AVAILABILITY OF ALUMINUM, IRON, AND CALCIUM PHOSPHATES IN SOILS

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
James Ray Melton
1964

ABSTRACT

AVAILABILITY OF ALUMINUM, IRON, AND CALCIUM PHOSPHATES IN SOILS

by James Ray Melton

Greenhouse experiments were conducted to study two methods for measuring the relative availability of different forms of soil phosphorus to plants. Measuring the change in soil phosphorus both before and after cropping appeared to give reliable information concerning the relative availibility of aluminum, iron, and calcium phosphates.

The change in aluminum phosphate during cropping was highly correlated with the initial aluminum phosphate content of the soils. Soils containing greater than 58 ppm phosphorus as aluminum phosphate lost aluminum phosphate during cropping, and soils containing less than 58 ppm aluminum phosphate gained aluminum phosphate during cropping.

Iron phosphate contributed significantly to the phosphorus change in five of the six soils studied.

The calcium phosphate in acid Warsaw, Plainfield, Kalamazoo and Iron River soils was more available than the calcium phosphate in two calcareous soils. Calcium

phosphate in the calcareous Gilford soil was apparently more available than that in the Conover soil, even though they both had the same pH.

The correlation coefficient between the change in aluminum, iron, and calcium phosphates during cropping and a function of the initial aluminum, iron, and calcium phosphate content of the soils [$F = 0.59(\text{Al phos.} - 57) + 0.49(\text{Fe phos.} - 72) + 1.0$ or $0.1 (\text{Ca phos.} - 62)$] was significant.

AVAILABILITY OF ALUMINUM, IRON,
AND CALCIUM PHOSPHATES
IN SOILS

By

James Ray Melton

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Soil Science

1964

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation and gratitude to Dr. B. G. Ellis for his helpful suggestions and guidance throughout the course of this investigation, and also in the preparation of the thesis. Grateful acknowledgment is also extended to Gary M. Lessman for taking photographs of various portions of the greenhouse experimentation. The ideas presented by Dr. E. C. Doll, and the securing of soil samples by Mr. Akira Suzuki and Drs. K. Lawton, and E. C. Doll are gratefully acknowledged. Also, appreciation is extended to my wife, Sue R. Melton, for typing the rough draft and for giving untiring moral support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Phosphorus has long been recognized as an essential element for plant growth. The low availability of soil phosphorus to plants, however, was not recognized until 1850 when it was reported in Europe that soil had the ability to retain phosphorus. The greatest efforts in understanding the basic chemistry of the phosphorus-plant relationships have been made since 1930 (20).

Many investigators (22, 30, 49) have reported that the predominant form of phosphorus available for plants was some form of calcium phosphates. Chang and Juo (6), however, found a high correlation between soils that contained large quantities of iron phosphate and the availability of phosphorus as determined by employing extractants that had been used most often by soil scientists. Suzuki, et al. (41), on the other hand, found a high correlation between soils that contained large quantities of aluminum phosphate and the availability of phosphorus as determined by methods similar to those studied by Chang and Juo. None of these investigators directly determined the quantity of calcium, iron, and aluminum phosphates removed from the soil by plants.

This investigation was, therefore, designed to study the relative availability of different soil phosphorus forms to plants. The objectives of this study were:

1. To compare two methods of determining the change in aluminum, iron, and calcium phosphate during cropping.

2. To determine the relative availability of aluminum, iron and calcium phosphate.

REVIEW OF LITERATURE

Availability of Iron, Aluminum, and Calcium Phosphates

Variscite, strengite, and a variscite-barrandite-strengite crystal series were formed when phosphorus fertilizers were added to acid soils that contained soluble iron and aluminum (8). The formation of these compounds was explained on the basis of solubility product principal (25, 26).

Chang and Jackson (5) derived pK values for strengite as follows:

$$FePO_4 + 2H^+ \longrightarrow Fe^{+3} + H_2PO_4^-$$

$$K = (Fe^{+3})\ (H_2PO_4^-)\ (OH^-)^2$$

$$pK = pFe^{+3} + pH_2PO_4^- + 2pOH^-$$

The pK values were determined as 33.6 to 35.1 when 0.1 to 10 grams of iron phosphate were suspended in 0.05M KCl and heated, and the pK values ranged from 33.0 to 33.2 when 0.12 to 6.0 millimoles of NaH_2PO_4 and 0.04 to 2.0 millimoles of $FeCl_3$ were added to 120 milliliters of 0.05 M KCl solution and digested in a water bath with occasional shaking each day. An average value of 33.5 was suggested as a good representation of the pK value.

Cole and Jackson (8) derived pK values for variscite as follows:

$$AlPO_4 + 2H^+ \longrightarrow Al^{+3} + H_2PO_4^-$$

$$K = (Al^{+3})\ (H_2PO_4^-)\ (OH^-)^2$$

$$pK = pAl^{+3} + pH_2PO_4^- + 2pOH^-$$

An average pK value of 28 was obtained upon addition of 0.10 to 5.00 grams of variscite to 50 milliliters of water. A pK value of 29.2 was found when 1 to 10 grams of kaolinite were added to 0.10 grams variscite.

Lindsay, et al. (31) found the pK value of a highly purified synthetic variscite to be 30.5 at 25° C. They obtained solubility data which indicated that intermediate products were more soluble than variscite, but were transformed into variscite when aged. Equilibrium for the ionization of variscite was obtained very slowly.

According to Bray and Dickman (1), all phosphorus fractions contributed significantly to plant growth. All the adsorbed fractions increased when soluble sources of phosphorus were added to the soil, but rock phosphate was converted to adsorbed forms only at pH 4.8 to 5.0. Rock phosphate was effective for plant growth up to a certain point; beyond this point addition of soluble phosphates was required for maximum yields.

Hsu and Jackson (22) found that the solubilities of iron and aluminum phosphates, represented by strengite and variscite respectively, were very close in the pH range of most soils. Solubilities of iron and aluminum phosphates were approximately equal to calcium phosphate--represented by hydroxyapatite--at a pH range of 6 to 7. Cation activities of aluminosilicates, calcium carbonate, gibbsite, hydrous iron oxides, exchangeable calcium, and possibly soluble salts were largely responsible for the solubilities of phosphates between pH 6 and 7.

Taylor, et al. (43) studied the availability of seven iron and aluminum phosphates for three successive crops of corn grown in a phosphorus deficient soil in the greenhouse. Potassium taranakite, $H_6K_3Al_5(PO_4)_8 \cdot 18\ H_2O$, calcium ferric phosphate, $H_4CaFe_2(PO_4)_4 \cdot 5H_2O$, colloidal iron phosphate, and colloidal aluminum phosphate were relatively good sources of phosphorus. Acidic potassium iron phosphate, $H_8KFe_3(PO_4)_6 \cdot 6H_2O$ was found to be practically unavailable and synthetic aluminum and iron leucophosphates, $KAl_2(PO_4)_2OH \cdot 2H_2O$ and $KFe_2(PO_4)_2OH \cdot 2H_2O$, were only slightly available for plant growth.

Lindsay and DeMent (29) studied the availability of four iron phosphates and fluorapatite for three successive crops of corn grown in the greenhouse. Strengite was completely unavailable in acid soils and only slightly available when soils were limed to pH 7.6. Hydrogen ammonium ferric phosphate, $H_8NH_4Fe_3(PO_4)_8 \cdot 6H_2O$, was approximately 70 per cent as available as monocalcium phosphate and increased proportionally with cropping. The two colloidal ferric phosphates were approximately 78 per cent as available as monocalcium phosphate and increased proportionally with cropping and liming. Fluorapatite was of very low availability for plant growth in basic soils.

According to Huffman, et al. (23) strengite and colloidal ferric phosphate were readily soluble in stable triple point solution. Calcium ferric phosphate, $H_4CaFe_2(PO_4)_4 \cdot 5H_2O$, was much more soluble in water than strengite and colloidal ferric phosphate. Strengite and colloidal ferric phosphate were approximately equally soluble in water, but both had a lower solubility than fluorapatite. Strengite and colloidal ferric phosphate were found to be similar in availability for plant growth.

Lindsay and Moreno (30) selected a calcium ion concentration of 0.005 M and assumed the activity of water to be unity in deriving equations to express the solubilities of strengite, variscite, dicalcium phosphate dihydrate, octacalcium phosphate, hydroxyapatite, and fluorapatite. These respective equations are as follows:

(1) $pH + pH_2PO_4 = pK_v - pK_g + pK_w$

$pH_2PO_4 = 10.7 - pH$

*(2) $pH + pH_2PO_4 = pK_{st} - pK_{gt} + pK_w$

$pH_2PO_4 = 10.9 - pH$

---

*Values of 38.1 for pK_{gt} and 35.0 for pK_{st} were adopted.

