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THE AVAILABILITY OF PHOS-
PHATES IN CALCAREOUS
OR ALKALINE SOILS

By J. F. Breazeale and P. S. Burgess

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FOREWORD

Although a large amount of field experimental work has been done upon the subject of commercial fertilizers, the fundamental reasons that underlie the practice are little understood. Some soils respond to a certain fertilizer, while other soils, apparently of the same chemical and physical composition, do not. If the human race is to survive, the fertility of the soil must be maintained, and the maintenance of soil fertility probably always will involve the use of commercial fertilizers.

When brought under cultivation, the soils of the arid West and Southwest generally are rich in the mineral elements of plant food and are wonderfully productive, but it is only a matter of time when this native fertility will be reduced, so as to make the application of fertilizers necessary. In many places crop yields are now on the decline, due, in part, to the loss of fertility of the soil. Of the mineral elements in these soils phosphorus seems to be the most deficient, and there are indications that this element is the limiting factor in crop production in many soils.

Western soils are known to differ from many soils in the humid regions, in that they often respond to applications of acid or superphosphates but not to insoluble phosphates, such as floats or bone meal. This phenomenon has been made the subject of this bulletin.

In order to conduct experimental work with fertilizers intelligently, it is necessary to have a knowledge of the reactions in the soil under different conditions. This bulletin deals with the chemical reactions that take place when both soluble and insoluble phosphates are added to calcareous or alkaline soils; it explains the role of carbon dioxide in the soil solution, interprets observed phenomena, and offers a sensible working hypothesis for future work.

J. J. THORNBER,

Director.

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By J. F. Breazeale and P. S. Burgess

INTRODUCTION

It has been shown repeatedly that, in certain localities, insoluble phosphate* such as finely ground phosphate rock—commonly known as floats—is rendered available, if first mixed with manure or other organic matter and then applied to the soil. Furthermore, it is well known that soils high in organic matter, such as the fertile soils of the Middle West, are more likely to respond to applications of insoluble phosphate than are soils that are low in organic matter. Upon much of the red clay soil in the Piedmont section of the South, where such marked effects with soluble or acid phosphates are obtained in growing cotton, little or no effects are obtained from applications of floats. These cotton-producing soils are usually very low in organic matter.

In the Southwest, especially in the Lower Colorado Valley, and in other places in Arizona, the same phenomenon is noticed under a set of conditions different from those existing in the South. Although these soils may contain an abundance of organic matter, no effects are obtained from applications of insoluble phosphates. However, the effect of soluble phosphate upon a variety of crops is very pronounced.

Nearly all of the arid soils of the West, when brought under cultivation, are rich in total phosphorus, and the soils of the Lower Colorado Valley and Arizona are no exceptions to this general rule. Yet, while these soils are known to contain a relatively high percentage of total phosphorus, or of the phosphates that are soluble in strong acids, many of them respond markedly to applications of soluble phosphate. The increase in yields of crops that have been fertilized with soluble phosphate has been noticed repeatedly upon our experimental plots, and upon private farms in different parts of the State.

Acid phosphate is a comparatively cheap fertilizer, and there is no reason why it should not play an important part in the maintenance of soil fertility in the Southwest. An accurate knowledge of the conditions under which a benefit from its application may or may not be expected,

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*In deference to custom, the term "insoluble phosphate" will be used in this bulletin to designate the slightly soluble forms, such as finely ground apatite, South Carolina or Florida rock, or bone meal. It is recognized that all of these so-called insoluble phosphates have a low solubility. It should be noted also that, while these phosphates usually are referred to as tri-calcium, $Ca_3(PO_4)_2$, it is the opinion of many investigators that they are either a solid solution of di-calcium phosphate in calcium oxide, $Ca_2(HPO_4)_2 + CaO$, or tri-calcium phosphate with an excess of calcium hydroxide, $3Ca_3(PO_4)_2.Ca(OH)_2$.

is, therefore, exceedingly important.   These facts seemed to justify research work upon this subject.

The reaction of plants toward applications of phosphates under western conditions, has interested a great many people.   Hilgard recognized the importance of fertilizing arid soils with soluble phosphates, and he also observed the lack of positive results from applications of insoluble phosphate.   On page 393 of "Soils," he says:

"The forecast that for most California soils, fertilization with phosphates is of exceptional importance, has already been abundantly confirmed by cultural experience. Few definite data are, as yet, available from other arid states, where fertilization is thus far sporadic and unsystematic. But it is predictable that in view of the presence of this excess of lime carbonate in arid soils, and the unfavorable effect of this compound on the rapid solubility of tri-calcic phosphate demonstrated by Schloesing, Jr., by Bottcher and Kellner, and Nagaoka, fertilization with readily available phosphate fertilizers will be found necessary among the first, all over the arid region, especially in view of the scarcity of humus in arid soils."

Practically all of the arid, upland soils of the West are calcareous and it is evident that Hilgard attributed the results of applications of insoluble phosphates to this fact.   This, no doubt, has an effect, in a manner that will be explained later, but there are other reasons that are probably more potent than is the mere presence of an excess of calcium carbonate in the soil.

EXPERIMENTS WITH SOILS FROM THE LOWER COLORADO VALLEY

Four large soil samples representing soils that respond to applications of soluble phosphates, were collected from the Experiment Station plots of the United States Department of Agriculture, Bard, California. These soils were collected in the autumn of 1925, and had received the treatments described in Table I in the spring of that year. The soil samples were dried and shipped to Tucson, where the experiments were conducted. The soils were calcareous, and showed a trace of black alkali.

TABLE I—TREATMENT OF SOILS

1. Control plot (D 23)
2. Plot that had received an application of bone meal at the rate of 600 lbs per acre (D 22).
3. Plot that had received an application of 16 percent acid phosphate at the rate of 900 lbs per acre (D 23)
4. Plot that had received an application of 44 percent superphosphate at the rate of 545 lbs per acre (D 26).

The soils were used as collected from the field, without additional applications of phosphate.

PREPARATION OF THE SOIL EXTRACTS

Two thousand grams of each soil were weighed out, placed in a large bottle and 4,000 c.c. of distilled water added. This mixture was shaken in a machine for about half an hour, allowed to stand overnight, and the solutions or extracts were filtered through porous filter cores under pressure. The same core was used for soil No. 1 throughout the experiment, and the core was not washed between filtrations. Another core was used for soil No. 2, and so on. These cores had been in use in the laboratory for several months, and gave up no phosphorus to the extract and absorbed practically nothing from it.

One hundred seedlings of oats or barley were grown in about 2,000 c.c. of each of these extracts, and the extracts were changed every day. In order to make this change, the plants were allowed to grow in one portion of the extract for one day while the soil was being shaken and digested with another part of the same extract. When the extract was filtered off from the soil on the following day, the extract that the plants had been growing in during the previous day was poured back upon the soil. None of the extracts were thrown away, but in this way were used over and over again, and allowed to become saturated by standing in contact with the soil every other day.

PREPARATION OF CULTURE PLANTS

Under the conditions that existed during these experiments, it was found best first to malt the oat and barley seeds by soaking them in water for a few hours and then roll them in wet towels until the plumules and radicals appeared. They were then sprinkled upon perforated aluminum discs that floated in pans of tap water. A photograph of one of these discs, showing the glass floats, is given in figure 1.

When the plumules had reached a length of about one centimeter, they were counted out and, one at a time, removed from the seed-bed discs, and placed upon other discs that were floating on the pans containing the soil extracts. Under ordinary conditions, the little seedlings, when thus transplanted, will send their roots down through the perforations of the discs and grow readily. A disc of seedlings that was removed from one of the culture pans, after 3 weeks' growth, is shown in figure 2.

After the seedlings had grown in the culture solutions for the required period, from 25 to 50 representative plants were removed from each culture pan, dried, weighed, and analyzed for phosphorus. The increase in the phosphorus content of the plants over that contained in the control, or in the plants that grew in distilled water, represents the phosphorus that had been absorbed from the solution.

By using the plant in this way as an indicator, a distinction may be made between the plant food that is soluble and the plant food that is available.

