PHOSPHATE FERTILIZER REACTIONS UNDER VARIOUS SOIL CONDITIONS

by

ARTHUR B. ONKEN

Bachelor of Science

Texas College of Arts and Industries

Kingsville, Texas

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Thesis Approved:

Lester V. Reed
Thesis Adviser

Dale E. Weibel

John F. Stone

Eddie Basler

Billy B. Tucker

Robert MacVicar
Dean of the Graduate School

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CHAPTER I

INTRODUCTION

Many soils throughout the world are known to be deficient in one or more of the nutrient elements needed for good plant growth. The fact that plants grew better, in some areas, when fertilized was apparently recognized fairly early in man's cultivation of crops. The use of such materials as animal manures, bones, wood ashes, wool wastes, guano, fish, chalk, and marl can be traced back several thousand years. The idea of elemental needs did not, however, start to be understood until the early part of the nineteenth century.

One element that is frequently lacking, in sufficiently available quantities, is phosphorus. Harper (20)[1] states that the first limiting factor to crop production in central and eastern Oklahoma is phosphorus.

Experiments to determine the magnitude of the need for phosphorus were started as early as 1837 when Lawes founded Rothamsted Experimental Station. (14) Through the years, as the experimentation has progressed, it has been found that chemical reactions in the soil in conjunction with added phosphate compounds are diverse and subject to the chemical environment of the soil. Warrington (41) was one of the first investigators to realize this complexity. In the present study some of the effects of this environment were investigated.

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[1] Figures in parenthesis refer to Literature Cited.

The objectives of the study were: 1. To determine the pattern of phosphorus release with time from an acid soil treated with lime, rock phosphate and superphosphate. 2. To determine some of the compounds formed by the phosphorus of rock phosphate and superphosphate as influenced by plant growth, liming and time of application.

CHAPTER II

REVIEW OF LITERATURE

In view of the objectives as stated in the introduction the effects of certain conditions and treatments with regard to phosphorus applied to soils were considered. These were: liming, time of application, reaction products and rate of release.

Effect of Liming

Lime applications to acid soils have been observed to have a diversity of effects on phosphorus availability. These effects appear to form a pattern dependent upon particular conditions existing in the soil. Soil conditions to which these effects can be ascribed include source of phosphorus, resulting percent base saturation, incubation periods and the presence of iron and aluminum.

Army and Miller (2) investigated the effects of liming on two acid soils, Bladen fine sandy loam and Georgeville silty clay loam. After liming, the soils had a range of 10% to 100% base saturation. No fertilizers were added. Application of lime to both soils increased uptake of phosphorus by turnips. It was noted that on the Bladen soil the exchange complex had to be highly saturated with calcium before a marked increase in phosphorus availability was apparent. Acid extractable phosphorus (.02 N H_2SO_4) at the end of the experiment had increased. The soil lowest in organic matter exhibited the greatest conversion of acid insoluble to acid soluble phosphorus. It was suggested that this was due to conversion of inorganic phosphates. Beater (4) reported that liming an acid soil increased the availability of native soil phosphorus to sugar cane and maize.

Finn, Cook and Harrison (17) applied rock phosphate and superphosphate to three acid soils on the basis of equal amounts of citrate soluble phosphorus. The fertilizers were applied in conjunction with no lime and lime at one and four tons per acre. All treatments were added just prior to planting. Superphosphate plus lime was the best treatment for oats, however, rock phosphate produced an increase in yield over the check. Increased yield due to superphosphate over rock phosphate was attributed to greater water solubility of superphosphate.

Taylor, Gurney and Lindsay (38) reported greater phosphorus uptake by corn from monocalcium phosphate applied with lime, on an acid soil, than under unlimed conditions. They also found more phosphorus uptake from the check and monocalcium phosphate when the plants were seeded immediately after fertilization than when the treatments were allowed to incubate for three months. Efficiency of less soluble phosphates was found to increase with the use of an incubation period. Olson et al. (27) found that addition of lime to acid soils reduced the effectiveness of all phosphate fertilizers used except superphosphate. In more acid soils, pH 5.6 to pH 6.0, a two month incubation period at field capacity increased superphosphate and rock phosphate availability to the Bray No. 1 extractant. Less acid soils, pH 6.4 to pH 7.6, did not exhibit this increase due to incubation.

The capacity of New Zealand soils to retain phosphorus was reported by Saunders (31) to be due to aluminum. Addition of calcium carbonate to the soil depressed the release of phosphorus into solution until pH 7 was reached. On unlimed soil, when pH 6 was reached the release of phosphorus was markedly increased. He states that the results indicate that unless the exchange complex is almost fully saturated the calcium is held too firmly by the exchange complex to allow much calcium in solution. Consequently, reactions between calcium and phosphorus could not take place. This would be in agreement with Marshall's (26) concepts and experimental results on the activities and bonding energies of cations held by the colloidal fraction of the soil.

Terman, Bouldin and Lehr (39) found hydroxyapatite to be a poorer source of phosphorus than more soluble forms of phosphate fertilizers on acid and basic soils. Ryegrass with a subsequent crop of sudangrass were used as indicator plants. They found no dependence of yield and phosphorus uptake on a phosphorus interaction with pH. Cropping lowered the soil pH. Lime treatments were applied at time of fertilization. The authors concluded that the nature of iron, aluminum and other substances in various soils, as influenced by lime, were important to plant response to phosphorus.

Time of Application

From the above discussion it would be expected that time of lime applications with respect to superphosphate and rock phosphate applications would be important. This would be due to the apparent dependence of the above observations upon the chemical composition of the soil solution.

Roberts (29) reported that when lime alone increased availability of native soil phosphorus significantly as compared with superphosphate; rock phosphate did well in the presence of lime. The converse also was found to be true. Roberts suggested that finely ground limestone used far enough in advance of rock phosphate, to permit all of the lime to react with the soil, might be a solution to the difficulty where lime interferes with the rock phosphate availability.

Ames and Kitsuta (1) found that simultaneous addition of lime with rock phosphate and superphosphate decreased phosphorus availability. The effect was most pronounced with rock phosphate. Lime added well in advance of rock phosphate had less depressing effect. Lime added after rock phosphate decreased phosphorus availability. Lime increased the availability of native soil phosphorus.

Ellis, Quader and Truog (16) reported that in pot cultures rock phosphate applied one month before lime gave greater availability of phosphorus to oats than when the reverse procedure was used. It was concluded that rock phosphate should be added one year or more prior to liming. Rock phosphate released phosphorus rapidly at pH 5.1 to pH 5.7. Ellis et al. pointed out that the released phosphorus could react with goethite to form strengite. It was thought that a subsequent addition of lime to pH 7 would release the phosphorus in a more soluble form.

Reaction Products

Results from experiments discussed in the two previous sections indicate a chemical change in the phosphorus compounds after application to the soil. This was made evident by the increasing or decreasing phosphorus availability as the chemical nature of the soil solution was changed. Chemical changes that affect phosphorus availability could be produced by the applied phosphorus sources added as well as by lime.

Warrington (41), in 1868, reported in a series of experiments that two calcium free soils would remove phosphorus from solution. Soil A removed 50.8% and Soil B removed 96.1% of the phosphorus from solution. Soil B contained twice as much iron and aluminum oxides as Soil A. He concluded that iron and aluminum oxides in the soil were responsible for the removal of phosphorus from solution making it unavailable for plant growth.

Stoddart (37) found that the ratio of iron and aluminum phosphates to calcium phosphates for acid soils was greater than non-acid soils. He stated that low soil pH would then be conducive to the formation of iron and aluminum phosphates which would be unavailable to plants. Chandler (8) states that it appears that formation of iron and aluminum phosphates is responsible for adsorption of phosphates in acid soils; while precipitation of tricalcium phosphate is responsible for decreasing the solubility of phosphorus in neutral or alkaline soils. Cho and Caldwell (12) also found more phosphorus in the aluminum and iron fractions in acid soils and more in the calcium fraction of calcareous soils. However, pH differences between soils did not correlate with the form of phosphorus in the case of acid soils. Soils having approximately the same pH varied widely in the distribution of the phosphorus fractions.

Hsu and Jackson (22) reported that the solubility and formation of calcium, iron and aluminum phosphates were dependent on pH. They found calcium phosphate formation increased as soil pH increased with aluminum and iron fractions decreasing. Further they reported that reducing conditions favored formation of aluminum phosphates instead of iron phosphates. The statement was made that at pH's below seven, calcium carbonate rapidly disappears from soil and exchangeable calcium regulates the solubility of hydroxyapatite.

Chang and Jackson (11) fractionated soil phosphorus into iron, reductant soluble iron, calcium and aluminum forms. They found that application of lime had little effect on these discrete forms of native phosphorus in the fertilized soil. Application of soluble phosphorus fertilizer increased the amount of aluminum and iron phosphorus at all lime levels, but calcium phosphorus only slightly at the highest lime level. Reductant soluble iron phosphorus was not affected by liming or fertilization. The relatively small increase in calcium phosphorus, regardless of lime level, was thought to be due to crop removal plus precipitation of applied phosphorus as the less soluble iron and aluminum forms. However, liming did keep more of the fertilizer phosphorus in the calcium form. Formation of reductant soluble iron phosphorus was thought to be related to soil genesis since it was not affected by fertilizer application. Wright and Peech (44) also found that most phosphate fertilizer added to soils went to the aluminum and iron fraction except in the case of rock phosphate. Even after more than thirty years a large part of the rock phosphate remained in the calcium form. They concluded that these results supported the solubility criteria with respect to fertilizer products in acid soils. Further they concluded that soil characteristics determined the dominant residual phosphorus compounds. Williams (42) added superphosphate and rock phosphate to soil in equivalent rates. He reported half as much calcium phosphate and twice as much iron and aluminum phosphates formed from superphosphate as from rock phosphate.