*(3) $-pH + pH_2PO_4 = pk_{dcpd} - pK_2 - pCa$

$$pH_2PO_4 = -3.14 + pH$$

(4) $-5pH + 3pH_2PO_4 = pK_{ocp} - 3pK_2 - 3pK_3 - 4pCa$

$$pH_2PO_4 = -7.22 + 5/3\ pH$$

(5) $-14pH + 6pH_2PO_4 = pK_{ha} - 6pK_2 - 6pK_3 - 2pK_w - 10pCa$

$$pH_2PO_4 = -9.40 + 7/3\ pH$$

(6) $-12pH + 6pH_2PO_4 = pK_{fa} - pK_{ft} - 6pK_2 - 6pK_3 - 9pCa$

$$pH_2PO_4 = -5.18 + 2pH$$

These investigators found that strengite, variscite, hydroxyapatite, and fluorapatite came to equilibrium with soil solution very slowly, but dicalcium phosphate, octacalcium phosphate, and the more soluble alkali and ammonium iron and aluminum phosphates dissolved or precipitated rapidly thereby regulating the phosphorus acitivty in solution. The less soluble compounds attained equilibrium so slowly that Lindsay and Moreno suggested that solubility measurements for these compounds found in soils probably did not represent any known solubility product.

Lehr, et al. (28) observed pellets of monocalcium phosphate monohydrate after placement in several soils. Capillary flow seemed to be principally responsible for the movement of phosphorus away from the pellets, the necessary moisture apparently transported to the pellet in the vapor phase. Significant quantities of anhydrous or

---

*The expressions pK_2 and pK_3 are equibalent to products in equations 1 and 2 respectively.

dihydrated dicalcium phosphate were discovered at the pellet site after dissolution of the monocalcium phosphate monohydrate; the dissolution process was affected by soil moisture content, humus content, soil type, capillarity of pellet and soil, temperature, and microbiological activity.

Lindsay and Stephenson (32) found rapid dissolution of monocalcium phosphate monohydrate for a few minutes while shaking with water at room temperature, but between one and twenty four hours the solution was in equilibrium with newly formed dicalcium phosphate dihydrate and undissolved monocalcium phosphate monohydrate. However, the dicalcium phosphate dihydrate later began to dissolve and anhydrous dicalcium phosphate slowly precipitated. Equilibrium was finally attained between undissolved monocalcium phosphate monohydrate and anhydrous dicalcium phosphate.

Moisture accumulated near the fertilizer band when Lindsay and Stephenson (32) banded monocalcium phosphate monohydrate in soil. The solution at the fertilizer pellet had a very similar composition to that of metastable triple point solution consisting of 3.98 M phosphorus, 1.44 M calcium, and pH 1.48. This highly concentrated solution moved away from the fertilizer band into the drier surrounding soil and dissolved iron, aluminum, manganese, and other constituents. The solution continued to move farther into the surrounding soil after monocalcium phosphate monohydrate had dissolved because of continued water movement into the fertilizer zone. Solution composition remained near metastable triple point solution for quite a while because dicalcium phosphate dihydrate dissolved much faster than anhydrous dicalcium phosphate precipitated, but the composition changed to stable triple point solution as dicalcium phosphate dihydrate was allowed sufficient time to precipitate.

Equations were derived to illustrate the processes occurring when monocalcium phosphate monohydrate was dissolved in water. These equations are:

$$(1)\quad Ca(H_2PO_4)_2 \cdot H_2O \longrightarrow CaHPO_4 + H_3PO_4 + H_2O$$

$${}^{*}(2)\quad Ca(H_2PO_4)_2 \cdot H_2O + XH_2O \underset{\longleftarrow}{\overset{\longrightarrow}{\text{metastable}}} CaHPO_4 \cdot 2H_2O + MTPS$$

$$(3)\quad Ca(H_2PO_4)_2 \cdot H_2O + XH_2O \underset{\longleftarrow}{\overset{\longrightarrow}{\text{stable}}} CaHPO_4 + TPS$$

According to Moreno, <u>et al</u>. (34), octacalcium phosphate precipitated when dicalcium phosphate dihydrate was hydrolyzed in dilute phosphoric acid solutions at 25°C. and pH values greater than 6.8; the higher initial pH corresponded to a larger extent of hydrolysis. The solubility product constant for dicalcium phosphate dihydrate was calculated to be 2.77×10^{-7} (33), and was found to be 1.25×10^{-47} for octacalcium phosphate (34). Moreno, <u>et al</u>. (33) also found that both dissolution and precipation

---

*The symbol X should be less than 13.3.

of dicalcium phosphate dihydrate in dilute phosphoric acid solutions occurred with a calcium to phosphorus ratio of one if the pH range was between 3.5 and 7.5.

Lehr and Brown (27) stated that some applied phosphorus obtained by plants was taken up directly from such compounds as anhydrous dicalcium phosphate, octacalcium phosphate, tricalcium phosphate, and hydroxyapatite; the stability of these compounds and the close root association with the crystals were the supporting evidence. The greatest plant response resulted when dicalcium phosphate dihydrate was applied to acid soils and when monocalcium phosphate monohydrate was applied to basic soils (27, 33). Anhydrous dicalcium phosphate was much less available than dicalcium phosphate dihydrate, but hydroxyapatite and tricalcium phosphate were the poorest sources of phosphorus for plant growth. Larger plant responses appeared to be related to the solubility of the calcium phosphate added, except for the lower availability of monocalcium phosphate monohydrate in acid soils.

These investigators (27) also found that phosphorus became more available for plants when dicalcium phosphate dihydrate was hydrolyzed to form octacalcium phosphate or apatite. One suggestion for the enhanced availability was that the phosphorus released during the hydrolysis was readily available to the plant. The hydrolysis of dicalcium phosphate dihydrate to octacalcium phosphate was illustrated by the equation:

$$4(CaHPO_4 \cdot 2H_2O) \longrightarrow Ca_4H(PO_4)_3 \cdot 3H_2O + H_3PO_4 + 5H_2O.$$

Another explanation was that the removal of calcium ions by the precipitation of octacalcium phosphate resulted in a higher concentration of phosphorus in the soil solution.

Withee (49) found that a compound similar in solubility to octacalcium phosphate controlled the amount of phosphorus in solution in calcareous soils. Dicalcium phosphate dihydrate was converted to this more basic phosphate when the soils were subjected to wetting and drying cycles. There was no conversion to hydroxyapatite after addition of phosphorus to calcareous soils.

Phosphorus Fixation

Phosphorus fixation was first recognized in 1850 when it was reported in Europe that soil had the ability to retain phosphorus. Similar reports of phosphorus fixation originated in the United States shortly after 1900. The greatest efforts in understanding the basic chemistry of phosphorus fixation and how to alter the amount fixed, however, have been made since 1930 (20).

As the subject of phosphorus fixation is most easily discussed as fixation in acid soils and fixation in alkaline soils, the literature review will be subdivided accordingly. It must be realized, however, that the mechanisms primarily involved in each occur to some extent under both types of conditions.

Phosphorus Fixation in Acid Soils

Many investigators (15, 24, 36, 42) have reported that oxides and hydroxides of iron and aluminum contribute significantly to phosphorus fixation is acid soils. According to Toth (45), removal of free iron oxides from soil colloids reduced the amount of phosphorus fixation, thus illustrating that these compounds must be involved in phosphorus fixation.

Coleman (9) studied hydrogen and ammonium saturated clays of various sizes at several pH values both before and after free iron and aluminum oxides were removed. The fine kaolinite and montmorillonite clays fixed appreciable amounts of phosphorus, but the coarse clay minerals were unable to fix phosphorus. Fixation by both coarse and fine clays was altered by pH and exchangeable cations if iron and aluminum oxides were present, but no alteration occurred when the oxides had been removed. Ellis and Truog (14) found that hydrogen saturated montmorillonite free of iron and aluminum oxides would not fix phosphorus against water or weak acid extractions.

Phosphorus fixing capabilities of iron and aluminum saturated cation exchange resins were determined by Haseman, et al. (18). These systems were capable of fixing phosphorus; therefore, it was suggested that a similar relationship could exist in the clay mineral fraction of soil.

Seventy five per cent of the phosphorus retained by the ferrated exchange resin was readily exchangeable phosphorus, indicating that it must have been fixed by an adsorption mechanism, the exchangeability being improbably high for a precipitate (18). An anion exchange reaction could possibly be responsible for adsorption of the phosphorus (12, 39, 45).

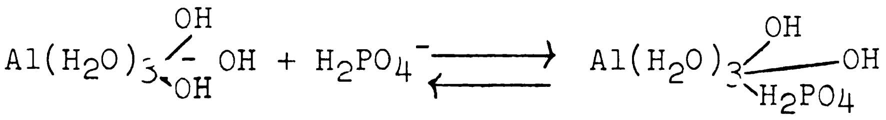
Haseman _et al_. (17) studied montmorillonite, illite, kaolinite, gibbsite, and goethite to determine phosphate fixation under varying conditions. The experiments were conducted at temperatures of 26, 49, and 95 decrees C, at pH values of 3, 5, 7, and at 1.0, 0.1, and 0.01 molar concentrations of phosphate. It was found that a rapid fixation and a slow fixation occurred. The rapid fixation was attributed to readily available aluminum and iron; the slower fixation was suggested to occur because of decomposition of minerals which released iron and aluminum. The rate of fixation by clay minerals increased with concentration of phosphate, increasing temperature, and lowering pH. Rate of phosphorus fixation by gibbsite, hydrous oxides, and goethite increased with increased temperature but was affected very little by pH in 0.1 molar phosphate solutions. Fixation of phosphorus was found to be in the order:

gibbsite > goethite > illite > kaolinite > montmorillonite.