Certain plant foods may be in the form of an aqueous solution and yet not be available to plants.*

PROBABLE ERROR

While there is always a variation in seedlings, even with the most skilled technique, every care was taken to reduce this error to a minimum. Seedlings, even when grown in distilled water, will vary in ash content, if results of analyses are expressed in terms of a hundred plants. This variation is due largely to the difference in the size and composition of the original seeds. Even if it is assumed that the original seeds were of uniform size and composition, a variation must be expected in the seedlings.
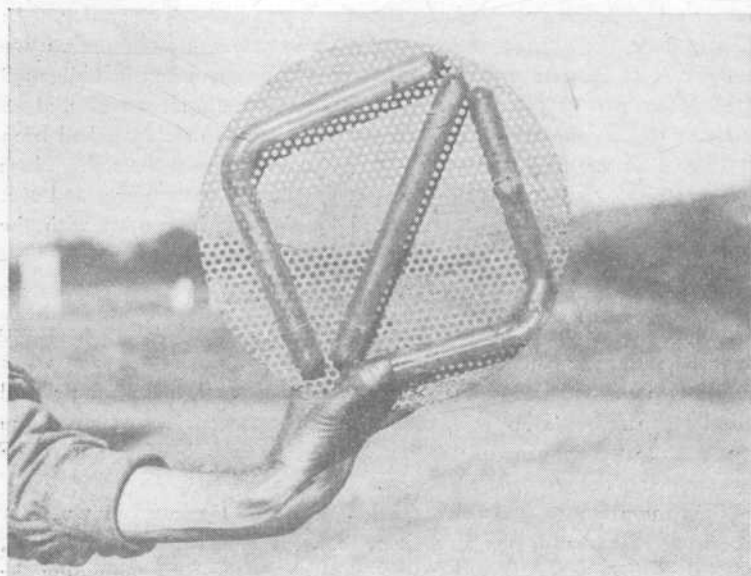
Fig. 1.—Aluminum culture disc, showing glass floats.

That is, a set of a hundred barley seedlings, if grown for a few weeks in distilled water, will not necessarily analyze exactly the same as a set that is grown from the same kind of seed at another time. The variation in such cases is usually small, but in working with a few parts per million, it must be considered. Barley, oat, and wheat seedlings, if soaked in water preparatory to germination, will exude a certain amount of salts, particularly potassium and phosphate ions, into the solution. This phos-

*Breazeale, J. F., Jour. Agr. Res. Vol. XX, No. 8. Jan. 15, 1921. Concentration of Potassium in Orthoclase Solutions, not a Measure of its Availability to Wheat Seedlings.

phate or other plant food will be absorbed by the seedlings as soon as they start growing. One hundred grams of barley were soaked overnight in about 125 c.c. of water, and the seeds exuded .0148 gram of phosphorus into the solution, and more phosphorus might have been exuded if the measurements had been continued throughout the germination process. It is almost impossible to carry on seedling work under uniform conditions, as there is no practical way of determining how much salt has been exuded, or how much has been reabsorbed by the plants. This error will depend largely upon the amount of water that the seeds have come in contact with, upon the temperature of the water, and upon other factors.
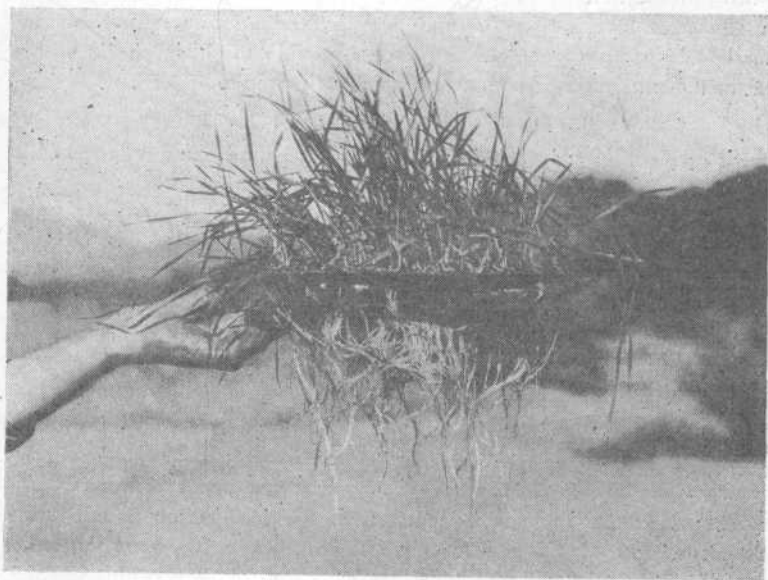
Fig. 2.—A disc of seedlings, three weeks old.

In these experiments the seeds were treated as the occasion seemed to justify. The seeds were always malted in order to get the best germination. Occasionally they were soaked in a large amount of water, but usually they were only moistened and wrapped in wet towels before they began to sprout prior to placing them upon the aluminum discs that were used as seedbeds. The seedlings were carefully counted as they were withdrawn from the seedbed, and particular attention was given that no unsprouted seed should be carried along with the sprouted seedlings, as the plant food from unsprouted seeds diffuses into the solution and is absorbed by the growing seedlings.

In running the controls of these experiments, it seemed advisable to have a control culture pan for each set, and to base all calculations upon this control.   These control plants were selected from the same seedbeds as were the rest of the set, they had the same treatment, they looked alike, they had the same average-size plumules, and approximately the same root development.   This seemed to be about as fair a control as it was possible to get, and in the determination of very small amounts of plant food in the seedlings, this matter of fair control is an exceedingly important one.   In the experiments that follow, different varieties of seeds were used, so the control of one set must not be compared with the control of another.

The error involved in the analytical determinations was probably too small to be of any consequence.   It was possible to obtain checks within 0.3 or 0.4 milligram of phosphorus upon each sample.

EXPERIMENTS WITH SOIL EXTRACTS

Barley seedlings were grown for 19 days in the soil extracts described in Table II, and then analyzed for phosphorus.

TABLE II.—ABSORPTION OF PHOSPHORUS FROM EXTRACTS BY BARLEY SEEDLINGS.

	Grams in 100 plants	
	Dry wt.	Phosphorus
1. Distilled water control	2 560	01387
2. Extract of soil from the control plot	2 472	01425
3. Extract of soil from bone-meal plot	2 840	01409
4. Extract of soil from 16% acid-phosphate plot	2 744	01566
5. Extract of soil from 44% superphosphate plot	2 742	01630

The plants that grew in the extracts of the acid-phosphate and super-phosphate plots, Nos. 4 and 5, were distinctly better than were those that grew in the extracts of the bone-meal and control plots. This effect is not shown in the dry weights of the crops.   However, this is often the case; the dry weights of seedlings are not a safe criterion in culture work, when working with the effect of phosphorus.   The phosphorus content of the plants that were grown in the extracts was different, however. The plants that were grown in the bone-meal extract showed little or no increase in phosphorus over the control soil extract or the distilled water control.   The most marked increase in phosphorus was in the plants that had been grown in the superphosphate-soil extract.   As the plants in the control soil extract contained very little more phosphorus than did those that were grown in distilled water, it is reasonable to assume that practically no phosphorus went into solution from the control soil. If any had gone into solution, the little seedlings unquestionably would have absorbed

it, and it would have been shown in the analysis of the ash. These results are distinct and cannot be explained upon the basis of the possible error of the experiment.

Oat seedlings also were grown in these soil extracts under conditions similar to those under which the barley seedlings were grown. In Table III are shown the analyses of oat plants that were under observation for 15 days.

TABLE III.—ABSORPTION OF PHOSPHORUS FROM EXTRACTS BY OAT SEEDLINGS.

	Grams in 100 plants	
	Dry wt.	Phosphorus
1. Distilled water control	3 040	01371
2. Extract of soil from control plot	3 592	01355
3. Extract of soil from bone-meal plot	3 160	01296
4. Extract of soil from 16% acid-phosphate plot	3 176	01528
5. Extract of soil from 44% superphosphate plot	3 800	01555
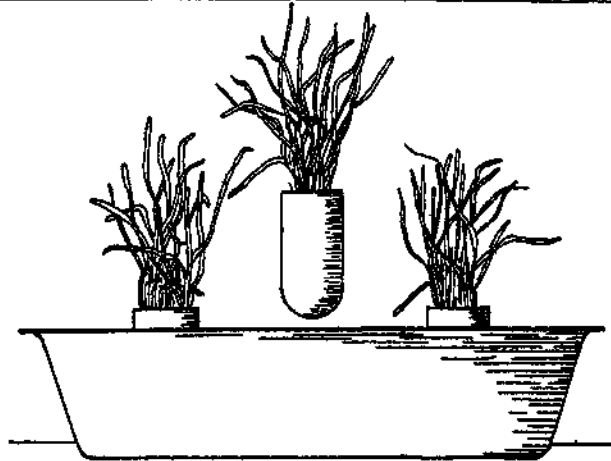
Fig. 3.—A drawing illustrating culture scheme, using filter paper thimbles.