Chang and Chu (9) studied the fate of phosphorus added to soils, as KH_2PO_4 and superphosphate, under different moisture conditions and lengths of time. Six soils were used with pH values ranging from 5.3 to 7.5.

When KH_2PO_4 was allowed to react for three days with soils moistened to field capacity, the phosphorus fractions were found mainly in the aluminum phosphate fraction, followed by iron phosphate and calicum phosphate. For the same moisture conditions, but for a reaction period of 100 days, they found that iron phosphate increased at the expense of aluminum and calcium phosphates. Iron phosphate was the dominant form found in soils flooded for 100 days. When KH_2PO_4 in solution was shaken with the soils for three hours the dominant form found was iron phosphate.

They also found that phosphorus from superphosphate applied to a soil over a period of 31 years was dominantly in the iron phosphate fraction, with aluminum phosphate next, and calicum phosphate last. Liming did not change the distribution pattern.

Bhangoo and Smith (6) used seven acid soils in a fractionation and incubation experiment. They incubated 200 grams of soil at field capacity for five weeks. Samples were removed and available phosphorus determined by the Bray and Kurtz No. 1 method using a 1:50 soil-solution ration. An increase of from three to fourteen pounds of phosphorus per acre was found. This increase was attributed to mineralization. Good correlation was found for available phosphorus before and after incubation versus phosphorus uptake of wheat. Available phosphorus due to mineralization gave a somewhat lesser degree of correlation. It was found that soil with most of its phosphorus in iron and aluminum fractions has less phosphorus available for plant growth than soil where most of the phosphorus was in the calcium fraction. Adsorbed phosphorus showed little correlation with plant growth. It was concluded that fractionation was of value in evaluation of phosphorus supplying abilities of soils.

Cook (15) reported that addition of hydrogen saturated clay to soil increased the availability of rock phosphate to oats, corn, and millet, but not to a high calcium feeder such as buckwheat. It was concluded that this was in accordance with the law of mass action regarding the solubility expression of rock phosphate. The hydrogen clay removed calcium from solution, driving the dissolution reaction toward completion. Graham (19) carried this concept a step further. He found a good correlation between bonding energies of various exchange complexes for calcium and hydrogen and release of phosphorus into solution by rock phosphate. The greater the bonding energy for calcium and the smaller the bonding energy for hydrogen the more phosphorus released. Initial pH of the colloidal system could not be used to explain the difference in release. Schaller (32) found that as percent base saturation increased, release of water soluble phosphorus from rock phosphate decreased. A slightly better correlation of release was found with pH than percent base saturation. Heck (21) concluded that increased percent base saturation decreased the ability of soils to combine phosphorus in difficultly available forms. Further he stated that variation of percent base saturation does not usually cause more than 20-30% change in fixation. Eighty to ninety percent base saturation was found to be the best range.

Saunders (30) reported on the effect of superphosphate on the pH of soil. He topdressed moist soil in a beaker with ninety pounds of superphosphate per acre and measured the pH at intervals. At the end of the first day the pH had dropped from 5.8 to 5.2 and at the end of eighteen weeks the pH was up to 6.2. The initial decrease in pH was attributed to the acid nature of the fertilizer and replacement of hydrogen ion by calcium ions on the clay. Phosphate was found to increase as pH of the soil and water suspension increased. At a pH of approximately 5.5 the curve of phosphorus in solution versus pH rose steeply. The pH and not exchangeable calcium was thought to be the dominant factor determining the amount of phosphorus released into soil solution. Further, it was concluded that the effect of phosphorus fertilizer on soil pH determined the amount of phosphorus released into the soil solution.

Lindsay and Stephenson (25) found that a wetted zone formed around a granule of monocalcium phosphate in the soil. A pH as low as 2.06 was observed in some soils five millimeters from the granule. Calcium, aluminum and iron were found in solution. Calcareous soils had large amounts of calcium ions in solution and acid soils large amounts of iron and aluminum. The conclusion was reached that these ions, brought into solution by the acid fertilizer solution, precipitate out at higher pH values, in the outer edges of the wetted zone, forming compounds with the phosphate ion.

Coleman, Thorup and Jackson (13) reported a positive correlation between formation of aluminum phosphate with exchangeable aluminum. It was also found that formation of aluminum phosphate was pH dependent. The formation of aluminum phosphate increased as pH increased. This was thought to be due to reaction of phosphorus in solution with aluminum exchanged by calcium.

Laverty and McLean (23) fertilized soil samples from differentially limed field plots with 240 pounds of ammonium dihydrogen phosphate per acre. The soil samples were wetted to the moisture equivalent and incubated for ten days. Samples were removed and fractionated for phosphorus compounds according to Jackson. It was found that only the calcium fraction correlated with pH. Calcium phosphate increased with an increase in pH. The amounts of water soluble, iron and aluminum phosphates increased in the fertilizer treatments over the check. The largest portion of recovered phosphorus was in the aluminum and iron fractions. Percent recovery ranged from 90 to 120%. Bray and Kurtz No. 1 extraction method was used to determine available phosphorus. That phosphorus, not recovered from the fertilizer treatment by this method was termed as fixed. More iron and less aluminum phosphate was found in soils where fixation was highest. Another set of soil samples were treated with various phosphorus fertilizers and subjected to the ten day equilibrium period. Oats were then planted and grown for one month. It was found that water soluble, iron and aluminum phosphate fractions were positively correlated with phosphorus taken up by the plant. Apatite was found to remain for the most part in the calcium form. Ammoniated phosphates were found to be rendered less available than superphosphate. South Carolina rock phosphate at 4,000 pounds per acre and superphosphate at 240 pounds per acre were found to be almost equal on the basis of uptake. Virginia apatite treatments were not significantly different from the check.

Williams (43) reported 57% of the phosphorus in wheat was derived from calcium phosphate and 30% from adsorbed iron and aluminum phosphates when superphosphate was added to the soil. In a field experiment he found correlation between calcium phosphate and yield, aluminum plus iron plus adsorbed phosphate and yield and the sum of all fractions and yield. The conclusion was reached that fractionation was a good tool for evaluation of phosphorus in soils.

Rate of Release

Since the primary step in phosphorus nutrition is dissolution of relatively insoluble compounds, it would not be unreasonable to expect that rate of release studies might furnish some useful criteria for evaluation of phosphorus availability.

Fried et al. (18) reported that the rate of release of phosphorus from soil by water leaching decreased rapidly, at first, with successive extracts. A point was reached, however, where the amount of phosphorus released held constant. This value was taken as the rate of release of phosphorus to plants. It was reported that this rate was 250 times the rate of uptake of phosphorus by excised barley roots for the soils used. Shapiro and Fried (33) derived an equation for the release of phosphorus into soil solution. They assumed a psuedo first-order reaction. When the equation was applied to the results of a water leaching experiment two forms of phosphorus were found on the basis of rate of release. One form was rapidly released and decreased rapidly with time and the other form was released rather constantly with time. An equation for equilibrium adsorption was also derived. When applied to experimental results indications were that two forms existed; one held tightly and one held loosely.

CHAPTER III

Rock Phosphate and Superphosphate Reactions With an Acid Soil and Their Effect on Plant Nutrition

1. Rates of Reaction[1]

Arthur B. Onken and Lester W. Reed[2]

Abstract

A laboratory experiment was conducted to determine the pattern of release of phosphorus with time from an acid soil treated with lime, rock phosphate and superphosphate. The experiment consisted of placing Parsons silt loam soil in beakers with a total of 21 treatments consisting of lime, rock phosphate and superphosphate. These were equilibrated for 14 weeks at 1/3 atmosphere of moisture tension. Each week a soil sample was removed from each beaker and available phosphorus determined by the Bray and Kurtz No. 1 method as modified by Smith et al. (35).

The rate of release of available phosphorus from the rock phosphate treated soil was found to fit over the time interval investigated, a first

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[2] Graduate assistant and Professor of Agronomy, Oklahoma State University, Stillwater, Oklahoma.

order kinetic relation. Rate of release of phosphorus from the soil treated with superphosphate presented a much more complex situation. A large decrease in available phosphorus occurred in the first week and was related to the amount of phosphorus added. From the first week through the fifth week an increase in available phosphorus extracted occurred. A decrease in available phosphorus released occurred from five through 14 weeks. A tentative explanation of this behavior is presented. This explanation is based on the effect of superphosphate on the chemistry of the soil solution.

Rock Phosphate and Superphosphate Reactions with an Acid Soil and Their Effect on Plant Nutrition

Timing of the application of phosphorus fertilizers to the soil in order to obtain maximum benefit for plant nutrition involves two considerations. The first is to apply relatively insoluble sources, such as rock phosphate, so that enough phosphorus is in solution at the time the plant starts to grow that the rate of release from the source is sufficient to maintain an adequate supply of phosphate ion in solution. This implies that equilibrium conditions of phosphorus from the source with the soil solution would be the ideal time to initiate plant growth. It further implies that enough unreacted source must be present to maintain an adequate supply of phosphorus in solution.

When rock phosphate reacts with an acid soil, compounds more soluble than the original rock phosphate are formed[3] (23, 35). Thus rock phosphate

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[3] Onken, Arthur B. Phosphate fertilizer reactions under various soil conditions. Unpublished M.S. thesis, Oklahoma State University, Stillwater, Oklahoma. 1963.

must be added in quantities so that the formation of the more soluble compounds will take place at a rate rapid enough to keep adequate phosphorus in solution. The necessary formation rate of the more soluble compounds will be dependent upon the rate at which they release phosphorus into solution.