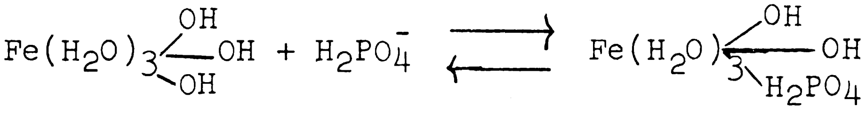
Hemwall (21) made a quantitutive characterization of the reaction of phosphorus with kaolinite and montmorillonite. The solubilities of both clays and the aluminum phosphate formed upon reaction with phosphorus were determined. It was found that clays which could fix phosphorus supported a higher soluble aluminum concentration than the aluminum phosphate. Also, type of clay, time of contact between clay and phosphate, or concentration of phosphate did not alter the solubility product of aluminum, thus indicating that a definite compound had been formed. They concluded that phosphorus is fixed in acid soils by clay minerals reacting with soluble aluminum to form an insoluble aluminum compound, the aluminum originating from lattice dissociation and from exchange sites of the clays.

Some investigators have suggested that phosphorus is fixed by an anion exchange of a phosphate ion for a hydroxide ion on the surface of the clay lattice (11, 39, 45). Ravikovitch (39) hypothesized that the amount of phosphate in solution increased with pH because the increased concentration of hydroxide ions caused a replacement of the phosphate ions on the clay surface. Dean and Rubins (11) determined that varying species of anions are not absorbed by the soil to the same magnitude, i.e., phosphate will replace all arsenate, but arsenate will not replace all phosphate. The fact that chelating compounds would free phosphorus stimulated a deduction that phosphorus was fixed by methods other than anion exchange. The anion exchange theory for phosphorus fixation seems to have only a few supporters today.

According to Swenson, Cole, and Sieling (42), maximum precipitation of iron phosphates occurred at a pH of 2.5 to 3.5, and aluminum phosphates at pH of 3.5 to 4.0. It is probable that the anion which reacted with iron and aluminum to form chemically combined phosphate was $H_2PO_4^-$; the pH values of the reaction medium were in the range where $H_2PO_4^-$ predominates. One phosphate ion was the maximum amount of phosphorus which would react chemically with one iron or aluminum ion. Two hydroxide ions were required to complete the chemical precipitation. They proposed equations which represented phosphorus fixation by aluminum and iron. The respective equations are:

(1) 

$$\mathrm{Al(H_2O)_3}\begin{matrix}\mathrm{OH}\\\mathrm{OH}\\\mathrm{OH}\end{matrix} + \mathrm{H_2PO_4^-} \rightleftarrows \mathrm{Al(H_2O)_3}\begin{matrix}\mathrm{OH}\\\mathrm{OH}\\\mathrm{H_2PO_4}\end{matrix}$$

(2) 

$$\mathrm{Fe(H_2O)_3}\begin{matrix}\mathrm{OH}\\\mathrm{OH}\\\mathrm{OH}\end{matrix} + \mathrm{H_2PO_4^-} \rightleftarrows \mathrm{Fe(H_2O)_3}\begin{matrix}\mathrm{OH}\\\mathrm{OH}\\\mathrm{H_2PO_4}\end{matrix}$$

Taylor, et al. (44) stated that aluminum hydroxide is the principle compound which causes the precipitation of phosphate in acid soils. The compounds precipitated when gibbsite was dissolved in potassium-free acidic calcium phosphate solutions were dicalcium phosphate, ($CaHPO_4$), calcium aluminum phosphates [$CaAlH(PO_4)_2 \cdot 6H_2O$ and $CaAl_6H_4(PO_4)_8 \cdot 2H_2O$], and amorphous aluminum phosphate ($AlPO_4$). More calcium aluminum phosphates were formed as the acidic calcium phosphate solution became more diluted. Almost all the phosphate was precipitated as aluminum compounds unless there was a large amount of iron oxides in the soil sample.

Phosphorus Fixation in Calcareous Soils

Phosphorus fixation in calcareous soils is usually attributed to the formation of a calcium phosphate compound. Eisenberger, et al. (13) stated that between the compounds $CaHPO_4$ and CaO there is a continuous series of compounds having an apatite structure. The apatite structure is very stable, permitting many unusual types of isomophous substitutions involving a large number of ions. Therefore, it is rare when the composition of any calcium phosphate can be expressed by a chemical formula which would suggest a definite chemical compound. Further, calcium phosphate can create a more complicated system by adsorbing additional phosphorus. The identification of a specific compound in a dynamic medium like soil is obviously a very difficult task.

Burd (2) found that some form of calcium phosphate was the primary source of phosphorus in calcareous soils. The concentration of calcium in the soil solution was the principle factor in determining phosphorus concentration. Various calcium phosphates were formed depending upon conditions at time of formation; rate of solution was largely determined by surface area.

Clark and Peech (7) stated that monocalcium phosphate must be converted to some other form if added as fertilizer because of its instability in soils. They also discovered that dicalcium phosphate could be found only in soils in which the phosphorus concentration in solution was unusually high. They concluded that hydroxyapatite was the predominant phosphorus containing mineral aggregate in neutral and calcareous soils, even though fluoroapatite was found to occur in important quantities in certain soils.

Clark and Peech (7) proposed chemical equations illustrating the formation of dicalcium phosphate, hydroxyapatite, and also proposed a general case equation. These respective equations are:

(1) $Ca(OH)_2 + Ca(H_2PO_4)_2 \longrightarrow 2CaHPO_4 + 2H_2O$

(2) $7Ca(OH)_2 + 3Ca(H_2PO_4) \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 12H_2O$

(3) $mCa(OH)_2 + nCa(H_2PO_4)_2 \longrightarrow X \text{ solid phase} + yH_2O$

Fuller and McGeorge (16) found that the solubility of phosphorus added to calcareous soils had not been clearly characterized. They stated, however, that phosphorus fixation may be due to sorption reactions or the chemical reaction of calcium with soluble phosphorus to form variably soluble phosphate precipitates. The more insoluble phosphates appeared to possess properties similar to carbonatoapatite.

These investigators distinguished "active" calcium from carbonate calcium by determining the amount of soil calcium that reacted with 0.2 N ammonium oxalate. A larger quantity of "active" and carbonate calcium in the subsoil than in the topsoil was associated with a lower solubility of phosphorus in the subsoil. "Active" to carbonate calcium increased, and carbon dioxide soluble phosphorus decreased with depth. The lowest "active" and carbonate calcium content was found in soils showing the least response to phosphorus for plant growth.

Wild (48) suggested that phosphorus can be fixed by exchangeable calcium. Naftel (35) stated that this type of fixation could occur up to an approximate pH of 6.5, but apatite and tricalcium phosphate would be precipitated at higher pH values. Phosphorus was not precipitated from solution by calcium ions at a pH lower than 5.0 (48). The initial phosphorus fixing step in calcareous soils seemed to be an adsorption to the surface of calcium carbonate particles rather than the formation of an insoluble phosphate precipitate.

Pratt and Thorne (37) suggested that adsorbed calcium on the clay minerals could fix phosphorus in addition to that fixed by calcium compounds in the soil. Calcium saturated clays fixed much more phosphorus than sodium saturated ones. Also, the calcium clays fixed larger amounts of phosphorus as pH increased, as might be expected from the decreasing solubility of calcium phosphates with increasing pH.

According to Dean (10), the concentration of phosphorus added, time of reaction, temperature, and pH must be rigidly controlled when studying the effects of calcium on phosphorus fixation. Also, rates of phosphorus application should approximate those normally used on field crops, and a uniform definition of "fixed phosphorus" should be established.

Ragland and Seay (38) defined "retained phosphorus" as phosphorus removed by clay from water solution, and defined "fixed phosphorus" as the portion of retained phosphorus not recovered from the clay with 0.005 N H_2SO_4. They found that phosphorus retention and fixation by initially acid saturated clays increased proportionally with per cent calcium saturation after sixty per cent saturation. Practically no increase occurred until the clays were approximately sixty per cent saturated. Phosphorus fixation in natural base saturated clays decreased with an increase in pH. They concluded that acid saturated clays may not be indicative of phosphorus fixation as it occurs under natural soil conditions.

According to Hsu and Jackson (22), the phosphorus in calcareous soils was mainly bonded to calcium. Tricalcium phosphate decreased and $AlPO_4$ and $FePO_4$ increased as the calcium carbonate was leached out and the pH dropped below 7. Some phosphorus dissolved from tricalcium phosphate and was precipitated as $FePO_4$ and $AlPO_4$ when soil pH was above 7, probably in acid root and leaching channels. Iron oxide coatings and the slow rate of ion diffusion along moisture films seemed to be responsible for the slow back transformation to tricalcium phosphate when lime was added to acid soils. They concluded that the transformations were mainly controlled by pH.

Wild (47) suggested that exchangeable cations such as calcium determine the extent formation of basic $AlPO_4$. His evidence was that monovalent as well as divalent cations caused an increase in phosphorus retention. Cation effect was found with an aluminum-saturated exchange resin, but not with a hydrogen resin or an aluminum sulfate solution, and exchangeable aluminum was affected by exchangeable cations.

Chang and Chu (3) found that latosols fixed more phosphorus than other soils. Further, iron and aluminum phosphates were more prevalent than calcium phosphate, and the change of aluminum and calcium phosphates to iron phosphate was highly significant. They suggested that surface area of the solid phase associated with calcium ions, rather than the ionic activity of calcium in soil solution, determined the nature of the phosphates formed. They concluded that calcium was not instrumental in the fixation of phosphates because of the gradual transformation of calcium and aluminum phosphates to iron phosphate; the rate of transformation increased proportionally with moisture content.

