Factors Influencing the Availability of Native Soil Phosphate and Phosphate Fertilizers in Arizona Soils

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FACTORS INFLUENCING THE AVAILABILITY OF NATIVE SOIL PHOSPHATE AND PHOSPHATE FERTILIZERS IN ARIZONA SOILS

By

W. T. McGeorge

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FACTORS INFLUENCING THE AVAILABILITY OF NATIVE SOIL PHOSPHATE AND PHOSPHATE FERTILIZERS IN ARIZONA SOILS

By W. T. McGeorge

INTRODUCTION

In view of the widespread importance and interest in phosphate fertilization in Arizona, the study of the fundamental principles involved in the availability of phosphate in Arizona soils has been a major project at the Arizona Agricultural Experiment Station for some years.

Studies on several phases of the problem have been reported in previous bulletins. These investigations have involved: effect of phosphate on the maturity and yield of lettuce (8); effect of mechanical composition of the soil on phosphate availability and phosphate nutrition (18, 22); availability of phosphate (4); solubility studies (21); application of electrodialysis to phosphate studies and the nature of the phosphate compounds predominating in calcareous soils (23); the behavior of iron, aluminum, and organic phosphates in calcareous soils (16); the effect of high *p*H values on the absorption of phosphate by plant roots (3); physicochemical studies on the phosphate compounds present in calcareous soils (5); and fertilization of alfalfa with phosphates (17). In addition to these bulletins a number of articles dealing with the problem have been published in technical journals.

Since the publication of the above, field observations have been made on the important crops grown in the state, such as truck, grain, alfalfa, cotton, and citrus, and much additional information on the availability of phosphate has been gained.

In general, field experience has shown that truck crops, with few exceptions, grains, and alfalfa give profitable response to phosphate fertilization. Cotton often gives profitable response on light soils but less often on heavy soils.

The phosphate fertilization of citrus is still an open question, since in some cases there has been evidence of response in an improved quality of fruit, in others no apparent response. There are several theories which may explain this. Recent analyses of grapefruit made in this laboratory have shown that only approximately 30 pounds of phosphate (expressed as P_2O_5) are sold off an acre of orchard annually as fruit. This would be represented by only 10 parts P_2O_5 per million parts of an acre foot of soil. It is evident from this that the phosphate requirement of citrus is not great. Furthermore, the citrus tree is vegetatively active throughout the most of the year and may be continuously drawing upon the soil phosphate over this period. Finally crops with high calcium requirement are usually considered strong phosphate feeders, and citrus has a very high calcium requirement.

To explain further, carbon dioxide, as a product of root respiration, is the solvent employed by roots in dissolving soil compounds which are not readily soluble in the soil solution. In calcareous soils the products of the reaction involved in the solubility of phosphate are Ca, HCO_3, and HPO_4 or H_2PO_4 ions. Since both the calcium and phosphate ions must be removed from solution to make the reaction continuous, obviously the plant with a high Ca requirement, thereby absorbing both ions, will have a more sustained supply of phosphate. If the Ca is not adequately absorbed by the roots, its accumulation will reduce the solubility of phosphate.

The present status of the problem is one of ascertaining the reasons for the variable behavior of crops on soils which are apparently low in available phosphate, some of the factors influencing phosphate availability, and the relative value of different forms of phosphate fertilizer. Few, if any, of Arizona's alkaline calcareous soils are actually deficient in phosphate. That is, the total amount of phosphate present is ample to support crops for many years. Even though this phosphate is readily soluble in dilute acids when the soil is examined in the laboratory, it may not react readily to the solvent processes employed by plant roots in extracting phosphate from the soil. The important factors contributing to this low availability are calcium carbonate (caliche) and alkalinity. Calcium carbonate functions in the chemical fixation of phosphate as carbonate-phosphate and also contributes to the development of high *p*H, since the *p*H of calcium carbonate is 9.4 to 9.7. It has been clearly demonstrated that a reduction in *p*H of the soil by means of acid in the irrigation water or heavy manure applications will greatly increase the absorption of phosphate by crops. This increased availability has been demonstrated both by chemical analyses of the soil and of plants grown on soils thus treated (19). Since such a reduction in *p*H can not always be economically accomplished, phosphate fertilization on calcareous soils is essential for good crop yields. On account of the difference in phosphate requirement and feeding power of different crops, no single fertilizer program can be employed for all crops and on all soil types. There is a wide difference in physiology, growth habits, and root distribution of plants and an equally wide difference in structure, reaction (*p*H), and calcium carbonate content of Arizona soils.

EXPERIMENTAL

METHODS FOR DETERMINING AVAILABLE PHOSPHATE IN SOILS

There is a constant demand from farmers for specific information on the available phosphate in their soils. In response to this demand many new analytical procedures have been developed.

They may be divided into quick field chemical tests, laboratory chemical tests, and plant tests.

The quick field test has proved an excellent method for estimating the approximate phosphate deficiencies in many soils. It has the advantage that many tests can be made at little cost and in a very short period of time. However, there are certain soils in which the quick tests are not applicable. In the Southwest, phosphate availability is primarily a question of soil reaction. Phosphate in these soils is largely present as carbonate-phosphate, a complex composed of tricalcium phosphate and calcium carbonate. This compound is readily available at soil reactions of near neutrality or at acid soil reactions. Since a buffered acid solvent is used in all these quick tests, they will show, without exception, a high phosphate availability in practically all Arizona soils, but without any correlation with the response of the soil to phosphate fertilization. Furthermore, the ratio of volume of solvent to weight of soil influences the field test so greatly that large errors are encountered in the approximate methods which must be used in field tests. They produce a greater reduction in *p*H and dissolve larger amounts of phosphate than would be dissolved in the field.

In order to illustrate the magnitude of this error the following data are submitted. Three soils were extracted with sodium acetate buffer solution of *p*H 5.0 and carbonic acid. Extraction with carbonic acid was conducted by passing CO_2 gas through the soil-water mixture for 15 minutes. Extraction with sodium acetate solution was conducted by shaking the soil with this solution for 1 hour. Extractions were made with soil-water ratios of 1:2.5, 1:5, 1:10, 1:20, and 1:50. The solutions obtained from these extractions were analyzed colorimetrically for phosphate, and the results obtained are given in Table 1, expressed as parts per million soil.

TABLE 1.—VARIATION IN PHOSPHATE SOLUBILITY WITH VARIATION IN RATIO OF SOIL TO VOLUME OF SOLVENT (PARTS PO_4 PER MILLION PARTS SOIL).

Ratio of soil to solvent	Acetate buffer	Carbon dioxide	Acetate buffer	Carbon dioxide	Acetate buffer	Carbon dioxide
1:2.5	9	10	16	12	34	18
1:5	42	19	46	18	67	36
1:10	114	39	132	63	180	75
1:20	456	75	360	123	504	150
1:50	1,350	225	1,200	300	1,770	360
Soil no.	36	36	45	45	32	32

While many other data have been accumulated in studying the solubility of soil phosphate in weak acid solvents, the data in

Table 1 are sufficient to illustrate the limit of their utility in field tests. It is doubtful whether a field method can be devised which will eliminate the error arising from slight variations in the soil-water ratio with calcareous soils. In view of this tests have been confined on Arizona soils to the laboratory, and a carbonic acid method of extraction is being used. This acid is employed because it is the weakest acid adaptable to such tests and because it is the vehicle employed by plant roots in extracting phosphate from the soil. The method is essentially as follows: A 50 gram portion of air-dry soil is weighed into a liter wide mouth bottle containing 250 cc. of distilled water, and carbon dioxide is passed through the soil-water mixture, with occasional shaking, for 15 minutes. The whole is then filtered and the phosphate determined in an aliquot of the filtrate by the molybdic blue colorimetric method.

From an extensive survey of the truck crop fields of the state a correlation between soil analysis and field performance has been developed which is useful. In order for soil analyses to be useful such a correlation is highly essential.

0 to 5 ppm PO_4	very deficient in phosphate
5 to 10 ppm PO_4	usually deficient in phosphate
above 10 ppm PO_4	usually not deficient in phosphate

An interesting summary of field experiments with lettuce showing a correlation between the determination of available phosphate in the soil and yield and quality of lettuce is given in Table 2 (24).

TABLE 2.—RELATION BETWEEN AVAILABLE PHOSPHATE IN SOIL AND RESPONSE IN HEAD WEIGHT OF LETTUCE.

Soil no.	Ppm PO_4 in soil	Weight of heads (pounds)		
		Check plots	Fertilized plots	Increase in wt. of heads
1	2.3	1.06	1.22	0.16
2	2.6	1.06	1.49	0.43
3	8.4	1.50	1.57	0.07
4	9.6	1.47	1.56	0.09
5	11.2	1.37	1.38	0.01
6	25.0	1.70	1.73	0.03

In this series the data show little response to phosphate fertilization in soils above 10 ppm available phosphate, and below this there is a good correlation between available phosphate and response in head weight.

Plant tests

Plant culture tests are of value but principally as a research tool in soil and fertilizer investigations. Because of the time and expense involved in plant tests they have found only limited application in the routine examination of soils. The Neubauer test has reduced this to a minimum and is now extensively employed in determining the availability of phosphate in soils and fertilizers. During the past 10 years many hundred Neubauer tests have been made in this laboratory on Arizona soils, and it is believed that the method is clearly indicative of the availability of phosphate in alkaline calcareous soils. It is also a valuable method for studying the relative efficiency of the numerous phosphatic fertilizers as well as the factors which influence phosphate availability and absorption.

The original Neubauer method suggests 18 days as the most desirable period for growing the rye plants. In view of the difference in our climatic conditions, some attention has been given to the time factor during our extensive studies of the method. Experiments were conducted with sand and four representative soils in which the plants were harvested and analyzed at 12, 14, 16, and 18 day periods. The data from this experiment are given in Table 3. These data show that a 14 to 16 day period is ample under our conditions, and in view of this a 15 day period is employed when the test is used in this laboratory.

TABLE 3.—INFLUENCE OF TIME ON NEUBAUER VALUES (MGM. PO_4 PER 100 PLANT CULTURE).