It will be seen that the results with oat seedlings were similar to those with barley, that is, no absorption of phosphorus was obtained from the control soil extract as shown by a comparison with the distilled water control. The plants in the bone-meal soil extract were even slightly deficient in phosphorus. There was, apparently, no soluble phosphorus either in the control soil or in the bone-meal soil extract. The plants that grew in the extracts of the superphosphate and acid-phosphate soils were distinctly higher in phosphorus than were the others. Evidently these soils were transmitting their good or poor properties to their extracts.

EXPERIMENTS WITH FILTER PAPER THIMBLES

This method of study, that involved the use of filter paper extraction thimbles, was probably never before adapted to soil culture work, but it appears to have promising possibilities. A drawing of the culture scheme is shown in figure 3.

In this method, 5,000 grams of soil were weighed out and placed in a porcelain pan. This amount of soil was sufficient to fill the pan almost to the top. Six filter paper thimbles such as are ordinarily used in the determination of crude fiber, were then imbedded in the soil around the outer edge of the pan. The thimbles were made of thick filter paper and were 33 mm. in diameter and 80 mm. in length, and when pushed into the soil in the pan, they stood about 10 mm. above the soil. Twenty-five seedlings were placed in each of these thimbles and held in place with cotton batting. A little well was then made in the center of each pan of soil, and distilled water was poured into these wells and allowed to soak out through the soil and into the filter paper thimbles. The plant roots grew in the soil extract inside the thimbles.

In the first trials the roots grew through the filter paper and out into the soil, but this trouble was obviated by taking the seedlings lightly between the forefinger and thumb and turning them about half a revolution each day. With this treatment, the roots grew in a bunch and remained inside the thimbles. It would have been an easy matter to have added nitrogen, potash, and other plant foods to the solution inside the thimbles, and to have carried the plants to maturity, but this was not done. The soil in the pans was kept saturated during the experiment.

As is well known, it is exceedingly difficult to grow young plants in a saturated soil without drainage, as they usually turn yellow and die within a few days. With the thimble method, the plants grow in the soil extract and behave like ordinary water cultures.

The thimble method eliminates certain serious objections which have been raised to many soil fertility investigations. In this method the soil extract filters through the thimbles and comes in contact with the roots, clear and free from suspended matter. The whole plant may then be used for analysis. This is not possible in culture studies when direct contact of the plant root and the soil is made, as it is practically impossible to get all of the roots out of the soil and have them free from adhering material. Plants that have the same top development may have a different root system. The plant food is distributed between the top and the root, so it is evident that the anaylsis of the top of a plant having a small root, may show more plant foot than the analysis of the top of a plant having a large root.

With the thimble method we also eliminate the possibility of the plant

exuding acids or solvents, that may dissolve insoluble soil constituents and thereby bring plant foods into solution that otherwise would not be available.

Several times during the experiment the solutions were drawn out from the inside of the thimbles, and conductivity measurements made upon them. It is interesting to note that the ohms resistence of these solutions was practically the same as was that of the extracts that were made by shaking the soils with twice their weight of water and filtering the extracts through porous filter cores, as was done in the experiments previously described. The solutions in both cases appeared to have been saturated with respect to the slightly soluble salts.

During the latter part of the experiment, a vigorous growth of blue-green algae appeared upon the surface of the soil of the superphosphate plot, a less vigorous growth appeared upon the acid-phosphate soil, while no growth was noticed upon the control or upon the bone-meal soil. These algae are plants, and although of a lower order than barley and oats, they require phosphorus as a plant-food constituent. This growth upon the soil that had been treated with soluble phosphate was, therefore, very significant.

After 23 days of growth, a set of oat plants was taken from the thimbles, and analyzed for phosphorus. These results are given in Table IV.

TABLE IV.—ABSORPTION OF PHOSPHORUS FROM SOLUTIONS BY OAT SEEDLINGS.

		Grams phosphorus in 100 plants
1.	Soil from control plot	01047
2.	Soil from bone-meal plot	01058
3.	Soil from 16% acid-phosphate plot	01129
4.	Soil from 44% superphosphate plot	.01307

It will be seen that the plants when grown in the thimbles, behaved very much like those that had been grown previously in the soil extracts, the plants grown in the superphosphate soil looked better and contained more phosphorus than did the others. The plants from the acid-phosphate soil were next best in appearance and next highest in phosphorus content, while the plants in the bone-meal soil grew no better and contained very little more phosphorus than did the control plants.

After 26 days of growth, a set of barley plants was withdrawn from the thimbles and analyzed for phosphorus.

TABLE V.—ABSORPTION OF PHOSPHORUS FROM SOLUTIONS BY BARLEY SEEDLINGS.

		Grams phosphorus in 100 plants
1.	Control soil	01296
2	Bone-meal soil	01210
3.	16% acid-phosphate soil	01297
4.	44% superphosphate soil	01856

These results, while probably not so definite as some of the others that have been given, indicate that the soil that had received an application of superphosphate had more phosphorus in its solution than did any of the others.

ANALYSES OF THE SOIL

An analysis of the soil from the control plot for total phosphorus was made by igniting a sample of the soil over a Bunsen burner, to destroy the organic matter, and digesting it with a mixture of hydrochloric and nitric acids. This treatment brought 0.0510 percent of phosphorus, or an equivalent of 0.1147 percent of P_2O_5 into solution. Upon the basis of dry soil, this percentage of phosphorus corresponds to about the average total phosphate content of soils in humid areas.

This soil from Bard which contains 0.1147 percent of P_2O_5, or an equivalent of about 4,500 pounds per acre-foot, would probably be classified by many as one that contains enough phosphorus to last ordinary crops many years.

Analyses of the water extracts of these soils were made by two methods. First, the soils were shaken with twice their weight of distilled water until the solutions came to equilibrium, filtered through porous filter cores, and analyzed for phosphorus. Second, 500 grams of each of the soils were placed in glass extraction tubes, percolated with 1 liter of distilled water, and the percolate analyzed for phosphorus. When calculated upon the basis of dry soil, the results were practically the same in both cases, and the average is shown in Table VI.

TABLE VI.—ANALYSES OF SOIL EXTRACTS.

		Parts per million of phosphorus in dry soil
1	Soil from control plot	0
2.	Soil from bone-meal plot	0
3	Soil from 16% acid-phosphate plot	1 0
4.	Soil from 44% superphosphate plot	2 0

Further percolations of the control and bone-meal soil failed to bring any phosphorus into solution, but the acid-phosphate and superphosphate soils continued to give up phosphorus, although in very small amounts.

From these analyses it seemed safe to assume that the soil solution in the control plot at Bard, is exceedingly low in phosphorus, and that the addition of phosphates in an insoluble form does not tend to bring any more phosphorus into solution. The so-called insoluble phosphates, floats, bone meal, etc., have each a definite solubility, they go into solution to the extent of a few parts per million, and should be available to plants in that concentration, yet under the conditions that exist at Bard and in many other places in the Southwest, the phosphate ion does not appear in the soil solutions.

EXPERIMENTS WITH CULTURE SOLUTIONS OF LOW CONCENTRATIONS

When seedlings of wheat, oats, or barley are placed in solutions of low concentrations of plant food, they show that they are able to feed quite readily. This phenomenon is more marked in the case of potassium than it is with phosphorus, and it is, in many cases, hardly noticeable with nitrogen. In Table VII are shown the analyses of wheat, oats, and barley plants, that were grown for 20 days in the solutions of nitrogen as sodium nitrate, potassium as potassium chloride, and phosphorus as sodium phosphate. These solutions were changed every day. The analyses for phosphorus, alone, are given.

TABLE VII.—ABSORPTION OF PHOSPHORUS BY WHEAT, OAT, AND BARLEY SEEDLINGS.