According to Heck (19), a high ratio of active calcium to active iron and aluminum resulted in readily available calcium phosphate, the reverse situation resulting in fixed phosphorus being only slightly available. Calcium, aluminum, and iron inhibited the downward movement of phosphorus in soils directly proportional to amount present and inversely proportional to solubilities of phosphorus compounds. They stated that with large amounts of calcium and small amounts of iron and aluminum, the phosphorus was fixed as tricalcium phosphate, which was only slightly soluble in water but easily soluble in 0.002 normal sulfuric acid.

Dean (10) concluded that H_2O, CaO, CO_2, and P_2O_5 probably combined to form a series of insoluble calcium phosphate compounds. These compounds formed solid solutions and were difficult to characterize chemically. There was also evidence that phosphorus may have been fixed by Al^{+3} or $Al\ (OH)_3$ in the clay fraction of alkaline soils, depending on the amount of other cations present.

EXPERIMENTAL PROCEDURES

Several soil samples were collected by Suzuki *et al.* (41) from various locations in Michigan as shown in Table 1. Iron River, Warsaw, Conover, Plainfield, Kalamazoo, and Gilford soil series were selected from these samples. Selection of these particular series was made because of large variabilities of aluminum and calcium fractions of phosphorus, according to Suzuki, *et al.* (41).

The pH was determined on all the soil samples with a Beckman (model G) pH meter. A soil to water ratio of one to one was used in this determination.

Uptake of Various Soil Phosphorus Fractions as Determined by Soil Analysis

A quantative determination of aluminum, iron, and calcium phosphates was made on the six soils. Extraction and colorimetric determinations of aluminum, iron, and calcium phosphates were made on all soils as described by Chang and Jackson (4).

Three thousand five hundred grams of quartz sand previously washed with hydrochloric acid and leached with distilled water were placed in a circular one gallon paper container. Five hundred grams of each soil series were distributed on top of the sand, and an additional 500 grams

TABLE 1.--The pH and sampling sites of six Michigan Soil series.

Soil Series	pH	Horizon	*Location
Iron River	5.5	Surface and Subsoil	Raiko Petroff, RFD 3, Iron River. SE1/4 NE1/4 Sec. 14 R35W T42N. Southeast corner of field north of house.
Conover	7.8	Surface and Subsoil	MSU Farm
Plainfield	5.6	Surface and Subsoil	Rose Lake Experimental Farm, 1/2 mile west of headquarter's building on south side of road.
Gilford	7.8	Surface and Subsoil	Fritz Montey Farm. Two miles north, two miles west of Caro. NE1/4 NE1/4 Sec. 30 T13N R9E. West side of road.
Warsaw	5.4	Surface and Subsoil	Lee Rhoda, RFD, Schoolcraft, Michigan. One mile south of Schoolcraft on west side of road. SE1/4 SW1/4 Sec. 19 T4S R11N. Sample taken in old garden area directly south of house.
Kalamazoo	5.3	Surface and Subsoil	Don Lutz, RFD, Marshall, Michigan. Two and one half miles west of Marshall. SE1/4 SE1/4 Sec. 30 T25 R6W. Field between railroad tracks and river, west of lane.

*Taken from report by Suzuki, Lawton, and Doll.

of sand were placed above the mixed fraction, thus inserting the mixed soil fraction about two inches below the surface. A double layer of cheesecloth was placed both below and above the mixed fraction of soil to later facilitate separation of the soil from sand.

Forty wheat seeds were placed one-half an inch below the surface within the sand layer, and the container brought to twenty per cent moisture with Hoagland's nutrient solution containing no phosphorus. A cycle whereby the plants were brought up to weight with distilled water for six days and with nutrient solution the seventh day was followed.

There are four replications of each series. Wheat was grown in the greenhouse for seventeen weeks with no additional phosphorus other than that contained in the soil.

The 500 gram mixed fraction layer of soil was carefully removed from all containers and dried after the seventeen week termination. Extraction and a quantitative determination of aluminum, iron, and calcium phosphates present in the soil after plant growth was conducted by the same procedure described earlier.

Uptake of Various Soil Phosphorus Fractions as Determined by Plant Analysis

The six soils were fractionated according to the method of Chang and Jackson (4). The aluminum phosphate was removed with 0.5N NH_4F to obtain a sample containing iron and calcium phosphate, the aluminum phosphates were removed with 0.5N NH_4F, and iron phosphate was removed with 0.1N NaOH to obtain a second fraction which contained only calcium phosphates. Calcium and iron phosphates were removed from a third fraction to obtain a sample containing aluminum phosphates. A 0.1N hydrochloric acid solution was used to remove the calcium phosphates, and a sodium dithionite-citrate solution was employed to remove the iron phosphate (4). A fourth fraction had no phosphates removed and therefore served as a check. All fractions were washed three times with a NaCl solution after extraction and prior to cropping.

Five hundred grams of sand were placed in a circular thirteen ounce paraffin coated paper container. The sand had been previously washed with concentrated hydrochloric acid and leached with distilled water to remove any phosphorus that might be present. Five grams of each soil fraction were distributed evenly above the 500 grams of sand and an additional 195 grams of sand were added above the mixed fraction, the mixed fraction being enclosed about two inches below the surface. Each fraction was replicated three times.

Forty wheat seed were inserted one-half inch below the surface within the sand, and the container was brought to twenty per cent moisture by weight with Hoagland's nutrient solution that contained no phosphorus. A cycle whereby the plants were brought to weight with distilled water for six days and with nutrient solution the seventh day was followed. All essential minor nutrients were added to the solution except iron; a foliar application of five per cent iron in the form of ferrous sulfate solution was administered once per week.

The wheat plants were grown in the greenhouse for one month, and at the termination of this period the tops were removed and analyzed for total phosphorus. Phosphorus was extracted from plant tissue by the method described in the Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists (1950, p. 196). The residue was dissolved in 5 milliliters of 2N hydrochloric acid and filtered into a 200 milliliter flask. Two drops of 2-4 dinitrophenol indicator were added to the solution, 1N sodium hydroxide was added until the solution turned yellow, and the neutralized solution was brought up to volume with distilled water. A 50 milliliter aliquot was taken from the 200 milliliter flask, and phosphorus was determined by the Deniges colorimetric method as modified by Truog and Meyer (46). Per cent transmission was determined on a Coleman Universal Spectrophotometer.

RESULTS AND DISCUSSION

Soil pH values for the six soils studied are given in Table 1. The Iron River, Plainfield, Warsaw, and Kalamazoo soils were acid ranging in pH from 5.3 to 5.6 while the Conover and Gilford soils were calcareous both with pH 7.8.

Change in Soil Phosphorus Fractions Upon Cropping as Determined by Soil Analysis

Soil phosphorus was removed by cropping with wheat. The media in which the wheat plants grew is shown in Figure 1. Plant roots were highly concentrated in the 500 gram layer of the mixed soil fraction creating a large stress upon the soil, thus promoting maximum phosphorus removal by cropping.

The concentration of aluminum, iron, and calcium phosphates before and after growth of wheat and the total decrease in phosphorus for each soil are given in Table 2. The quantity of aluminum phosphate in the six soils before cropping ranged from 29 in the Kalamazoo soil to 233 ppm phosphorus in the Warsaw soil. The aluminum phosphate fraction of the Iron River, Conover, and Kalamazoo soils, showed a net gain of 4, 14, and 17 ppm phosphorus respectively during plant growth; these soils contained less than 50 ppm

Figure 1. Root Distribution in Soil-Quartz Sand Media.

