and Amount of Phosphate

Added to each Jar in a single Plant Series.

Jar No.	Kind of Phosphate	Amount of Phosphate	Nutrient Sol.
I	None	-	No. 1
2 & 3	Acid phosphate	5.9 gms.	No. 1
4 & 5	Raw rock "	5.0 "	No. 1
6 & 7	" " "	5.0 "	No. 2

The phosphates were thoroughly mixed with the sand by

means of a rubber cloth and mixing pan.

All plants except the tobacco were started from seeds and, immediately after planting, each jar was watered with distilled water to 13% of the weight of the sand, this moisture content being maintained throughout the growth of the plants. More seeds were planted than the number of plants desired, the plants being thinned soon after they were up. In the case of the tobacco very small plants were transplanted from a hot bed. The following number of plants were left in the various jars: buckwheat 7, oats 16, barley 16, millet 20, rape 5, alfalfa 20, corn 2, tobacco 2, sunflower 2, turnip 5.

The nutrient solutions, previously described, were added to the jars soon after the plants were up. Each jar received 25 cc. of nutrient solution in a 500 cc. dilution with water and also a few drops of FeCl_3 .

Small amounts of nutrient solution were added to the larger plants later as required. As the second crop was grown in the same jars as the first, 10 cc. of nutrient solution was added to each jar before the second planting. No addition of phosphate was made but the sand was well mixed and the crops grown in the same order as before. Uniformly favorable conditions were maintained in the greenhouse throughout the growing period. The seasonal conditions being more favorable for the second crop, as might be expected, it grew more rapidly than did the first.

Table II Date of Planting, Date of Harvesting, and Length
of Growing Period for each Crop.

Plant	First Crop			Second Crop		
	Date of Planting	Date of Harvest	Days of Growth	Date of Planting	Date of Harvest	Days of Growth
Buckwheat	Oct. 14	Dec. 15	62	Mar. 4	Apr. 23	50
Oats	"	"	62	"	"	50
Millet	"	Dec. 22	69	"	May 18	75
Barley	"	Dec. 15	62	"	Apr. 23	50
Rape	"	Dec. 22	69	"	May 13	70
Alfalfa	"	Feb. 22	130	"	May 18	75
Corn	"	Dec. 15	62	"	May 13	70
Tobacco	"	Feb. 22	130	"	May 18	75
Sunflower	"	Dec. 22	69	"	"	75
Turnip	"	"	69	"	May 13	70

Notes on Growth of Plants.

Buckwheat did very poorly on all jars supplied with raw rock phosphate, the leaves curling and dying at the margin early in the growth of both crops. Although all plants blossomed, the growth even on acid phosphate was unsatisfactory. This may have been due to some unfavorable action of the sand used.

Oats made poor growth on all raw rock phosphate jars, exceeding but slightly the growth on the blank. Acid phosphate gave fair results.

Millet seemed unable to utilize raw rock phosphate but made a good growth on acid phosphate.

Barley gave evidence of a depressing effect of soluble calcium in the nutrient solution. Growth with acid phosphate was only fair.

The presence or absence of soluble calcium did not effect the growth of rape, results being practically the same in

all jars containing raw rock phosphate. Rape proved to be a strong feeder on insoluble phosphate making a growth almost equal to that made with acid phosphate. The growth in the blank jar was negligible.

Alfalfa on raw rock phosphate seemed to be slightly favored by the presence of a soluble calcium salt. All alfalfa plants did well on raw rock phosphate, more particularly the second crop.

Tobacco at first grew very slowly and seemed to be unable to utilize raw rock phosphate. Later, however, it made a very satisfactory growth. The presence of a soluble calcium salt had a depressing effect in all cases, the difference in favor of its absence being especially apparent in the second crop. The blank made little growth.

Corn made a poor growth on raw rock phosphate, both with and without soluble calcium.

Sunflower, where soluble calcium was present, utilized raw rock phosphate to quite an extent, but did poorly where soluble calcium was omitted. The plants of the second crop blossomed in all jars except the blank.

Turnips grew well on raw rock phosphate, the presence or absence of soluble calcium making little difference in the amount of growth.

The plants were harvested by cutting them off at the surface of the sand except in the case of the turnips which were made to include roots and tops. The harvested plants were placed in paper sacks, dried at 110° C. and weighed.

Table III Dry Weight of Different Crops in Grams.