		Grams phosphorus in 100 plants		
		Wheat	Oats	Barley
1.	Control, distilled water	0095	0113	0124
2.	1 p.p.m. each N.K. and P.	0294	0213	0219
3.	2 p.p.m. each N.K. and P.	0304	0231	0215
4.	10 p.p.m. each N.K. and P.	0453	0268	0364
5.	25 p.p m. each N.K. and P	0542	0336	0346
6	50 p p m. each N.K. and P.	0589	0336	0378
7.	100 p.p.m. each N.K. and P.	0536	0404	0410

It will be seen that the absorption of phosphorus increased at a fairly uniform rate as the concentration of the nutrient solution was increased.

When the concentration was decreased even below one part per million of phosphorus, which is the only plant food now being considered, marked results were obtained. This has been shown several times with both oat and barley seedlings. It is true that in distinguishing between one-fourth and one-half parts per million of phosphorus, a large percentage of error may occur, yet there is no doubt but that plants do feed readily in these low concentrations. In Table VIII are shown the analyses of barley seedlings that were grown in low concentrations of plant food for 14 days.

TABLE VIII.—ABSORPTION OF PHOSPHORUS BY BARLEY SEEDLINGS FROM SOLUTIONS OF LOW CONCENTRATIONS

		Grams phosphorus in 100 plants
1.	Control, distilled water	0112
2.	¼ p p.m each N.K. and P.	0167
3.	½ p.p.m. each N K. and P.	0162
4.	1 p p m. each N.K and P.	0227
5	10 p.p.m. each N.K. and P.	0367

The results with oats were even more striking, as shown by the analyses of seedlings that were kept under observation for 11 days.

TABLE IX.—ABSORPTION OF PHOSPHORUS BY OAT SEEDLINGS FROM
SOLUTIONS OF LOW CONCENTRATIONS.

		Grams phosphorus in 100 plants
1.	Control, distilled water	.01134
2.	¼ p.p.m. each N.K. and P.	01620
3.	½ p.p.m. each N.K. and P.	02190
4.	1 p.p.m. each N.K. and P.	02527
5.	10 p p.m. each N.K. and P.	02826

It will be seen that, even in a concentration as low as ¼ of a part per million, the absorption of phosphorus was marked. Every day each of these culture pans was given 2,500 c.c. of water, containing a total of 0.005 gram of phosphorus in solution. The plants were able to extract all of the phosphorus, while transpiring only a few centimeters of water. This is a striking example of the ability of the plant to extract nutrient material from a solution without absorbing and transpiring very much water.

The absorption of phosphorus may be detected from concentrations as low as 1/10 part per million, provided that concentration is maintained. In Table X are shown the analyses of a control and of 34 oat seedlings that were grown in a solution of 1/10 part per million of phosphorus, for a period of 20 days. These 34 plants grew in 3 liters of culture solution containing a total of .0003 gram of phosphorus and the solutions were changed daily. Nitrogen and potassium in concentrations of about 20 parts per million each were also added every few days.

TABLE X.—ABSORPTION OF PHOSPHORUS FROM CULTURE SOLUTIONS
OF LOW CONCENTRATIONS.

		Grams phosphorus in 34 plants
1.	Control, distilled water	.00436
2.	1/10 parts per million of phosphorus	.00569

· This experiment was repeated with similar results. There is no doubt but that a plant may feed in infinitely low concentrations of plant food, in fact there seems scarcely a limit to the possible dilution.

In the case of the Bard soil extract, therefore, if phosphorus had been present and available in concentrations as low as ¼, or even 1/10 of a part per million, the seedlings would have absorbed it. Evidently the untreated Bard soil does not give up an appreciable amount of phosphorus to an aqueous solution.

It is not doubted that the plants growing in this soil in the field, do absorb a certain amount of phosphorus from the soil solution. They must do this, or they would soon die. This phenomenon presents a problem upon which work is now being done. It seems as if the plant, in some way, can extract nutrient material from a soil, that would not otherwise

be dissolved by the soil moisture. Whether this is due altogether to the exudation of carbon dioxide by the roots remains to be proved.

Plants are often known to respond to very small applications of fertilizers, and our experiments in the laboratory and in the field indicate that minute amounts of phosphorus may exert a very marked effect upon crops. However, as is well known, the effect of phosphorus upon vegetative development is not often marked during the first stages of growth. Phosphorus is more concerned with the formation of the seed or fruit, than it is with vegetative tissue.

Professor Franklin H. King often said that fertilizers seemed to act like certain medicines and that they were often effective in exceedingly small doses. He seemed to think that minute differences in the amounts of plant food in different soils might often account for their differences in productivity, and he was constantly asking chemists for methods that could be used in determining plant food accurately, in concentrations of less than a part per million. It seems to be a fact, that, under the conditions existing in many of the soils of the Southwest, phosphorus, at least, acts in homeopathic doses.

CARBON DIOXIDE IN THE SOIL SOLUTION

The experiments with insoluble phosphates, in the past, have been carried on almost exclusively in humid regions, and upon neutral or slightly acid soils. The soil from Bard, California, which is representative of many soils in the West, is calcareous, and has an alkaline reaction, showing that it contains free hydroxyl ions. These hydroxyl ions may be derived from calcium or other soluble bases, but they are often derived from sodium carbonate and indicate the presence of black alkali. The results obtained by Hopkins in Illinois. Thorne in Ohio, and others, are, therefore, not applicable to our southwestern conditions.

The soil atmosphere in the humid regions, especially when organic matter is present, is usually relatively high in carbon dioxide, and it is well known that carbon dioxide or carbonic acid in the soil solution exercises an important function in dissolving and bringing the slightly soluble plant foods into an available form.

The effect of carbon dioxide upon the availability of the phosphorus in floats and other slightly soluble phosphates, was determined. Wheat seedlings were grown in culture pans in the way that has been described in the presence of a slight excess of the treated and untreated phosphates. (See Table XI.) The phosphates were shaken each day with the culture solutions, and, as some of the solid material would adhere to the roots of the plant, the tops alone were used in the analyses. Soluble nitrogen and potassium also were added to these culture solutions in order to get

vigorous plants. The seedlings were grown for 21 days, then ashed and analyzed for phosphorus.

TABLE XI.—EFFECT OF CARBON DIOXIDE UPON THE AVAILABILITY OF PHOSPHORUS IN FLOATS, TRI-CALCIUM PHOSPHATE, AND DI-CALCIUM PHOSPHATE.

No.	Treatment.	Grams phosphorus in 100 tops
1.	Control, distilled water	0073
2.	Floats, shaken in culture solutions	0095
3.	Floats, shaken with water and saturated with CO_2	0115
4.	Phosphate made by dissolving floats in HCl, reprecipitating the phosphate with ammonia, and washing free from impurities. Used while wet	0093
5.	Same as No. 4, except that the culture solution was saturated with CO_2	0119
6.	Same as No. 4, except that phosphate was dried and ground fine, and used alone	0096
7.	Same as No. 6, except that the solution was saturated with CO_2	0106
8.	Phosphate made by precipitating calcium phosphate from a saturated solution of $CaSO_4$ with Na_2HPO_4, and ammonia, and washing free from impurities. Used while wet	0120
9.	Same as No. 8, but phosphate dried and ground fine	.0102
10.	Same as No. 8, dried, ground fine, and solution saturated with CO_2	0124
11.	Phosphate made by dissolving calcium carbonate, $CaCO_3$ in HCl, adding Na_2HPO_4 and ammonia, and washing until pure. Used while wet	0115
12.	Same as No. 11, but solution saturated with CO_2	0127
13.	Five parts per million of phosphorus as mono-calcium phosphate	0126

These results show the effect of carbon dioxide upon the tri- and di-calcium phosphates. The phosphorus of the mono-calcium phosphate, No. 13, is readily soluble in water and available in low concentrations. The floats, No. 2, represent the tri-calcium or insoluble, while the phosphate used in numbers 4 and 5, represents the di-calcium or reverted form. It will be seen that the effect of carbon dioxide is shown in every case. Experiments similar to the above were conducted with barley seedlings with equally conclusive results. It should be borne in mind that while the culture solutions were saturated daily with carbon dioxide, they stood in open pans for 24 hours and some of the gas was doubtless lost.

THE EFFECT OF CARBON DIOXIDE UPON THE AVAILABILITY OF PHOSPHORUS IN BONE ASH

A sample of ignited bone ash was washed free from soluble impurities, and small amounts of this solid were added to water cultures as described in Table XII. The plants were kept under observation for 15 days and their analyses are shown in the table.