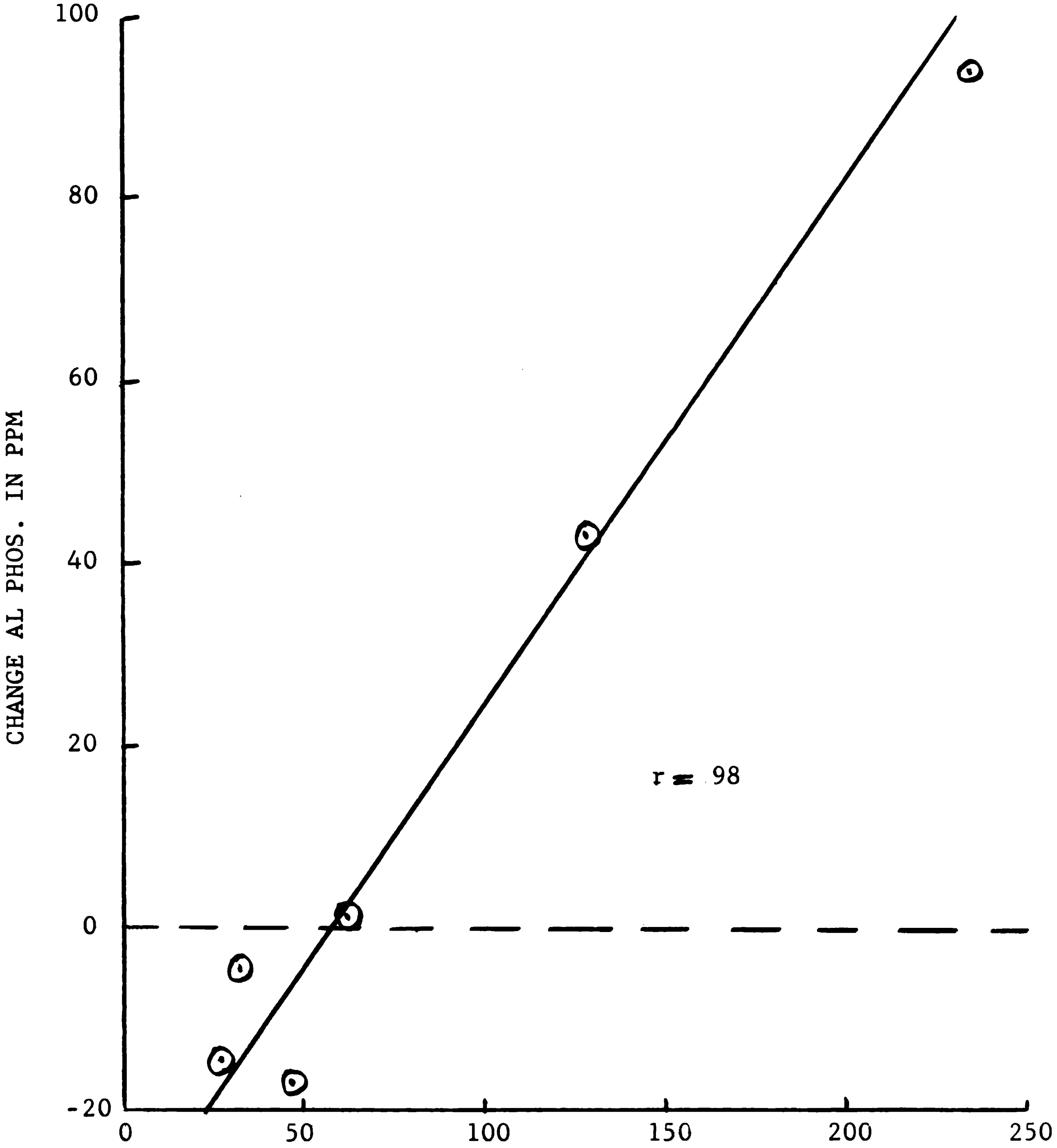
TABLE 2.--Aluminum, iron, and calcium phosphate content of the six soils.

	ppm Al Phos.		ppm Fe Phos.		ppm Ca Phos.		Total P
Soil Series	Before Growth	*After Growth	Before Growth	*After Growth	Before Growth	*After Growth	Rem. From Soil (ppm)
Iron River	48	65	175	153	81	75	11
Warsaw	233	138	168	126	50	51	136
Conover	33	37	54	52	174	170	2
Plainfield	128	84	132	106	92	56	106
Kalamazoo	29	43	166	116	93	57	72
Gilford	63	61	126	71	175	154	78

*Average of four replicas.

phosphorus as aluminum phosphate prior to cropping. There may have been a transformation of calcium and/or iron phosphates to aluminum phosphate when these soils were subjected to plant growth. The differences may have been due to experimental error; however, each result reported is a mean of four replications performed under identical conditions. There was little change in aluminum phosphate content of the Conover and Gilford soils, but the aluminum phosphate in the Plainfield and Warsaw soils decreased 44 and 95 ppm phosphorus respectively during cropping. The Warsaw soil lost 40.8 per cent and the Plainfield soil lost 34.4 per cent of the initial aluminum phosphate during cropping. It should be noted that the plants grown in the Warsaw soil, where over two-thirds of the total phosphorus removed by the plant came from the aluminum phosphate fraction, were about one and one-half times as large as the plants grown in the other soils.

Figure 2 gives the change in aluminum phosphate during cropping as a function of the initial aluminum phosphate content of the soils. These two variables were highly correlated. Figure 2 confirms that aluminum phosphate plays an important role in the phosphorus activity within the soil. Soils containing greater than 58 ppm phosphorus as aluminum phosphate would be expected to lose aluminum phosphate during cropping, and soils containing less than 58 ppm phosphorus as aluminum phosphate would



PPM AL PHOS.

Figure 2. Change in Aluminum Phosphate Upon Cropping as a Function of Initial Aluminum Phosphate Content.

be expected to gain aluminum phosphate during cropping under these experimental conditions. Fifty-eight ppm phosphorus as aluminum phosphate could be considered the point whereby aluminum phosphate is in equilibrium with other phosphate forms in the soils studied, an attempt to reach this equilibrium point being the reason for increases and decreases of aluminum phosphate.

The highly significant correlation between aluminum phosphate initially present and change in the aluminum phosphate fraction upon severe cropping stress suggest that this fraction is very important in furnishing phosphorus for plant growth. Consequently, any extracting solution used to measure available soil phosphorus must reflect the level of aluminum phosphate in the system.

Nearly equal quantities of iron phosphate were present in five of the six soils studied; the Conover soil was about 100 ppm lower in phosphorus as iron phosphate than the other soils (see Table 2). Five soils, the Iron River, Warsaw, Plainfield, Kalamazoo, and Gilford, showed a net loss in iron phosphate of from 22 to 55 ppm phosphorus during plant growth; these were the five soils that initially contained 126 to 175 ppm phosphorus as iron phosphate. The Conover soil showed little change in iron phosphate content upon cropping.

Figure 3 gives the change in iron phosphate during cropping as a function of the initial iron phosphate content of the soils. The correlation between these two variables was not significant. These data did not give much information about the relationship between these two variables because five of the six points on the graph are concentrated in a small area. It should, however, be noted that iron phosphate contributed significantly to the phosphorus change in five of the soils. For example, in the Warsaw soil 30.9 per cent of the total phosphorus loss came from the iron phosphate fraction, even though this soil was very high in aluminum phosphate.

Calcium phosphate content of the soils before cropping ranged from 50 in the Warsaw soil to 175 ppm phosphorus in the Gilford soil. The calcium phosphate fraction of the Plainfield, Kalamazoo, and Gilford soils decreased from 21 to 36 ppm phosphorus during plant growth, but there was no significant change in the calcium phosphate content in the Iron River, Warsaw, and Conover soils.

Figure 4 shows the change in calcium phosphate during cropping as a function of the initial calcium phosphate content of the soils. Correlation between the two variables on the Iron River, Plainfield, Warsaw, and Kalamazoo soils was not significant; these soils were separated from the Conover and Gilford soils because of pH

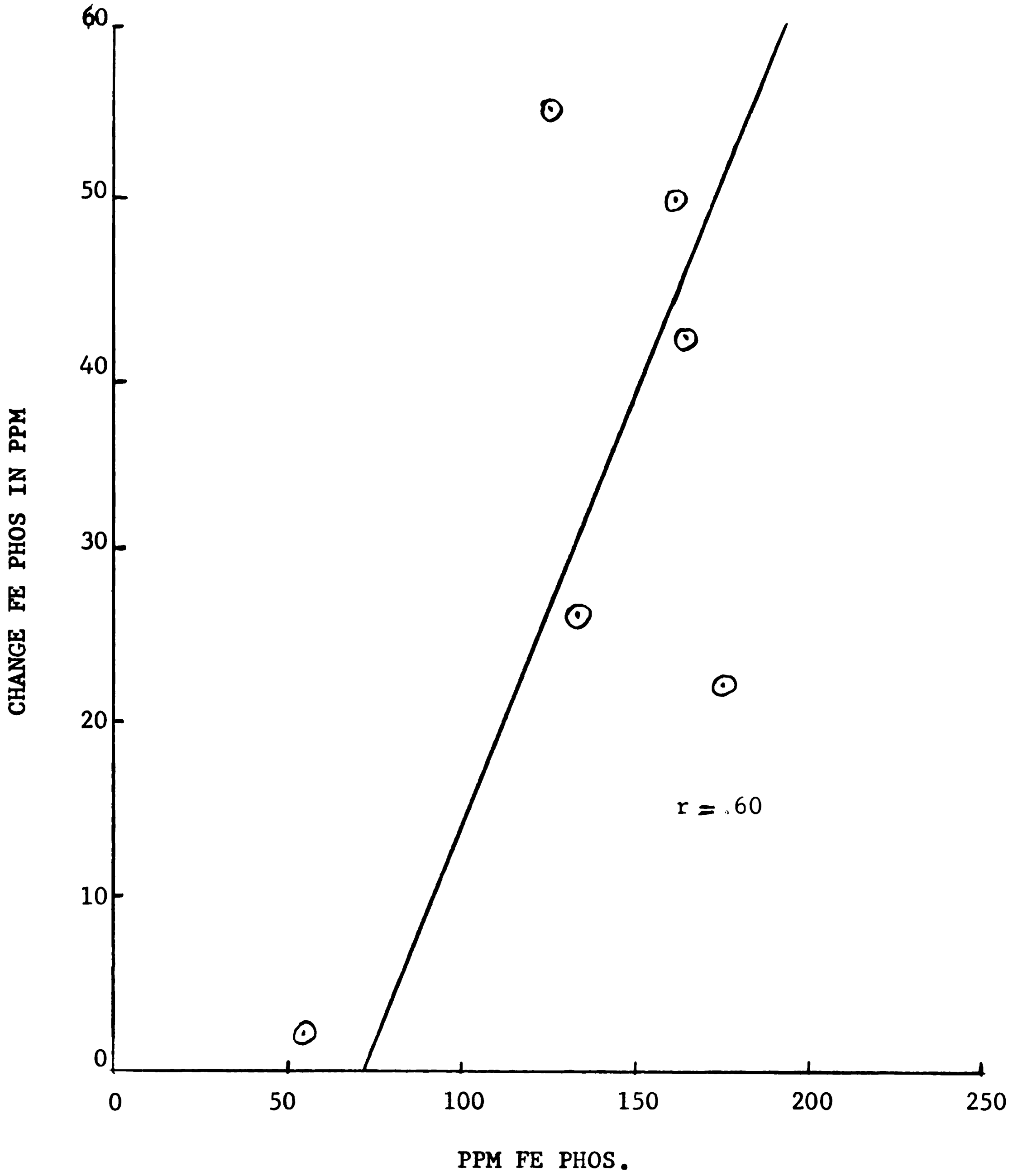


Figure 3. Change in Iron Phosphate Upon Cropping as a Function of Initial Iron Phosphate Content.