Days	Sand	Soil PV	Soil P	Soil T	Soil NF
12	24.8	27.2	28.0	34.0	28.0
14	27.7	30.5	31.0	37.5	32.1
16	27.2	29.1	31.1	33.5	28.8
18	23.8	31.2	30.0	32.6	29.6

As an illustration of the availability of phosphate in Arizona soils, Neubauer values from 103 soils are submitted below. The data are given as milligrams PO_4 instead of P_2O_5. Limit values for deficiency as established by Thornton (34) are 5.3 PO_4, which is equivalent to 4.0 P_2O_5. That is, all soils giving Neubauer values less than this are classified as deficient in available phosphate. The per cent of soils with Neubauer values below 5 is 81.

Neubauer values	No. of soils
0 to 1	25
1 to 2	18
2 to 3	17
3 to 4	13
4 to 5	8
5 to 6	5
6 to 8	7
8 to 10	4
above 10	6

It is evident from these data that the Neubauer values confirm the evidence which has been obtained from many chemical analyses of Arizona soils and that gathered from many field experiments and observations. That is, there is a decided deficiency of available phosphate in Arizona calcareous soils.

EFFECT OF MAGNESIUM ON THE ABSORPTION OF PHOSPHATE

In a study of phosphate availability in North Dakota soils Kellogg (15) found that assimilation of phosphate was greatly enhanced by the addition of magnesium salts to the soil. This was noticeable on soils cropped to flax and wheat. He surmised that since magnesium functions in phosphate nutrition and is deposited in the seed as magnesium phosphate, an apparent phosphate deficiency may often be related to a deficiency of magnesium. In an investigation of phosphate availability in the magnesium deficient soils of some Atlantic coastal lands, Willis (36) was unable to confirm the results obtained by Kellogg. Soybeans were used in his experiments, and he concludes: "With an abundance of calcium a deficiency of magnesium does not limit the absorption of phosphates . . . magnesium deficiency and phosphate deficiency have no mutual relation." On the other hand, experiments conducted by Bartholomew in Arkansas (1) confirm the work of Kellogg. His studies indicate that type of soil or kind of crop must be taken into consideration when drawing conclusions. He found that the addition of magnesium sulphate to the soil caused a decrease in dry matter (Sudan grass) and phosphate absorption by the plant when no phosphate fertilizer was added to the soil. However, when magnesium sulphate was added to phosphate fertilized soil there was a definite increase in the amount of phosphate absorbed by the plant. This was especially true when magnesium sulphate was used with phosphate materials low in availability.

In order to determine whether magnesium is in any way related to phosphate availability and absorption in alkaline calcareous soils of Arizona, a number of representative soils were selected and the problem studied by employing the Neubauer test. These soils were Palo Verde loam, Pinal sandy loam, a sandy loam from Peoria, Arizona, a clay loam from the University Farm at Yuma, and a clay loam from the University Farm in Tucson. All these soils were deficient in available phosphate. The Neubauer tests were conducted in the usual manner. Both the magnesium sulphate and super-phosphate were added in solution to the 100 gram portions of soil and mixed thoroughly with them just before planting. One Neubauer test was made on the soil for control. Magnesium sulphate at the rates of 0.25, 0.1, and 0.025 grams per 100 grams of soil with and without phosphate were used in the test. An equal amount of phosphate, 12 milligrams PO_4, was added to another series to determine phosphate absorption without the addition of magnesium sulphate. Each treatment was made in triplicate. The data obtained in this study are given in Table 4.

TABLE 4.—EFFECT OF $MgSO_4$ ON ABSORPTION OF PHOSPHATE BY RYE PLANTS (MGM. PO_4 PER 100 PLANTS).

	Palo Verde loam	Pinal sandy loam	Peoria soil	U. F. Yuma	U.F. Tucson
Control	26.2	25.7	29.8	28.1	....
$MgSO_4$ 0.25 gm.	25.5	23.6	29.8	29.0	....
$MgSO_4$ 0.10 gm.	26.3	24.8	29.6	27.9	....
$MgSO_4$ 0.025 gm.	27.4	26.8	31.6	29.9	....
$MgSO_4$ 0.25 gm. + 12 mgm. PO_4	33.7	30.8	35.8	33.6	32.9
$MgSO_4$ 0.10 gm. + 12 mgm. PO_4	35.3	33.0	38.2	35.8	32.7
$MgSO_4$ 0.025 gm. + 12 mgm. PO_4	35.6	34.3	39.1	35.1	35.9
12 mgm. PO_4 no $MgSO_4$	34.5	28.9	38.2	34.7	30.7

These Neubauer studies indicate a slight increase in absorption of phosphate by rye plants when magnesium sulphate is added to the soil. This was true for the cultures to which phosphate fertilizer was added, as well as in the unfertilized soils. This increased phosphate absorption, while apparently consistent, is too small to be greatly significant. The results indicate, however, that an excess of magnesium will depress phosphate absorption in unfertilized Neubauer cultures.

Pot experiments

In addition to the Neubauer cultures some experiments were conducted in pots using Sudan grass and cotton as test crops. One gallon glazed pots holding 4½ kilos of soil were used. Sudan grass was used because of its value as an indicator of phosphate deficiency in soils, and cotton was used because in the field the soil used in this experiment, even though apparently deficient in available phosphate, has not shown any response to phosphate fertilization. The following is the plan of the experiment used for Sudan grass.

1. Checks, no fertilization
2. Magnesium sulphate
3. Magnesium sulphate plus treble super
4. Magnesium sulphate plus phosphate rock
5. Treble super
6. Phosphate rock
7. Trimagnesium phosphate

Magnesium sulphate was added at the rate of 2.25 grams per 4½ kilos of soil and all the phosphates on an equivalent phosphate basis of 2.5 grams P_2O_5 per 4½ kilos. The fertilizer was applied by mixing it thoroughly with the upper half of the soil in the pot. Seed was planted the day after the fertilizer application, December 8, and observations were made on January 2 and February 9 which showed the characteristic purple color of phosphate deficiency in the plants growing in pots 1, 2, 4, and 6, while the color was normal in 3, 5, and 7. The plants in the latter showed plainly a response to phosphate fertilization. They were harvested at the heading-out stage, dried, and the dry weight per plant and phosphate content were determined. The data obtained from these analyses are given in Table 5.

TABLE 5.—DRY WEIGHT PER PLANT, P_2O_5 PER PLANT, AND PER CENT P_2O_5 IN SUDAN GRASS.

	Wt. per plant (gm.)	P_2O_5 per plant (mgm.)	Per cent P_2O_5 (dry basis)
Control	0.187	0.36	0.190
Magnesium sulphate	0.119	0.25	0.214
Magnesium sulphate plus treble super	0.486	1.57	0.322
Magnesium sulphate plus phosphate rock	0.125	0.36	0.284
Treble super	0.486	1.53	0.315
Phosphate rock	0.073	0.25	0.314
Trimagnesium phosphate	0.348	1.44	0.414

All these pots were replanted, without any further addition of fertilizer, on April 24 and harvested June 15. For the first planting only ten plants per pot were grown and to maturity. In the second planting fifty plants per pot were grown and the plants not grown to the heading-out stage. The same quantitative determinations were made, and the data are given in Table 6.

TABLE 6.—DRY WEIGHT PER PLANT, P_2O_5 PER PLANT, AND PER CENT P_2O_5 IN SUDAN GRASS.

	Wt. per plant (gm.)	P_2O_5 per plant (mgm.)	Per cent P_2O_5 (dry basis)
Checks	0.054	0.169	0.310
Magnesium sulphate	0.042	0.146	0.342
Magnesium sulphate plus treble super	0.104	0.450	0.434
Magnesium sulphate plus phosphate rock	0.057	0.299	0.522
Treble super	0.102	0.367	0.367
Phosphate rock	0.046	0.263	0.571
Trimagnesium phosphate	0.126	0.368	0.371

On the percentage basis, the analyses show little or nothing of value, as there was such a wide variation in the size of plants in the differently treated pots. When calculated to weight of P_2O_5 per plant, the data are highly significant. Magnesium sulphate in the unfertilized soil showed a slight reduction in the absorption of phosphate by the Sudan grass. When applied with treble superphosphate or rock phosphate, there is a slight increase in absorption of phosphate in presence of magnesium sulphate. The same relationship applies for weight of plants. Where trimagnesium phosphate was applied as fertilizer, absorption of phosphate was equal to that from treble super and the weight of plants was greater.

Many of our phosphate deficient soils do not show a response in growth of cotton when fertilized with phosphate. The soil used in this experiment (University Farm at Tucson) being one of these, a pot experiment was conducted with cotton to determine the effect of magnesium on the absorption of phosphate. Two-gallon glazed pots holding 8 kilos of soil were used. The phosphate and magnesium sulphate were thoroughly mixed with the upper half of soil, just as in the Sudan grass experiment. Cotton was planted December 8 and plants grown to May 2. Two plants were grown in each pot and when prepared for analysis the roots and tops were analyzed separately. The size of plants showed a good response to phosphate which had not been obtained under field conditions. The phosphate analyses are given in Table 7.

TABLE 7.—P_2O_5 PER PLANT AND PER CENT P_2O_5 IN COTTON PLANTS.

	Mgm. P_2O_5 per plant		Per cent P_2O_5 (dry basis)	
	Roots	Tops	Roots	Tops
Check, no fertilizer	0.84	5.95	0.309	0.402
Magnesium sulphate	0.67	4.87	0.267	0.358
Magnesium sulphate plus treble super	2.71	9.16	0.436	0.536
Treble super only	3.72	16.02	0.402	0.576

These data indicate that magnesium sulphate has reduced the absorption of phosphate by cotton in both the fertilized and unfertilized pots.

Briefly summarizing the magnesium studies, it appears that for alkaline calcareous soils, rye and Sudan grass show a slight increase in absorption of phosphate when fertilized with magnesium sulphate, which is hardly of economic significance, and the absorption of phosphate by cotton is reduced. The experimental data are in agreement with the conclusions of Bartholomew (1) in that type of soil and kind of crop must be taken into consideration in drawing conclusions regarding the effect of magnesium on the absorption of phosphate by plants.

It is of interest that there was considerable difference in size of cotton plants fertilized with phosphate and those unfertilized. In these pots the phosphate was thoroughly mixed with the soil. In view of the fact that cotton does not respond to phosphate on this soil in the field, it appears that the field method of application may have been faulty.