TABLE XII.—THE EFFECT OF CARBON DIOXIDE UPON THE AVAILABILITY OF PHOSPHORUS IN BONE ASH.

No.	Treatment	Grams phosphorus in 100 tops
1.	Control, distilled water	.0063
2.	Solid bone ash shaken daily with solution of 50 p.p.m. Na_2CO_3	0114
3.	Solid bone ash shaken with water and saturated daily with CO_2	0161

The addition of sodium carbonate to No. 2 was made, not for the purpose of its solubility effect upon the bone ash, nor in order to have a toxic body present. Sodium carbonate in the concentration used, is a stimulant to plants, and we often add it in small amounts to water cultures, when good plants are desired. In this experiment the plants receiving sodium carbonate were decidedly better and had a better root development than did those grown in the carbon dioxide solution, yet they did not contain as much phosphorus. Roots of growing plants exude carbon dioxide and if this gas had been present in solution in culture No. 2, it would have had an effect, although probably small, upon the solid bone ash. The sodium carbonate was, therefore, added in order to keep this exuded carbon dioxide out of solution, and only enough was used to accomplish this purpose. The sodium carbonate, when first added to the culture solution, gave a color with phenolphthalein, indicating an hydroxyl-ion concentration, but this color would become more and more faint, due to the conversion of the sodium carbonate into bicarbonate, until the next day when no color was obtained. It may be said, therefore, that the sodium carbonate fulfilled its mission and kept the carbon dioxide out of solution. The difference in the phosphorus content of the plants in culture 3 over that of culture 2, can, therefore, be safely attributed to the effect of carbon dioxide upon the insoluble bone ash.

CARBON DIOXIDE NOT ALWAYS PRESENT IN THE SOIL SOLUTION

We have shown that carbon dioxide, in solution, will bring insoluble phosphates into an available form. We are taught, furthermore, that carbon dioxide exists in the soil atmosphere in relatively large amounts, especially when decomposing organic matter is present. If carbon dioxide exists in these soils and in the soil solutions under field conditions, it is reasonable to assume that it would exert an effect upon the insoluble phosphates in the soil and bring some phosphorus into solution. The assumption that carbon dioxide exists in all soils, however, may be unwarranted.

Attention has been called to the fact that the soils under consideration are calcareous and contain a little black alkali, and thus have free hydroxyl ions in the soil solution. It is impossible to conceive of sodium carbonate, with its free hydroxyl ions, and carbon dioxide, or carbonic acid, existing in the same solution, so we are forced to the conclusion that these soils contain little or no carbon dioxide, either in the soil solution or in the soil atmosphere. Black alkali soils cannot contain an appreciable amount of carbon dioxide, and, as a reverse, soils that contain carbon dioxide cannot

contain black alkali.* In a black alkali soil, therefore, the effect of carbon dioxide upon the insoluble phosphates is reduced to a minimum, if any such action exists at all, and plants may actually suffer for phosphorus in a soil that is rich in that element.

EXPERIMENTS WITH CALCAREOUS SOILS AND CARBON DIOXIDE

A sample of Bard soil which contained .051 percent of phosphorus in insoluble form, but no soluble phosphorus, was mixed with twice its weight of water, (1,000 grams soil—2,000 c.c. of water), and this mixture saturated daily with carbon dioxide. The mixture was shaken in a machine after the addition of carbon dioxide, allowed to stand overnight, the extract decanted but not filtered, and a set each of barley and oat seedlings were grown in the extract. The extracts were used over and over again, that is, the solutions were allowed to stand in contact with the soil one day and used in the culture pans the next, while the extract that the plants had grown in on one day would be poured back into the bottle, saturated with carbon dioxide, and allowed to stand until the next day. One hundred parts per million of nitrogen, as sodium nitrate, were added to the culture solutions in three different applications.

TABLE XIII.—EFFECT OF CARBON DIOXIDE UPON THE AVAILABILITY OF PHOSPHORUS IN A CALCAREOUS SOIL.

No.	Treatment	Grams phosphorus in 100 plants	
		Barley	Oats
1.	Extract of untreated soil control ___ ___ _ ___	.01301	01339
2.	Extract saturated daily with carbon dioxide ___	01215	.00978

These experiments gave results opposed to those that were expected at the time, that is, they indicated that the presence of carbon dioxide in calcareous soil solutions would tend to diminish rather than to increase the availability of the phosphates.

CARBON DIOXIDE NOT EFFECTIVE IN CALCAREOUS SOILS

If insoluble phosphates, when applied to neutral or acid soils, produce beneficial effects, and if these effects are due largely to the presence of carbon dioxide in the soil, it would seem as if western soils which contain no black alkali, should respond to applications of insoluble phosphates, assuming that an excess of carbon dioxide is dissolved in the soil solution. However, we have at hand no data which prove that applications of floats to western calcareous soils, even when accompanied by applications of manure, produce beneficial results. This failure is due probably to the presence of

*Breazeale, J. F. & Burgess, P. S. Technical Bulletin No. 6, Ariz. Agri. Exp. Sta., "The Reaction between Calcium Sulphate and Sodium Carbonate, and its Relation to the Reclamation of Black Alkali Lands."

calcium carbonate, which keeps the carbon dioxide out of solution. What is true as to the presence of carbon dioxide in a black alkali soil, is also true, in a lesser degree, in a soil containing an excess of calcium carbonate. When carbon dioxide is generated in a calcareous soil, it is dissolved by the soil moisture with the formation of carbonic acid, which dissolves calcium carbonate and brings calcium bicarbonate into solution. While this reaction between calcium carbonate and carbonic acid may not run completely to an end, it certainly is effective in keeping carbonic acid out of solution until the soil solution is practically saturated with calcium bicarbonate.

AVAILABILITY OF PHOSPHORUS IN FLOATS, IN THE PRESENCE OF CARBON DIOXIDE, CALCIUM CARBONATE, AND CALCIUM SULPHATE

Cultures of barley were grown for 16 days in the solutions that are described in Table XIV. The solutions were first placed in large bottles and were saturated daily with carbon dioxide. The solutions were allowed to stand 24 hours in order that the sediments might settle, and the clear liquids were then decanted into the culture pans. In this method, the plants came in contact with the solution only, and not with floats, calcium carbonate, or calcium sulphate in solid phase.

TABLE XIV.—AVAILABILITY OF PHOSPHORUS IN THE PRESENCE OF CARBON DIOXIDE, CALCIUM CARBONATE, AND CALCIUM SULPHATE

No.	Treatment of solution	Grams phosphorus in 100 plants
1.	Control, distilled water	.01280
2.	Floats, saturated daily with carbon dioxide	01512
3.	Floats with calcium carbonate saturated daily with carbon dioxide	01210
4.	Floats with excess calcium sulphate, saturated daily with carbon dioxide	01557

The plants that grew in the solutions containing calcium carbonate, No. 3, were found to contain even less phosphorus than did those that grew in the distilled water. The difference is probably within the limits of error of the experiment, yet it is clear that carbon dioxide in the presence of calcium carbonate had brought no phosphorus into solution. There was considerable increase in the phosphorus content of the plants in solution No. 2 where floats occurred alone, and saturated daily with carbon dioxide. The plants in the cultures containing calcium sulphate also showed a decided increase in their phosphorus content.

SOLUBILITY OF FLOATS IN SOLUTIONS OF CARBON DIOXIDE, CALCIUM CARBONATE, AND CALCIUM SULPHATE

Heretofore our experiments have dealt largely with the available rather than with the soluble phosphorus. Some experiments were now made

upon the solubility of floats in solutions of carbon dioxide, calcium carbonate, and calcium sulphate.

Two grams of floats and 2,000 c.c. of water were placed in each of five bottles and treated as shown in Table XV. The bottles were shaken at intervals for 2 days, allowed to stand overnight, the solutions filtered through filter papers and 1,000 c.c. of each evaporated to a small volume and analyzed for phosphorus.

TABLE XV.—SOLUBILITY OF FLOATS IN SOLUTIONS OF CARBON DIOXIDE, CALCIUM CARBONATE, AND CALCIUM SULPHATE.