Plant	Crop No.		Blank	Acid Phosphate	Raw Rock Phosphate With Ca	Raw Rock Phosphate Without Ca
Oats	1	a	.90	4.45	1.00	.80
		b		2.50	.80	1.10
	2	a	1.50	7.00	3.00	3.05
		b		8.00	2.80	2.80
Millet	1	a	.10	2.50	.04	.08
		b		2.80	.04	.09
	2	a	.20	15.60	1.30	1.35
		b		16.00	1.25	1.40
Buckwheat	1	a	.40	2.35	.50	.85
		b		2.80	.55	.70
	2	a	1.20	6.50	2.40	3.00
		b		5.90	2.70	2.60
Barley	1	a	.95	4.55	1.25	1.80
		b		4.00	1.20	1.70
	2	a	3.70	7.00	4.60	4.70
		b		7.00	4.50	4.80
Rape	1	a	.02	5.45	1.10	1.10
		b		5.40	2.55	2.10
	2	a	.10	6.20	3.40	2.20
		b		5.60	3.30	2.30
Alfalfa	1	a	-	1.30	1.25	.50
		b		1.40	1.00	1.10
	2	a	-	8.35	5.00	5.20
		b		8.20	6.20	5.40

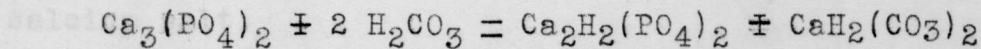
considerable extent, while oats, barley, corn and millet were rather weak feeders on the insoluble phosphate.

Table III Continued

Plant	Crop No.		Blank	Acid Phosphate	Raw Rock Phosphate With Ca	Raw Rock Phosphate Without Ca
Corn	1	a	2.15	14.00	4.00	4.80
		b		14.20	2.60	4.40
	2	a	4.00	16.00	4.70	5.70
		b		18.20	4.90	4.80
Tobacco	1	a	.20	12.50	2.80	4.90
		b		10.80	1.90	2.40
	2	a	.10	11.40	6.90	7.60
		b		11.50	1.90	7.20
Sunflower	1	a	.20	5.50	.90	.60
		b		2.90	1.00	.55
	2	a	.35	12.50	5.25	2.00
		b		14.50	5.50	2.60
Turnip	1	a	.05	5.30	.20	.25
		b		5.75	.17	.45
	2	a	.05	6.30	3.60	4.40
		b		7.00	-	4.60

From the foregoing table it will be seen that in every case acid phosphate was superior to raw rock phosphate. The difference, however, was not great with alfalfa, rape, turnip and tobacco, these plants being very good feeders on raw rock phosphate. Of the other plants grown, buckwheat and sunflower seemed to utilize raw rock phosphate to a considerable extent, while oats, barley, corn and millet were rather weak feeders on the insoluble phosphate.

of phosph Mr. E. Truog,⁽¹²⁾ of this station, after compiling much data from this station and others on the ability of different plants to utilize raw rock phosphate, found that there was a direct relation between the plants feeding power on this phosphate and its lime content. He found that in general, plants of high lime content are strong feeders on raw rock phosphate and plants of low lime content are weak feeders on the same phosphate. He explains this as follows. Plant roots excrete large amounts of carbon dioxide which acts upon the raw rock phosphate as indicated by the following reaction:



This reaction will of course be largely localized, going on only in close proximity to the plant root hairs. Plants high in lime will not only remove from the zone of action the $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$, but also the $\text{CaH}_2(\text{CO}_3)_2$, thus permitting the continuance of the reaction. Plants low in lime will remove such small amounts of the $\text{CaH}_2(\text{CO}_3)_2$ that the solution will soon become saturated with this salt, and according to the law of mass action the reaction will stop. Precipitation of the $\text{CaH}_2(\text{CO}_3)_2$ would have to take place in order for more phosphate to go into solution, but the carbon dioxide would then react with the precipitated carbonate rather than with the calcium phosphate.

If this theory is valid, it would be expected that the presence of a soluble calcium salt in the nutrient solution of plants low in lime would decrease the amount

(12) Science April 23, 1915.

of phosphorous made available and hence the amount of growth, for if their calcium requirements are thus easily filled, the concentration of the calcium bicarbonate in the previously mentioned reaction will increase still faster and the reaction cease still earlier. Plants high in lime, however, might be expected to show but small differences in growth due to the presence or absence of a soluble salt as they would in either case be able to absorb sufficient amounts of the calcium bicarbonate to allow the continuance of the reaction. Indeed, plants extremely high in lime might even make a better growth in the presence of a soluble calcium salt.