INFLUENCE OF NITROGENOUS FERTILIZERS ON PHOSPHATE AVAILABILITY

Semiarid soils are predominantly deficient in organic matter and therefore in nitrogen. In view of this, most cultural programs in Arizona require nitrogenous fertilizers or a crop rotation designed to conserve or build up the nitrogen supply of the soil. Obviously under arid conditions available nitrogen may become a limiting factor in phosphate response, and a knowledge of the nitrogen-phosphate relationship becomes of interest. Nitrogenous fertilizers may affect phosphate availability in two ways. First by their residual acidity or alkalinity and second by a stimulation in root growth. These may not, however, be of sufficient magnitude to be measured quantitatively in a short growing period.

Fudge (9) studied the residual effect of several nitrogenous fertilizers on phosphate availability and utilization on soils from the long-time fertilizer plats of the Alabama, Rhode Island, and New Jersey Experiment Stations. All these soils were acid, but it is significant that the residually alkaline nitrogenous salts increased phosphate availability by supplying monovalent and divalent bases to combine with the phosphate and thus reduce the degree of fixation. In alkaline calcareous soils where calcium carbonate and *p*H are the principal factors involved in low phosphate availability, a greatly different situation exists. Very little difference and very little effect from these salts, unless it be an increase in the feeding activity of the roots, should be expected.

In order to study this phase of the problem, Neubauer studies were conducted with several nitrogen compounds. These were urea, calcium nitrate, sodium nitrate, ammonium sulphate, and ammonium hydroxide. All were added at the rate of 50 milligrams of nitrogen per 100 grams of soil, 24 hours prior to planting the rye seed. The Neubauer values (mgm. PO_4) obtained, each treatment being run in quadruplicate, are given in Table 8.

TABLE 8.—INFLUENCE OF NITROGENOUS FERTILIZERS ON NEUBAUER VALUES.

	Mgm. PO_4
Control (no fertilizer)	2.8
Ammonium hydroxide	1.3
Ammonium sulphate	3.0
Calcium nitrate	3.4
Sodium nitrate	2.6
Urea	2.4

These differences are very small but indicate a slightly better absorption with ammonium sulphate and calcium nitrate. There is a definite reduction with ammonium hydroxide which is undoubtedly due to a temporary alkalinity. In view of the fact that this should gradually disappear as the ammonium hydroxide becomes nitrified we should expect an improvement in phosphate absorption over a longer growing period.

A second experiment was conducted in which the soils were incubated in one series for 30 days after addition of the nitrogen salts, while in another series the same salts were added just prior to planting. The data obtained from this experiment are given in Table 9 as milligrams PO_4 per 100 plants.

TABLE 9.—INFLUENCE OF NITROGENOUS FERTILIZERS ON ABSORPTION OF PO_4 BY RYE PLANTS WITH AND WITHOUT INCUBATION.

	Mgm. PO_4	
	Incubated	Not incubated
Control (no fertilizer)	26.6	27.2
Ammonium sulphate	27.1	26.5
Calcium nitrate	26.9	26.6
Cyanamid	27.8	24.6
Sodium nitrate	26.3	27.2
Urea	26.8	28.2

As should be expected, there was a slight increase from incubation as compared to nonincubation of cyanamid, but the other data are not conclusive. It seems safe to conclude that little improvement in phosphate availability will accompany nitrogen fertilization in alkaline calcareous soils.

In addition to the direct and residual effect of nitrogen fertilizers upon phosphate absorption there is another phase of the problem which must be considered. Due to the increase in growth obtained with phosphate fertilization, a maximum response will be limited by the amount of nitrogen available in the soil. That is, when phosphate is applied in amounts to meet the maximum absorbing capacity of the soil and the phosphate requirement of the crop, if nitrogen or any other essential element is deficient, growth will be limited according to the magnitude of the deficiency. This is illustrated in other experiments with tomato plants (24). Unfertilized plants absorbed 0.100 gram nitrogen and 0.024 gram P_2O_5, per 100 plants, from the soil. On fertilization with treble superphosphate (but no nitrogen) the plants absorbed 0.268 gram nitrogen and 0.124 gram P_2O_5 per 100 plants. In this case the phosphate deficiency limited nitrogen absorption and probably nitrification of soil nitrogen as well. In the next experiments it will be shown that when phosphate was supplemented with nitrogen there was an increase in phosphate absorption over phosphate alone.

These pot experiments were conducted to obtain some further information on the nitrogen-phosphate relationship. For this experiment 2-gallon glazed pots containing 8 kilos of soil were used. All fertilizers were thoroughly mixed with one half of the soil, as in the previous pot experiments. Nitrogenous materials were added at the rate of 1 gram nitrogen per pot, and phosphate at the rate of 2.7 grams P_2O_5 per pot. The following is a list of fertilizer treatments used in this experiment.

1. Calcium nitrate
2. Sodium nitrate
3. Ammonium sulphate
4. Urea
5. Calcium nitrate and treble super
6. Sodium nitrate and treble super
7. Ammonium sulphate and treble super
8. Urea and treble super
9. Treble super only

The experiment was composed of two pots of each treatment. They were planted to Sudan grass on December 8 and harvested on April 15. The plants were dried, weighed, and analyzed for phosphate. The data are given in Table 10.

TABLE 10.—INFLUENCE OF NITROGEN FERTILIZERS ON ABSORPTION OF P_2O_5 BY SUDAN GRASS.

	Weight per plant (gm.)	P_2O_5 per plant (mgm.)	Per cent P_2O_5 (dry basis)
1. Calcium nitrate	0.086	0.29	0.337
2. Sodium nitrate	0.070	0.28	0.398
3. Ammonium sulphate	0.052	0.23	0.440
4. Urea	0.132	0.43	0.327
5. Calcium nitrate and treble super	0.377	1.14	0.302
6. Sodium nitrate and treble super	0.095	1.71	0.287
7. Ammonium sulphate and treble super	0.257	0.91	0.254
8. Urea and treble super	0.326	1.42	0.437
9. Treble super only	0.469	1.34	0.286
10. Soil—no N or P fertilizer	0.199	0.59	0.305

At the conclusion of this experiment these pots were replanted on April 24 and harvested on June 13 as immature plants. The same quantitative determinations were made, and these data are given in Table 11. These data represent the residual effect of the fertilizer, as no additions were made to this second crop.

TABLE 11.—RESIDUAL EFFECT OF NITROGEN FERTILIZERS ON ABSORPTION OF P_2O_5 BY SUDAN GRASS.

	Weight per plant (gm.)	P_2O_5 per plant (mgm.)	Per cent P_2O_5 (dry basis)
1. Calcium nitrate	0.076	0.25	0.324
2. Sodium nitrate	0.090	0.40	0.419
3. Ammonium sulphate	0.104	0.36	0.346
4. Urea	0.147	0.48	0.322
5. Calcium nitrate and treble super	0.310	1.17	0.393
6. Sodium nitrate and treble super	0.327	1.64	0.503
7. Ammonium sulphate and treble super	0.363	1.48	0.408
8. Urea and treble super	0.333	1.50	0.452
9. Treble super only	0.297	1.21	0.405
10. Soil—no N or P added	0.119	0.45	0.376

In previous experiments with tomato plants (24) it has been observed that the phosphate-fertilized plants absorb more nitrogen per plant (as per cent nitrogen) than those not receiving phosphate fertilizer. From this the question arose as to whether phosphate response is in part a nitrogen response. In this Sudan grass experiment when nitrogenous salts only were added, there was no increase in absorption of phosphate by the plants either in the original or the residual test. The greatest absorption of phosphate and dry weight of plants in the nitrogen-only series was obtained with urea.

In the pots receiving both nitrogen and phosphate, residually, there was a greater absorption of phosphate than when phosphate alone was used. There is also a greater dry weight of plants. The data indicate that the variable response to nitrogen alone, phosphate alone, and the two combined is purely a limiting factor relationship. That is, phosphate response may be limited by nitrogen deficiency and nitrogen response by phosphate deficiency, but phosphate deficiency is by far the greater limiting factor.

Neubauer and Schneider (26) found that additions of nitrogen had no effect on the absorption of phosphate. This is essentially in agreement with our Neubauer method studies. Apparently during the short growing period employed in this method a nitrogen deficiency is without effect on growth and the nitrogen content of the seed is ample to supply the requirement of the rye plant for this period.

On growing plants for a longer period the nitrogen deficiency makes itself evident. Chapman (7) found that a nitrogen deficiency caused an accumulation of inorganic phosphate within the oat plant even in soils deficient in phosphate. In studies on Sudan grass (6) he found an increase in phosphate availability when using residually acid nitrogenous fertilizers on calcareous soils of high and medium available phosphate content. The magnitude varied with the phosphate and calcium carbonate content of the soil. Gilbert, McLean, and Adams (10) found that low nitrate may cause inorganic phosphate to accumulate in the plant and conversely low phosphate causes an accumulation of nitrate. In other words, if a limiting element retards the growth of the plant, high concentrations of other elements may appear in the plant. This is shown by the author's studies in that the percentage of phosphate in the plant shows no correlation with fertilization. Results must be calculated on the basis of the amount of phosphate per plant. Haas (14) has shown that in citrus, nitrate remains largely unchanged in the tissues when phosphorus is deficient.

RELATION BETWEEN BASE SATURATION OF THE CLAY AND PHOSPHATE AVAILABILITY

In view of the fact that the availability of phosphate is influenced by the chemical properties and structural composition of the soil, a study was made of the effect of base saturation of the clay on absorption of phosphate by plants.

The Neubauer method was used in this study. Five soils were selected and large portions saturated with sodium, calcium, and magnesium. This was accomplished by leaching the soils with solutions of the respective chlorides and then washing them with distilled water until practically free of excess salt. They were then dried and 100 gram portions used for Neubauer tests with the rye plants. In one series 30 milligrams of PO_4, as treble superphosphate, was added in solution and well mixed with the 100 grams of soil, while in another series no phosphate was added. As a control a Neubauer test on each soil in its original state was included in the experiment. The values obtained in this experiment are given in Table 12 and are expressed as milligrams PO_4 per 100 plants. That is the amount of PO_4 removed from 100 grams of soil by 100 rye plants.