The second consideration is the formation of more insoluble phosphorus compounds from the more soluble fertilizers, such as superphosphate. The formation rates of the compounds less soluble than those added have been found to be quite rapid. In some cases, only a matter of several hours or a few days are required (9, 23, 24). Desirability of equilibrium conditions, as described above, are again implied. The amount of phosphorus in solution at any given time would be dependent upon the rate of release from the compounds formed. Thus, the amount of superphosphate required for optimum plant growth would be dependent upon the solubility of the phosphorus compounds formed.

This study was conducted to determine the pattern of phosphorus release with time from an acid soil, treated with lime, rock phosphate and superphosphate, to an extracting reagent that might be used for the determination of available phosphorus. Available phosphorus was taken to be that phosphorus extractable in a given reagent that could be used in prediction of plant response to phosphate fertilization.

Materials and Methods

A rate of release study was conducted in the laboratory using Parsons silt loam, a phosphorus deficient acid Planosol (pH 5.3). The soil was 66.1% base saturated and contained 2.55% organic matter. Available phosphorus measured by the Bray and Kurtz No. 1 extraction, as modified by Smith et al. (35), was 26.9 pounds of P per acre. There was 27.0 percent moisture at 1/3 atmosphere of moisture tension.

Superphosphate used in this experiment was made with reagent grade monocalcium phosphate and gypsum. The amounts applied were adjusted to be equivalent to application of the specified amounts of 0-20-0. Rock phosphate was Florida land pebble containing 14.67% total phosphorus as determined by the method recommended by the AOAC (3). The rock phosphate was ground to pass a sieve with 74 micron diameter holes, before use.

After air drying, the soil was passed through a quarter inch mesh screen. Two hundred grams of the soil were placed in 250 ml. beakers. The following lime and fertilizer treatments were added in three replications. Lime at 0%, 25%, 50%, 75%, and 100% of the lime requirement; rock phosphate at 1,000, 1,500, 2,000, and 2,500 pounds per acre; superphosphate at 680, 1,020, 1,360, and 1,700 pounds per acre; 2,000 pounds of rock phosphate per acre plus lime at 25%, 50%, 75%, and 100% of the lime requirement; and superphosphate at 1,360 pounds per acre plus lime at 25%, 50%, 75%, and 100% of the lime requirement. The soil was brought to 1/3 atmosphere of moisture tension with distilled water, by weight, and maintained throughout the experiment by the same method.

A sample was removed each week for 14 weeks from each beaker. After air drying the sample was crushed to pass a 20 mesh sieve. Available phosphorus was determined on each sample by the Bray and Kurtz No. 1 method as modified by Smith et al. (35). The experiment was a randomized block and analyzed accordingly (36).

Results and Discussion

Duncan's new multiple range test showed that all the rock phosphate treatments produced significant differences in available phosphorus at the 1% level except that 2,000 pounds per acre was not significantly different from 1,500 or 2,500 pounds per acre. Release of available phosphorus with time was significant at the 1% level. The release curves obtained are shown in Figures 1 and 2. The interaction of rock phosphate with weeks was significant at the 5% level. Use of Duncan's new multiple range test (36) showed that at the 1% level the first 4 weeks released significantly less available phosphorus than the next 12 weeks. Weeks 1, 2 and 3 were significantly different from each other. Week four was not significantly different from week three. Weeks 5 through 14 were not significantly different, except week 11 was significantly less than weeks 5, 8, 10, 13, and 14.

In considering the kinetic characterization of available phosphorus release, the assumption was made that rock phosphate did not appreciably change the chemical nature of the soil solution. The criteria for testing the order of the kinetic reactions were taken from Benson (5).

This experiment as set up and conducted was an equilibrium system. First-order opposing reactions would be the simplest equilibrium system.

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

$$K = \frac{K_1}{K_2} = \frac{Beq.}{Aeq.}$$

Where: A = Concentration of reactant

B = Concentration of product

K_1 = rate constant for forward reaction

K_2 = rate constant for reverse action

K = equilibrium constant

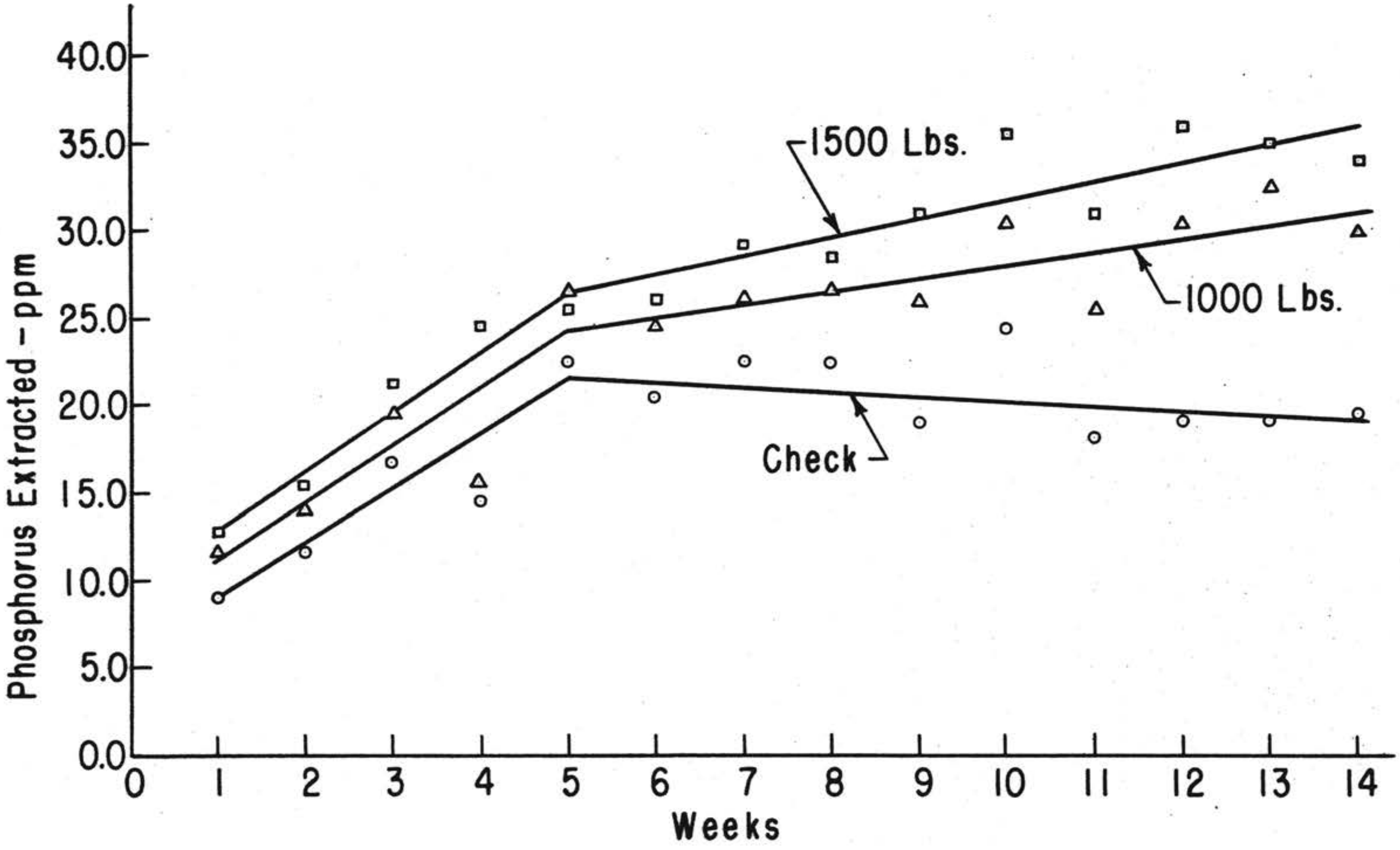

Figure 1. Available Phosphorus Released Versus Time for the Check, 1,000 and 1,500 Pounds of Rock Phosphate Per Acre.