These suppositions are well born out by the results. Of all the plants grown, alfalfa, rape and sunflower made better growth with the soluble calcium than without it. These are plants high in lime. Of these three plants, the sunflower alone showed a marked difference in favor of the presence of soluble calcium. The rape and alfalfa seemed to be but slightly influenced by it. Tobacco, a plant rather high in lime, however, showed a decided preference for the absence of soluble calcium. Turnips and buckwheat also showed a slight preference for the absence of soluble calcium. Millet, which is very low in lime, made considerably better growth where the soluble calcium was omitted. The remaining plants; corn, barley and oats, plants not high in lime content, although they proved to be weak feeders on raw rock phosphate, showed fairly well marked differences

in favor of the absence of soluble calcium. Dry Weight

Lime Content of Plants.

It has been well established that the composition of plants is influenced somewhat by the content of their nutritive media. In general, plants having access to large amounts of soluble calcium salts will be higher in lime content than plants whose feeding solution is low in this element. It was thought, however, that plants depending upon raw rock phosphate for their supply of phosphorous might, in order to secure sufficient phosphorous, absorb larger amount of calcium than they would were soluble phosphates supplied. The tobacco, corn, barley and sunflower were analyzed to see if this was true.

Analysis for the lime content of the plants was made in the following manner: the air dried plants were ground to a fine powder in a steel mill and samples taken for moisture determinations. Duplicate samples of from .5 gm. to 2 gms., depending on the amount of material available, were ignited in porcelain crucibles until all organic matter was completely oxidized. After taking up with 5 cc dilute HCl, the ash was transferred to a 500 cc beaker and diluted with 300 cc of water. Five cc FeCl_3 was added and the solution neutralized with NH_4OH until one drop would form a precipitate. Two basic acetate separations were then made, the calcium precipitated as the oxalate, filtered, washed, dissolved in H_2SO_4 and titrated with standard KMnO_4 .

Table IV Per cent CaO in Plants on Basis Dry Weight

Treatment	Corn	Barley	Sunflower	Tobacco
Blank	1.14	2.07	3.16	3.53
Acid Phosphate	1.11	2.79	3.52	3.02
Raw Rock (With Ca)	1.13	1.77	3.04	3.40
Raw Rock (No Ca)	.95	1.51	1.98	3.30

Results of analyses show that only in the case of the tobacco were plants grown on raw rock phosphate higher in lime than those grown on acid phosphate. Also, in all cases it was found that plants grown on raw rock phosphate having soluble calcium in their nutrient solution were higher in lime than those grown without soluble calcium. This increased absorption of calcium when it is present in a soluble condition may help explain why plants low in lime grow better on raw rock phosphate in the absence of soluble calcium salts.

Experimental Part II.

Plan of Investigation

It has been held by some investigators⁽¹³⁾ that while the freshly precipitated normal phosphates of iron and aluminum are quite readily available to most plants, that the phosphates of these metals occurring in the soil have become,

(13) U. S. Bureau of Soils Bul. 41.

through leaching and removal of phosphoric acid by plants, basic phosphates of relatively much less solubility than normal phosphates. In this investigation an attempt has been made to imitate the weathering processes taking place in the soil by treating freshly precipitated phosphates with carbonated water, filtering off the residue and in sand cultures observing its availability as compared to the original phosphate.

For this purpose the phosphates of iron, aluminum, and calcium were freshly precipitated in this laboratory. As a source of the basic radicals, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were used. In each case Na_3PO_4 contributed the phosphoric acid radical. These salts were weighed out in molecular proportions so as to yield theoretically 100 gms. of each phosphate.

Table V Amount and Dilution of Salts in Phosphate Preparation

Salt used	Wt. gms.	Dilution	Precipit.	Wt. gms.	Dilution
		cc.	ant.		cc.
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	271	500	Na_3PO_4	309	309
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	212	"	"	245	245
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	91	"	"	254	254

The Na_3PO_4 was diluted before precipitation 5 to 1 with water and the salts contributing the bases were each diluted to one liter. For the precipitation of the iron and aluminum phosphates, the portions of Na_3PO_4 were made

acid with acetic acid, boiled, and the hot solutions of aluminum sulfate and ferric chloride added slowly with constant stirring. The precipitates were then filtered on a Büchner funnel, washed free of sulfates and chlorides respectively, and dried at 110°C . Calcium phosphate was precipitated in a cold neutral solution and washed free of chlorides. The dry salts were ground to a fine powder and analyzed for moisture, phosphoric acid and base as follows:

Water was determined by the loss on ignition of a 2 gm. sample in a platinum crucible over a Meker burner.

