ABSTRACT

EVALUATION OF CERTAIN CHEMICAL TRANSFORMATIONS OF SOLUBLE FERTILIZER PHOSPHORUS APPLIED TO THREE MICHIGAN SOILS

By Carlostadio Sánchez

Field, greenhouse and laboratory studies were initiated in 1964 to evaluate certain chemical transformations that soluble phosphate may undergo when applied to three Michigan soils. The products of the transformations were related to the "available P", extracted by the Bray P-1 test, and to "P fixed." Corn was grown in the field and in the greenhouse in order to evaluate the yield response of this crop to fertilizer P.

The use of fertilizer P in the field and greenhouse, caused significant increases in yield. However, the response in the field was not nearly as large as that obtained in the greenhouse. Corn grown on the Conover loam from Shiawassee county responded more to P fertilizer than that grown on a similar soil type from Ingham county. On the Pewamo silty clay loam an intermediate response to P was obtained in the greenhouse.

The P content of the leaves of corn grown in the field was positively correlated with the use of increasing amounts of P fertilizer. However, the correlation was highest early in the season.

The P uptake by corn plants and the P left in the soil after the application of fertilizer, as measured with the Bray P-1 test accounted for only a small fraction of the total fertilizer P used. This effect was most evident on the Pewamo silty clay loam.

An incubation study showed that the percent P fixed decreased significantly as the amount of fertilizer P increased. This was most evident on the soil from Ingham county, which contained the lowest quantity of colloidal material. Although most of the applied P was fixed during the first week after application, there was a tendency for the percent P fixed by each of the soils to increase with time, especially where high rates of P were used.

The fractionation of the inorganic P at the end of twenty-two weeks, showed that from 70 to 99 percent of the applied P was recovered as water soluble, aluminum, iron, and calcium phosphate. The aluminum phosphate fraction contributed the most to these values, followed in order by the iron, the calcium, and finally, by the water soluble fraction.

A multiple regression study showed that the P extracted from the soil with the Bray P-1 method, was predominately aluminum phosphate followed by iron and then by calcium phosphate.

The relative importance of the calcium phosphate fraction with respect to other P forms was discussed. It is thought that some dicalcium phosphate may have been included in the fraction generally labeled as "aluminum phosphate."

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I. INTRODUCTION

When soluble phosphates are applied to soils, most of the P is rapidly converted to relatively insoluble forms. The specific reactions and the resulting discrete compounds are poorly defined since many factors play a part in determining the chain of events that take place between the time fertilizer is added to the soil and the formation of the ultimate products in the reaction sequence. A true equilibrium may never be established since the soil system is a complex and heterogeneous mixture of many dynamic components.

Chang and Jackson (17) suggested a fractionation procedure based on the solubility in various solutions of discrete phosphate compounds. This method offers an approximation to study the amounts of specific compounds formed after phosphates are applied to soils.

The available soil P, as determined by the Bray P-1 test (11), is used as the basis for fertilizer recommendations in Michigan. High correlations with plant growth have been obtained under variable conditions. Therefore, by relating the Bray P-1 test and the yield response of applied P to the several phosphate fractions, it should be possible to characterize the available forms of P in the soil.

This study was initiated in 1964 with the following objectives:

(a) To determine the effect of several rates of fertilizer P upon the water soluble, aluminum, iron, and calcium phosphate levels in three soils.

(b) To relate the Bray P-1 soil test after various time intervals of P addition to the several P fractions and to the use of applied P by corn.

II. REVIEW OF LITERATURE

A. Reactions of Phosphorus in the Soil

1. Mechanisms of phosphorus fixation.

The removal of phosphates from the soil solution, after soluble phosphate fertilizers are applied, is a common phenomenon. The immediate recovery of fertilizer P by a crop is equal to only 10 to 30 percent of the quantity added to the soil (45). It is assumed that the remaining 70 to 90 percent is converted to forms less soluble and not immediately available to plants. The process by which the availability of P is decreased and its mobility restricted is designated as "phosphorus fixation" (10, 51, 63).

Several mechanisms have been proposed to explain P fixation. These include: (1) adsorption of phosphates by the soil complex; (2) precipitation of P from the soil solution; and, (3) biological immobilization, which includes the use of P by soil micro-organisms. This discussion is concerned with the first two mechanisms. Very little is known about the role of soil microflora in P immobilization.

(a) Sorption reactions. It is known that soil colloids adsorb anions. The practical significance of such reaction has not been determined. Several workers (51, 66, 72) suggested a reversible exchange between phosphate and hydroxyl on the edges of the crystal lattice of clay minerals. Murphy (66), however, found that kaolinite fixes large amounts of phosphate but only when the mineral was very finely ground. This condition does not generally exist in the soil. Ellis and Troug (37), Coleman (29), Coleman, Thorup and Jackson (30) and Black (6) concluded that any fixation of phosphate by clay minerals is due to an alteration of the clay crystal by the phosphate solution which liberates soluble aluminum. Aluminum and free iron precipitates the phosphate. This type of reaction was described by Coleman et al. (30) as follows:

$$\text{Al-Clay} + MH_2PO_4 + 2\ MOH \rightleftharpoons M_3\text{-Clay} + \underbrace{Al(OH)_2\ H_2PO_4}_{\text{variscite type}} + 2H_2O$$

Where M is a metal cation which encourages the hydrolysis of aluminum.

Ravikovitch (67) suggested that P is fixed by clay in a H_2PO_4-Ca-clay linkage. This theory was later supported by Scarseth (68) and Allison (1). Wild (84), however, found an increase in P fixation by clay with monovalent as well as with divalent cations.

Whatever the mechanism of P fixation by clay is, its relative importance, in regard to other soil components, is not well understood. Thus, Franklin and Reisenauer (40), while correlating several soil properties with P fixation, found that there was not any relation to the type or content of clay. Kanwar (50), working with lateritic podzols in Australia, also concluded that the clay fraction contributed to only 20% of the total P retention. Most of the retention capacity resided in the coarser fractions as related to the presence of reactive sesquioxides.

In addition to the above mechanisms, Cole *et al.* (28) hypothesized that phosphates in calcareous soils may form a monomolecular layer deposit upon $CaCO_3$ surfaces.

(b) Chemical precipitation. It is possible that the three ionic forms of P into which orthophosphoric acid may dissociate, $H_2PO_4^-$, HPO_4^{-2}, and PO_4^{-3}, are involved in the chemical reactions of P in the soil.

Considerable evidence is available indicating that phosphate may be chemically fixed by precipitation with soil bases. In acid soils aluminum and iron play important roles in removing phosphate from the soil solution (41, 45, 47, 63). Aluminum and iron phosphate may be present as members of the isomorphous series variscite (aluminum phosphate), redondite (ferrian variscite), barrandite (aluminum strengite) or strengite (iron phosphate) (41). Cole and Jackson (26, 27) showed that iron and aluminum phosphate freshly precipitated from solutions, produce minute crystals, which correspond to members of the variscite-barrandite-strengite isomorphous series.

In alkaline soils the activity of calcium in solution seems to control the formation of insoluble P compounds (41, 51, 63). However, the iron and aluminum compounds may be responsible for some fixation in soils with high pH's (18, 45). The exact nature of the calcium phosphate compounds in alkaline soils, has not been established. According to Hemwall (45), who cited Eisenberg <u>et al</u>. there are between $CaHPO_4$ and CaO a series of solid compounds having an apatite $(CaF)\ Ca_4\ (PO_4)_3$ structure. The structure of apatite is remarkably stable, permitting a number of unusual types of substitutions which involve several ions.