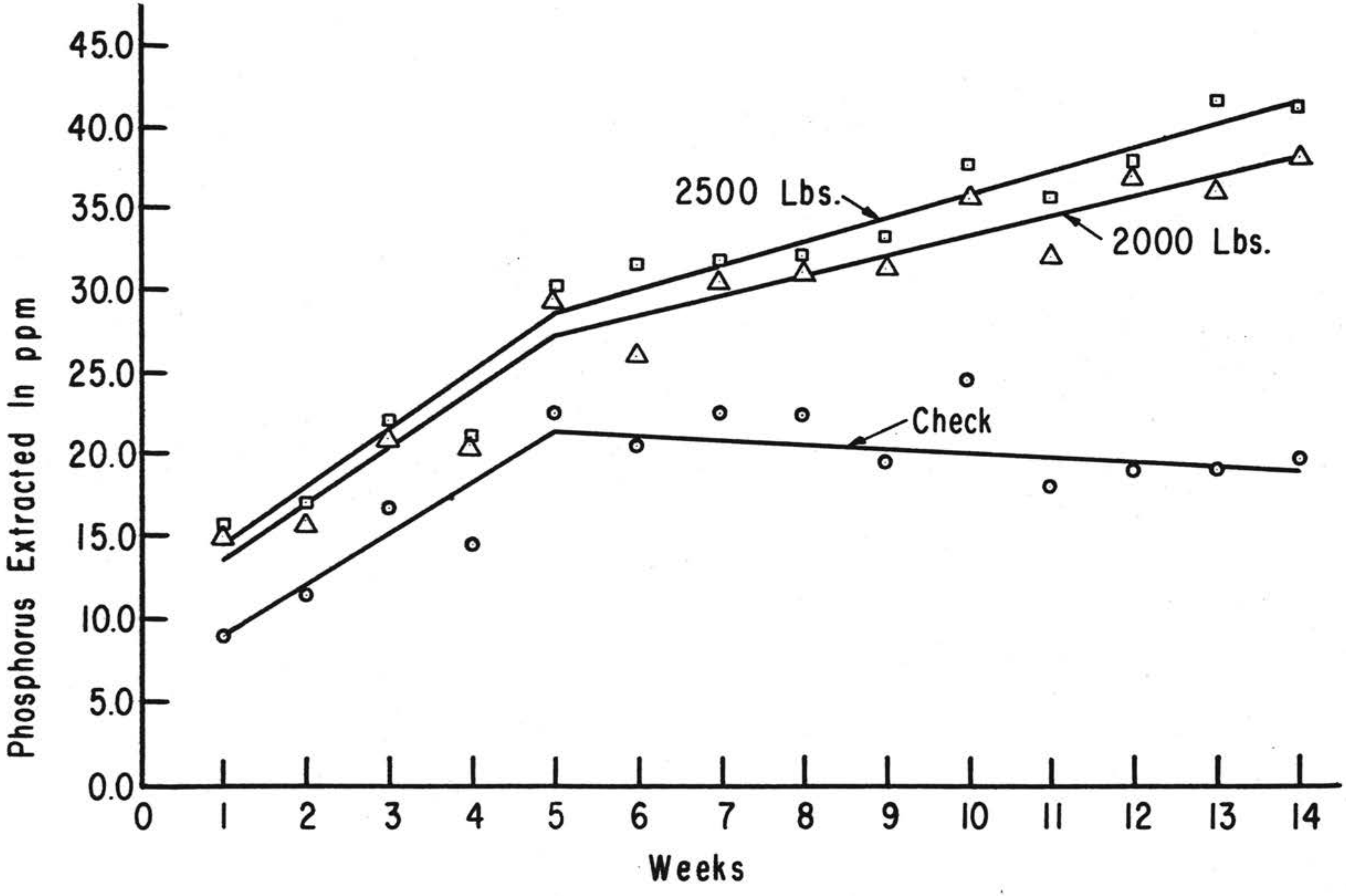

Figure 2. Available Phosphorus Released Versus Time for the Check, 2,000 and 2,500 Pounds of Rock Phosphate Per Acre.

Beq. = Concentration of product at equilibrium

Aeq. = Concentration of reactant at equilibrium

If the assumption is made that Beq. will be large compared to Aeq. ($k > 100$) then the reaction reduces to a simple first-order reaction. This assumption was made on the basis of the acid nature and low available phosphorus content of the soil used; plus the relatively steep slope of the 5 to 14 week portion of the release curves with as much as 25% of the phosphorus added, released.

A first-order reaction is one in which the rate of the reaction is proportional to the concentration of only one of the reacting substances. The first-order reaction

$$aA + bB + \ldots\ldots \xrightarrow{K} \text{products}$$

is represented algebraically

$$\frac{dC_A}{dt} = -K_A C_A$$

Where C_A is the concentration of reactant A in the system at time "t" and K_A is the specific rate constant. The minus sign denotes decreasing concentration of A. Upon integration the differential equation yields:

$$\ln C_A = -K_A t + \ln C_{Ao}.$$

This form of the first-order equation gives a simple graphical method for the determination of reaction order and specific rate constant. A plot of $\ln C_A$ versus time would yield a straight line with a slope $-K_A$ and intercept $\ln C_{Ao}$.

Plots of this nature were made for the four rates of rock phosphate. They are given in Figure 3. The lines in the graphs were fitted by the method of least squares. Calculated equations for these lines and the values for $\ln C_{Ao}$ are given in Table 1. The pounds of phosphorus per acre added as rock phosphate was taken as C_{Ao}. C_A was calculated by subtracting the amount of phosphorus released by the check at time "t" from the amount of phosphorus released from the respective treatment at time "t" and this in turn was subtracted from C_{Ao}. This assumes that rock phosphate had no appreciable effect on the chemical properties of the soil solution.

Table 1 shows that the intercept of each calculated line is very close to the value of ln C_{Ao}. The slopes of these lines should not have varied. Three possibilities should be considered in explaining this variance. These are analytical error, sampling error and the assumption of non-chemical change of the soil solution by rock phosphate. Sampling error is illustrated in Figure 3 by the scatter of points. Very small quantities of rock phosphate were mixed with the 200 grams of soil which made uniform mixing difficult. Sampling error decreased as amounts of rock phosphate increased. Secondly, the assumption of no effect of rock phos- on the chemistry of the soil solution might not have been true. However, since each rate used satisfies the criteria for first-order reactions this is a useful characterization. These data indicate that the release of phosphorus to the extracting reagent used was dependent only upon the amount of rock phosphate present over the time interval tested.

Analysis of variance and multiple range tests for available phosphorus released from the superphosphate treatments showed that time, treatments and the interaction of time with treatments produced significant differences at the 1% level.

Each additional increment of superphosphate produced a significant increase in available phosphorus released. Weeks 1, 2, and 4 were significantly different from each other and all other weeks. No significant

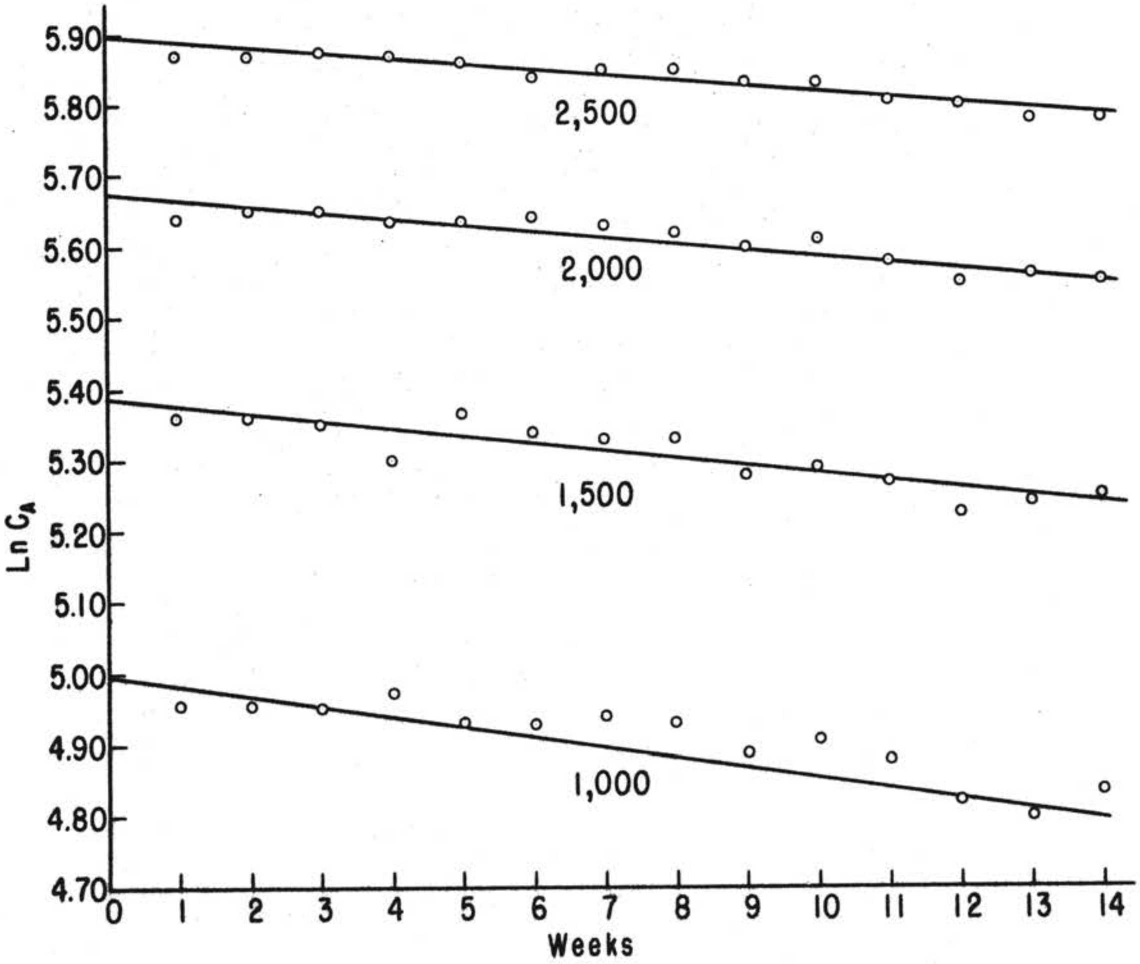

Figure 3. Plot of Ln C_A Against Time for 1,000; 1,500; 2,000 and 2,500 Pounds of Rock Phosphate Per Acre.

difference was found between weeks 5, 6, 7, 8 and 10. A tendency for decreased available phosphorus release after reaching a peak was shown by weeks 9, 11, 12, 13 and 14 being significantly less than weeks 5, 6, 7 and 8.

Interactions of the superphosphate treatments with time are illustrated in Figures 4 and 5. In drawing the line from zero to one week it was assumed that at zero time all the phosphorus added as superphosphate would have been extractable in the Bray and Kurtz reagent. This amount of phosphorus was added to the extractable phosphorus of the original soil to

Table 1

C_{Ao}, Ln C_{Ao} And Equations of Lines Fitted

To the Kinetic Plots

Experimental Values Equation Calculated	Values for Treatment Added C_{Ao} lbs./Ac.	 Ln C_{Ao}
$\ln C_A = -0.01\ t + 4.99$	146.70	4.99
$\ln C_A = -0.01\ t + 5.38$	220.05	5.40
$\ln C_A = -0.008\ t + 5.67$	293.40	5.68
$\ln C_A = -0.008\ t + 5.90$	336.75	5.90

obtain the zero time point. A decrease in available phosphorus from superphosphate after a short term reaction with soil was also found by Laverty and McLean (23).

A plot of ppm. of phosphorus extractable at zero time minus ppm. of phosphorus extractable at one week versus ppm. of phosphorus extractable at zero time is shown in Figure 6. The fact that these data fitted a straight line so well indicates that the mechanism of reduction was the same for all concentrations used and that the amount of reduction was in some manner dependent upon the concentration.