TABLE 12.—EFFECT OF BASE SATURATION ON PHOSPHATE AVAILABILITY (MGM. PO_4).

	Yuma soil	Santa Rita soil	Davis soil 1	Davis soil 2	U.F. soil
		No phosphate added			
Control, original soil	29.4	27.0	30.5	27.3	28.7
Sodium saturated soil	27.7	23.3	29.2	24.5	27.5
Calcium saturated soil	30.8	27.8	30.5	27.3	28.2
Magnesium saturated soil	....	27.2	....	....	29.7
		30 mgm. PO_4 added			
Control, original soil	37.7	44.2	43.2	37.0	40.3
Sodium saturated soil	33.8	35.4	31.1	29.5	34.4
Calcium saturated soil	37.5	44.0	37.4	37.8	43.3
Magnesium saturated soil	....	43.4	....	....	43.9

When no phosphate fertilizer was added there was a slight increase in phosphate absorption by the rye plants in the calcium saturated soils, while in the sodium saturated soils phosphate absorption was consistently reduced. Absorption from the magnesium saturated soils was in close agreement with that from the calcium saturated soils. When phosphate was added to the cultures, there was little difference in absorption in the controls, the calcium saturated soils, and the magnesium saturated soils, while sodium saturation again depressed phosphate absorption.

This experiment shows that sodium saturated soils will materially reduce the availability of phosphate as measured by plant absorption.

EFFECT OF CARBON DIOXIDE AND *p*H ON PHOSPHATE AVAILABILITY

Throughout the extensive experiments which have been conducted in this laboratory, it has been consistently demonstrated that the phosphate problem, insofar as the availability of the phosphate naturally present in Arizona soils is concerned, is largely one in which the soil reaction, *p*H, is the principal limiting factor. The Neubauer method was therefore employed in gaining more information on this phase of the problem.

The adaptability of the Neubauer test to nutritional plant and soil investigations is further illustrated by this experiment dealing with the effect of carbon dioxide on the availability of phosphate in an alkaline calcareous soil. When the *p*H of the soil indicates the presence of black alkali the soluble phosphate present in the soil is usually high because of the solvent effect of NaOH. Within a *p*H range of 7.6 to 8.5 where carbon dioxide in the soil solution is at a minimum, there is usually found a minimum range of phosphate solubility. At lower *p*H values where carbon dioxide comes into play, the solubility and availability of phosphate increases. This is shown by the effect of organic matter on the availability of phosphate and in the solvent action of carbon dioxide obtained in the quantitative method presented earlier in this bulletin.

The next experiment was devoted to a study of the effect of carbon dioxide on the availability of phosphate in an alkaline calcareous soil in which the carbon dioxide was added to the water used in irrigating the plants. The usual Neubauer procedure was followed and two phosphate deficient soils were used. Each treatment was conducted in quadruplicate. One set was irrigated with carbon-dioxide-free water and the others with waters containing 50, 100, 330, and 500 ppm carbon dioxide respectively.

The data obtained from this experiment are given in Table 13 as PO_4 Neubauer values. That is, they represent milligrams PO_4 absorbed by the plants from the soil minus the PO_4 content of the control plants grown in silica sand.

TABLE 13.—EFFECT OF CO_2 ON AVAILABILITY OF PHOSPHATE.

Ppm CO_2	PO_4 Neubauer value U.F. soil	PO_4 Neubauer value Smith soil
0	1.8	2.0
50	1.9	2.6
100	2.4	5.7
330	4.8	4.5
500	4.8	12.8

This experiment clearly confirms the observations which have led to the statement that carbon dioxide is a major growth limiting factor in alkaline calcareous soils. There is a decided improvement in the availability of phosphate in the above experiment with increase in carbon dioxide content of the water. A similar response to organic matter additions to the soil has been previously noted on similar soil types (20).

In another experiment designed to study the influence of soil reaction, the Neubauer cultures were irrigated with waters which had been adjusted to *p*H values of 4, 6, 7, 8, and 9 with acid and alkali in one case, and 3, 7, and 9 in another.

In the first experiment a calcareous soil and a noncalcareous soil (Santa Rita Range) were used. To one series of cultures 60 milligrams of PO_4 were added, while the other series received no phosphate. The usual Neubauer procedure was followed except as stated above, waters of different *p*H values were used to irrigate them. The effect of reaction on the absorption of phosphate is shown in Table 14 as milligrams PO_4 removed from 100 grams of soil by 100 rye plants.

TABLE 14.—EFFECT OF *p*H ON AVAILABILITY OF PHOSPHATE.

*p*H of water	Calcareous soil		Noncalcareous soil	
	Not fertilized mgm. PO_4	Fertilized mgm. PO_4	Not fertilized mgm. PO_4	Fertilized mgm. PO_4
4	28.8	49.6	31.5	55.4
6	28.5	50.8	30.2	53.0
7	29.6	52.3	29.1	51.5
8	26.7	52.3	27.8	50.0
9	27.6	47.0	28.4	48.5

In the second experiment a similar procedure was followed except that only three *p*H values were studied—namely, 3, 7, and 9. Tests were made on three additional soils and with silica sand, and to the fertilized cultures 30 milligrams of PO_4 were added instead of 60 as in the first experiment. The data from this ex-

TABLE 15.—EFFECT OF *p*H ON AVAILABILITY OF PHOSPHATE (MGM. PO_4)

*p*H value of water	Davis soil	Univ. Farm soil	Yuma soil	Silica sand
		Not fertilized		
3	28.5	29.0	30.0	30.0
7	27.5	25.0	25.0	28.0
9	27.0	27.5	26.0	29.0
		Phosphate fertilized		
3	37.0	38.0	38.0	36.0
7	38.0	35.5	39.0	33.0
9	36.0	38.5	39.0	34.0

periment are given in Table 15 as milligrams PO_4 absorbed from 100 grams of soil by 100 rye seedlings.

These experiments show that the Neubauer method can be used to illustrate the effect of soil *p*H on the availability of phosphate and its absorption by plants. In growing 100 plants in 100 grams of soil a very large mass of roots per unit weight of soil will be present, and it is quite evident that this explains the high absorption of phosphate in the alkaline cultures. The carbon dioxide produced by the respiration of this mass of roots is undoubtedly greater than would be produced under field conditions.

EFFECT OF CALCIUM CARBONATE AND CALCIUM HYDROXIDE ON PHOSPHATE AVAILABILITY

In this department's field studies, as well as some of the laboratory investigations, there has been evidence that the alkalinity arising from $Ca(OH)_2$ and solid phase $CaCO_3$ is instrumental in reducing the availability or absorption of phosphate by plants in alkaline calcareous soils. The Neubauer method has been employed in an attempt to study this phase of the problem. In this experiment a fertilized and unfertilized series of rye plants were grown. Calcium hydroxide solution was used for irrigation as a saturated solution, as a mixture of one part saturated $Ca(OH)_2$ solution and one part water, and as a mixture of one part saturated $Ca(OH)_2$ solution to five parts water. Calcium carbonate was added at the rate of 1 gram per 100 grams of soil to some other cultures. The data obtained from this experiment are given in Table 16 as milligrams PO_4 absorbed by 100 rye plants from 100 grams of soil.

TABLE 16.—INFLUENCE OF $Ca(OH)_2$ AND $CaCO_3$ ON ABSORPTION OF PO_4 IN NEUBAUERS (MGM. PO_4 PER 100 PLANTS).

	Soil 1	Soil 2	Soil 3	Sand
	Not fertilized			
Control	29.7	28.3	30.2	23.8
1:5 $Ca(OH)_2$	28.2	29.7	25.6	......
1:1 $Ca(OH)_2$	28.3	28.7	28.5	......
Saturated $Ca(OH)_2$	27.7	27.6	30.9	......
$CaCO_3$	27.6	27.2	31.7	......
	Fertilized with phosphate			
Control	40.6	34.5	36.9	36.3
1:5 $Ca(OH)_2$	42.9	33.9	37.3	30.3
1:1 $Ca(OH)_2$	40.8	34.4	37.3	30.0
Saturated $Ca(OH)_2$	38.7	29.6	36.7	27.5
$CaCO_3$	41.0	34.6	36.0	38.2

As in the previous experiments with the Neubauer method where a large mass of roots is respiring in a small unit of soil, the differences are very small in these data. However there does appear to be a definite trend. All these soils were highly calcareous and the additional amounts of $CaCO_3$ which were added appear to have had no effect in the fertilized cultures, but a slight reduction in phosphate absorption in the unfertilized soils. In soil 3 there is a reduction in phosphate absorption in the unfertilized cultures but none in the fertilized, while for soils 1 and 2 there is a reduction in absorption in both cases.

The influence of excessive amounts of calcium carbonate on the availability of phosphate is by no means confined to southwestern calcareous soils. So-called overliming injury has often been noted on acid soils and while some of this is due to a reduction in the availability of such elements as iron, manganese, and zinc, a part has been attributed to reduced phosphate availability (27). On liming acid soils the P_2O_5 availability increases with increase in *p*H up to approximately 7.0. When too much solid phase calcium carbonate is present, overliming, availability is again reduced. The overliming effect disappears when the calcium carbonate and soil have come to equilibrium. In studying the effect of $CaCO_3$ on the phosphate availability in soil colloids, Gile (11) obtained greatest yield with 0.4 gram $CaCO_3$ and reduced yield with 1.6 grams per 5,000 grams of soil. Benne, Perkins, and King (2) found that calcium ions cause a maximum precipitation of phosphate at 7.5. Above this point the solubility will depend upon the presence of solid phase $CaCO_3$ and whether the alkalinity is due to NaOH or $Ca(OH)_2$. Scarseth (31) found that at high *p*H values phosphate ions may be replaced by hydroxyl ions. If the colloid system contains free $CaCO_3$ all the PO_4 ions will be precipitated at approximately 8.2. If sodium ions are in excess, phosphate will be held in solution. This is in agreement with the author's observations on Arizona soils. Scarseth and Tidmore (32) found that supersaturating the colloids with calcium decreases the availability of applied phosphate, but the native soil phosphate is made more available. Apparently there is plenty of evidence to support our observations that phosphate availability is unfavorably influenced by $CaCO_3$, $Ca(OH)_2$, and the alkalinity arising therefrom in alkaline calcareous soils.