The identification of the phosphate compounds in soil is difficult. X-ray and optical methods cannot be used without first concentrating the phosphate fraction. The process of concentration generally brings about changes in phosphate forms. In recent years this problem has been approached by use of solubility criteria. This relates the solubility of the soil phosphates to the solubility of known pure phosphate compounds (25, 41, 53, 60). Thus, the existence of a crystalline solid phase in soils will result, at equilibrium, in a fixed relation between its component ions in solution, and therefore, it should be possible to prove the existence of specific phosphate compounds in soils by the use of the solubility criteria. Lindsay and Moreno (60) developed a solubility diagram for variscite ($AlPO_4.2H_2O$), strengite ($FePO_4.2H_2O$), fluoroapatite ($Ca_{10}(PO_4)_6F_2$), hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), octocalcium phosphate ($Ca_4H(PO)_3.3H_2O$) and dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$). The activity isotherms for these compounds were represented on a single solubility diagram in which a function of the phosphate activity in solution was plotted against pH, assuming that Al^{3+} activity was limited by the solubility of gibbsite, Fe^{3+} activity by that of goethite, F^- activity by that of fluorite, and Ca^{2+} activity was that of a 0.005M solution. This diagram emphasizes the effect of pH on the relative stabilities of phosphate compounds that may be present in the soil.

Clark and Peech (25) represented the solubilities of calcium phosphate on a single solubility diagram in which the functions of the chemical potentials of $Ca(OH)_2$

and $Ca(H_2PO_4)_2$ are used as coordinates. They found that in the presence of solid phase $CaCO_3$, the chemical potential of lime (the value of pH - 1/2 Ca) depends upon the partial pressure of CO_2 in the atmosphere. This approach permitted them to conclude that monocalcium phosphate cannot persist in soils and dicalcium phosphate can exist only in soils in which the phosphate concentration in solution is unusually high; hydroxyapatite is probably the predominant solid phase in neutral and alkaline soils.

The use of methods based on the selective extraction of chemical solutions permit a more or less complete characterization in the soil of the soil phosphate compounds. Chang and Jackson (17) developed a method based on this principle. They subdivided the different forms of soil phosphate into aluminum phosphate, iron phosphate, calcium phosphate, reductant soluble iron phosphate, occluded aluminum phosphate, and occluded aluminum-iron phosphate, with successive extraction with neutral 0.5 N NH_4F, 0.1 N NaOH, 0.5 N N_2SO_4, Na_2SO_4, $Na_2S_2O_4$- citrate, neutral 0.5 N NH_4F, and 0.1 N NaOH, respectively. This method was used to follow the weathering process of phosphates in soils (18, 20, 46). Thus, Chang and Jackson (18) concluded that in the initial stage of weathering, calcium phosphate and aluminum phosphates were more likely to be formed because of the higher activities of the ions of calcium and aluminum than iron.

Since some calcium phosphates are more soluble than other forms, this phosphate changes rapidly to other less soluble forms. As time elapses, the calcium and aluminum phosphate gradually changes into iron phosphate which is the least soluble. This was supported by Chang and Chu (20) who found that superphosphate applied to the soil over 31 years, was present primarily as iron phosphate. However, three days after P was added to the soil in an incubation study aluminum phosphate was the predominant form.

Since the publication of the paper on fractionation of soil phosphorus by Chang and Jackson (17), criticisms and modifications have been suggested by Fife (38, 39), Glen _et al_. (42), and Khin and Leeper (52) as to the delineation of the four first main forms of inorganic phosphate. Thus, dicalcium phosphate and some iron phosphate may be dissolved in the neutral 0.5 _N_ NH_4F, which increases the amount of extracted aluminum phosphate. The use of an alkaline (pH 8.0 to 8.5) NH_4F solution prevents this dissolution. However, Chang and Liaw (22) found that the pH of the NH_4F solution in the range 7 to 8.5 does not affect the amount of P extracted. On the other hand, Chang (21) accepted the possibility of some dissolution of dicalcium phosphate in the neutral NH_4F when the phosphate ion in solution is unusually high. He added that NH_4F with a pH of above 8.0 may hydrolize more iron phosphate than the neutral solution in some soils (21).

The possibility exists that the extraction of calcium phosphate with 0.5 N H_2SO_4 following the extraction with NH_4F and NaOH, produces some error because sulfuric acid may dissolve some of the occluded phosphate. Khin and Leeper (52) demonstrated that the quantity of occluded phosphate dissolved may be great, if the soll contains a large amount of it. Glenn et al. (42), therefore, suggested the possibility of extracting the reductant soluble and the occluded iron and aluminum phosphate after the removal of the iron phosphate with 0.1 N NaOH and before extracting the calcium phosphate with 0.5N H_2SO_4.

2. Behavior of phosphorus fertilizer in soils

When a water-soluble salt such as monocalcium, monoammonium or diammonium phosphate is placed in moist soil, water moves from the surrounding soil into the granule to form an almost saturated solution of phosphate. The water movement is due to the osmotic potential gradient between the saturated solution and the soil water (56).

The concentrated solution is drawn off by the surrounding soil so that the solution touches and reacts with the soil minerals (47). The process of inward movement of moisture and outward movement of solution continues until the concentration of the solution is decreased by dilution or precipitation of the phosphate to the level at which no osmotic gradient remains (56, 57). The reactions that occur in the shell of soil surrounding the granule depend upon the compositions of both, the soil and the solution. The dissolution of monocalcium phosphate has been studied by Lindsay and Stephenson (57), Brown and Lehr (16) and Lehr <u>et al</u> (56), who showed that the initial saturated solution approximates that of a metastable triple-point solution in the system $CaO-P_2O_5-H_2O$ in equilibrium with $Ca(H_2PO_4)_2.H_2O$ and $Ca\ HPO_4.2H_2O$, and in which phosphorus is 3.98 <u>M</u>, Ca 1.44 <u>M</u> and pH 1.48. Anhydrous dicalcium phosphate slowly replaces the metastable calcium dihydrate and the solution composition approaches that of the stable triple point (8, 57) in which $Ca\ (H_2PO_4)_2.H_2O$ and $Ca\ HPO_4$ are in equilibrium. The stable triple point solution is 4.50 <u>M</u> with respect to P, 1.34 <u>M</u> with respect to calcium and has pH of 1.01 (58). Brown and Lehr (16) emphasized that the composition of the solution leaving the granule of monocalcium phosphate is independent of the composition of the surrounding soil. The validity of the approach was shown by their success in calculating, from phase rule data, the quantity of dicalcium phosphate that should remain as residual material at the site of the original pellet. According to this calculation, the fraction f of the original phosphate remaining is given by the equation:

$$f = \frac{(1-R)}{(2-R)}$$

Where R is the mole ratio of CaO/P_2O_5 in the composite solution removed from the granule. Bouldin et al. (8), however, showed that when superphosphate is mixed with other salts, the phase rule relationships of the three component system $Ca\text{-}P_2O_5\text{-}H_2O$ are inadequate. Mixtures of monocalcium phosphate and potassium chloride, for example, constitute a five component system in which six salts - $Ca(H_2PO_4).H_2O$, $CaHPO_4$, $CaHPO_4.2H_2O$, KCl, KH_2PO_4 and $Ca_2KH_7(PO_4)_4.2H_2O$ are the possible solid phases. In such systems, the composition of the released solution is controlled by the rate at which fertilizer is dissolved and the new phases precipitate.