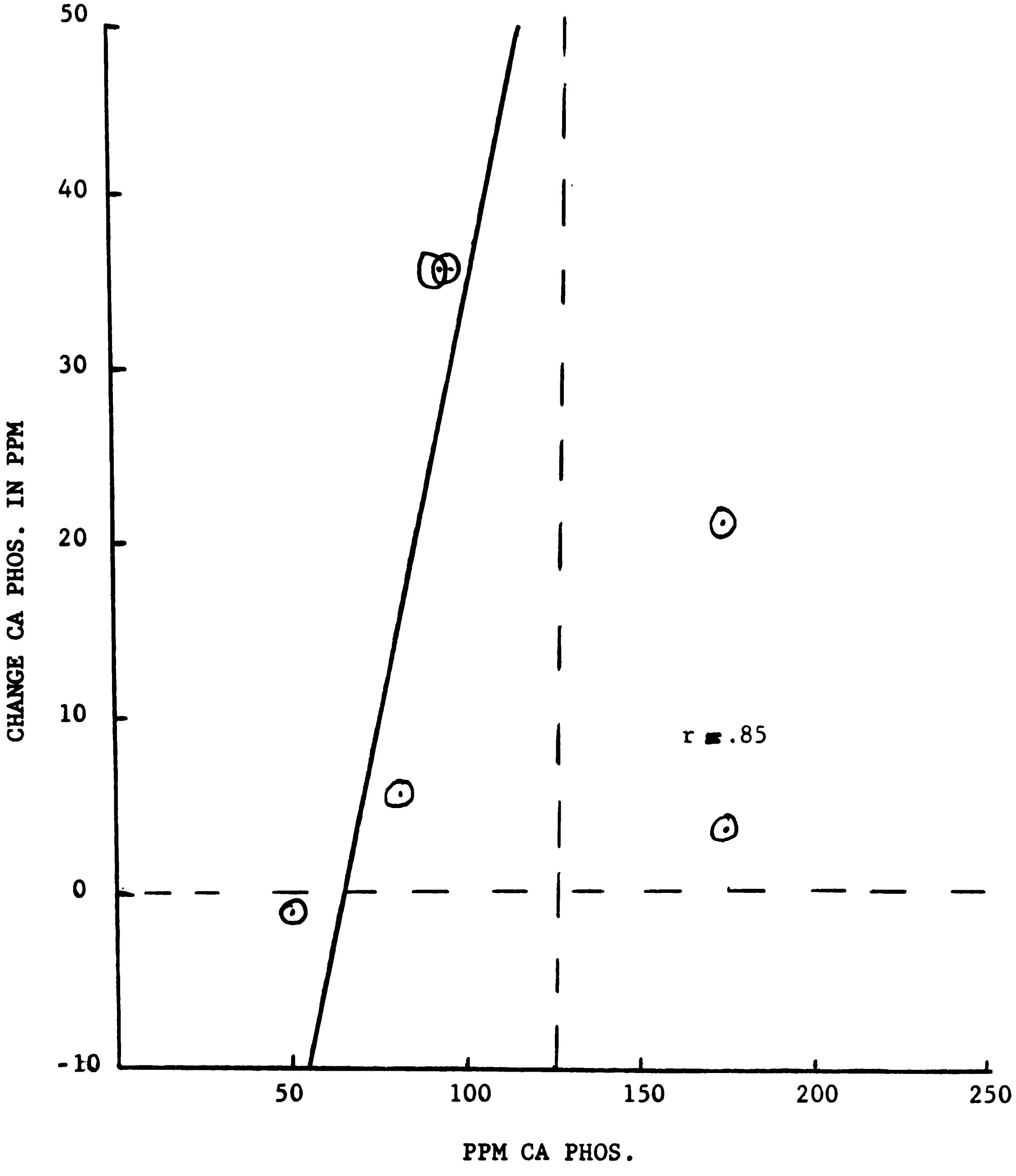


Figure 4. Change in Calcium Phosphate Upon Cropping as a Function of Initial Calcium Phosphate Content.

differences (see Table 1). These data did not give much information about the relationship between these two variables because there were only four points on the graph and two of these points were extremely close.

Certain trends seemed to occur, however, when the soils were divided according to pH. There was little change in calcium phosphate content in the Conover soil during cropping, but the Gilford soil lost 21 ppm phosphorus as calcium phosphate even though the soils had the same pH and nearly the same calcium phosphate content initially, suggesting that the calcium phosphate in the Conover soil was in a less available form than that in the Gilford soil. According to Lindsay and Moreno (30) the forms of calcium phosphate, which may be expected to exist at pH of 7.8 are hydroxyapatite, dicalcium phosphate dihydrate, and octacalcium phosphate; the differences in solubilities between the hydroxyapatite and octacalcium phosphate were greater than between the octacalcium phosphate and the dicalcium phosphate dihydrate, and the hydroxyapatite showed little solubility at this pH. It is quite possible, therefore, that the predominant form of calcium phosphate in the Conover soil was hydroxyapatite, and that the predominant form of calcium phosphate in the Gilford soil was octacalcium phosphate. A direct relationship between ppm phosphorus as calcium phosphates in the soil before cropping and uptake during cropping on all four acid soils would suggest that a similar form or forms of calcium phosphates were present. Lindsay and Moreno (30) suggested that forms of calcium phosphates present in soils at pH 5.5 were fluorapatite, hydroxyapatite, and dicalcium phosphate dihydrate, and all three forms were quite soluble in the order, dicalcium phosphate dihydrate > hydroxyapatite > fluorapatite; there was very little difference in the solubilities of dicalcium phosphate dihydrate and hydroxyapatite at this pH.

Total phosphorus removed from each soil was calculated by adding the differences in ppm phosphorus as aluminum, iron, and calcium phosphates before and after cropping. The Iron River and Conover soils did not lose a significant quantity of phosphorus when cropped, but the Warsaw, Plainfield, Kalamazoo, and Gilford lost from 72 to 136 ppm phosphorus.

Figure 5 gives the change in aluminum, iron, and calcium phosphates during cropping as a function of the initial aluminum, iron, and calcium phosphate content of the soils. Each form of soil phosphorus was weighted by a factor obtained from the slope of the individual regression lines shown in Figures 2, 3, and 4. In addition the proposed function takes into account where each individual regression line crosses the axis. It was assumed that there was no change in calcium phosphate content in the calcareous soils when 62 ppm phosphorus as calcium phosphate was present and that there was a ten