No.	Treatment	Parts per million in solution	
		Ca	P
1.	Floats in carbon-dioxide-free water	1 5	30
2.	Floats in water saturated with carbon dioxide	31 5	4 48
3.	Floats in carbon-dioxide-free water with excess of calcium carbonate	19 5	23
4.	Floats with excess of calcium carbonate saturated with carbon dioxide	322 0	Trace
5.	Floats with excess of calcium sulphate saturated with carbon dioxide	637 0	3 33

The floats used in the control had been washed free from calcium carbonate with dilute nitric acid, yet more calcium went into solution than that required to balance the phosphorus in the formula $Ca_3(PO_4)_2$. This indicates the presence of other salts of calcium in the floats.

It will be seen from the table that the solubility of phosphorus in floats in distilled water, was increased 15 times by the addition of carbon dioxide to the solution. The presence of calcium carbonate alone, No. 3, did not materially affect the solubility of the phosphorus. When carbon dioxide was introduced into the solution containing floats and calcium carbonate, No. 4, it brought 322 parts per million of calcium into solution which forced the phosphorus existing as tri-calcium phosphate, almost completely out of solution. In a saturated solution of calcium sulphate and carbon dioxide, No. 5, while the solubility of the phosphorus was slightly reduced from that obtained with carbon dioxide alone, the solution contained about 12 times as much as did the control. These reactions will be discussed later.

The solubilities of the slightly soluble phosphates under the conditions just described, are in accordance with chemical laws, and the solubilities were all indicated in advance by the behavior of the seedlings in the experiments that have been described. Our results correspond fairly well with those of Cameron and Seidel.*

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*Jour. Amer. Chem. Soc. 26.1454, 1904.

TRI-CALCIUM PHOSPHATE AND CARBON DIOXIDE

It is common agricultural practice, where available phosphorus is low, to apply floats or finely ground, steamed bone meal to the neutral or slightly acid soils of the humid regions, where considerable quantities of organic matter are present. Such applications are usually beneficial. The explanation commonly offered is that the carbon dioxide evolved during the decomposition of the organic matter changes the inert tri-calcium phosphate into more available forms. This action is well illustrated in Table XIV where the solubility of tri-calcium phosphate was raised from less than 1 p.p.m. of phosphorus to nearly 5 p.p.m. by the addition of carbon dioxide alone. The reaction may be represented as follows:

$$Ca_3(PO_4)_2 + 2H_2CO_3 \rightleftharpoons Ca_2H_2(PO_4)_2 + Ca(HCO_3)_2$$
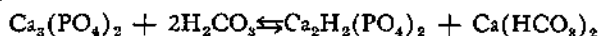
This equation is but slightly reversible under field conditions, i. e., di-calcium phosphate does not react with calcium carbonate to form tri-calcium phosphate and carbonic acid. In our studies it was found that, at approximate equilibrium, 4.48 p.p.m. of phosphorus were brought into solution by carbon dioxide. While in field soils probably less would be dissolved, nevertheless, sufficient carbon dioxide is usually present, under humid conditions, to bring sufficient phosphate into solution to produce marked effects upon crop growth if tri-calcium phosphate is present.

The reaction above cited represents the action of carbonic acid upon tri-calcium phosphate, providing it had the molecular formula, $Ca_3(PO_4)_2$, but probably very few naturally occurring phosphates have their phosphate and lime present in exactly these proportions. According to most authorities, rock phosphate is in reality a series of solid solutions of di-calcium phosphate, and calcium oxide, and in varying proportions, together with other materials (often calcium carbonate). When such solid solutions come in contact with pure water or with water charged with carbon dioxide, the resulting aqueous solutions carry an excess of phosphoric acid or base depending upon the composition of the rock.* The solid solution thus goes into true aqueous solution as di-calcium phosphate and calcium bicarbonate. In the presence of a great excess of the latter more soluble salt, however, much less of the phosphate will be dissolved due to the "common-ion effect." This has been found to be the case in our solubility studies. As is well known, tri-calcium phosphate is of little value as a source of phosphorus to plants when acting alone. It must first be changed to the more available mono- or di-calcium form, either by carbonic acid or by means of stronger acids, before it is of value.

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*It has been found that the phosphate ion is more rapidly leached from these solid solutions than is the lime, hence as time goes on and leaching progresses, the naturally occurring phosphate becomes more and more basic and increasingly insoluble. See, "The Action of Water and Aqueous Solutions Upon Soil Phosphates" by Cameron and Bell, Bul. 41, Bureau of Soils, U. S. D. A., for an extensive discussion of this subject.

TRI-CALCIUM PHOSPHATE, CALCIUM CARBONATE, AND CARBON DIOXIDE

The reactions above discussed might be expected to take place in neutral or slightly acid soils containing little solid calcium carbonate. The soils of the Southwest, however, usually carry from 1 to 10 percent of calcium carbonate, and occasionally much more. Conditions here, therefore, are decidedly different. The addition of calcium carbonate to an aqueous suspension of floats has little effect upon the solubility of the phosphate, as shown in Table XIV, but when carbon dioxide is introduced into the suspension an entirely different set of conditions prevails. This reaction may be represented as follows:

$$Ca_3(PO_4)_2 + CaCO_3 + H_2CO_3 \rightleftharpoons Ca_3(PO_4)_2 + Ca(HCO_3)_2$$
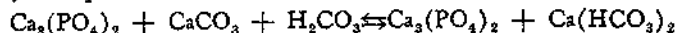
It has been found that the tri-calcium phosphate does not enter appreciably into this reaction, hence practically no phosphorus is brought into solution. Carbonic acid is a weak acid, hence when present with a mixture of calcium phosphate and calcium carbonate, the action is entirely with the latter, more basic salt. As long as calcium carbonate is present, no attack will be made upon the tri-calcium phosphate. Kelley also has shown this to be true for the nitrous and nitric acids biologically formed in calcareous soils.

The solubility of calcium bicarbonate is over 1,000 p.p.m. in pure water, while that of tri-calcium phosphate is extremely low. Thus, in a solution containing both, we would expect to find less soluble phosphorus than in one carrying tri-calcium phosphate alone. This is shown to be the case in Table XIV.

In field practice, the beneficial effects of applications of floats and organic matter to neutral or acid soils and the absolute lack of response to such treatments in calcareous soils are explained. The addition of organic matter (carbonic acid) with the floats in the latter case (see Table XIV) tends actually to decrease, rather than increase, the slight solubility of the phosphate.

TRI-CALCIUM PHOSPHATE, GYPSUM, AND CARBON DIOXIDE

Where floats is applied to a neutral soil containing gypsum and carbon dioxide, another set of conditions prevails. In our experiments, floats and gypsum were suspended in pure water which was kept saturated with carbon dioxide, and shaken for several days until an approximate equilibrium had been attained. The carbonic acid had practically no effect upon the solubility of the gypsum but did react to a limited extent with the tri-calcium phosphate. The equation may be represented as follows:

$$Ca_3(PO_4)_2 + CaSO_4 + 2H_2CO_3 \rightleftharpoons Ca_2H_2(PO_4)_2 + CaSO_4 + Ca(HCO_3)_2$$
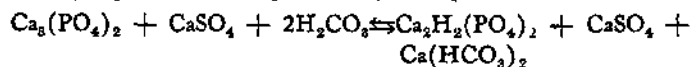
The gypsum present in solution, carrying the common calcium ion, had a slight tendency to retard the solution of the tri-calcium phosphate. This effect is shown in solutions No. 2 and No. 5 of Table XIV. As the tri-calcium phosphate has a marked solubility in carbonic acid solutions, and as gypsum does not take up carbonic acid on dissolving, the retarding effect of the latter salt is but slight.

SOLUBLE PHOSPHATE APPLICATIONS TO CALCAREOUS SOILS

Our experiments confirm Hilgard's early statements that, in western calcareous soils, plants usually respond to applications of soluble phosphates, while showing no response to the insoluble tri-calcium form. The water-soluble, mono-calcium phosphate will remain in solution only in the presence of an excess of hydrogen ions. It is well known that, when this phosphate is added to a soil containing calcium carbonate or other basic material, it quickly reverts to the most insoluble form which it is capable of assuming under these conditions. The reaction may be written as follows:

$$CaH_4 (PO_4)_2 + 2CaCO_3 \rightleftharpoons Ca_3H_2 (PO_4)_2 + Ca(HCO_3)_2$$
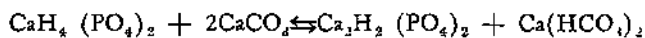
This reaction quickly runs to completion from left to right, and is but slightly reversible. Di-calcium phosphate, furthermore, is stable in the presence of an exce s of calcium carbonate, and does not go over into the tri-calcium form. Now, as di-calcium phosphate is slightly soluble in water, we would expect that an application of any soluble phosphate (acid phosphate or double superphosphate) would be beneficial to a calcareous soil. Field experience has shown this to be true.