It is expected that the highly acid phosphate solution that moves out from the dissolving granule attacks clays and oxides of iron and aluminum and dissolves calcium compounds with the formation of various phosphates of iron, aluminum and calcium. These will be precipitated differently depending upon the compositions of the soil and the fertilizer (44, 47, 57, 58, 59). The stable triple point solution in contact with the soil dissolves manganese more readily than aluminum, and aluminum more readily than iron (58). With time, the precipitation of these cations is in the order $Fe > Al > Mn$. Potassium tarankite, $H_6K_3Al_5(PO_4)_8 \cdot 18\ H_2O$ has been identified as a product of the reaction of the metastable triple point solution with the soil (59). With ammonium phosphates, the ammonium analogue, $H_6(NH_4)_3\ Al_5(PO_4)_8 \cdot 18H_2O$, was identified by Lindsay, according to Taylor et al. (74).

In other laboratory studies of the reactions of soils with concentrated phosphate solutions more than 30 compounds were identified as possible reaction products (61).

Chang and Chu (20) in fractionation of soil P studies, found that the added soluble phosphate in six soils, with pH varying between 5.3 to 7.5, after three days fixed P mainly as aluminum phosphate, and followed by iron phosphate and calcium phosphate. After 100 days, the amount of iron phosphate increased while that of the aluminum and calcium phosphate decreased. They suggested that the initial stage of the reaction of soluble phosphate with various cations is governed by the surface area of the solid phases with which the phosphates come into contact. As time elapses, the stability of the newly formed phases will be in accordance with the principle of the solubility product.

B. Availability of Primary Phosphorus Sources

Terman *et al.* (75) studied the relative availabilities of several phosphorus containing compounds. He grew rye-grass and sudan grass in the greenhouse on three acid and two alkaline soils. Monocalcium phosphate was slightly more available than dicalcium phosphate on alkaline soils but less available on acid soils. Dicalcium phosphate dihydrate was considerably more available than dicalcium phosphate anhydrous on all soils. Hydroxyapatite had very low availability on all soils. Octocalcium phosphate produced yields intermediate between those of anhydrous dicalcium phosphate and hydroxyapatite. After this greenhouse study had been completed, Lehr and Brown (55) made a petrographic study of the reaction products of the primary P sources and the alterations that had been made on the material that had been placed in the soil. They concluded that the availability of P from different sources may be increased by: (a) simple dissolution of crystalline products with the resultant build-up in P concentration in the soil solution; (b) an increase in the solubility of some of the products as a result of biological activity in the zone where the calcium phosphates are found; (c) the root hairs interact with crystalline materials of low solubility, and, therefore, increase the solubility of the materials at the interface between the crystals and the living root; and (d) hydrolysis in which a product with a low solubility reacts with water to yield an even more insoluble product and a compound with higher solubility than the original material. Thus, under certain conditions dicalcium phosphate dihydrate may be converted to octacalcium phosphate by hydrolsis, as follows:

$$4\ [CaHPO_4.2H_2O] \rightarrow Ca_4H(PO_4)_3.\ 3H_2O + H_3PO_4 + 5H_2O$$

The phosphorus released in this reaction may be readily available to the plant.

Bouldin and Sample (7) reported the relative availability of monocalcium phosphate, monoammonium phosphate, and diammonium phosphate when applied to an acid and a calcareous soil. They found good correlations between the uptake of P by plants in the greenhouse and the integrated solubility of the reaction products of soil P. The order of availability of the various phosphates on the acid soil was diammonium phosphate > monoammonium phosphate > monocalcium phosphate. On the calcareous soil, the availability was reversed: monocalcium phosphate > monoammonium phosphate > diammonium phosphate. The presence of the ammonium ion in the acid soil seemed to increase the availability of the reaction products.

Taylor et al. (74), comparing the effectiveness of various iron and aluminum complexes believed to be formed by the action of acid fertilizer solutions upon roots, found that these materials are relatively good sources of P and cannot be regarded as responsible for the "fixation" of phosphate from water soluble fertilizers. Chang and Chu (19) found that iron phosphate in a hydrated form as it occurs in lowland rice soils under flooding conditions, seems to be the most important source of available P to rice in Taiwan. Laverty and MacLean (54) found that the iron and aluminum phosphate fractions are used by the oat seedlings.

C. Prediction of Phosphorus Availability to Plants

The Bray P-1 method (11) in which 0.3 N NH_4F plus 0.025 N HCl is used as extractant is now widely utilized (3, 34, 40, 65, 71, 76, 80). In Michigan, this method provides an acceptable basis for P fertilizer recommendations (5, 31, 43, 70, 73).

Quantitative studies of plant growth as related to the applied P have resulted in several proposals of mathematical expressions. To this category belongs the Mitscherlich equation (83), which is based on the assumption that the yields brought about by successive increments of a plant nutrient followed a diminishing returns curve. This equation was stated as follows:

$$\frac{dy}{dx} = (A-y).C$$

in which dx represents the increment of fertilizer that produces a given increment of yield dy; A is the maximum yield that could be produced by indefinitely increasing the amount of fertilizer. When integrated, assuming y = o when x = o becomes:

$$\log (a-y) = \log A - CX$$

One of the important points in this equation is the constancy of the factor C. Mitscherlich and his colleagues (83) considered that C for each nutrient is constant regardless of the kind of plant, type of soil, or other factors. However, other investigations (14) indicated that C should vary with: (a) kind of plant; (b) form of nutrient; (c) fertility pattern; and, (d) planting rate and pattern.

Bray (12) modified the original Mitscherlich equation to:

$$\log (a-y) = \log A - C_1 b - CX$$

In this equation, A = maximum yield; y = yield obtained when X units of a nutrient are added to the soil; b = original nutrient content present in the soil expressed in units of the added nutrient X; C and C_1 are the proportionality constants (efficiency factors) of the original nutrient content in the soil and of the added nutrient, respectively. Working with this equation, Bray (12) adopted the percentage yield concept originally described by Baule.

Empirical equations based in statistics methods have been used to explain the relationship between different soil testing procedures and plant growth under particular conditions.

Plant analyses also have been used as a diagnostic tool to indicate the availability of mineral elements. It is based on the assumption that there is a relationship between the amount of a nutrient present in the soil and its uptake by plants. The choice of the kind of tissue and time of sampling for a particular plant are some of the factors affecting the interpretation of plant analysis as a guide of the nutritional status. Tyner and Weed (78) and Tyner (79) selected the corn leaf for analysis because it represents a seat of very active synthesis. The sixth leaf from the base of the plant was selected for sampling, because this position is easily recognized, and because it is the leaf immediately below the leaf in whose axil the uppermost ear is born. Generally, leaf samples have been collected at silking time (4, 32, 79, 81), although Ellis _et_ _al_. (36) and Webb and Pesek (82) observed that the effect of P applications was reflected primarily in the early growth stages.

III. EXPERIMENTAL PROCEDURE

A. Field experiments

Three field experiments were established at the following locations:

1. Ingham County - in the S.W. corner of section 15, Wheatfield township.
2. Shiawassee county - in the N.W. corner of section 26, Rush township.
3. St. Clair county - in the N.W. corner of section 6, Columbus township.