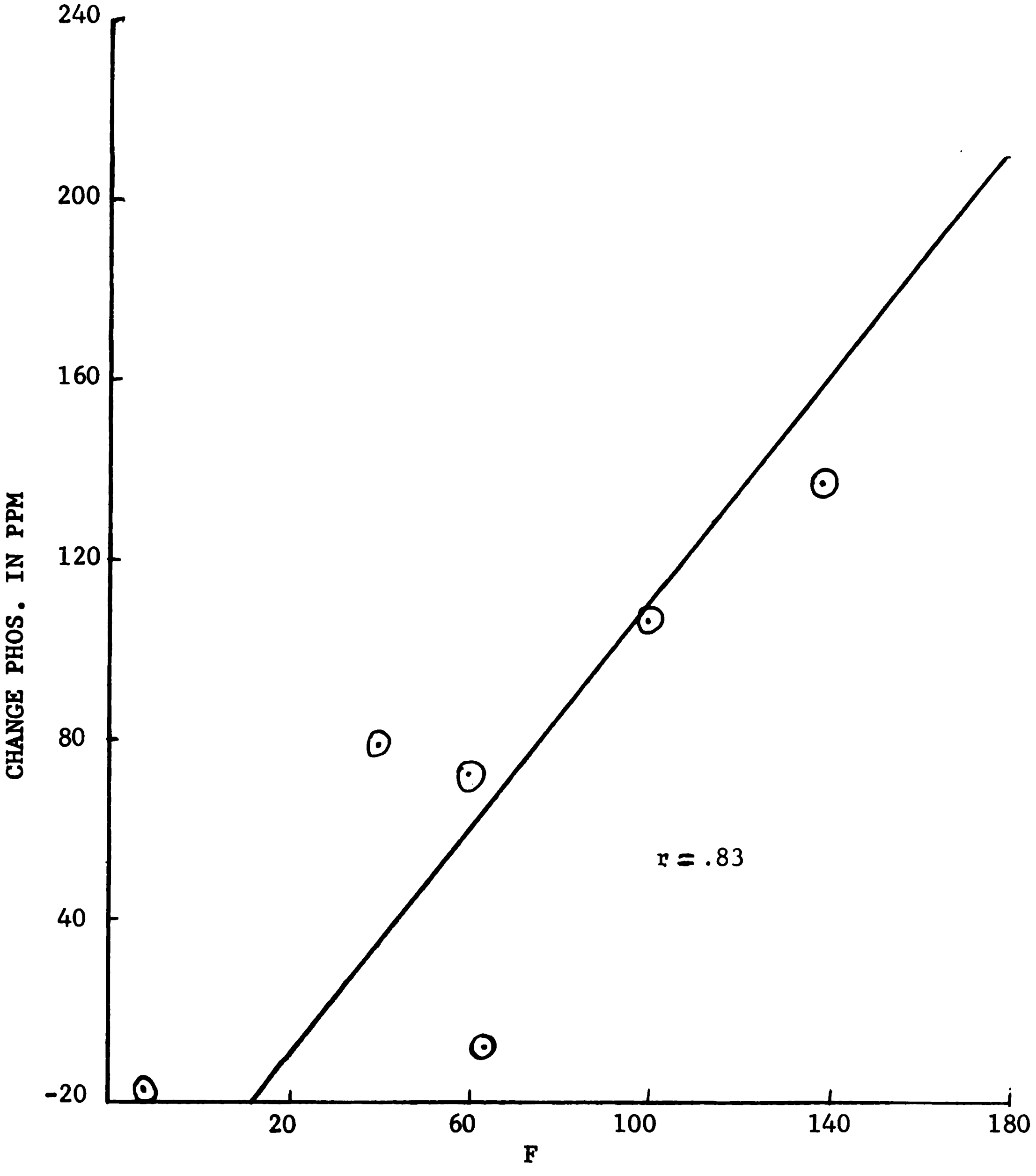


Figure 5. Total Change in Soil Phosphorus Upon Cropping as a Function of Aluminum, Iron, and Calcium Phosphates. [F = 0.59 (Al Phos. - 57) + 0.49 (Fe phos. - 72) + 1.0 or 0.1 (Ca phos. - 62)].

per cent change above 62 ppm phosphorus in these calcareous soils. The correlation coefficient between the two variables was significant. This would indicate that the forms of soil phosphorus must not be added directly to obtain an estimation of the total available phosphorus.

In general, the fraction of phosphorus taken up in largest quantities by the plants was dependent upon the predominant form of phosphorus in the soil before cropping. A notable exception was the calcareous Gilford soil where the calcium phosphate appeared quite unavailable.

Change in Soil Phosphorus Fractions Upon Cropping as Determined by Plant Analysis

The second part of this investigation was conducted primarily to study an alternate method of measuring the relative availability of different forms of soil phosphorus to plants. In this method a portion of the soil phosphorus was removed by procedures described in the experimental methods and the remaining phosphorus fractions cropped in a soil-quartz sand mixture. It is very likely that some or all of the remaining phosphorus fractions were altered greatly during the extraction procedures. Other soil properties such as pH, structure, and exchangeable ions were also altered; however, these effects should have been minimized by the final NaCl washing and the large dilution with quartz sand.

Table 3 gives the quantity of phosphorus that was present in the six soils studied after they were subjected to various fractionation processes. Only 79, 11, 59, 14, 71, and 45 per cent of the initial aluminum phosphate remained in the Iron River, Warsaw, Conover, Plainfield, Kalamazoo, and Gilford soils, respectively, when the calcium and iron phosphates were extracted. The attempt to extract the iron and calcium phosphates without extracting the aluminum phosphate, therefore, was not very successful.

The average weights of plants are given in Table 4 and the total phosphorus uptake is given in Table 5. Differences in plant weight and phosphorus uptake due to soils, phosphorus sources and interaction of soils and phosphorus sources were all highly significant; there were no significant differences due to replication.

The difference between weights of plants grown in soils containing calcium and iron phosphates and soils with the other three treatments was highly significant; the only exception was that plants grown in the Warsaw soil containing calcium and iron phosphates weighted more than plants grown in the check pots. Ross, et al. (40), found a large response in yield of alfalfa plants when lime was applied to this same Warsaw soil. It is

TABLE 3.--Quantity of phosphorus in five grams of soil in various phosphate forms.*

Soil	Al + Ca + Fe Phos. (mg)	Ca + Fe Phos. (mg)	Ca Phos. (mg)	Al Phos. (mg)
Iron River	1.52	1.28	.41	.19
Warsaw	2.26	1.09	.25	.14
Conover	1.31	1.14	.87	.10
Plainfield	1.76	1.12	.46	.09
Kalamazoo	1.44	1.30	.47	.10
Gilford	1.82	1.51	.88	.14

*Seed contained 3.29 milligrams phosphorus.

TABLE 4.--Plant weights when grown in various soil phosphate fractions.

Soil	Al + Ca + Fe Phos.*	Ca + Fe Phos.*	Ca Phos.*	Al Phos.*	Av.
Iron River	1.77	1.16	1.80	1.63	1.59
Warsaw	1.51	1.79	1.78	1.73	1.70
Conover	1.61	1.16	1.45	1.79	1.50
Plainfield	1.67	1.56	1.66	1.63	1.63
Kalamazoo	1.69	1.43	1.55	1.62	1.57
Gilford	1.73	1.24	1.79	1.72	1.62
Av.	1.66	1.39	1.67	1.69	

L.S.D. Soils (.05) = .08
(.01) = .11

L.S.D. Phos. Forms (.05) = .05
(.01) = .06

*Average of three replications, values reported in grams dry weight.

TABLE 5.--Total phosphorus uptake in plants when grown in various soil phosphate fractions.

Soil	Al + Ca + Fe Phos (mg)*	Ca + Fe Phos. (mg)*	Ca Phos. (mg)*	Al Phos. (mg)*	Av.
Iron River	2.49	2.40	2.85	2.75	2.62
Warsaw	2.54	2.56	2.38	2.43	2.48
Conover	2.31	1.98	2.38	2.26	2.23
Plainfield	2.27	2.22	2.65	2.48	2.41
Kalamazoo	2.89	2.41	2.75	2.63	2.67
Gilford	2.75	2.35	2.32	1.96	2.34
Av.	2.54	2.32	2.55	2.42	

$$\text{L.S.D. Soils} \begin{Bmatrix} (.05) \\ (.01) \end{Bmatrix} \begin{matrix} = .15 \\ = .20 \end{matrix}$$

$$\text{L.S.D. Phos. Forms} \begin{Bmatrix} (.05) \\ (.01) \end{Bmatrix} \begin{matrix} = .12 \\ = .16 \end{matrix}$$

*Average of three replications

quite possible, therefore, that the removal of aluminum phosphate from the Warsaw soil resulted in larger plants because of the decrease in aluminum content, i.e., the aluminum may be present in sufficiently large quantities in the Warsaw soil to be toxic to plants.

There were no statistical differences between plant weights when plants were grown in soils containing aluminum phosphate, calcium phosphates, or aluminum, calcium, and iron phosphates when plant weights from all soils were averaged. There was, however, a highly significant decrease in plant weight when aluminum and iron phosphates were removed from the Conover soil; the calcium phosphate which remained in this calcareous soil was quite unavailable for plant growth which confirms results of the first method.

On the other hand, removal of aluminum phosphate with NH_4F may have resulted in a calcium phosphate form such as fluorapatite which was less soluble than the initial calcium phosphate, or that three washings with NaCl solution left sufficient fluorine in solution to be toxic to the wheat plants. Either possibility might explain why the plant weight and phosphorus uptake was less in almost all soils when the aluminum phosphate was extracted.

The forty wheat seed that were added to each container contained an average of 3.29 milligrams phosphorus, which was more phosphorus than was found in any of the plant tops. Consequently, the stress on the soil phosphorus was less than desired.

SUMMARY AND CONSLUSIONS

Greenhouse experiments were conducted primarily to study two methods for measuring the relative availability of different forms of soil phosphorus for plants. Six soils, the Iron River, Warsaw, Conover, Kalamazoo, Gilford, and Plainfield, were selected because of their variability in quantity of aluminum and calcium phosphates. Wheat plants, because of their extensive root systems were utilized to remove phosphorus from these soils by cropping. In the first experiment, quantity of different phosphates removed from the soil was determined by measuring the quantity of aluminum, iron, and calcium phosphates both before and after cropping. In the second experiment, each of the six soils was fractionated to give samples containing all forms of phosphates, calcium and iron phosphate, only calcium phosphate, and only aluminum phosphate. The relative availability of the phosphorus in each of the fractions was measured by plant uptake.

Of the two methods studied, the first appeared to reflect better the relative availability of the phosphorus forms to plant growth.

It was found in the first experiment that the change in aluminum phosphate during cropping was highly correlated with the initial aluminum phosphate content of the soils. Soils containing greater than 58 ppm phosphorus as aluminum phosphate lost aluminum phosphate during cropping, and soils containing less than 58 ppm aluminum phosphate gained aluminum phosphate during cropping under these experimental conditions.

Iron phosphate contributed significantly to the phosphorus change in five of the six soils studied.

The calcium phosphate in the acid Warsaw, Plainfield, Kalamazoo and Iron River soils was apparently more available than the calcium phosphate in the two calcareous soils. The calcium phosphate in the calcareous Gilford soil was apparently more available than that in the Conover soil, even though they both had the same pH.