PHOSPHATE AVAILABILITY

The fertilizer industry supplies a rather formidable variety of phosphate fertilizers extending over a wide range of availability and solubility with phosphate rock on the one extreme and liquid phosphoric acid on the other. The economy and efficiency of these various phosphates depend in large part upon the soil type and other soil characteristics.

Thornton (35) has shown that the Neubauer test is well suited to a study of the availability of various forms of phosphate in soils. It has therefore been employed in a rather extensive study of the suitability of various forms of phosphate for Arizona soils.

The following is a description of the method as employed in this study. One hundred grams of air-dry soil were mixed with 50 grams of silica sand and spread uniformly over the bottom of a dish with a diameter of 11 centimeters. Over the surface of this were spread 150 grams of silica sand and then 100 carefully selected rye seed which had been previously treated with a 0.25 per cent "Uspulin" solution. One hundred grams of sand were carefully spread over this seed, and 80 grams of distilled water were added.

For a control the same number of plants were grown in sand alone. At the end of 15 days the plants were washed free from adhering sand and soil, dried, ashed at low temperature, and the phosphate in the ash was determined. The results may be used in several ways. The difference between the phosphate content of the plants grown in sand and in soil represents the so-called Neubauer value. For comparative purposes it is often suitable just to express the results as grams PO_4 removed by 100 plants from 100 grams of soil. In testing the comparative efficiency of phosphate fertilizers the value which represents the difference in PO_4 content of the plants grown in the fertilized soil and the unfertilized soil is useful. All three methods of expressing the results are used in this bulletin.

In the first experiment a study of the less available phosphates was made. While it was known that phosphate rock is extremely ineffective in alkaline calcareous soils, it appeared of interest to study the availability of some of the modified forms and especially the relation of degree of fineness to availability. This opportunity was presented in a set of materials used in co-operative studies with the Association of Official Agricultural Chemists in 1937. Table 17 gives a list of materials used in the experiment and the mesh of these phosphates as well as their total phosphate and citrate insoluble phosphate (30) content.

TABLE 17.—MESH, TOTAL P_2O_5, AND CITRATE INSOLUBLE P_2O_5 IN PHOSPHATE MATERIALS.

	Mesh	Total P_2O_5	Citrate insoluble P_2O_5
Control, no fertilizer	......	....	....
Calcined phosphate	20	37.40	7.80
Calcined phosphate	40	37.36	4.72
Calcined phosphate	80	37.18	3.73
Calcined phosphate	200	37.20	3.68
Calcined phosphate	20-40	37.30	9.53
Calcined phosphate	60-80	37.20	5.63
Calcined phosphate	100-150	37.05	4.46
Monocalcium phosphate	40	56.76	0.00
Fused phosphate rock	80	28.97	4.60
Tenn. brown raw phosphate rock	100	33.75	31.37
Basic slag	100	18.46	3.61

Calcined phosphate is prepared by heating 40 mesh raw rock to 1,400 degrees C. for 30 to 60 minutes in the presence of silica and water vapor. This treatment removes 95 to 100 per cent of the fluorine by volatilization and converts 85 to 95 per cent of the phosphorus into a citrate soluble form (29). The low availability of phosphorus in phosphate rock has been attributed to the fluorine which is combined as fluorapatite. The fused phosphate rock is prepared by blowing wet air through fused Tennessee brown rock phosphate and is quite similar to the calcined rock.

The comparative efficiency of these materials, as measured by the Neubauer test, is shown graphically in Figure 1 as Neubauer values. That is, the analysis of the plants grown in sand is subtracted from that of the plants grown in soil. It is clearly evident again that raw phosphate rock is of little or no value on Arizona's alkaline calcareous soils. The chemical composition of phosphate rock is quite similar to that of the native soil phosphate, except that the former is a fluorapatite while that in calcareous soil is a carbonate apatite. Both exhibit very low availability in alkaline soils and are of little value unless the *p*H of the soil can be reduced. This evidence is made all the more conclusive by the fact that the rock used in this experiment was all less fine than 100 mesh and 86 per cent of it 400 mesh. Also, it was thoroughly mixed with the 100 grams of soil so as to obtain intimate contact with the roots.

The calcined phosphate increases in availability with fineness and at 200 mesh can be given a fairly high efficiency rating when thoroughly mixed with the soil in the root zone so as to get a maximum root-soil contact. It compares very well with the monocalcium phosphate which the author finds is one of the most available materials for these soils in Neubauer and pot tests. Fused rock is slightly more effective than raw rock but not equivalent to the calcined phosphate of the same mesh. Serralles (33), in studying the comparative efficiency of calcined phosphates, using a Morrison Sandy loam of *p*H 6.2, found that they were equal to superphosphate and far superior to rock phosphate. The experiment indicates that 200 mesh calcined phosphate and 100 mesh basic slag should be useful in band fertilization on Arizona's calcareous soils.

In the next experiment all the important phosphate fertilizers were used. As in the previous experiment, they are added in amounts to give 30 milligrams PO_4 per 100 grams of soil. Each test was made in triplicate. Four soils were used—namely, a heavy clay from the Yuma Valley, a silt loam from Peoria, Arizona, and two clay loams from near Tucson—namely, the City Farm and the University Farm. All these soils are phosphate deficient soils. In addition to the fertilizer materials a number of chemically pure and other phosphate salts were included in the experiment in order to learn the availability of magnesium, sodium, and potassium phosphates, the metaphosphates of calcium

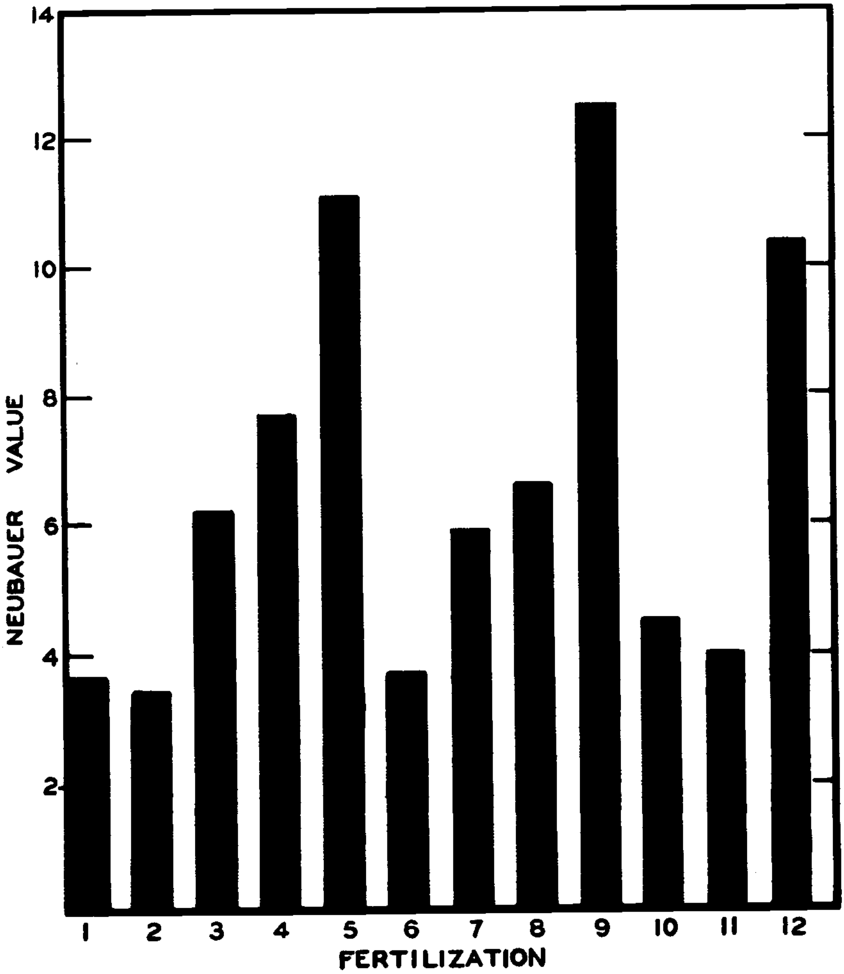

Figure 1.—Relative availability of phosphates: *1*, control; *2*, calcined phosphate, 20 mesh; *3*, calcined phosphate, 40 mesh; *4*, calcined phosphate, 80 mesh; *5*, calcined phosphate, 200 mesh; *6*, calcined phosphate, 20-40 mesh; *7*, calcined phosphate, 60-80 mesh; *8*, calcined phosphate, 100-150 mesh; *9*, monocalcium phosphate, 40 mesh; *10*, fused phosphate rock, 80 mesh; *11*, Tennessee brown raw phosphate rock, 100 mesh; *12*, basic slag, 100 mesh.

and sodium, and the organic phosphate phytin. The data obtained from this experiment are given in Table 18 as milligrams of PO_4 removed from each fertilized soil. That is, in each case a control was run with unfertilized soil and this subtracted from the phosphate content of the plants fertilized with 30 milligrams of PO_4 from the different materials. The relative absorption of PO_4 is also given on the basis of 100 for monocalcium phosphate.

The data are quite illuminating and indicate little or no choice between treble superphosphate and ammonium phosphate which are the principal phosphate fertilizers now in use in this state. Monocalcium phosphate appears to be the most consistently effective form of phosphate on all the soils, which may be due to its fineness being greater than that of superphosphate and ammonium phosphate which were used in commercial form. Slight variations in the utilization of the several phosphates are probably related to the difference in fixing power of different soils.

It is of special interest to note the effective utilization of magnesium, sodium, and potassium phosphates, and especially the trimagnesium phosphate as compared with tricalcium phosphate. These differences are probably related to the difference in solubility and *p*H of the solutions of these salts. Calcium phosphate is least soluble under alkaline conditions, while this is not true for sodium and potassium phosphates.

Except for the crystalline Baker's sodium metaphosphate, the metaphosphates are all very effective and appear to be readily utilized by plants, especially the sodium metaphosphates.

TABLE 18.—MILLIGRAMS PO_4 ABSORBED BY NEUBAUER PLANTS FROM PHOSPHATE FERTILIZERS AND RELATIVE ABSORPTION BASED ON MONOCALCIUM PHOSPHATE AS 100.