The soils in experiments 1 and 2 are Conover loams which are imperfectly drained Gray-Brown Podzolic soils developed on loam or silt loam calcareous till. A description of the most important horizons occurring in these two profiles is as follows:

Conover loam (Ingham County)

Horizon	Depth (inches)	Description
Ap	0-6	Loam; dark grayish brown (10YR4/2); weak, granular structure; very friable when moist and slightly hard when dry; pH 6.2
A2	6-14	Loam; pale brown (10YR6/3) mottled with abundant yellowish brown (10YR5/6) and light brownish gray (10YR6/2); moderate, medium granular to weak, thin, platty structure; friable when moist and slightly hard when dry; pH 5.9

Horizon	Depth (inches)	Description
B_t	14-24	Sandy clay loam; yellowish brown (10YR 5/6) mottled with grayish brown (10YR 5/2); moderate, medium to coarse, subangular blocky structure; firm when moist and hard when dry; pH 7.0

Conover loam (Shiawassee County)

Ap	0-8	Loam; dark grayish brown (10YR4/2); fine, granular structure; friable when moist and slightly hard when dry; pH 6.3
B_1	8-14	Clay loam; brown (10YR4/2), mottled with 10% of grayish brown (2.5Y5/2) with 25% yellowish brown (10YR5/6); subangular blocky structure; firm when moist and hard when dry; pH 6.8
B_2	14-24	Clay loam; brown (10YR5/3) mottled with light brownish gray (10YR6/2 and yellowish brown (10YR5/6); subangular blocky structure; firm when moist and hard when dry; pH 7.2

Experiment 3 was located on a Pewamo silty clay loam. This soil is a poorly drained Humic Gley in the Gray Brown Podzolic Region, developed in calcareous silty clay loam or clay loam till. The description of this profile at the site of the experiment is:

Horizon	Depth (inches)	Description
Ap	0-7	Silty clay loam; very dark brown (10YR2/2); granular structure; firm when moist, slightly plastic when wet, and hard when dry, pH 6.1

Horizon	Depth (inches)	Description
A_2	7-10	Clay loam. Very dark gray (10YR3/1); granular structure; firm when moist; pH 6.1
B_{21g}	10-17	Silty clay loam; dark gray (10YR4/1) mottled with olive brown (2.5Y4/4) and dark brown (10YR4/3), coating of gray (10YR5/1) and grayish brown (10YR5/2) on faces of peds; fine angular blocky structure; very firm when moist; pH 6.1
B_{22g}	17-40	Silty clay; mottled with grayish brown (10YR5/2-2.4Y5/2), olive brown (2.5Y4/4), dark gray (10YR4/1), and yellowish brown (10YR5/6-5/8), mottles are many; medium, angular blocky structure; firm to very firm when moist; pH 6.5
C_1	40+	Silty clay loam; yellowish brown (10YR5/6-5/8), mottled with grayish brown (2.5Y5/2)-(10YR5/2) and dark grayish brown (2.5Y4/2), mottles are common; weak, coarse, angular blocky to massive structure; very firm when moist; pH 7.1

Certain chemical and physical characteristics of the surface horizon of each soil are shown in Table 1.

The field plots in the three experiments were arranged in a randomized block design with four replications of each treatment. There were 4 rows, 42 inches apart and 50 feet long for each plot. Six levels of P, namely 0, 10, 20, 40, 80 and 160 pounds per acre of elemental P were studied.

Table 1. Some chemical and physical characteristics of the three soils where field experiments were located

Soil Type	County	Organic Matter %	C.E.C.[1/] me/100gr.	P (Bray P-1) ppm	pH	Mechanical Analysis: Sand (%) 2.-.02mm	Mechanical Analysis: Silt (%) .02-.002mm	Mechanical Analysis: Clay (%) .002 mm	Kind and approximate composition of the clay fraction[2/]	
Conover loam	Ingham	2.0	10.9	8.8	6.2	53.2	27.0	19.8	(C-1)[1]	30%
									V	10%
									K	20%
									I	30%
Conover loam	Shiawassee	2.3	12.6	8.1	6.3	42.2	31.0	26.8	V	20%
									K	30%
									I	40%
Pewamo silty clay loam	St. Clair	3.5	26.5	15.9	6.1	15.2	42.0	42.8	(C-V-M)	10%
									K	30%
									I	50%

1/ Cation exchange capacity

2/ C chlorite; V vermiculite; K kaolinite; I illite; parenthesis, random interstratification

Corn was the indicator crop. The other major nutrients were made adequate by adding 150 pounds per acre of nitrogen and 166 pounds per acre of potassium. P, N, and K were applied as diammonium phosphate, ammonium nitrate and potassium chloride, respectively. One-half of the P and all the N and K were broadcasted on the surface of the soil before plowing. The remaining P was applied after plowing and disked in. Soil samples consisting of 20 borings per plot to a depth of six inches, were taken prior to fertilizer application and after harvesting the corn. A second composite soil sample composed of 50 subsamples from each experimental area, was taken before fertilizer was applied. This soil was used in the greenhouse and in the incubation studies.

The experiments in Ingham, Shiawassee, and St. Clair counties were planted, respectively, on May 11, May 25 and May 21 of 1964. The crop in St. Clair was lost because of a poor stand caused mainly by lack of rainfall for some time after planting.

Leaf samples were collected at different stages of growth. Each sample consisted of 10 leaves selected randomly from 10 plants in one of the central rows of each plot. The fifth leaf from the base of the plant was selected. In Ingham county, samples were taken on June 25, July 20 and August 18; in Shiawassee county on July 9, August 4, and September 1. The last sampling was made when the ears were completely developed.

In Ingham County, grain harvests were made on October 13. Two areas per plot, each being 1/1000 acre in size were harvested. Areas were selected that contained the equivalent of exactly 15,000 plants per acre.

In Shiawassee county, one central row per plot with a population of 12,000 plants per acre, was harvested on October 13.

The corn grain yields were calculated at a 15.5% moisture content.

B. Greenhouse Trials

For greenhouse work, the soil samples from the three experimental areas were air-dried and crushed to pass a 2-mm sieve. Six levels of P equivalent to 0, 20, 40, 80, 160 and 320 pounds per two-million pounds of soil were applied as diammonium phosphate. Uniform applications of N and K were added to all treatments.

Ammonium nitrate was used to bring the total N up to a rate equivalent to 300 pounds per acre of N. Potassium chloride was used to supply K at the equivalent rate of 332 pounds per acre of K.

The treatments in the three experiments were set up as randomized block experiments with four replications of each treatment. All fertilizer materials were thoroughly mixed with the soil. Corn was grown in the greenhouse in 3-gallon glazed jars, each filled with 13.0 kgr. of soil. Eight seeds were planted. After seedling emergence, the population was reduced to four plants per jar. Distilled water was used as needed. Plants were grown for 35 days. Then, the plants were cut off at the level of the soil, dried in a draft oven at 60°C and weighed. Samples for chemical analysis were ground in a Wiley Mill. After the crop harvest, soil samples consisting of 5 borings in each jar were taken.

C. Laboratory Studies

1. Incubation Study

Nine P levels, 0, 10, 20, 40, 80, 160, 320, 640 and 1280 ppm P were established with the use of KH_2PO_4. One hundred grams of soil for each treatment were placed in 200 ml beakers. Phosphorus was added from a standard solution and well mixed with the air-dried soil. Each soil sample was adjusted to the moisture equivalent level and tightly covered with plastic Saran wrap, which permitted the air to diffuse in and out but limited the passage of water vapor. The samples were incubated at 25°C. There were three replications for each treatment. At the end of one, two, eight and twenty-two weeks, soil samples were taken and air-dried for chemical analysis.