AVAILABILITY OF PHOSPHATES IN THE PRESENCE OF IRON AND ALUMINUM

All soils contain oxides, or hydrated oxides, of iron and aluminum, and it has been a matter of much speculation as to the effects which these materials have upon the availability of soil phosphorus. It is known that iron and aluminum phosphates are much less soluble in water than is the so-called tri-calcium phosphate; also, that a mixture of slightly soluble substances approaching equilibrium conditions in a water solution at constant temperature, follows certain definite chemical laws. Such a heterogeneous equilibrium, as between tri-calcum phosphate, ferric hydroxide, and carbon dioxide in pure water, involves both solution and reprecipitation. If a solid is in contact with its saturated solution (partially or wholly ionized), and the ion product is in any way lowered by the removal of either ion from solution, more of the solid will dissolve, and enter into reaction until the substances finally resulting are the most insoluble

possible combinations of the ions involved.   Thus, if floats and organic matter are added to a non-calcareous soil containing hydrated oxides of iron, carbon dioxide will be evolved as decomposition progresses, and we may expect a reaction taking place within the soil solution between these compounds.   Tri-calcium phosphate is soluble to the extent of 3 or 4 p.p.m., ferric hydroxide less than 1 p.p.m., while carbon dioxide in cold water is soluble to the extent of over 1,000 p.p.m.   Due to these differences in solubility, the tri-calcium phosphate will be fairly rapidly dissolved as di-calcium phosphate while the ferric hydroxide will be but slowly attacked.   The following reactions may represent such changes:

$$Ca_3(PO_4)_2 + 2Fe(OH)_3 + 6H_2CO_3 \rightleftharpoons 3Ca(HCO_3)_2 + 2FePO_4 + 6H_2O$$
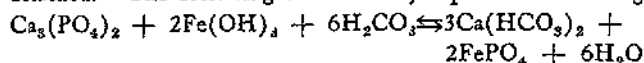
It is thus very probable that, in non-calcareous soils, some of the phosphates added, either as mono-, di-, or tri-calcium phosphate, enter into combination with iron or aluminum if not first taken up by plants, and we are led to believe that the phosphorus in soils, which is insoluble in carbonated water, but soluble in the stronger mineral acids, exists largely as iron or aluminum phosphates.

The apparent insolubility of the iron and aluminum phosphates has contributed to the belief that their phosphorus is largely lost to the plant. However, it has been repeatedly shown that *artificially prepared* iron and aluminum phosphates are available sources of this element for plants, while, for reasons that have not yet been explained, the finely ground, *naturally occurring* phosphates of these metals are almost wholly unavailable.   Two definite reasons for this apparent anomaly present themselves:

First: The precipitated compounds are much more finely divided and expose a much greater surface to the action of the solvent.   Thus, while *at equilibrium* the same amounts of phosphorus may be rendered soluble from both sources, the actual *rate* at which solution progresses may be many times greater in the case of the finely divided, precipitated materials. Professor F. H. King, many years ago, while in the Federal Bureau of Soils, accumulated many data which indicated that the *rate* of solution of the more insoluble plant nutrients is of far more importance to the growing plant than are *the absolute amounts* of these substances which may be dissolved from a soil when equilibrium conditions between it and the solvent are approached.

·Second: The action of water and carbonated water upon the phosphates of iron and aluminum is similar to that of like solutions upon the phosphates of calcium, although somewhat slower.   When aqueous solutions come in contact with all of these phosphates, the phosphate ion is removed more rapidly than is the calcium ion, resulting in the formation

of a more basic residue. The basic phosphates are thus more insoluble than are the neutral phosphates, and in the naturally occurring minerals which have been leached for ages, these basic phosphates greatly predominate. On the other hand, freshly precipitated ferric phosphate invariably contains an excess of phosphate ions over that required to form $FePO_4$.* It is thus acidic rather than basic, and hence much more soluble and available.

In order to study the reactions taking place between floats, ferric hydroxide and calcium carbonate when suspended in carbonated water, several large bottles were prepared as indicated in Table XVI. The ferric hydroxide used was the mineral limonite, ground to an impalpable powder in a ball mill. Two grams of each of the solids indicated in the table were added to 2 liters of cold water saturated with carbon dioxide, and shaken intermittently, with additions of carbon dioxide, over the periods stated. One liter of each solution was evaporated and analyzed for phosphorus.

TABLE XVI.—SOLUBILITY OF FLOATS IN THE PRESENCE OF FERRIC HYDROXIDE, CALCIUM CARBONATE, AND CARBON DIOXIDE.

| | | Parts per million of phosphorus in solution | |
		After 18 hours	After 12 days
No.	Treatment		
1.	Floats in solution saturated with carbon dioxide _____	2 03	2 70
2.	Floats, with ferric hydroxide in solution, saturated with carbon dioxide. . _____	1 28	88
3.	Floats with calcium carbonate, in solution saturated with carbon dioxide _____	Trace	00

As here shown, floats is soluble to the extent of about 10 p.p.m. in water saturated with carbon dioxide. It is also evident that all of this soluble phosphorus has not been removed as the insoluble ferric phosphate (No. 2) at the end of the 12-day period. Under humid soil conditions, where organic matter is present, the carbonic acid will progressively react with the tri-calcium phosphate to maintain soluble phosphorus in the soil solution at all times, even though some may be slowly precipitated, possibly as the basic ferric phosphate. This action will continue as long as any tri-calcium phosphate remains in the soil.

In a calcareous soil, however, the carbonic acid reacts first with the calcium carbonate rather than with floats as we have previously shown, and

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*An excellent discussion of this subject appears in Bul. 41, Bureau of Soils, U. S. D. A., "The Action of Water and Aqueous Solutions upon Soil Phosphates," by Cameron and Bell.

we have a soil solution partially saturated with calcium bicarbonate. This will prevent any action on the tri-calcium phosphate, so that no reaction can be expected between it and the hydroxides of either iron or aluminum. This effect is shown in No. 3, Table XVI.

The hydrated oxides of iron exist in considerable quantities in all soils while *soluble* phosphorus is usually present in extremely small amounts. The relative solubilities of ferric hydroxide and ferric phosphate will determine the possibility of the formation of the latter compound in soils. Both are extremely insoluble in pure water, and even less soluble in alkaline solutions. Hence we may expect no reaction whatever in calcareous soils, where hydroxyl ions are always present in excess.

PRECIPITATION OF PHOSPHORUS FROM SOLUTION BY FERRIC HYDROXIDE WHEN NO CARBON DIOXIDE IS PRESENT

A solution containing .00655 gm. per 100 c.c., or 65.5 p.p.m. of phosphorus was prepared by shaking a small amount of commercial superphosphate with an excess of calcium carbonate, allowing the mixture to stand for three days, and filtering off the clear solution. The phosphorus in this solution was largely in the form of reverted, or di-calcium phosphate.

One liter of this solution was placed in a bottle, and 1.5 grams of finely pulverized limonite added. The solution was allowed to stand for 24 hours with occasional shaking, and 100 c.c. were filtered off and analyzed for phosphorus. The solution was then shaken and allowed to stand for 1 day more and analyzed again for phosphorus. This was continued for 7 days, and the results of the analyses are shown in Table XVII.

TABLE XVII.—PROGRESSIVE REMOVAL OF SOLUBLE PHOSPHORUS FROM SOLUTION BY LIMONITE.

No.	Grams phosphorus in each 100 c.c. solution
1. Original solution	00655
2. After standing 1 day in contact with ferric hydroxide	00634
3. After standing 2 days in contact with ferric hydroxide	00624
4. After standing 3 days in contact with ferric hydroxide	00620
5. After standing 4 days in contact with ferric hydroxide	00605
6. After standing 5 days in contact with ferric hydroxide	00591
7. After standing 6 days in contact with ferric hydroxide	00577
8. After standing 7 days in contact with ferric hydroxide	00570

It will be seen that, after standing in contact with the solution of di-calcium phosphate of a concentration of 65.5 p.p.m. of phosphorus for 7 days, the ferric hydrate had removed only 8.5 p.p.m of phosphorus from solution. This concentration of phosphorus (65.5 parts per million) is

probably 20 times as great as that ordinarily found in the soil solution. In a concentration of 1 or 2 p.p.m. of phosphorus the reaction with ferric hydrate thus must be *exceedingly slow.*

The reaction just described took place in a solution that contained neither carbon dioxide nor an excess of calcium carbonate. The presence of these two compounds would have prevented even this slow reaction between the phosphate and the ferric hydroxide.