The initial decrease in available phosphorus, as illustrated in Figures 4 and 5, might be explained by a combination of chemical and physical phenomena.

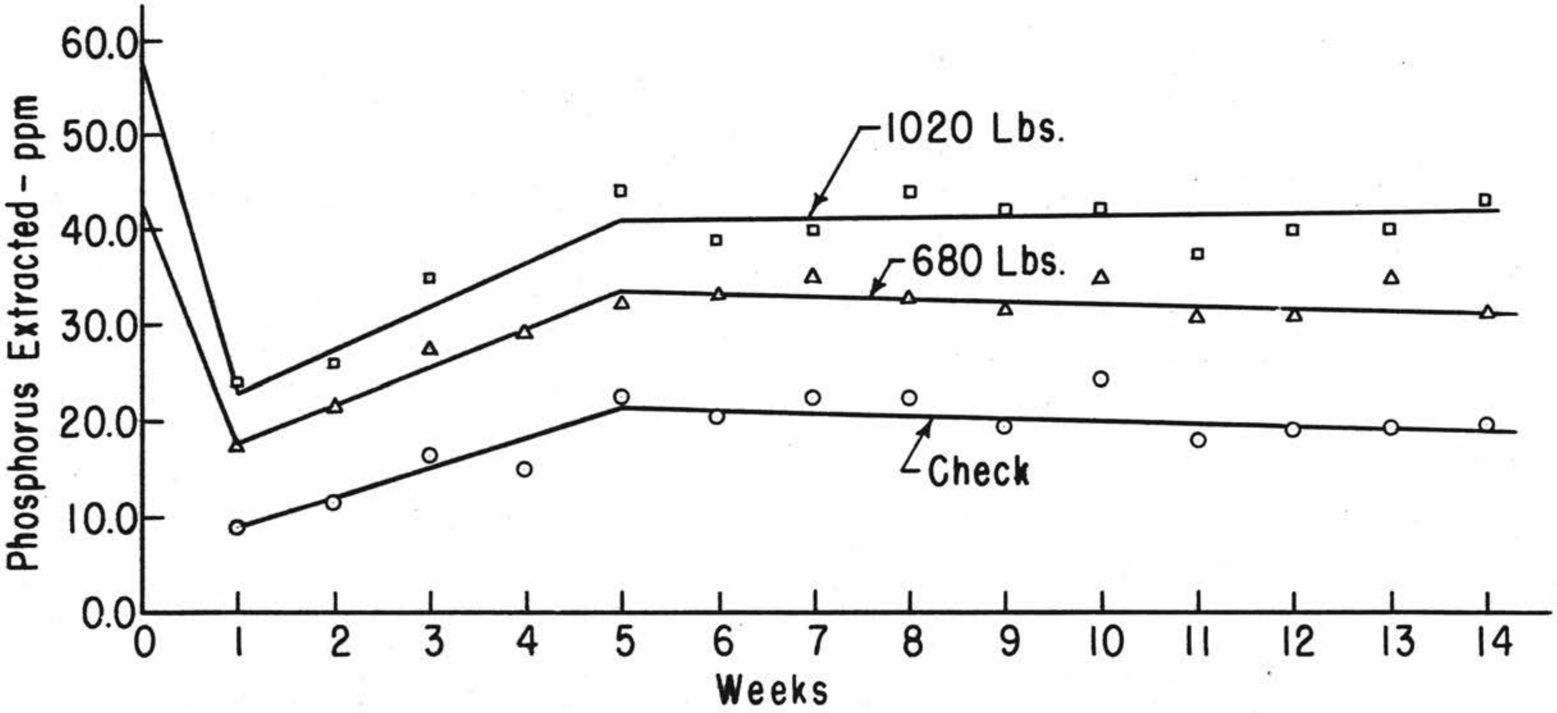

Figure 4. Available Phosphorus Released Versus Time for the Check, 680 and 1,020 Pounds of Superphosphate Per Acre.

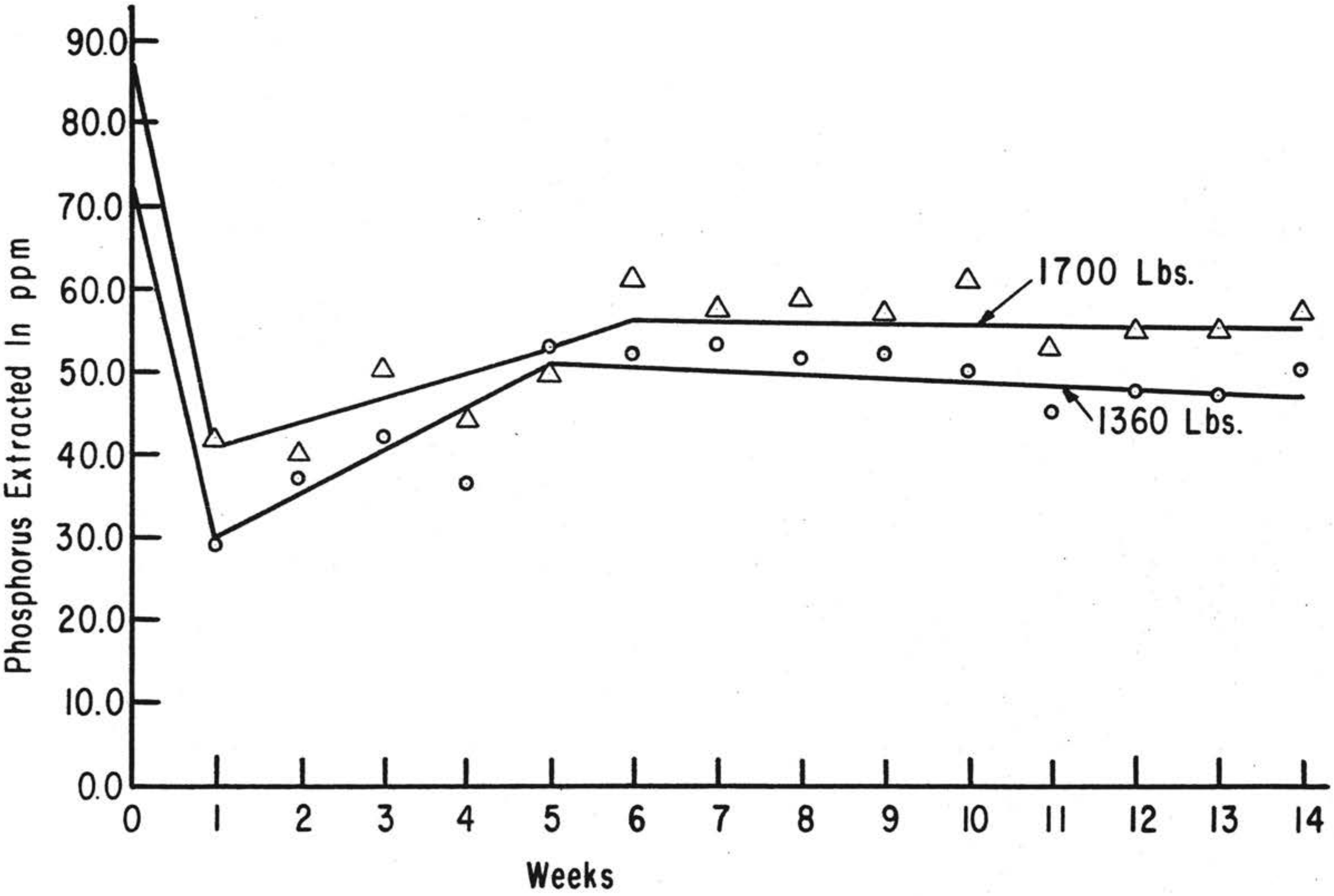

Figure 5. Available Phosphorus Released Versus Time for 1,360 and 1,700 Pounds of Superphosphate Per Acre.

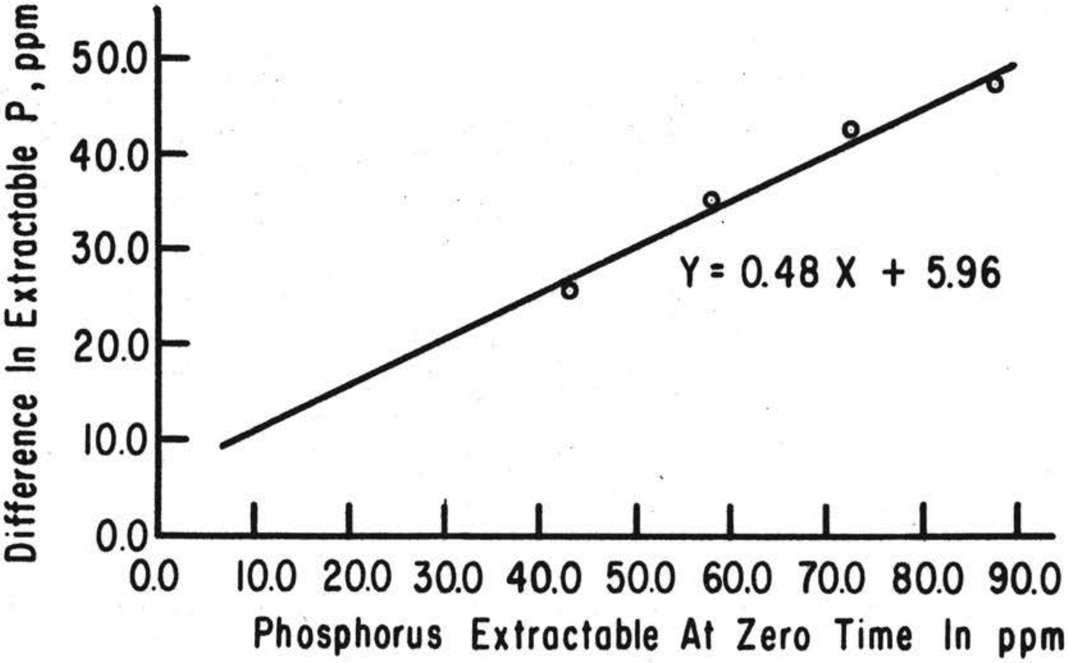

Figure 6. Plot of Available Phosphorus Extractable at Zero Time in ppm. Minus Available Phosphorus Extractable at one Week in ppm. Against Extractable Phosphorus at Zero Time in ppm.