2. Soil Analysis

Available phosphorus was determined by the Bray P-1 method (11), using an extracting solution of 0.03 N NH_4F plus 0.025 N HCl. The soil to extracting solution ratio was 1 to 8. Water soluble phosphates, aluminum phosphates, iron phosphates and calcium phosphates were determined by the methods of Chang and Jackson (17).

Organic matter was determined by the method of Walkley-Black (49). The cation exchange capacity was evaluated with NaOAc at a pH of 8.2, as described by Jackson (49). The Bouyoucos (9) method was used for mechanical analysis. The identification and approximate composition of the clay fractions were made with X-rays, DTA, surface area, cation exchange capacity, and infrared absorption spectra, with procedures described by Jackson (48). The pH was determined in a 1:1 soil-water ratio with a potentiometer.

3. Plant Analysis

Corn plants grown in the greenhouse and leaves from plants grown in the field were analyzed for P. Ground tissue was dried at 65°C. To 0.2 grams of plant tissue was added 5 ml. of alcoholic $Mg(NO_3)_2$. The sample was dry ashed in a muffle furnace at 500°C. The ash was dissolved in 2N HCl and filtered into a 200 ml. flask. The pH was adjusted to 3.0 with the indicator 2-4 dinitrophenol. A 50 ml. aliquot was taken and phosphorus was determined by the Deniges colorimetric method as modified by Truog and Meyer (77). Percent of transmission at 660λ was determined in a Bauch and Lomb spectrophotometer.

IV. RESULTS AND DISCUSSION

A. Field experiments

Corn was planted at three locations. The weather at each location during the entire growing season was characterized by significantly less than normal precipitation. This is an important consideration in interpreting the data obtained from each field experiment.

Corn yields were not obtained from the Pewamo silty clay loam because an extended dry period immediately after planting on this fine textured soil resulted in a very poor and uneven stand.

The grain yields produced in Shiawassee and Ingham counties are shown in Figure 1. As can be seen, the use of fertilizer increased the yields in each experiment, but more so in Shiawassee county. Maximum grain yields were produced with approximately 40 pounds of P in Ingham county and with 80 pounds in Shiawassee county, despite the fact that the soils in each experiment had similar soil test results before applying fertilizer and before planting the crop (Table 1).

The residual available P levels, as measured by soil tests, after the crops were harvested are shown in Table 2. In Ingham County, soil test levels for P increased only 42.8 pounds per acre where 160 pounds had been used.

Figure 1. Effect of Applied P to Two Locations on the Yield of Corn Grain (Field Experiments)

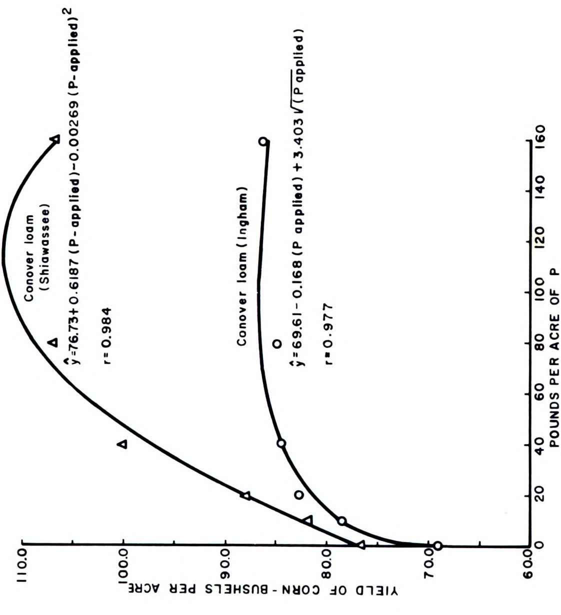
Conover loam (Shiawassee)
ŷ=76.73+0.6187 (P-applied)−0.00269 (P-applied)²
r= 0.984
Conover loam (Ingham)
ŷ=69.61 − 0.168 (P applied) + 3.403 √(P applied)
r=0.977
YIELD OF CORN-BUSHELS PER ACRE
110.0
100.0
90.0
80.0
70.0
60.0
POUNDS PER ACRE OF P
0
20
40
60
80
100
120
140
160

Figure 1.

TABLE 2 - Changes in P content (Bray P-1) of three soils as affected by the addition of P fertilizer and the production of one corn crop, (Field Experiments).

Treatments			P (pounds/acre) 1/								
			Conover Loam (Ingham)			Conover Loam (Shiawassee)			Pewamo Silty Clay Loam(St.Clair) 2/		
(Pounds/acre) N	P	K	Before P Addition	107 days after P addition	Change	Before P addition	169 days after P addition	Change	Before P addition	141 days after P addition	Change
150	0	166	19.4	25.8	+ 6.4	14.8	10.8	- 4.0	31.8	26.8	- 5.0
150	10	166	19.2	27.2	+ 8.0	17.2	11.4	- 5.8	33.2	30.4	- 2.8
150	20	166	17.0	28.0	+11.0	16.0	17.0	+ 1.0	30.4	31.2	+ 0.8
150	40	166	18.4	32.0	+13.6	15.6	16.4	+ 0.8	34.8	35.0	+ 0.2
150	80	166	17.2	36.2	+19.0	16.8	32.8	+16.0	33.2	44.0	+10.8
150	160	166	14.6	57.4	+42.8	16.4	51.8	+35.4	27.8	49.4	+21.6

1/ Average of 4 replications

2/ The corn population was very poor

In Shiawassee county, the change was even less, being equal to 35.4 pounds. Where no crop was harvested from the Pewamo silty clay loam, the value was equal to only 21.6 pounds per acre.

These data illustrate the very high P fixing power of these soils, in that corn has a relatively low requirement for P, much less than that suggested by the difference between the theoretical tests immediately after fertilization (available P in untreated soil as measured with soil test plus available P in fertilizer) and the actual tests after the crops were harvested.

Corn leaves were sampled for chemical analysis at three times during the season. The first sampling period occurred in the middle of the vegetating stage. The second was made at silking time while pollen was being dispersed. The last sampling date occurred after the ears were completely formed in the later part of the graining stage.

The P content of the leaves of corn plants grown in the field are shown in Table 3. The use of increasing rates of fertilizer P increased the percent P in the corn leaves. Generally speaking there was a reduction in percent P as related to sampling date. This was more apparent in Ingham than in Shiawassee county.

TABLE 3 - The P content of corn leaves at three stages of growth as affected by rates of P applied to two soils (Field experiments)

Treatments			Conover Loam (Ingham)			Conover Loam (Shiawassee)		
			Time of Sampling (days after planting)					
Pounds/acre								
N	P	K	44	70	100	46	72	100
			% P[1]					
150	0	166	0.22	0.20	0.20	0.21	0.26	0.20
150	10	166	0.23	0.25	0.23	0.27	0.27	0.22
150	20	166	0.25	0.26	0.24	0.28	0.28	0.25
150	40	166	0.26	0.26	0.24	0.30	0.30	0.29
150	80	166	0.31	0.28	0.25	0.32	0.30	0.29
150	160	166	0.35	0.28	0.26	0.34	0.35	0.32
L.S.D. .05			0.015	0.007	0.016	0.019	0.014	0.010
L.S.D. .01			0.027	0.010	0 021	0.026	0.020	0.013

---

[1] Average of four replications

The P content of the leaves was closely related to both the grain yield and the P applied (Table 4). The highest correlation coefficient involving yields from the Ingham county experiment were obtained with the July sampling. The same in Shiawassee county was obtained for the September date.