COMPETITION BETWEEN PLANTS AND FERRIC HYDROXIDE FOR SOLUBLE PHOSPHORUS

Knowing that ferric hydroxide slowly removes phosphorus from solution, especially in non-calcareous soils, and also knowing that plants absorb phosphorus from solution, it is evident that a competition must exist in many soils between plants and ferric hydroxide for this element. It has been shown that growing seedlings make a strong demand for phosphorus, that they are vigorous feeders, and that they are able to feed in extremely low concentrations.

A determination of the ability of barley seedlings to compete with ferric hydroxide for phosphorus was shown in the following experiment. Six solutions of 2 liters each, were prepared from commercial superphosphate, and treated as indicated in Table XVIII. Two of these solutions contained phosphorus and ferric hydroxide but no plants, two contained phosphorus alone with 100 barley seedlings, while the other two contained both phosphorus and ferric hydroxide with 100 barley plants. The experiment lasted 7 days, and the amount of phosphorus which remained in solution at the end of that period is shown in Table XVIII.

TABLE XVIII.—COMPETITION BETWEEN BARLEY SEEDLINGS AND FERRIC HYDROXIDE FOR SOLUBLE PHOSPHORUS.

No.	Treatment	Parts per million of phosphorus	
		Added	F'd in solution
	Without plants		
1.	Solution of calcium phosphate shaken with 1 gm. of limonite	5 57	4 95
2.	Solution of calcium phosphate shaken with 1 gm. of limonite	2 79	2 73
	With plants		
3.	Solution of calcium phosphate with 100 barley seedlings	5 57	27
4.	Solution of calcium phosphate with 100 barley seedlings	2 79	11
5.	Solution of calcium phosphate with 1 gm. limonite and 100 barley seedlings	5 57	0
6.	Solution of calcium phosphate with 1 gm limonite and 100 barley seedlings	2 79	0

It will be seen that ferric hydroxide removed only .62 part per million of phosphorus from solution No. 1 which originally contained 5.57 parts per million, and practically no phosphorus from solution No. 2 which contained 2.79 parts per million. At the same time 100 barley seedlings removed nearly all, or 5.3 parts per million of phosphorus from the solution that contained 5.57 parts per million, and all from the solution that contained 2.79 parts per million, while all of the phosphorus was removed from solution in the cultures containing both the plants and the ferric hydroxide.

It is evident that when a solution of soluble phosphorus is placed in contact with ferric hydroxide in the presence of growing plants under conditions represented by the above experiment, the absorption of phosphorus by the plants is a great deal more rapid than is the precipitation as insoluble ferric phosphate. When one considers the rapidity with which most plants feed, and the extreme slowness of the reaction between the soluble phosphates and the ferric hydroxide, there can be no doubt but that, under field conditions, the odds are greatly in favor of the plant in its competition for phosphorus with ferric or aluminum hydroxide.

COMPETITION FOR PHOSPHORUS IN NEUTRAL OR ACID SOILS

In an acid soil, or in a soil containing carbon dioxide but no calcium carbonate, conditions are somewhat different from those just described. Ferric hydroxide is slightly more soluble than is ferric phosphate in weak acids, so that the reaction between calcium phosphate and ferric hydroxide under such conditions should go on more rapidly, and this is indicated by the following experiment.

TABLE XIX.—COMPETITION BETWEEN FERRIC AND ALUMINUM HYDROXIDES AND BARLEY SEEDLINGS FOR SOLUBLE PHOSPHORUS IN THE PRESENCE OF CARBON DIOXIDE.

No.	Treatment	Grams phosphorus in 100 plants
1.	Control, distilled water	01280
2.	Floats saturated with carbon dioxide	01512
3.	Floats and ferric hydroxide saturated with carbon dioxide	01242
4.	Floats with aluminum hydroxide saturated with carbon dioxide	01296

Cultures of barley were grown for 16 days in the solutions described in Table XIX, and then analyzed for phosphorus. The solutions that contained the floats, and the floats plus ferric hydroxide or aluminum hydroxide (Nos. 2, 3, and 4), were placed in large bottles, saturated with

carbon dioxide, and allowed to stand for 24 hours. The clear solutions were then decanted into culture pans that contained the barley seedlings, and the solutions changed daily. In this way the plant roots did not come in contact with the solid floats or with solid ferric or aluminum hydroxides. Phosphorus that was brought into solution by the carbon dioxide from the floats, stood in contact with the finely divided ferric and aluminum hydroxides for 24 hours before the plants were put into the solutions. From the results of this experiment, the phosphorus seems to have been largely removed from solution during this time by the iron or aluminum salts, as no increase in the phosphorus content of the plants in cultures Nos. 3 and 4 was noted.

CONCLUSIONS

1. Neutral or acid soils in humid regions often respond to applications of floats, or insoluble phosphates, especially if there is an abundance of organic matter present.

2. Calcareous or alkaline soils in semi-arid regions do not respond to applications of insoluble phosphates, although they do respond to the soluble acid phosphates.

3. Certain western calcareous soils which have been fertilized with floats or bone meal, yield water extracts which contain little or no phosphorus, while such soils which have been fertilized with acid or superphosphates yield extracts which contain appreciable amounts of phosphorus.

4. Plants are able to absorb phosphorus readily from solutions as dilute as one-tenth of a part per million.

5. The presence of CO_2 in solution increases the solubility and availability of the phosphorus in both tri-calcium and di-calcium phosphates.

6. In western soils that contain black alkali, there is no free CO_2, so that in such soils the solvent action of CO_2 upon the insoluble phosphates is eliminated.

7. Floats is practically insoluble in carbon-dioxide-free distilled water and in carbon-dioxide-free water containing an excess of $CaCO_3$.

8. Floats in a saturated solution of CO_2 has a relatively high solubility, while in a saturated solution of CO_2 with $CaCO_3$, or $Ca(HCO_3)_2$, it is practically insoluble.

9. Floats in a saturated solution of CO_2 with $CaSO_4$ has an appreciable solubility, but slightly lower than in the absence of $CaSO_4$.

10. Tri-calcium phosphate alone seems to be of little value as a source of phosphorus to the plant.

11. The beneficial effect of the application of floats to eastern soils which contain decomposing organic matter, or CO_2, is due largely to the fact that the CO_2 changes the tri-calcium phosphate to di-calcium phosphate and thus renders the phosphorus available.

12. The lack of response of western calcareous or alkaline soils to applications of floats or bone meal is due chiefly to the fact that under these conditions there is no CO_2 to react with the tri-calcium phosphate as carbonic acid will react first with the more basic $CaCO_3$, or Na_2CO_3 if present.

13. The beneficial effects of applications of soluble phosphates to western soils are accounted for largely by the fact that, under these conditions, mono-calcium phosphate will revert to the di-calcium form which is available, but not to the tri-calcium or insoluble form.

14. The application of manure to western calcareous soil, while advisable from other considerations, will tend to decrease rather than increase the availability of the insoluble tri-calcium phosphates.

15. Ferric and aluminum hydroxides react slowly with calcium phosphate and form insoluble ferric and aluminum phosphates. This action is accelerated by the presence of carbonic acid alone, but retarded by carbonic acid plus calcium carbonate.

16. After an application of calcium phosphate to a soil, there is competition for the phosphate between the growing plants and the ferric and aluminum hydroxides. In a neutral soil containing no carbonic acid, in a black alkali soil, or in a soil containing an excess of calcium carbonate plus carbonic acid, the odds are greatly in favor of the plants. In a slightly acid soil, or in a soil containing carbonic acid but no calcium carbonate, the plants will have more difficulty in absorbing the phosphorus before it enters into combination with the iron and aluminum.

17. Explanations are offered as to why artificially precipitated iron and aluminum phosphates are more available sources of phosphorus than are the naturally occurring mineral phosphates of these metals.