When superphosphate was added to the moist acid soil it changed the chemistry of the soil solution. A large decrease in pH occurred with subsequent solution of iron, aluminum, and calcium compounds (24, 25). As time passed, the buffering system of the soil plus movement of compounds outward from the zone of concentration caused the pH to approach its original level.

Low solubility of phosphorus compounds at the end of one week might have been an effect of mixed compounds and low degrees of crystallinity. Increased solubility with time, 1 to 5 weeks, might be attributed to the formation of purer compounds with a higher degree of crystallinity.

According to the data in Figures 4 and 5, five weeks produced optimum conditions. The decrease in solubility noted after this period might be explained on the basis of physical phenomena.

Maximum solubility would indicate small crystals. Small crystals would continually go into solution and reprecipitate on other crystals (7). Thus, larger and larger crystals would be formed with a consequent decrease in solubility.

The 1,700 pounds per acre rate of superphosphate apparently did not reach its maximum solubility with the extracting reagent until the sixth week. This would mean, by the foregoing interpretation, that at this rate of superphosphate the buffering system of the soil took longer to compensate for the acid nature of the fertilizer. Apparently up to this point rate had little effect on the recovery time for soil solution pH.

Characterization of the rate of release of available phosphorus from the superphosphate treatments over the 1 to 14 week period could not be accomplished by the use of first-order kinetic criteria. Data for higher order testing were lacking. The effect of superphosphate on the chemistry of the soil solution is thought to be the primary reason for the failure of the system to fit simple first-order kinetic criteria.

Available phosphorus extracted from the soil with the lime treatments alone was not significantly different from the check. The release pattern exhibited by the check is in Figure 1. A change in the rate of release occurred at five weeks as with the other treatments discussed. The increase observed could be due to a conversion of inorganic phosphates (2), mineralization of organic phosphates (6), or both. The shapes of the release curves would be expected for mineralization of organic phosphates. In general, the shapes of these curves follow bacterial population and residue decomposition curves. If conversion of inorganic phosphates was the only mechanism responsible, equilibrium conditions should have been reached and the decrease from 5 through 14 weeks not observed. Both processes could have occurred with mineralization of organic phosphate predominating. The release curves from the lime treatments did not satisfy first-order kinetic criteria.

No significant difference was observed between the four treatments of 2,000 pounds of rock phosphate per acre plus lime or between these treatments and 1,000 pounds of rock phosphate per acre. Although lime depressed the amount of available phosphorus released it did not affect the time necessary for the rate of release to change. This still occurred at five weeks. A slight decrease in available phosphorus release from 5 through 14 weeks was observed. Thus, the release patterns of these treatments did not satisfy first-order kinetic criteria.

Lime added with superphosphate had little effect on the release of available phosphorus until the 100% base saturation level was reached. At the 1% level superphosphate plus lime at 100% of the lime requirement released a significantly greater amount of available phosphorus than superphosphate alone and superphosphate plus lime at 25% of the lime requirement. As with the other superphosphate treatments these did not satisfy first-order kinetic criteria for the rate of release.

CHAPTER IV

Rock Phosphate and Superphosphate Reactions With An Acid Soil and Their Effect on Plant Nutrition. II. Forms of Phosphorus Recovered by Fractionation.[1]

Arthur B. Onken and Lester W. Reed[2]

Abstract

Sugar Drip forage sorghum, Sorghum vulgare Pers., was grown in the greenhouse on Parsons silt loam soil treated with 24 combinations of rock phosphate, superphosphate and lime. Two orders of application, phosphorus equilibrium before lime and lime equilibrium before phosphorus, were used or a total of 48 treatments.

Soil samples were removed from the pots after the plants were harvested to determine the following: Phosphorus fractions, available phosphorus, exchangeable cations and pH. Fertilizer and lime application rates and

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[2] Graduate assistant and Professor of Agronomy, Oklahoma State University, Stillwater, Oklahoma.

the order of application affected the formation of the phosphorus fractions. Available phosphorus was affected in the same way as the phosphorus fractions. It was concluded that rock phosphate and superphosphate formed the same compounds upon application to the soil, but the chemical and physical reactions forming these products were quite different.

Rock Phosphate and Superphosphate Reactions With An Acid Soil and Their Effect on Plant Nutrition. II. Forms of Phosphorus Recovered by Fractionation.

Research reported herein was conducted to determine some of the phosphorus compounds formed by rock phosphate and superphosphate in relation to plant growth, liming and time of application.

Review of Literature

As early at 1868, Warington (41) concluded that iron and aluminum oxides in the soil were responsible for the removal of phosphorus from solution making it unavailable for plant growth. Stoddart (37) found that the ratio of iron and aluminum phosphates to calcium phosphate for acid soils was greater than non-acid soils. Cho and Caldwell (12) found more phosphorus in the aluminum and iron fractions in acid soils and more in the calcium fraction of calcareous soils. However, pH differences between soils did not correlate with the form of phosphorus in the case of acid soils. Hsu and Jackson (22) reported that the solubility and formation of calcium, iron and aluminum phosphates were dependent on pH.

Chang and Jackson (10) fractionated soil phosphorus into iron, reductant soluble iron, calcium and aluminum forms. They found that lime application had little effect on these discrete forms of native phosphorus in fertilized soil. Soluble phosphorus fertilizer increased the amount of aluminum and iron phosphate at all lime levels, but increased calcium phosphate only slightly at the highest lime level. Reductant soluble iron phosphate was not affected by liming or fertilization.

Schaller[3] found that as percent base saturation increased, release of water soluble phosphorus from rock phosphate decreased. A slightly better correlation of release was found with pH than percent base saturation. Heck (21) concluded that increased percent base saturation decreased the ability of soils to combine phosphorus in difficultly available forms. Laverty and McLean (23) found more iron and less aluminum phosphate in soils where solubility to the Bray and Kurtz No. 1 extractant was lowest.

Materials and Methods

Parsons silt loam soil used in this experiment had an exchange capacity of 11.8 me. per 100 gms. Calcium and magnesium dominated the exchange complex. Available phosphorus by the Bray and Kurtz No. 1 extractant as modified by Smith et al. (35) was 27.0 pounds per acre. Total phosphorus determined by the method of Shelton and Harper (34), was 570 pounds per acre. The soil contained 2.55% organic matter. Percent moisture at 1/3 atmosphere was 27.0. The soil pH was 5.3.

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[3] Schaller, C. C. Effect of base saturation, pH and exchange capacity on the release of phosphorus from acid soils containing rock phosphate. Unpub. M.S. thesis, Oklahoma State University, Stillwater, Oklahoma, 1960.

Rock phosphate used in this experiment was Florida land pebble rock phosphate containing 14.67% total phosphorus as determined by the method recommended by the Association of Official Agricultural Chemists (3). This material was ground to 200 mesh before use. Superphosphate was made with reagent grade monocalcium phosphate and gypsum. Reagent grade $CaCo_3$ was used as the liming material.

Two gallon glazed stoneware crocks were filled with 7,000 grams of air dry Parsons soil. Half the pots initially received four rates of rock phosphate and one rate of superphosphate. Rock phosphate was applied at 0, 1,000, 1,500, 2,000 and 2,500 pounds per acre; superphosphate at 1,360 pounds per acre. The pots were brought to approximately 1/3 atmosphere of moisture tension, by weight, with distilled water and covered with aluminum foil and white plastic. There were allowed to equilibrate for six weeks. This was the length of time, as indicated by a laboratory study previously reported, necessary for the rate of release of phosphorus to the Bray and Kurtz extraction to start decreasing.[4] The other half of the pots were limed at 0, 25, 50, and 100% of the lime requirement. At the end of five weeks of the equilibration period for phosphorus, the limed pots were brought to 1/3 atmosphere of moisture tension, covered and then allowed to equilibrate for one week. Laboratory results indicated that at the end of one week the calcium carbonate would be approaching equilibrium with the soil.

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[4] Onken, Arthur B. and Reed, Lester W. Rock phosphate and superphosphate reactions with an acid soil and their effect on plant nutrition. 1. Rates of reaction. Soil Sci. Soc. of Amer. Proc. in press.

The covers were removed from all pots at the end of the equilibration period. The pots were allowed to dry to a moisture condition conducive to the handling required by the next phase in the soil preparation.

The soil was removed from each pot; rescreened and additional treatments were applied. Lime was added at 0, 25, 50, and 100% of the lime requirement to the phosphorus equilibrium pots. Lime pots received rock phosphate at 0, 1,000, 1,500, 2,000, and 2,500 pounds per acre and superphosphate at 1,360 pounds per acre, making a total of 48 treatments. Thus, two situations were attained: 1. Phosphorus sources approaching equilibrium with the soil before lime as added. 2. Lime approaching equilibrium with the soil before application of phosphorus sources. The pots were placed on a bench in the greenhouse in a randomized block design with three replications.