	U.F. soil 1		C.F. soil		Davis soil		U.F. soil 2	
	Mgm. PO_4	Relative abs.	Mgm. PO_4	Relative abs.	Mgm. PO_4	Relative abs.	Mgm. PO_4	Relative abs.
Monocalcium phosphate	19.3	100	21.4	100	28.2	100	19.4	100
Treble superphosphate	20.9	102	21.9	102	21.3	76	19.9	103
Ammonium phosphate 11-48	17.4	85	20.2	94	27.6	98	18.2	93
Ammonium phosphate 16-20	......	......	18.6	87	23.8	84	16.6	86
Calcium metaphosphate	15.4	75	14.1	66	24.4	87	12.1	62
Single superphosphate	17.7	87	17.1	80	19.7	70	15.1	78
Basic slag	15.7	77	10.2	48	15.2	54	8.2	42
Fused phosphate rock	9.8	48	6.4	30	15.6	55	4.4	23
Raw phosphate rock	9.3	45	5.4	25	2.6	9	3.4	18
Dicalcium phosphate	12.6	62	15.5	72	23.1	82	13.5	70
Sodium metaphosphate Rosestone	17.9	88	18.0	84	24.4	87	16.0	82
Sodium metaphosphate Calgon	17.3	85	19.3	90	22.1	78	17.3	89
Sodium metaphosphate Baker's	12.9	63	15.2	71	19.4	69	13.2	68
Sodium pyrophosphate	18.5	91	15.1	71	22.6	80	13.1	67
Monosodium phosphate	16.8	82	18.5	86	25.9	92	16.5	85
Phytin	......	......	7.8	36	5.3	19	5.8	30
Trimagnesium phosphate	......	......	......	......	27.3	97	......	......
Dimagnesium phosphate	......	......	......	......	24.4	87	......	......
Tripotassium phosphate	......	......	......	......	21.5	76	......	......

The calcium metaphosphate is a sample of that prepared at Muscle Shoals by the T.V.A. by treating Tennessee brown phosphate rock at a temperature of 1,000 to 1,100 degrees C. with P_2O_5 fumes evolved in the smelting of phosphate rock in an electric furnace (25). It contained 63.87 per cent P_2O_5 and only 0.24 per cent citrate insoluble P_2O_5. Three forms of sodium metaphosphate were used. Rosestone is a hexametaphosphate containing some pyrophosphate and is used in irrigation water to prevent the precipitation of calcium as $CaCO_3$ when liquid ammonia is applied as fertilizer in the water. Calgon is a hexametaphosphate, also containing a small amount of pyrophosphate, which is used as a water softener. Baker's chemically pure sodium metaphosphate is a crystalline salt and of low solubility as compared with Rosestone and Calgon which are the glassy form.

As a supplement to the Neubauer tests on the various forms of phosphate, some pot experiments and additional Neubauer tests were conducted principally to check further the availability of the metaphosphates and colloidal phosphate. The latter is a natural rock phosphate of colloidal dimensions.

The first experiment was conducted in 1-gallon glazed pots holding 4 kilos of soil. All the phosphates were added so as to have equivalent amounts of P_2O_5 in all cases. Each treatment was in duplicate, and as previously described the phosphates were mixed thoroughly with the upper half of soil in the pots. Sudan grass was planted on December 8 and fertilizer mixed with the soil on December 7. The plants were harvested April 10. Dry weight per plant and phosphate were determined on the plants and the data are given in Table 19.

TABLE 19.—COMPARATIVE AVAILABILITY OF PHOSPHATES AS SHOWN BY WEIGHT OF PLANTS AND PHOSPHATE ABSORBED.

	Wt. per plant (gm.)	Wt. P_2O_5 per plant (mgm.)	Per cent P_2O_5 (dry basis)
Control, no fertilizer	0.256	1.12	0.437
Tricalcium phosphate	0.431	1.55	0.360
Trimagnesium phosphate	0.591	2.44	0.413
Dicalcium phosphate	0.556	2.40	0.431
Dimagnesium phosphate	0.418	1.08	0.258
Calcium metaphosphate, T.V.A.	0.788	2.63	0.334
Sodium metaphosphate, Rosestone	0.840	4.88	0.582
Ammonium phosphate 11-48	0.843	2.60	0.307
Treble superphosphate	0.770	1.52	0.199

All these pots were replanted on April 24 in order to determine the residual effect of these phosphates. They were har-

TABLE 20.—RESIDUAL AVAILABILITY OF PHOSPHATE FERTILIZERS.

	Weight per plant (gm.)	Weight P_2O_5 per plant (mgm.)	Per cent P_2O_5 (dry basis)
Control	0.064	0.21	0.327
Tricalcium phosphate	0.060	0.20	0.337
Trimagnesium phosphate	0.144	0.48	0.340
Dicalcium phosphate	0.123	0.42	0.339
Dimagnesium phosphate	0.124	0.44	0.354
Calcium metaphosphate	0.157	0.45	0.287
Sodium metaphosphate	0.267	1.04	0.423
Ammonium phosphate 11-48	0.104	0.48	0.464
Treble superphosphate	0.133	0.53	0.394

vested as immature plants on June 16, and the data from this residual test are given in Table 20.

The greatest dry weight per plant was obtained with sodium metaphosphate in both the original and the residual test. Calcium metaphosphate, 11-48 ammonium phosphate, and treble superphosphate gave quite similar yields and phosphate absorption per plant. Tricalcium phosphate showed the lowest availability. The residual availability of sodium metaphosphate is quite significant.

Another pot experiment was conducted in which two soils were used. One from the Yuma Valley Experimental Farm and the other from the Tucson Farm. Again all phosphates were added in equivalent amounts of P_2O_5 per pot and were thoroughly mixed with the upper half of the soil. They were planted to Sudan grass on May 3, and the plants were harvested June 13. The data obtained from this experiment are given in Table 21.

TABLE 21.—COMPARATIVE AVAILABILITY OF PHOSPHATES AS MEASURED BY WEIGHT OF PLANTS AND PHOSPHATE ABSORPTION.

	Wt. per plant (gm.)	Wt. P_2O_5 per 100 plants (gm.)	Per cent P_2O_5 (dry basis)
Yuma soil			
Control, unfertilized	0.097	0.030	0.305
Treble superphosphate	.126	.075	.600
Ammonium phosphate 11-48	.312	.119	.381
Monocalcium phosphate	.106	.081	.766
Calcium metaphosphate	.123	.067	.570
Colloidal phosphate	.052	.019	.361
Tucson soil			
Control	.039	.015	.385
Treble superphosphate	.084	.030	.356
Ammonium phosphate 11-48	.107	.037	.343
Monocalcium phosphate	.121	.029	.318
Calcium metaphosphate	.147	.071	.491
Colloidal phosphate	0.038	0.015	0.428

With the Yuma soil, response to ammonium phosphate is outstanding, but judging from the color of the plants the nitrogen was in part responsible for the superiority of this material. Treble super- and calcium metaphosphates agreed quite closely in availability, while the colloidal phosphate showed no more availability than has been obtained with other forms of the natural phosphate rock.

With the Tucson soil, calcium metaphosphate showed the greatest availability, and the colloidal phosphate again no better than the unfertilized control.

For the Neubauer tests both Rosen rye and Sacramento barley were used. While Neubauer specifies the rye plant for his method, the author has found barley quite suitable. It is better adapted to this climate, and a 15 day period will produce a heavier root and top growth and therefore extract more phosphate from the soil. Barley will also give uniform results. The data obtained from this experiment are given in Table 22 as milligrams PO_4 extracted by 100 plants from 100 grams of soil. The soil used was a University Farm soil and comparisons with silica sand are given.

TABLE 22.—COMPARATIVE AVAILABILITY OF PHOSPHATES AS MEASURED BY RYE AND BARLEY PLANTS IN THE NEUBAUER TEST.

	Rye (mgm. PO_4)	Barley (mgm. PO_4)
Sand		
Control, not fertilized	27.1	43.8
Treble superphosphate	38.5	67.3
Ammonium phosphate 16-20	36.4	67.0
Monocalcium phosphate	35.3	59.3
Calcium metaphosphate	35.9	57.2
Colloidal phosphate	26.0	43.4
Soil		
Control, not fertilized	27.6	44.8
Treble superphosphate	36.3	65.0
Ammonium phosphate 16-20	43.7	59.1
Monocalcium phosphate	40.6	62.7
Calcium metaphosphate	37.7	57.8
Colloidal phosphate	27.3	43.9

These results obtained with rye and barley confirm the results obtained in the pot experiments.

In all these experiments, both the Neubauer tests and the pot tests, the fertilizers were thoroughly mixed with the soil, much more so than could be accomplished under practical field methods. This should favor the less soluble phosphates in that there would be a greater opportunity for root contact and conversely more scattered fixation of the soluble phosphates.

Considering these experiments from all angles, the treble superphosphate and ammonium phosphate are superior forms of phosphate for alkaline calcareous soils. However, for the band method of fertilization which is now so extensively practiced, calcium metaphosphate and the less soluble phosphates such as dicalcium phosphate should definitely be highly efficient. Co-operative pot experiments conducted by the Association of Official Agricultural Chemists in 1937 (30) gave calcium metaphosphate a high rating of availability. However, Green (13) in some field experiments in Montana found that calcium metaphosphate was only slightly better than raw phosphate rock as a fertilizer for alfalfa.

During the course of these experiments one important observation was made. As already stated, plants with high calcium requirements are considered strong phosphate feeders because the accumulated calcium ions tend to reduce phosphate solubility in the soil solution and the root-soil contact film if the soluble calcium is not removed. There will be less or no calcium accumulation if both the calcium and phosphate ions are absorbed by the roots. Reitemeier (28) has shown that hexametaphosphate has the property of sequestering calcium ions as a stable soluble complex. Therefore, the activity or effective concentration of calcium ions in the soil solution will be reduced by the metaphosphate. In all Neubauer tests used in these experiments the plants were analyzed for calcium as well as phosphate. These analyses showed that the rye plants which were fertilized with metaphosphate contained less calcium and therefore had absorbed less. This may be highly significant in calcareous soils and is being studied further. The magnitude of the phosphate absorption from sodium metaphosphate was apparent throughout this investigation and the absorption of phosphate in the residual availability studies with Sudan grass (Table 21) is especially significant.