The relationship between the P content of leaves and applied P was highest at the first sampling date at each experiment. This observation agrees with those of Ellis _et al_. (36) and Moham (64).

B. Greenhouse Experiments

Before any fertilizer was applied in the field experiments, soil was collected from all three sites for use in the greenhouse. Similar rates of P, as were used in the field, were added to each soil. Corn was then planted. The data in Table 5 show the yield (dry weight), the percent of P content in the corn plants, and the P uptake by the plants.

In the greenhouse, the use of each increment of fertilizer P, increased the dry weight of the corn plants grown on all three soils. The use of even the highest rate of P, equivalent to 320 pounds per acre, was not sufficient to produce maximum yields. This was not the case in the field.

TABLE 4 - Linear correlation coefficients of the P content of corn leaves at three stages of growth as related to grain yields and fertilizer rates on two soils (Field experiments).

	P in Leaves					
	Conover Loam - Ingham			Conover Loam - Shiawassee		
	June 24 44 days after planting	July 20 70 days after planting	August 18 100 days after planting	July 9 46 days after planting	August 4 72 days after planting	September 1 100 days after planting
Corn grain yield	0.891**	0.941**	0.907**	0.903**	0.796**	0.959**
P applied	0.897**	0.759**	0.737**	0.925**	0.821**	0.856**

** Significant at 0.01 level

TABLE 5 - The dry weight, percent P, and P uptake of corn grown on three soils as related to rates of P fertilizer (Greenhouse experiments). 1/

Treatments (Pounds/acre)			P added mg/Pot	Conover Loam (Ingham)			Conover Loam (Shiawassee)			Pewamo Silty Clay Loam (St. Clair)		
N	P	K		Dry Weight (Grams)	% P	P uptake (mmg)	Dry Weight (Grams)	% P	P uptake (mmg)	Dry Weight (Grams)	% P	P uptake (mmg)
300	0	332	0	5.0	0.14	6.8	2.8	0.12	3.3	4.6	0.16	7.4
300	20	332	127	5.6	0.15	8.4	4.0	0.13	5.2	5.3	0.17	8.7
300	40	332	254	6.5	0.16	10.4	4.9	0.14	6.8	6.3	0.17	10.6
300	80	332	508	8.7	0.16	14.1	7.7	0.15	11.7	8.7	0.18	15.4
300	160	332	1,016	11.0	0.21	22.5	17.0	0.21	34.7	13.8	0.19	26.2
300	320	332	2,032	12.8	0.26	32.5	22.4	0.33	74.5	17.1	0.26	44.5
L.S.D. 0.05				0.78	0.010	1.62	0.50	0.011	1.09	0.82	0.008	1.14
L.S.D. 0.01				1.07	0.015	2.22	0.70	0.015	1.49	1.13	0.011	1.56

1/ Average results of 4 replications

Both the lowest and the highest dry weight of corn plants were produced in the soil from Shiawassee county. An explanation for this is not easily evident even when taking into consideration the natural differences in the three soils. Visual observations suggest that the Shiawassee county soil had a more stable structure which contributed to more rapid germination and emergence than on the other two soils.

The use of increasing rates of fertilizer P, generally raised the percent P in the corn plants on all three soils. At the highest fertilizer rate, the P content of the corn grown on the Ingham Conover loam and the St. Clair county Pewamo silty clay loam were very similar and substantially less than that in the corn on the Shiawassee county Conover loam soil.

The P uptake was obtained by multiplying the P content of the corn plants by the dry weight. Such a procedure accentuated the difference between the soils where high rates of P were used, because the Shiawassee county soil produced both the highest dry weight and percent P. This is schematically shown in Figure 2.

The linear relationships between yields produced in the greenhouse, the percent P in the corn plants, the P uptake, and applied P are shown in Table 6. All values

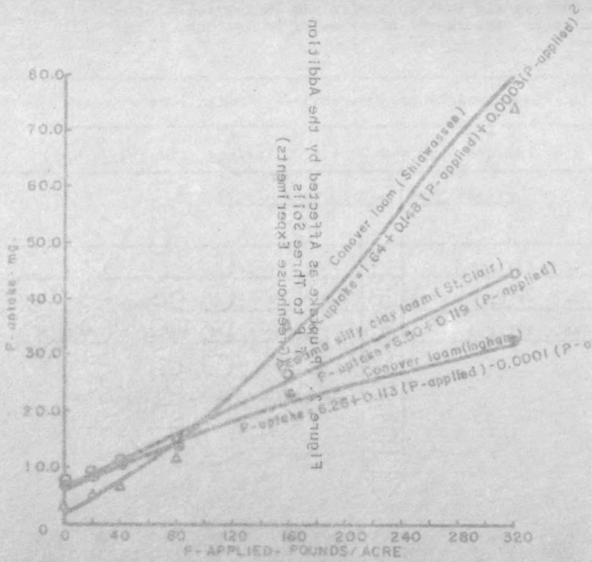
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
P-uptake - mg.
0
40
80
120
160
200
240
280
320
P-APPLIED- POUNDS/ACRE
Conover loam (Shiawassee)
P-uptake = 1.64 + 0.148 (P-applied) + 0.0003 (P-applied)^2
Sims silty clay loam (St. Clair)
P-uptake = 6.50 + 0.119 (P-applied)
Conover loam (Ingham)
P-uptake = 6.26 + 0.113 (P-applied) - 0.0001 (P-applied)^2

Figure 2

Figure 2. P uptake as Affected by the Addition of P to Three Soils (Greenhouse Experiments)

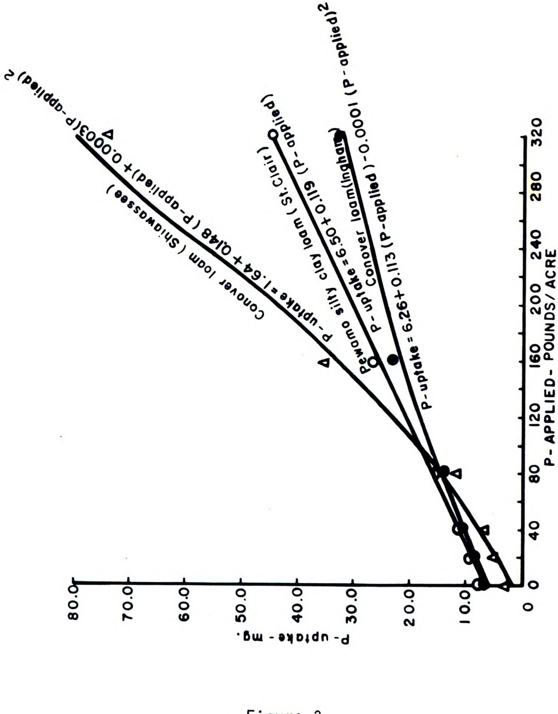
Conover loam (Shiawassee)
P-uptake = 1.64 + 0.148 (P-applied) + 0.0003 (P-applied) 2
Pewamo silty clay loam (St. Clair)
P-uptake = 6.50 + 0.119 (P-applied)
Conover loam (Ingham)
P-uptake = 6.26 + 0.113 (P-applied) - 0.0001 (P-applied) 2
P-uptake - mg.
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
0
40
80
120
160
200
240
280
320
P- APPLIED- POUNDS/ ACRE

Figure 2

TABLE 6 - Simple correlation coefficients of P uptake, percent P, dry weight of corn plants, and P applied to three soils (Greenhouse experiments).