Simultaneously, with the second set of treatments, 200 pounds of nitrogen per acre as urea were added plus potassium at 4% of the cation exchange capacity as potassium chloride. Each treatment was mixed thoroughly with the total soil mass. The soil was returned to the pots and planted to Sugar Drip forage sorghum, Sorghum vulgare Pers., on July 4, 1960. Distilled water was added to bring the pots to approximately 1/3 atmosphere of moisture tension. The amount of water necessary was determined by weighing. Plants started emergine on the third day and were periodically thinned until four plants remained per pot. Moisture in all pots was maintained at 1/3 atmosphere.

The plants were harvested twenty-four days after emergence. Soil samples were removed from the pots in the three days following harvest, then air dried and crushed to pass a 20 mesh sieve. Fractionation of the soil phosphorus into water soluble and loosely bound, aluminum, iron and calcium phosphorus fractions was carried out by the method described by Chang and Jackson (10). Available phosphorus was determined by the Bray and Kurtz No. 1 extraction as modified by Smith et al. (35). Exchangeable cations were determined by the method of Peech et al. (28). Soil reaction was determined on a soil-water saturation paste with a Beckman Zeromatic pH meter.

Results and Discussion

Rock phosphate and superphosphate will be discussed together under each variable, to compare the respective chemical systems involved.

Water Soluble and Loosely Bound Phosphorus Applications of 2,000 and 2,500 pounds of rock phosphate per acre produced significant increases in this fraction, at the 5% level, over the check. No significant difference was found between the four rates of rock phosphate applied. The range of this fraction extracted was 2 to 3 pounds of P per acre. It might be that below this concentration the sorghum was not capable of removal of this fraction, but any amount above this level was removed. Or, it might be that between harvest and when the soil samples dried out, equilibrium was established between this fraction and the rock phosphate.

Application of superphosphate increased the amount of this fraction found at the 1% level. In contrast to rock phosphate, the amount of this fraction extracted from the superphosphate treatments was dependent upon order of application (lime or fertilizer equilibrium). This was significant at the 5% level. Application of superphosphate after lime equilibrium yielded the most water soluble and loosely bound phosphorus.

Aluminum Phosphate Formation of aluminum phosphate from applying rock phosphate was significantly affected at the 1% level by order of application, amounts of lime and rock phosphate applied and the interaction of order with rock phosphate. The interaction of order with lime was significant at the 5% level.

Phosphorus equilibrium conditions were more conducive to aluminum phosphate formation from rock phosphate than lime equilibrium conditions. This was probably due to a longer reaction time and the solubility depressing effect of the common ion calcium.

Rate of lime had no statistically significant effect on the formation of aluminum phosphate when rock phosphate was allowed to react with the soil first. However, when lime was allowed to equilibrate with the soil there was a large reduction in aluminum phosphate. This reduction was significant at 25% of the lime requirement, but from 25% to 100% of the lime requirement, the amounts formed were not significantly different. There was probably enough calcium in solution at the 25% lime level to reduce the solubility of the rock phosphate enough so that additional amounts had little effect.

Considering both orders and all lime levels, only the 2,000 pound per acre rate of rock phosphate did not yield a significant increase in aluminum phosphate over the next lowest treatment. As the application rate of rock phosphate increased the formation of aluminum phosphate increased. However, the increase in aluminum phosphate formed per unit of rock phosphate was greater for phosphate equilibrium than lime equilibrium. Here again, the difference in order is thought to be a result of the same two factors previously discussed.

Correlations of the amount of aluminum phosphate extracted with exchangeable calcium and pH were poor.

Formation of aluminum phosphate in the superphosphate treated soil was affected, at the 1% level, by order of application, application of superphosphate and by the interaction of order with superphosphate application.

Adding superphosphate to the soil significantly increased the amount of aluminum phosphate extracted.

In contrast to the rock phosphate treatments, aluminum phosphate formation was increased by allowing the soil to come to equilibrium with lime before adding superphosphate. However, the added lime had no effect.

Iron Phosphate For the rock phosphate treatments, formation of iron phosphate was affected at the 1% level by order of application, lime level, rock phosphate level, the interaction of order with lime level and the interaction of order with rock phosphate level.

With each increasing increment of rock phosphate applied, the amount of iron phosphate extracted was significantly higher.

As with the formation of aluminum phosphate, phosphorus equilibrium conditions favored iron phosphate formation over those of lime equilibrium. The amount of iron phosphate formed per unit of rock phosphate added was greater for phosphorus than lime equilibrium conditions.

Lime level and the interaction of order with lime level also affected iron phosphate formation in much the same way as aluminum phosphate formation. The amount of iron phosphate extracted was significantly reduced by the first increment of lime added and was not significantly reduced further by the other two increments. Lime had little affect on the amount of iron phosphate formed under phosphorus equilibrium conditions, but that formed under lime equilibrium conditions was greatly reduced by application of lime.

The correlation coefficients between iron phosphate and aluminum phosphate in Table II further substantiate that both of these fractions were affected by the treatments in much the same way. Exchangeable calcium and pH did not appear to be related to the amount of iron phosphate extracted.

Factors that affected the amount of iron phosphate extracted from the superphosphate treatments were as follows: at the 1% level, order of application and addition of superphosphate; at the 5% level, the interaction of order with lime and the interaction of order with superphosphate.

As with aluminum phosphate, addition of superphosphate after lime equilibrium yielded more iron phosphate than phosphorus equilibrium.

In contrast to the formation of aluminum phosphate from superphosphate and in keeping with the formation of aluminum and iron phosphates from rock phosphate, iron phosphate formation from superphosphate was affected by the interaction of order with lime. Although the amount of iron phosphate formed with order was opposite that for rock phosphate, the effects of lime on each order were comparable. The first increment of lime greatly decreased the formation of iron phosphate for lime equilibrium conditions, while for phosphorus equilibrium conditions, all levels of lime had little effect. However, even with this decrease, lime equilibrium conditions produced more iron phosphate. The effect of lime would, therefore, appear to be more than a simple solubility effect.

<u>Calcium Phosphate</u> The amount of calcium phosphate extracted from the soil treated with rock phosphate was affected at the 1% level by order of application, amount of rock phosphate applied and the interaction of order

Table II

Correlation Coefficients Between Iron and Aluminum Phosphates for each Order of Application and Lime Level over all Rock Phosphate Levels

Lime Level*	Order No. 1	Order No. 2
0%	0.881	0.818
25%	0.787	0.882
50%	0.849	0.902
100%	0.825	0.924

*As percent of lime requirement

with rock phosphate level. If iron and aluminum phosphates were formed from some of the phosphorus of rock phosphate, it would be expected that factors favoring their formation would tend to decrease the amount of calcium phosphate extracted.

This was found to be true for order of application; lime equilibrium conditions favored calcium phosphate extraction. However, rate of rock phosphate and lime level did not follow the expected pattern.

With each additional increment of added rock phosphate, calcium phosphate extracted significantly increased. In conjunction with this, the fact that the untreated soil contained an average of about 15 pounds per acre of calcium phosphate indicates that most of the calcium phosphate extracted was from unchanged rock phosphate.

The order with rock phosphate interaction was a result of no order effect on the check pots, over all lime levels, and then having more aluminum and iron phosphates released under phosphorus equilibrium conditions. The increase in extracted calcium phosphate for each increment of added rock phosphate, above 1,000 pounds per acre, was the same for both orders. Neither pH nor exchangeable calcium correlated with the amount of calcium phosphate extracted.

The amount of calcium phosphate extracted from the soil treated with superphosphate was affected, at the 1% level, by order of application and addition of superphosphate and, at the 5% level, by lime level and the interaction of order with lime.

Lime equilibrium conditions were, when considered over all other treatments, more conducive to calcium phosphate formation from the phosphorus of superphosphate than phosphorus equilibrium conditions. The effects of lime added to each order were quite different. The first increment of lime added to the lime equilibrium treatments decreased the amount of calcium phosphate extracted while each additional increment added had little effect. For the phosphorus equilibrium treatments, the first increment of lime had little effect, but each increment increase after that increased the amount of calcium phosphate extracted. At the 100% lime level phosphorus equilibrium conditions yielded the most calcium phosphate, but the increase over lime equilibrium conditions was small. Lime effect on the phosphorus equilibrium treatments might be explained by additional amounts of calcium being present and thereby promoting the formation of calcium phosphate. However, as previously suggested, the lime effect on the lime equilibrium treatments appears to be more than a simple solubility effect.

The effects of lime level, when taken over both orders, were not so well defined. Only lime at the 25% level produced a significant increase in calcium phosphate over the check and it was not significantly different from the 50% and 100% lime levels.

Recovery of Added Phosphorus by Fractionation Percent recovery of added phosphorus was calculated by subtracting the amount of phosphorus found in the appropriate check from the amount of phosphorus found in the treatment and dividing by the amount of phosphorus added as rock phosphate or superphosphate. A greater percent recovery was made from the rock phosphate treatments under lime equilibrium conditions as shown in Table III. Since the check was subtracted out to calculate percent recovery, it would appear that either sampling error played a large role or rock phosphate added in mineralization of organic phosphate by increasing the number of microorganisms (40).

Percent recoveries of added phosphorus for the superphosphate treatments are given in Table IV. Mineralization of organic phosphorus apparently occurred under both orders of application to account for the high percent recovery. Since the appropriate check was subtracted out in calculation of each percent recovery, the application of superphosphate must have promoted mineralization by increasing the number of microorganisms in the soil (40). Except for the 1,360 pounds per acre superphosphate treatment at 0% lime, a greater percent phosphorus was extracted from the treatments under lime equilibrium conditions.