PHOSPHATE FIXATION

Arizona soils have a strong fixing power for soluble phosphates due to the large amount of solid-phase calcium carbonate present and to the high *p*H. However, there is plenty of evidence that unless this fixation proceeds as far as carbonate-phosphate the fixed phosphate will maintain a high degree of root-contact availability, probably as dicalcium phosphate.

In the next experiment the Neubauer method was used to study fixation. Three series of soil treatments were employed. In one series 30 milligrams of PO_4 from ten different phosphate materials were added to 100 grams of soil and incubated at optimum moisture content for 30 days. In a second the same plan was followed except that 0.05 gram of magnesium sulphate was added to each 100 grams of soil in order to determine the effect of magnesium on fixation and subsequent availability. In the third series the phosphate materials were added just before planting. The plants were analyzed after growing 15 days as in the regular Neubauer test. These data are given in Table 23 as milligrams of PO_4 per 100 plants.

These data show a measurable fixation of the more important phosphate materials over a 1 month period. The greatest fixation is noted in the ammonium phosphates closely followed by the soluble monocalcium phosphate. Incubation had no effect upon the availability of phosphate in the unfertilized soil, and likewise there was no improvement in the availability of raw phosphate rock. The analyses of the plants fertilized with dicalcium phosphate serve as an excellent check on the method, as there should be no change on incubation, and the data showed that none took place. It is of interest that in spite of the greater fixation of the ammonium phosphates and monocalcium phosphate these materials still show the greatest utilization by the

TABLE 23.—EFFECT OF INCUBATION ON PHOSPHATE FIXATION.

	Incubated 1 mo. after P added	Incubated 1 mo. after Mg and P added	Not incubated after P added
Monocalcium phosphate	46.7	48.4	53.5
Ammonium phosphate 11-48	45.5	45.6	55.9
Ammonium phosphate 16-20	43.0	44.0	52.6
Trimagnesium phosphate	49.9	47.9	52.1
Calcium metaphosphate	50.3	48.3	48.1
Rosestone (sodium metaphos.)	48.4	47.6	52.4
Dicalcium phosphate	46.7	43.8	47.0
Treble superphosphate	44.4	46.7	49.7
Single superphosphate	42.9	46.5	45.7
Tennessee rock phosphate	31.2	29.6	30.7
Control, no fertilizer	31.2	30.7	30.8

plants. This confirms our field observations—namely, that the soluble phosphates in spite of rapid fixation give a notable residual response in Arizona soils.

Another fixation study was conducted in which the soils were kept for 18 months after the addition of phosphate prior to determining the availability. The experimental procedure was as follows. Four phosphate deficient soils were selected. Dilute solutions of 11-48 ammonium phosphate and treble superphosphate were added to portions of each of the four soils at the rate of 22 milligrams of PO_4 per 200 grams of soil. For control another portion of soil was maintained under the same conditions as those to which no fertilizer was added. In other words, for each soil one portion was fertilized with treble superphosphate and maintained at optimum moisture content for 18 months and another allowed to dry after the original addition of water and remain dry for 18 months. The same procedure was followed for portions of the same soil fertilized with ammonium phosphate and for unfertilized portions. At the end of 18 months tests were made by the Neubauer method and by extraction with carbon dioxide to determine the chemical availability. These data are given in Table 24.

These data illustrate the degree of fixation as well as the ability of the plant to utilize the fixed phosphate. In every case the solubility of the fixed phosphate in carbonic acid is high. Likewise in every case the Neubauer values are 5.3 or greater which is the minimum value used in the Neubauer studies below which a soil is considered deficient in available phosphate. There is further confirmation, therefore, in these data that soluble phosphate, after fixation, will remain available in these soils for a reasonable period. The data also show a greater fixation of both forms of phosphate in the soils maintained at optimum moisture content over the 18 month period. Furthermore, as measured by

TABLE 24.—EFFECT OF 18 MONTHS' INCUBATION ON PHOSPHATE AVAILABILITY.

Treatment	Neubauer PO_4 value	Sol. in CO_2 (ppm)	Treatment	Neubauer PO_4 value	Sol. in CO_2 (ppm)
U. F. soil			Smith soil		
Dry, am. phos.	6.9	47	Dry, am. phos.	8.1	70
Dry, treble	7.6	47	Dry, treble	9.8	70
Dry, none	1.6	12	Dry, none	1.6	11
Wet, am. phos.	5.4	50	Wet, am. phos.	7.1	52
Wet, treble	5.7	50	Wet, treble	6.7	45
Wet, none	1.7	9	Wet, none	1.6	11
Turly soil			Davis soil		
Dry, am. phos.	5.9	47	Dry, am. phos.	7.1	40
Dry, treble	7.1	50	Dry, treble	9.9	35
Dry, none	2.6	4	Dry, none	1.1	tr.
Wet, am. phos.	5.3	27	Wet, am. phos.	5.5	45
Wet, treble	6.1	27	Wet, treble	5.7	32
Wet, none	2.6	4	Wet, none	1.1	tr.

the Neubauer test, treble superphosphate maintained a greater availability under both wet and dry conditions.

Field experiments have also shown the high availability of soluble phosphate fertilizers after fixation. In a fertilizer experiment in which 200 pounds per acre of 11-48 ammonium phosphate were applied, increased yields were obtained for 3 successive years during which six cuttings of hay were made each year (17).

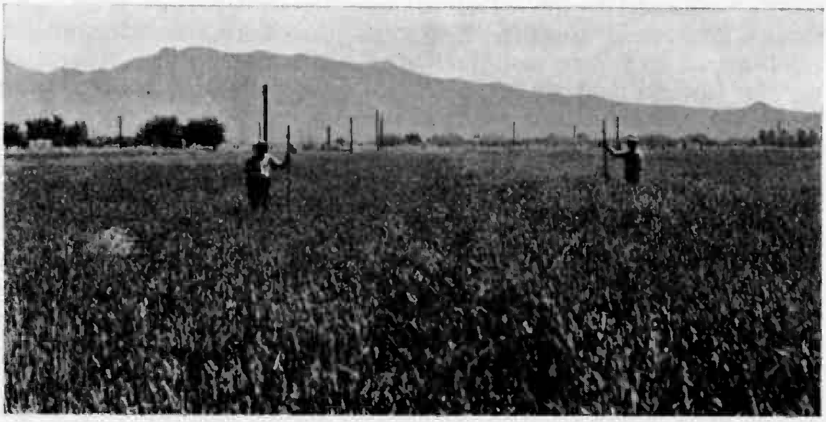

Plate I.—Residual response to ammonium phosphate: left, check border; right, 600 pounds of 11-48 ammonium phosphate applied to alfalfa, followed by hegari, and then planted to the grain crop shown.

In another case an application of 600 pounds per acre of 11-48 ammonium phosphate applied to alfalfa gave an increase of 3 tons of hay per acre. The alfalfa was followed by hegari and then grain. The residual response in the grain crop was outstanding and is shown in Plate I.

METAPHOSPHATES

In the past orthophosphates have been employed exclusively as phosphate fertilizers. Recently interest has arisen in metaphosphates (25) and this interest has been largely stimulated by the production of calcium metaphosphate by the Tennessee Valley Authority at Muscle Shoals. Calcium metaphosphate $Ca(PO_3)_2$ as a fertilizer, has been discussed by MacIntire, Hardin, and Oldham (25). It contains an approximate 65 per cent P_2O_5 equivalent, the water solubility of which varies quite widely. In four analyses given by MacIntire this variation is 10.2 to 61.7 per cent in samples containing 63.5 to 65.11 per cent total P_2O_5. Obviously, for Arizona soils, the value of calcium metaphosphate will be largely governed by its solubility in water.

In the irrigated regions of the West sodium metaphosphate is being used in small amounts in the irrigation water to prevent the precipitation of calcium when liquid ammonia is applied as a nitrogenous fertilizer. These facts prompted the inclusion of metaphosphates and pyrophosphates in the availability studies already presented. It is clearly demonstrated by these experiments that both meta- and pyrophosphates are readily available forms of phosphate and are readily absorbed by crops.

It is the general opinion among plant physiologists that plants absorb ions only in their most highly hydrated and most highly oxidized forms. How then does this apply in the case of metaphosphates, for both the meta- and pyrophosphates are dehydrated orthophosphates?

$$H_3PO_4 \rightarrow HPO_3 + H_2O$$
$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

The pot experiments and Neubauers clearly demonstrated the ready availability of both the calcium and sodium metaphosphates. Also, in the case of the latter, the glassy form which is the more soluble is more effective than the less soluble crystals. The next experiments were designed to study the absorption of metaphosphates and their behavior in the soil.

In the first set of experiments the absorption of metaphosphate by plants from water cultures was studied. The culture solutions were prepared by adding sufficient soluble phosphate to give a solution of 30 ppm of PO_4 from monocalcium phosphate and PO_3 from the sodium metaphosphates, Rosestone and Calgon. The basic culture solution was 60 ppm of KNO_3 in tap water. One-liter wide mouth bottles were used for growing the plants, and there were twenty-two plants in each culture. Each treatment was conducted in triplicate and the experiment repeated three times. A typical set of data is submitted in Table 25, the rye seedlings being grown from October 14 to November 5, 1936, at which date the plants were dried, weighed, and analyzed.[1]

TABLE 25.—ABSORPTION OF PHOSPHORUS BY RYE PLANTS FROM ORTHO- AND METAPHOSPHATES.

	Dry weight per 100 plants (gm.)	Mgm. P_2O_5 per 100 plants
Control	2.96	27.3
Monocalcium phosphate	3.32	84.1
Sodium metaphosphate (C)	4.00	114.1
Sodium metaphosphate (R)	3.16	96.3

These data leave no doubt as to the ability of plants to utilize phosphate from metaphosphates, and this absorption is apparently of greater magnitude in culture solutions than orthophosphate as $Ca(H_2PO_4)_2$.