Variables	---Conover Loam (Ingham)-----			Conover Loam (Shiawassee)--			Pewamo Silty Clay Loam- (St.Clair)		
	% P	Dry Wt.	P applied	% P	Dry Wt.	P applied	% P	Dry Wt.	P applied
				Simple Correlation Coefficients					
Dry Weight	--	--	0.941**	--	--	0.975**	--	--	0.969**
% P	--	0.919**	0.980**	--	0.945**	0.990**	--	0.881**	0.968**
P uptake	0.979**	0.972**	0.988**	0.995**	0.963**	0.992**	0.962**	0.975**	0.998**

** Significant at 0.01 level

are statistically significant at the one percent level. The correlation coefficients obtained from the Shiawassee county soil tend to be slightly higher than those from the other two soils.

Soil tests were made before fertilizer was added to the soil in the greenhouse and immediately after the crops were harvested. The results are shown in Table 7.

The level of P, before fertilizer was used, in the two Conover soils was similar. Each value is considered to represent a "low" level of P availability. The level in the Pewamo silty clay loam is considered as "medium".

After the crops were harvested, soil test levels increased with the use of fertilizer P. In Ingham county soil, up to one-half of the fertilizer P remained in an available form; whereas, only up to one-fourth was available in the Shiawassee and St. Clair county soils.

The P removed by the crops and P left in the soil as measured by standard soil test procedure do not account for all of the applied fertilizer P. Therefore, some must have been converted into non-extractable forms or "unavailable forms" not measured by the Bray P-1 test. This effect was more evident in the soils from Shiawassee and St. Clair counties. The effect was greatest at low levels of applied P.

TABLE 7 - Change in P content (Bray P-1) of three soils as affected by the addition of P fertilizer and the production of one corn crop (Greenhouse experiments)

Treatments (pounds/acre)			P (Pounds/acre)[1]								
			Conover Loam (Ingham)			Conover Loam(Shiawassee)			Pewamo Silty Clay Loam (St. Clair)		
N	P	K	Before addition	35 days after P addition	Change	Before addition	35 days after P addition	Change	Before addition	35 days after P addition	Change
300	0	332	17.6	18.8	+ 1.2	16.2	14.0	- 2.2	31.8	28.0	- 3.8
300	20	332	17.6	30.6	+ 13.0	16.2	17.2	+ 1.0	31.8	32.9	+ 1.1
300	40	332	17.6	36.4	+ 18.8	16.2	21.4	+ 5.2	31.8	37.8	+ 6.0
300	80	332	17.6	55.4	+ 37.8	16.2	31.0	+14.8	31.8	46.8	+15.0
300	160	332	17.6	95.2	+ 77.6	16.2	60.0	+43.8	31.8	71.8	+40.0
300	320	332	17.6	171.2	+153.6	16.2	108.6	+92.4	31.8	122.3	+90.5

1/ Average of 4 replications

Data obtained in the greenhouse and in the field clearly demonstrated that the three soils were deficient in available P. The response to fertilizer P was greatest in the greenhouse experiment. The explanation of this undoubtedly is related to the fact that in the greenhouse stands were not as variable, deficiencies in water were not as prolonged, and there were more plants per unit of soil than in the field. This situation probably resulted in a greater density of roots in the greenhouse soils and, therefore, a better opportunity for the roots to contact the P containing fertilizer particles.

C. Laboratory Experiments

A laboratory experiment was conducted with samples of each of the three soils in order to determine what happens to fertilizer P after it is added to the soil. P containing fertilizer was added to each soil. The soils were then incubated at a constant temperature of 25 degrees centigrade.

The data in Table 8 summarize the Bray P-1 test on the three soils as they were affected by the addition of various rates of P. In general, available P increased with each increment of fertilizer added, but decreased with time, even at the high rate of 1,280 ppm P. These data illustrate the tremendous P fixing power of each of these soils.

TABLE 8 - Effect of time of incubation and rates of P application to three soils on available P as determined by Bray P-1 soil test.

ppm P added	Conover Loam (Ingham)				Conover Loam (Shiawassee)				Pewamo Silty Clay Loam (St. Clair)			
	Incubation time (weeks)											
	1	2	8	22	1	2	8	22	1	2	8	22
	ppm P (Bray P-1) 1/											
0	13.6	12.3	10.0	10.7	10.4	9.2	8.2	8.0	16.0	16.0	13.0	13.3
10	15.2	15.2	12.4	11.8	11.2	9.8	8.5	9.0	16.0	16.0	13.4	13.5
20	20.8	18.4	16.5	16.2	12.8	10.4	8.8	9.7	16.0	16.0	14.2	13.4
40	32.0	28.8	22.4	23.9	25.6	16.0	13.8	14.4	22.4	25.6	22.4	22.5
80	72.8	62.4	40.0	38.3	32.0	30.4	27.2	25.6	30.4	35.2	38.4	33.3
160	124.8	124.8	78.1	76.2	74.2	73.6	54.4	51.2	77.2	73.6	64.0	57.6
320	220.6	211.2	177.9	181.0	169.6	144.0	134.4	146.3	195.2	195.2	147.2	140.9
640	576.0	512.0	384.0	382.3	336.0	320.0	304.0	319.6	339.2	339.2	339.2	284.9
1,280	1,170.0	1,120.0	864.0	854.9	896.0	880.0	825.6	802.0	852.0	816.0	704.0	511.9
L.S.L. 0.05	1.7	1.8	0.7	4.5	2.2	19.5	0.6	1.4	0.7	0.7	2.9	0.6
L.S.D. 0.01	2.3	2.5	1.0	6.2	3.0	26.8	0.8	1.9	1.0	1.0	4.0	0.8

1/ Average of three repetitions

Soil test results and fertilizer rates were closely associated as is shown by the correlation coefficients in Table 9. The difference between the coefficients for the three soils are exceptionally small.

The data in Table 10 were calculated from the soil test results. These data show the amount of P that was fixed by each soil. The fine textured Pewamo silty clay loam fixed the most fertilizer P. This was especially evident at the two highest rates of P used. At rates of less than 320 ppm, the difference in fixation in the Pewamo and Conover (Shiawassee) was reduced to a very low level. Shiawassee county Conover loam fixed more than did the Ingham county Conover loam.

Apparently the fixation process was not complete when these studies were terminated because the values were still increasing at the time of the last sampling. Therefore, these data cannot be used to estimate the total P fixing capacities of these three soils.

The highly significant correlation coefficients presented at the bottom of Table 10 suggest that the relationship between rates of fertilizer P and fixed P becomes more direct with time in that, for each soil, the coefficients increased with each successive soil sampling date.

TABLE 9 - Simple correlation coefficients between P applied and soil tests for P (Bray P-1), after various incubation times.