The favoring of organic phosphorus mineralization by lime equilibrium conditions could have been due to the acid nature of the superphosphate. As stated previously superphosphate produces a very acid condition when placed in the soil. This strongly acid environment would not have been conducive to the growth of microorganisms. With lime being in equilibrium before the addition of the superphosphate, the acidic effect of the

Table III

Percent Recovery of Added Phosphorus, by Fractionation, From the Rock Phosphate Treatments

Treatment*	Lime Equilibrium	Phosphorus Equilibrium
R. P. -1000 L-0%	83.22%	89.18%
R. P. -1500 L-0%	100.92%	102.81%
R. P. -2000 L-0%	117.16%	98.98%
R. P. -2500 L-0%	99.74%	105.20%
R. P. -1000 L-25%	117.59%	95.15%
R. P. -1500 L-25%	117.02%	100.55%
R. P. -2000 L-25%	116.31%	101.26%
R. P. -2500 L-25%	104.06%	108.38%
R. P. -1000 L-50%	122.70%	100.54%
R. P. -1500 L-50%	111.30%	108.12%
R. P. -2000 L-50%	112.05%	106.79%
R. P. -2500 L-50%	103.94%	102.59%
R. P. -1000 L-100%	112.77%	98.55%
R. P. -1500 L-100%	104.52%	103.57%
R. P. -2000 L-100%	106.94%	107.93%
R. P. -2500 L-100%	113.60%	102.48%

*R. P. = Rock Phosphate expressed in pounds per acre

L = Lime as percent of the lime requirement

Table IV

Percent Recovery of Added Phosphorus, by Fractionation, From the Superphosphate Treatments

Treatment*	Lime Equilibrium	Phosphorus Equilibrium
S. P. -1360 L-0%	132.70%	142.87%
S. P. -1360 L-25%	185.80%	134.80%
S. P. -1360 L-50%	155.15%	137.60%
S. P. -1360 L-100%	143.32%	135.85%

*S. P. = Superphosphate expressed in pounds per acre

L = Lime as percent of the lime requirements.

superphosphate would have lessened. Thus, an environment more conducive to microorganism growth would have been produced. Also, during the period of lime equilibration the population of microorganisms could have increased.

It is concluded that rock phosphate and superphosphate formed the same compounds on application to the soil, but the chemical and physical reactions forming these products were quite different.

Available Phosphorus For the rock phosphate treatments significant differences, at the 1% level, of available phosphorus released were produced by order of application, lime level, rate of rock phosphate, the interaction of order with rock phosphate and the interaction of lime with rock phosphate.

Phosphorus equilibrium conditions, decreasing lime levels and increasing rates of rock phosphate were conducive to increased release of available phosphorus from the rock phosphate treatments. The increase in available phosphorus per unit increase in rock phosphate added was greatest for phosphorus equilibrium conditions. Regardless of lime level, increasing rock phosphate increased the amount of available phosphorus released.

Release of available phosphorus followed a pattern similar, with respect to treatment effects, to that of aluminum and iron phosphates. Thus, the treatments promoting the change of the phosphorus of rock phosphate to aluminum and iron phosphates increased the release of available phosphorus. These findings are further substantiated by the correlation coefficients in Table V. The correlation coefficients between available phosphorus and calcium phosphate show the relationship of increasing rates of rock phosphate producing an increase in available phosphorus.

For available phosphorus released from the superphosphate treatments, order of application, lime level, application of superphosphate and the interaction of order with superphosphate application produced significant differences at the 1% level in the amount of available phosphorus extracted.

Lime equilibrium, application of superphosphate and no lime produced conditions that released the most available phosphorus.

The release of available phosphorus from the superphosphate treatments followed closely the extration patterns of aluminum, iron and calcium phosphates.

Table V

Correlation Coefficients Between Available Phosphorus And Aluminum, Iron and Calcium Phosphates for Each Order of Application and Lime Level over all Rock Phosphate Levels

Lime Level*	Order No. 1	Order No. 2
	Aluminum Phosphate	
0%	0.841	0.840
25%	0.843	0.938
50%	0.777	0.910
100%	0.937	0.937
	Iron Phosphate	
0%	0.774	0.949
25%	0.903	0.942
50%	0.811	0.919
100%	0.854	0.943
	Calcium Phosphate	
0%	0.782	0.942
25%	0.856	0.880
50%	0.861	0.873
100%	0.719	0.901

* As percent of the lime requirement

Chapter V

Summary and Conclusions

This investigation was concerned with two objectives. These were: 1. To determine the pattern of phosphorus release with time from an acid soil treated with lime, rock phosphate and superphosphate. 2. To determine some of the compounds formed by the phosphorus of rock phosphate and superphosphate as influenced by plant growth, liming and time of application. In order to carry out these objectives two experiments were designed and conducted, a laboratory experiment and a greenhouse experiment.

The laboratory experiment was conducted to determine the pattern of release of phosphorus with time from an acid soil treated with lime, rock phosphate and superphosphate. The experiment consisted of placing Parsons silt loam soil in beakers with a total of 21 treatments consisting of lime, rock phosphate and superphosphate. These were equilibrated for 14 weeks at 1/3 atmosphere of moisture tension. Each week a soil sample was removed from each beaker and available phosphorus determined by the Bray and Kurtz No. 1 method as modified by Smith et al. (35).

The rate of release of available phosphorus from the rock phosphate treated soil was found to fit over the time interval investigated, a first-order kinetic relation. Rate of release of phosphorus from the soil treated with superphosphate presented a much more complex situation. A large decrease in available phosphorus occurred in the first week and was related to the amount of phosphorus added. From the first week through the fifth week an increase in available phosphorus occurred. A decrease in available phosphorus released occurred from 5 through 14 weeks. A tentative explanation of this behavior is presented. This explanation is based on the effect of superphosphate on the chemistry of the soil solution.

Superphosphate added to a moist soil produces a large decrease in pH with subsequent solution of iron, aluminum and calcium compounds. After a period of time the soil buffering system brings the pH back to its original level.

Low solubility of phosphorus compounds at the end of one week might have been due to mixed compounds and low degrees of crystallinity. Increased solubility from 1 to 5 weeks, might be attributed to the formation of purer compounds with a higher degree of crystallinity.

Maximum solubility would indicate small crystals. The observed decrease in solubility from 5 to 14 weeks might have been due to the small crystals continually going into solution and reprecipitating on larger crystals.

Thus, it is concluded that rock phosphate had little effect on the chemistry of the soil solution while superphosphate had a large effect.

Sugar Drip forage sorghum was grown in the greenhouse on Parsons silt loam soil treated with 24 combinations of rock phosphate, superphosphate and lime. The orders of application, phosphorus equilibrium before lime and lime equilibrium before phosphorus, were used or a total of 48 treatments.

Soil samples were removed from the pots after the plants were harvested to determine the following: Phosphorus fractions, available phosphorus, exchangeable cations and pH. Fertilizer and lime application rates and the order of application affected the formation of the phosphorus fractions. Available phosphorus was affected in the same way as the phosphorus fractions. It was concluded that rock phosphate and superphosphate formed the same compounds upon application to the soil, but the chemical and physical reactions forming these products were quite different.

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APPENDIX

Table VI

PROFILE DESCRIPTION OF PARSONS SILT LOAM[1]

Samples were taken 825 feet east and 330 feet north of the southwest corner of Section 18, Township 5 North; Range 19 East, on the Wilburton station in Latimer county.

Parsons silt loam is a Planosol developed on acid clay shales and is found on upland flats having nearly level relief.

A_1	0-10"	Light brownish-gray (10 YR 6/2; 4/2 moist) silt loam; weak medium granular; friable; permeable; pH 6.0; occasional fine pores and root holes; grades to layer below.
A_2	10-16"	Very pale brown (10 YR 7/3; 6/3 moist) silt loam with a few light yellowish-brown spots and dark brown ferruginous films; weak granular; friable; pH 6.0; contains a few fine and medium black concretions and rests abruptly on the layer below.
B_2-1	16-24"	Yellowish-brown (10 YR 5/4; 4/4 moist) clay; weak fine blocky; very firm; very slowly permeable; pH 6.0; a few specks of light yellowish-brown and a few round black concretions; sides of peds slightly darker than the interiors; grades to layer below.
B_2-2	24-42"	Yellowish-brown (10 YR 5/5; 4/5 moist) clay; weak medium blocky; very firm; very slowly permeable; pH 6.5; many fine black concretions; occasional gypsum crystals in the

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[1] Description by H. M. Galloway.

lower part. This layer seems slightly more compact than the B_2-1 and grades to the layer below.

C_1 42-52" Light yellowish-brown (10 YR 6/4; 5/4 moist) clay with a few streaks of grayish-brown and a few strong brown specks; weak blocky; firm; slowly permeable; pH 7.0; numerous ferruginous films and fine black concretions; less compact than the B_2-2 and contains occasional water-worn sandstone and silt-stone pebbles and an occasional small posket lined with gypsum crystals. No shale partings were evident in the deepest material sampled.

VITA

Arthur Blake Onken

Candidate for the Degree

Master of Science

Thesis: PHOSPHATE FERTILIZER REACTIONS UNDER VARIOUS SOIL CONDITIONS

Major: Agronomy (Soils)

Biographical:

Personal data: Born August 13, 1935, in Alice, Texas, son of Arthur R. and Iley Belle Onken.

Education: Graduated from William Adams High School, Alice, Texas 1953. Undergraduate work at the Agricultural and Mechanical College of Texas 1953 to 1955 and Texas College of Arts and Industries 1955 to 1959. Graduate study at Oklahoma State University, 1959 to 1963.

Experience: Worked during summers of 1950 through 1953 in sheet metal and plumbing shop. Employed by Texaco as roustabout, draftsman and rod and chainman during summers of 1954 and 1955. Worked for Chiles Drilling Company during summers of 1956, 1958 and 1959. Part time employment as laboratory technician for Bureau of Reclamation during school years of 1957 through 1959 and summer of 1957. Graduate assistant, Oklahoma State University 1959 to 1963.

Member: Alpha Tau Alpha, Alpha Chi, Society of Sigma Xi, American Society of Agronomy and Soil Science Society of America.

Date of final examination: July, 1963.