The correlation coefficient between the change in aluminum, iron, and calcium phosphates during cropping as a function of the initial aluminum, iron, and calcium phosphate content of the soils [F = 0.59 (Al Phos. - 57) + 0.49(Fe Phos. - 72) + 1.0 or 0.1 (Ca Phos. - 62)] was significant. This would indicate that the forms of soil phosphorus must not be added directly to obtain an estimation of the total available phosphorus.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Bray, R. H., and Dickman, S. R. Adsorbed phosphates in soils and their relation to crop responses. Soil Sci. Soc. Amer. Proc. 6:312-320. 1941.

2. Burd, John S. Chemistry of the phosphate ion in soil systems. Soil Sci. 65:227-247. 1948.

3. Chang, S. C. and Chu, W. K. The fate of soluble phosphate applied to soils. Jour. Soil Sci. 12: 286-293. 1961.

4. Chang, S. C., and Jackson, M. L. Fractionation of soil phosphorus. Soil Sci. 84:133-144. 1957.

5. Chang, S. C., and Jackson, M. L. Solubility product of iron phosphate. Soil Sci. Soc. Amer. Proc. 21:265-269. 1957.

6. Chang, S. C., and Juo, S. R. Available phosphorus in relation to forms of phosphates in soils. Soil Sci. 95:91-96. 1963.

7. Clark, J.S., and Peech, Michael. Solubility criteria for the existence of calcium and aluminum phosphates in soils. Soil Sci. Soc. Amer. Proc. 19:171-174. 1955.

8. Cole, C. V., and Jackson, M. L. Solubility equilibrium constant of dihydroxy aluminum dihydrogen phosphate relating to a mechanism of phosphate fixation in soils. Soil Sci. Soc. Amer. Proc. 15:84-88. 1950.

9. Coleman, Russell. Phosphorus fixation by the coarse and fine clay fractions of kaolinitic and montmorillonitic clays. Soil Sci. 58:71-77. 1944.

10. Dean, L. A. Fixation of soil phosphorus. Advances in Agron. 1:391-411. 1950.

11. Dean, L. A., and Rubins, E. J. Anion exchange in soils: I. Exchangeable phosphorus and the anion-exchange capacity. Soil Sci. 63:377-387. 1947.

12. Dickman, S. R., and Bray, R. H. Replacement of adsorbed phosphate from kaolinite by fluoride. Soil Sci. 52: 263-273. 1941.

13. Eisenberger, Sidney, Lehrman, Alexander and Turner, William D. The basic calcium phosphates and related systems. Some theoretical and practical aspects. Chem. Revs. 26:257-296. 1940.

14. Ellis, Roscoe, Jr., and Truog, Emil. Phosphate fixation by montmorillonite. Soil Sci. Soc. Amer. Proc. 19:451-454. 1955.

15. Ensminger, L. E. The relationship between water lost and PO_4 adsorbed on phosphating clay minerals and soil colloids. Soil Sci. Soc. Amer. Proc. 13:170-174. 1948.

16. Fuller, W. H., and McGeorge, W. T. Phosphates in calcareous Arizona soils: I. Solubilities of native phosphates and fixation of added phosphates. Soil Sci. 70:441-460. 1950.

17. Haseman, J. F., Brown, Earl H., and Whitt, Carlton D. Some reactions of phosphate with clays and hydrous oxides of iron and aluminum. Soil Sci. 70:257-270. 1950.

18. Haseman, J. F., Lehr, J. R., and Smith, J. P. Mineralogical character of some iron and aluminum phosphates containing potassium and ammonium. Soil Sci. Soc. Amer. Proc. 15:76-84. 1950.

19. Heck, A. Floyd. Phosphate fixation and penetration in soils. Soil Sci. 37:343-355. 1934.

20. Hemwall, John B. The fixation of phosphorus by soils. Advances in Agron. 9:95-112. 1957.

21. Hemwall, John B. The role of soil clay minerals in phosphorus fixation. Soil Sci. 83: 101-108. 1957.

22. Hsu, P. H., and Jackson, M. L. Inorganic phosphate transformations by chemical weathering in soils as influenced by pH. Soil Sci. 90:16-24. 1960.

23. Huffman, E. O., Cate, W. E., and Deming, M. E. Rates and mechanisms of dissolution of some ferric phosphates. Soil Sci. 90:8-15. 1960.

24. Kelly, Joseph B. and Midgley, A. R. Phosphate fixation and exchange of phosphate and hydroxyl ions. Soil Sci. 55:167-176. 1943.

25. Kittrick, J. A., and Jackson, M. L. Application of solubility product principles to the variscite-kaolinite system. Soil Sci. Soc. Amer. Proc. 19:455-457. 1955.

26. Kittrick, J. A., and Jackson, M. L. Common ion effect on phosphate solubility. Soil Sci. 79:415-421. 1955.

27. Lehr, J. R. and Brown, W. E. Calcium phosphate fertilizers: II. A pertrographic study of their alteration in soils. Soil Sci Soc. Amer. Proc. 22:29-32. 1958.

28. Lehr, James R., Brown, Walter E., and Brown, Earl H. Chemical behavior of monocalcium phosphate monohydrate in soils. Soil Sci. Soc. Amer. Proc. 23:3-7. 1959.

29. Lindsay, W. L., and DeMent, J. D. Effectiveness of some iron phosphates as sources of phosphorus for plants. Plant and Soil. 14:118-126. 1961.

30. Lindsay, W. L., and Moreno. E. C. Phosphate phase equilibria in soils. Soil Sci. Soc. Amer. Proc. 24: 177-182. 1960.

31. Lindsay, W. L., Peech, Michael, and Clark, J. S. Solubility criteria for the existence of variscite in soils. Soil Sci. Soc. Amer. Proc. 23:357-360. 1959.

32. Lindsay, W. L. and Stephenson, H. F. Nature of the reactions of monocalcium phosphate monohydrate in soils: I. The solutions that reacts with the soil. Soil Sci. Soc. Amer. Proc. 23: 12-18. 1959.

33. Moreno, Edgard C., Brown, Walter E. and Osborn, Glen. Solubility of dicalcium phosphate dihydrate in aqueous systems. Soil Sci. Soc. Amer. Proc. 24:94-98. 1960.

34. Moreno, Edgard C., Brown, Walter, E. and Osborn, Glen. Stability of dicalcium phosphate dihydrate in aqueous solutions and solubility of octocalcium phosphate. Soil Sci. Soc. Amer. Proc. 24:99-102. 1960.

35. Naftel, James A. Soil liming investigations: II. The influence of lime on the sorption and distribution of phosphorus in aqueous and soil colloidal systems. J. Amer. Soc. Agron. 28:740-752, 1936.

36. Perkins, Alfred T., and King, H. H. Phosphorus fixation by soil minerals: II. Fixation by iron, silicon, and titanium oxides. Soil Sci. 58:243-250. 1944.

37. Pratt, Parke F. and Thorne, D. W. Solubility and physiological availability of phosphate in sodium and calcium systems. Soil Sci. Soc. Amer. Proc. 13:213-217. 1948.

38. Ragland, J. L. and Seay, W. A. The effects of exchangeable calcium on the retention and fixation of phosphorus by clay fractions of soil. Soil Sci. Soc. Amer. Proc. 21:261-264. 1957.

39. Ravikovitch, S. Anion exchange: II. Liberation of the phosphoric acid ions adsorbed by soils. Soil Sci. 38:279-290. 1934.

40. Ross, G. J., Lawton, K. and Ellis, B. G. Lime requirement related to physical and chemical properties of nine Michigan soils. Soil Sci. Soc. of Amer. Proc. 28:209-212. 1964.

41. Suzuki, A., Lawton, K., and Doll. E. C. Phosphorus uptake and soil tests as related to forms of phosphorus in some Michigan soils. Soil Sci. Soc. Amer. Proc. 27:401-403. 1963.

42. Swenson, Richard M., Cole, C. Vernon and Sieling, Dale H. Fixation of phosphate by iron and aluminum and replacement by organic and inorganic ions. Soil Sci. 67:3-21. 1949.

43. Taylor, A. W., Gurney, E. L., and Lindsay, W. L. An evaluation of some iron and aluminum phosphates as sources of phosphate for plants. Soil Sci. 90:25-31. 1960.

44. Taylor, A. W., Gurney, E. L., and Moreno. E. C. Precipitation of phosphate from calcium phosphate solution by iron oxide and aluminum hydroxide. Soil Sci. Soc. Amer. Proc. 28: 49-52. 1964.

45. Toth, S. J. Anion adsorption by soil colloids in relation to changes in free iron oxides. Soil Sci. 44:299-314. 1937.

46. Truog, E. and Meyer, A. H. Improvements in the Denignes Colorinetric method for phosphorus and arsenic. Ind. and Eng. Chem., Anal. Ed., 1:136-139. 1929.

47. Wild, A. The effect of exchangeable cations on the retention of phosphate by clay. Jour. Soil Sci. 4:72-85. 1953.

48. Wild, Alan The retention of phosphate by soil: A review. Jour. Soil Sci. 1:221-238. 1949-50.

49. Withee, L. Change of phosphate potentials of calcareous soils upon additions of phosphorus. Ph. D. Dissertation, Kansas State University. 1963.