Phosphorous was determined from a .2 gm. sample dissolved in nitric acid, diluted to 200 cc, and the phosphorous precipitated with $(\text{NH}_4)_2\text{MoO}_4$ at 65°C from a solution slightly acid with HNO_3 and containing 3 % NH_4NO_3 . The precipitate after being filtered and washed was dissolved on the filter with 2.5 % NH_4OH , diluted to 100 cc and made slightly acid with HCl . Ten cc each of NH_4Cl and magnesia mixture were then added, the solution heated to boiling and MgNH_4PO_4 precipitated by adding slowly 2.5 % NH_4OH to the hot solution. The precipitate was ignited and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

Aluminum was determined in the filtrate from the phosphorous determination by precipitating $\text{Al}(\text{OH})_3$ with NH_4OH in a boiling solution. The precipitate was dried, ignited and weighed as Al_2O_3 .

Iron was determined from a .3 gm sample dissolved in 2.5 % H_2SO_4 , reduced in a hot solution with H_2S for 20 minutes,

boiled and the excess H_2S washed out by passing in CO_2 . The solution was cooled and titrated with standard $KMnO_4$.

The calcium was determined by precipitating in a boiling hot acetic acid solution with $(NH_4)_2C_2O_4$ and after the precipitate was dried and ignited it was weighed as CaO . Results of analyses are reported in table VI.

Method of Extraction.

Twenty five grams of each phosphate were treated for seven days with ten liters of distilled water, saturated with CO_2 . The bottles used as containers were shaken twice a day and kept at room temperatures. The salts were then filtered washed and dried at $110^{\circ}C$ and then ground and analyzed as before.

Table VI Composition of Extracted and Unextracted Phosphates on Moisture Free Basis.

Phosphate		Theoretical	Prepared Unextracted	Prepared Extracted
$Ca_3(PO_4)_2$	CaO %	54.19	55.09	56.99
	P_2O_5 %	45.80	44.82	42.87
$AlPO_4$	Al_2O_3 %	41.85	40.21	41.41
	P_2O_5 %	58.15	57.70	56.69
$FePO_4$	Fe_2O_3 %	52.98	52.74	54.71
	P_2O_5 %	47.02	47.16	44.21

Corn and oats were used in determining the availability of these phosphates. Since six phosphates, (three extracted and three unextracted), in duplicate were used, twenty four jars were required. The jars were of the same size and contained the same amount of sand as those for the first experiment. The phosphates were thoroughly mixed with the sand and such amounts of each were used as to give approximately the same amount of phosphorous per jar, as follows: AlPO_4 , 3.3 gms., $\text{Ca}_3(\text{PO}_4)_2$, 3.9 gms., FePO_4 , 4.1 gms. Planting, thinning and watering was done as described in the previous work. Twenty five cc of nutrient solution No. I, previously described, were added after the plants were up and further applications were made from time to time as needed.

The plants in both series made a very good growth and showed only slight variations due to the treatment of the phosphates. In the case of the corn, aluminum phosphate gave the most rapid growth from the start, and at first the availability of the phosphorous seemed to be considerably decreased by treating with carbonated water, but the difference became less and less and less apparent as growth continued.

The iron phosphate gave almost as rapid a growth as the aluminum phosphate and the plants seemed to show a slight preference for the treated phosphate.

In the jars supplied with calcium phosphate the plants made a slower growth than in those supplied with the other

phosphates and also lacked the healthy appearance exhibited by the latter. This was also true in the case of the oats.

Both oats and corn were planted on February 22nd and harvested on April 29th, giving the plants a growing period of 66 days.