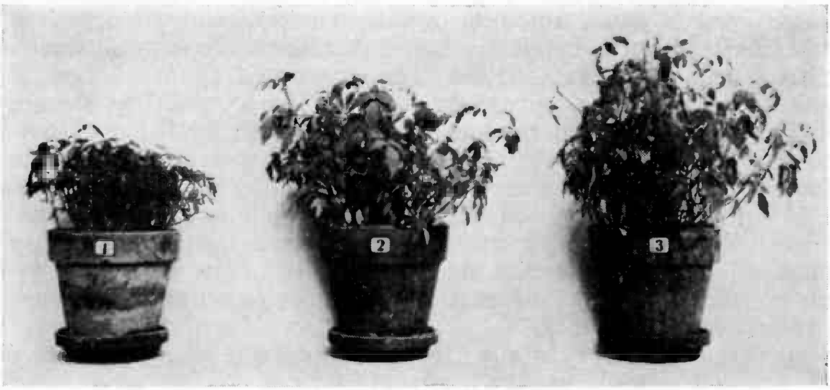

Plate II.—Comparative growth of tomatoes when fertilized with ortho- and metaphosphates: *1*, control, not fertilized; *2*, sodium metaphosphate (Rosestone); *3*, monocalcium phosphate. Both phosphates were added in amounts to give equal P_2O_5 applications.

In order to determine whether the phosphates had been absorbed as metaphosphate ions or whether they had been first hydrated to orthophosphate, a study was made of the changes in the amount of the two forms of phosphate in the culture solution. This study showed that when growing roots were present in the culture solution there was a surprisingly rapid hydration of the metaphosphate to orthophosphate. It was concluded from this that absorption takes place as orthophosphate.

[1] This experiment was performed by J. F. Breazeale.

This observation is supported by Weissflog and Mengdehl and by Kitsata as reported by MacIntire (25). Kitsata reports that an enzyme will induce hydrolysis, while Weissflog and Mengdehl report that root hairs can convert PO_3 into PO_4.

Glixelli and Boratinski (12) found that all forms of phosphate, H_3PO_4, $H_4P_2O_7$, alpha-$(HPO_3)_x$, and beta-$(HPO_3)_x$, are suitable sources of phosphorus for wheat and barley, the two plants used in their study. They report, however, that a considerably smaller amount of phosphorus is absorbed from meta solutions than from ortho solutions. This is not in agreement with the absorption data obtained by the author with rye, as given in Table 25. Glixelli and Boratinski attributed the differential absorption to the respective molecular sizes because the more highly polymerized beta form of metaphosphate was less readily absorbed than the alpha form, the pyro-, or the orthophosphates. They state that this differential absorption was less apparent in dilute nutrient solutions than in concentrated nutrient solutions.

Fixation of metaphosphates

Phosphate fixation in soils may take place either as an absorption phenomenon in which the clay fraction is largely involved or as a precipitation phenomenon in which the calcium ions and solid-phase calcium carbonate are involved. The *p*H of the soil is an associated factor in both types of fixation. Fixation in the alkaline calcareous soils of Arizona is largely, if not entirely, a precipitation phenomenon, for calcium phosphate is least soluble under alkaline conditions. The rate of reaction between monocalcium phosphate and $CaCO_3$ is very rapid and results in the formation of the less soluble though available dicalcium phosphate. The latter slowly reacts further with $CaCO_3$ to form some modification of tricalcium phosphate, probably $[Ca_3(PO_4)_2]CaCO_3$.

The absorption, by plants, of phosphate when applied to the soil as fertilizer may take place either from the soluble phosphate in the soil solution or directly from that fixed by the clay or precipitated as the several forms of calcium phosphate. Probably only a small portion of the phosphate used by plants is absorbed directly from the soil solution. It is an entirely different system from the root-soil contact system which supplies the plant with most of its phosphate. The dicalcium phosphate is readily soluble in the root soil contact film, but the final precipitated form, carbonate-phosphate, is much less so, for the root hair must break through the $CaCO_3$ to reach the phosphate and will meet the antagonism of a greater number of calcium ions. This explains the low solubility of native soil phosphate and phosphate rock and the difference in the ability of plants to dissolve phosphate from insoluble forms. In Arizona's alkaline calcareous soils an additional impediment is met, for the soil particles are often coated with a film of ferric hydroxide or oxide.

In view of the fact that metaphosphates—that is, the glassy forms—exist in solution in molecular form in several degrees of polymerization, their fixation is of interest. It was postulated that fixation would be less active and therefore this form of phosphate might penetrate deeper into the root zone than the ortho salts. The fixation of metaphosphate was therefore studied as a part of this investigation. The hexametaphosphate hydrates very slowly, in fact is practically stable at room temperature (28). An acidic environment hastens hydration, while a basic medium induces slow hydration.

One-kilogram portions of soil were weighed into glass percolators and leached with solutions containing 30 parts per million of PO_4, in the one case from monocalcium phosphate and the other from sodium metaphosphate (Rosestone). A third portion of soil was leached with tap water as a control. The leaching operations were conducted by pouring a liter of solution in the top of the percolator and when the leaching was complete from each separate liter, the phosphate in the leachate was determined. These data are given for ten leachates in Figure 2. Each part of the experiment was conducted in duplicate, and the experiment shows that the metaphosphate was fixed more completely by this calcareous soil than the orthophosphate.

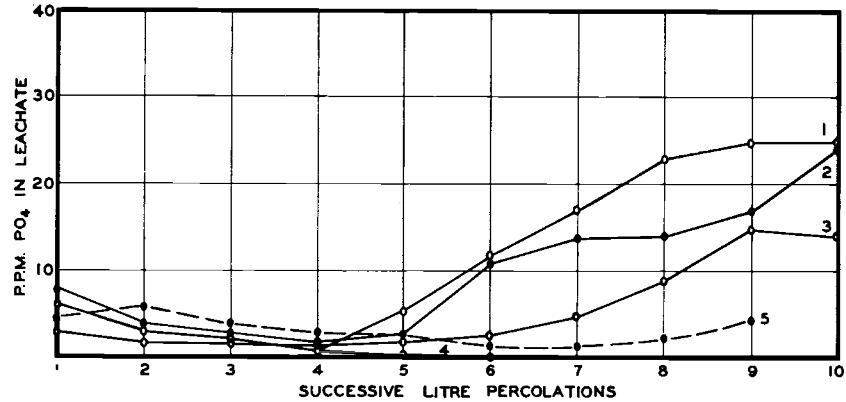

Figure 2.—Ppm PO_4 in successive leachings with solution of *1*, monocalcium phosphate; *2*, sodium metaphosphate (Rosestone); *3*, sodium metaphosphate (Calgon); *4*, tap water, control; *5*, sodium metaphosphate (Rosestone), heated soil.

Since metaphosphates do not react with ammonium molybdate as do the orthophosphates, it was possible to determine the form of phosphate present in the leachate. These analyses showed that the metaphosphate had undergone complete hydration during the time of its contact with the soil, since at no time during the leaching was metaphosphate detected in the leachate. It is impossible to state, therefore, whether the phosphate was fixed as meta or after hydration to ortho, but in all probability the latter.

In another experiment the soil was sterilized by heating in an oven at 110 degrees C. The purpose of this sterilization was to destroy bacteria and enzymes to determine if these were associated with the hydration of meta. The same concentration of phosphate and the same weight of soil were used, and the leachates from each successive liter were analyzed. The data are given in Table 26. These data show that the heated soils fixed metaphosphate more strongly than the unheated. In the previous experiment the phosphate did not begin to increase in the leachates until the sixth liter, while in the heated soils the concentration did not increase until the ninth liter. It seems fair to conclude from this that bacteria and enzymes are not involved in the fixation of metaphosphates.

TABLE 26.—FIXATION OF METAPHOSPHATE BY HEATED SOIL.

Leaching	Ppm PO_4 in leachate	
	Control	Metaphosphate
First liter	3.2	6.0
Second liter	2.2	7.0
Third liter	1.4	4.4
Fourth liter	0.8	3.2
Fifth liter	stopped	3.2
Sixth liter	......	2.0
Seventh liter	......	2.0
Eighth liter	......	2.6
Ninth liter	......	5.6
Tenth liter	......	10.0

These data are in agreement with MacIntire *et al.*, as they found a greater fixation of metaphosphate than ortho (25) in noncalcareous soils. Quantitatively this fixation was 2.4 to 2.05 times that of ortho.

These data show quite conclusively that metaphosphates are fixed strongly and quickly by calcareous soils, and there should be no greater penetration from their use than is now being obtained with the orthophosphates.

SUMMARY

1. Quick field chemical tests for phosphate availability in the alkaline calcareous soils of Arizona have not proved effective because of the influence of *p*H and ratio of soil to solvent on phosphate solubility.

2. Chemical determinations of phosphate availability can be effectively conducted in the laboratory by using carbonic acid as a solvent.

3. Neubauer plant tests have proved useful in studying phosphate availability in Arizona soils.
4. Absorption of phosphorus by plants on Arizona soils is faintly increased by magnesium sulphate, but it is not of sufficient magnitude to be significant as an aid to phosphate nutrition.
5. Absorption of natural soil phosphate was not significantly influenced by nitrogen fertilization, but when phosphate fertilization is practiced, a nitrogen deficiency will be a limiting factor in phosphate response.
6. Phosphate is absorbed more readily by plants from calcium saturated soils than from sodium saturated soils.
7. Carbon dioxide, because of its effect upon the *p*H value of the soil, increases the availability and absorption of phosphate by plants.
8. Calcium hydroxide and calcium carbonate, because of their effect upon the *p*H of the soil and as sources of calcium ions, reduce the availability and absorption of phosphate.
9. All the water soluble phosphates, ortho, meta, and pyro, are excellent sources of phosphate as plant food for phosphate deficient alkaline calcareous soils.
10. The value of calcined phosphate is directly related to its fineness, the 200 mesh being almost equal to monocalcium phosphate in the Neubauer test.
11. Raw rock phosphate, fused phosphate rock, and colloidal phosphate are of practically no value as a source of plant food phosphate on alkaline calcareous soils.
12. Sodium metaphosphate proved extremely effective as a phosphate fertilizer. This may be related to its property of sequestering calcium ions.
13. Soluble phosphate fertilizers are fixed in a form which is surprisingly available as shown by the residual response obtained in pots and in the field.
14. Metaphosphates exhibit greater fixation by calcareous soils than the orthophosphate.

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