Table VIII Dry Weight of Crops in Grams

Crop	No.	Ca Phosphate		Fe Phosphate		Al Phosphate	
		Unex-tracted	Ex-tracted	Unex-tracted	Ex-tracted	Unex-tracted	Ex-tracted
Corn	a	10.00	17.60	12.80	17.30	20.70	20.00
	b	10.50	10.50	15.40	17.50	21.60	11.50
	Ave.	10.25	14.05	14.10	17.40	21.15	15.75
Oats	a	12.45	13.50	13.70	13.00	13.50	13.40
	b	11.80	11.50	15.20	14.50	16.50	15.50
	Ave.	12.12	12.50	14.45	13.75	15.00	14.45

The yields of the crops show conflicting results as to the effect of treating aluminum, iron and calcium phosphates with carbonated water on their subsequent availability, but on the whole the effect was not great. It is noticeable, however, that the aluminum phosphate, which gave the best results with both crops, also gave an increased growth with the unextracted aluminum phosphate. As far as the availability of the untreated phosphates to corn and oats is concerned, the results bear out previous work at this station.

Conclusions.

1. Plants vary greatly in their ability to utilize raw rock phosphate. The plants of the leguminosae and cruciferae families grown, that is, alfalfa, rape and turnip are relatively strong feeders on raw rock phosphate. These are plants high in lime.

2. The gramineae, represented by oats, millet, barley and corn, are poor feeders on raw rock phosphate.

3. Buckwheat, tobacco and sunflower are able to use considerable amounts of raw rock phosphate.

4. Alfalfa, rape and sunflower made better growth on raw rock phosphate when soluble calcium was present in the nutrient solution than when it was withheld. This difference was slight with alfalfa and rape but marked with the sunflower.

5. All of the remaining plants grew better in the absence of soluble calcium, the difference being slight for turnip, tobacco and oats, but greater in the case of millet, corn, barley and buckwheat.

6. Plants which are strong feeders on raw rock phosphate are little affected by the absence or presence of soluble calcium in the nutrient solution.

7. Of the plants analyzed, corn, barley, sunflower and tobacco, there was a direct relation between their lime content and their ability to utilize raw rock phosphate. Arranging these plants in order as to their ability to use raw rock phosphate also puts them in order as to their percentage content of lime. The order is; tobacco, sunflower,

barley and corn, the first using raw rock phosphate to the greatest degree and also being the highest in lime.

8. Of the plants analyzed, those on acid phosphate had a higher lime content than those on raw rock phosphate, with the exception of tobacco.

9. Plants grown on raw rock phosphate having soluble calcium in the nutrient solution were in all cases found to be higher in lime than those grown on the same phosphate but having no soluble calcium in the nutrient solution.

10. Extraction of aluminum, iron and calcium phosphates with carbonated water causes the to become more basic and reduces the amount of phosphorous in the extracted material. The basicity obtained by the method used was not great, the added base being in each case about two percent.

11. The effect of leaching calcium phosphate was to increase the yield of both oats and corn.

12. Leached aluminum phosphate in all cases gave a poorer yield than the unleached phosphate.

13. Leached iron phosphate served the corn better than did the unleached but the oats made better growth on the unleached phosphate.

14. The amount of basicity obtained by the method of extraction used affected but little the availability of the phosphates.

15. With both plants aluminum phosphate gave the best results, iron phosphate being second.



Tobacco.

- No. 1. Blank.
- No. 2. Raw rock phosphate (with Ca).
- No. 3. " " " (without Ca).
- No. 4. Acid phosphate.



Sunflower.

- No. 1. Blank.
- No. 2. Raw rock phosphate (with Ca).
- No. 3. " " " (without Ca).
- No. 4. Acid phosphate.



Alfalfa.

- No. 1. Blank.
- No. 2. Raw rock phosphate (with Ca).
- No. 4. Acid phosphate.



Corn.

- No. 1. Blank.
- No. 2. Raw rock phosphate (with Ca).
- No. 3. " " " (without Ca).
- No. 4. Acid phosphate.



Rape.

- No. 1. Blank.
- No. 2. Raw rock phosphate (with Ca).
- No. 3. " " " (without Ca).
- No. 4. Acid phosphate.



Tobacco.

- No. 1. Blank.
- No. 2. Raw rock phosphate (with Ca).
- No. 3. " " " (without Ca).
- No. 4. Acid phosphate.



Turnip.

- No. 1. Blank.
- No. 2. Raw rock phosphate (with Ca).
- No. 3. " " " (without Ca).
- No. 4. Acid phosphate.



Alfalfa.

- No. 1. Blank.
- No. 2. Raw rock phosphate (with Ca).
- No. 3. " " " (without Ca).
- No. 4. Acid phosphate.

Approved

E. Truog.