Incubation time --weeks--	Conover loam (Ingham)	Conover loam (Shiawassee)	Pewamo silty clay loam (St.Clair)
	Simple correlation coefficient		
1	0.998**	0.991**	0.995**
2	0.997**	0.987**	0.996**
8	0.997**	0.990**	0.998**
22	0.997**	0.976**	0.998**

** Significant at 0.01 level

TABLE 10 - Amount of P fixed on three soils as related to time of incubation and rates of P applied.

ppm P Added	Conover loam (Ingham)				Conover loam(Shiawassee)				Pewamo silty clay loam (St.Clair)			
	Incubation Time (Weeks)											
	1	2	8	22	1	2	8	22	1	2	8	22
	ppm P fixed (Bray P-1) 1/											
10	8.4	8.1	7.6	8.9	9.2	9.4	9.7	9.0	10.0	10.0	9.6	9.8
20	12.8	13.9	13.5	14.5	17.6	18.8	19.4	18.3	20.0	20.0	18.8	19.9
40	21.6	23.5	27.6	26.8	24.8	33.2	34.4	33.6	33.6	30.4	30.6	30.8
80	20.8	29.9	50.0	52.4	58.4	58.8	61.0	62.4	67.6	62.8	54.6	60.0
160	48.8	47.5	91.9	94.5	96.2	95.6	113.8	116.8	98.8	102.4	109.0	115.7
320	113.0	121.1	152.1	149.7	200.8	185.2	193.8	181.7	139.4	140.8	185.8	192.4
640	77.6	140.3	266.0	268.4	314.4	329.2	344.2	328.4	309.2	316.8	313.8	368.4
1280	121.6	172.3	426.0	435.8	394.4	409.2	462.6	486.0	444.0	480.0	589.0	781.4
Simple Correlation Coefficients	0.827*	0.913**	0.991**	0.992**	0.953**	0.960**	0.972**	0.984**	0.984**	0.989**	0.998**	0.999**

1/ Average of 3 repetitions

* Significant at 0.05 level

** Significant at 0.01 level

The data in Table 11 were calculated from those presented in Table 10. The values in this table illustrate the percent of fertilizer P that was fixed by each soil. Generally the percent P fixed decreased with each increment of added fertilizer P. This was the situation for each soil and for each incubation period.

The fixation rate was slowest in the Conover loam from Ingham county, ranging between 10 and 84 percent at the end of 7 days and most rapid in the Pewamo silty clay loam which had a range in percent fixed P between 34 and 100 percent at the end of 1 week. The values at the end of 22 weeks of incubation were 34 to 89 for the Conover soil and 61 to 98 for the Pewamo. Such differences suggest that different kinds of reactions were involved in the P fixation process for each of the soils.

At high rates of applied P, the percent P fixed by all three soils increased with time. The greatest range occurred in the Pewamo soil, which received 1,280 ppm P. During the twenty-two week incubation period the percent P fixed increased from 35 to 61 percent.

The data in Table 11 suggest that the two samples of Conover were not as similar perhaps as they should be considering that each soil represented the same soil type. The percent P fixed in the Shiawassee county soil was much greater and, on the average, the fixation of fertilizer P occurred at a more rapid rate than in the Ingham county sample.

TABLE 11 - Percent P fixed by three soils as affected by time of incubation and rates of P application

ppm P added	Conover Loam (Ingham)				Conover Loam (Shiawassee)				Pewamo Silty clay loam - (St. Clair)			
	Incubation time (weeks)											
	1	2	8	22	1	2	8	22	1	2	8	22
	% P fixed 1/											
10	84.00	81.0	76.00	89.00	92.00	94.00	97.00	90.0	100.00	100.00	96.00	98.00
20	64.00	69.50	67.50	72.50	88.00	94.00	97.00	91.50	100.00	100.00	94.00	99.50
40	54.00	58.75	69.00	67.00	62.00	83.00	86.00	84.00	84.00	76.00	76.50	77.00
80	26.00	37.38	62.50	65.00	73.00	73.50	76.25	78.00	84.50	78.50	68.25	75.00
160	30.50	29.69	57.44	59.06	60.13	59.75	71.13	73.00	61.75	64.00	68.13	72.31
320	35.31	37.84	47.53	46.78	62.75	57.88	60.56	56.78	43.56	44.00	58.06	60.13
640	12.13	21.92	41.56	41.94	49.13	51.44	53.78	51.31	48.31	49.50	49.03	57.56
1,280	10.00	13.46	33.28	34.05	30.81	31.97	36.14	37.97	34.69	37.50	46.02	61.05

1/ Average of three repetitions.

Because fertilizer P was fixed by these three soils in different amounts and at different rates, the question naturally arises as to why such differences occurred. The results of the P fractionation after 22 weeks of incubation help to explain this situation. The fractions labeled by Chang and Jackson (17) as water soluble, aluminum, iron, and calcium phosphates are shown in Table 12. The data in this table show that where no fertilizer P was used, there was approximately four times the calcium phosphate in the Pewamo soil as in either of the two Conover soils. The Pewamo also contained about twice as much iron phosphate as the two Conover soils, as well as significantly more aluminum phosphate. All three soils, where no fertilizer P was used, contained only traces of water soluble phosphate while the greatest quantity of P was in the iron phosphate fraction.

In general all of the P fractions were increased by the use of increasing rates of fertilizer P. In all three soils the fraction labeled aluminum phosphate increased the most. The iron phosphate was also dominant where relatively low rates were used up to and including 80 ppm P. At 160 ppm P, in the Ingham county soil the values for the iron and aluminum P fraction were similar while in the other two soils the iron P continued to dominate. At the 320 ppm

TABLE 12 - Water soluble, aluminum, iron, and calcium phosphate in three soils after 22 weeks of incubation as affected by rates of P fertilizer.

ppm P Added	---Conover Loam (Ingham)---				Conover Loam(Shiawassee)---				Pewamo Silty Clay Loam (St.Clair)-----			
	H_2O Soluble Phosphate	Al-Phosphate	Fe-Phosphate	Ca-Phosphate	H_2O Soluble Phosphate	Al-Phosphate	Fe-Phosphate	Ca-Phosphate	H_2O Soluble Phosphate	Al-Phosphate	Fe-Phosphate	Ca-Phosphate
						ppm P [1/]						
0	Trace	21.3	49.6	21.6	Trace	16.0	56.3	19.4	Trace	31.9	109.3	80.2
10	Trace	26.3	52.0	21.8	Trace	19.0	60.7	19.6	Trace	36.3	109.8	82.3
20	Trace	29.9	55.0	24.9	Trace	23.4	62.7	20.1	Trace	41.7	111.0	85.2
40	5.6	37.5	58.4	24.9	Trace	28.9	72.4	29.3	Trace	50.8	123.9	85.7
80	6.2	57.5	76.0	25.5	Trace	42.4	88.3	30.2	Trace	71.6	130.6	98.9
160	21.8	100.3	101.3	25.5	11.5	79.4	112.9	30.6	8.3	111.7	135.2	105.3
320	53.0	192.9	123.1	30.1	43.3	170.2	165.5	31.3	21.1	218.3	137.5	118.6
640	117.5	287.7	150.1	37.3	106.9	307.7	228.3	37.1	57.9	366.3	293.7	121.8
1,280	231.8	654.5	225.8	43.8	229.5	654.2	338.8	53.9	143.8	847.6	300.0	124.7
L.S.D. 0.05	--	4.2	3.9	1.8	--	8.8	6.3	2.3	--	5.9	9.7	6.6
L.S.D. 0.01	--	5.8	5.4	2.4	--	12.1	8.7	3.2	--	8.1	13.3	9.0

[1/] Average of three repetitions

treatment, and at rates above this, the P in the soil was associated with the fraction labeled as aluminum phosphate. The aluminum phosphate content of the two Conover soils were relatively similar at all fertilizer rates, while the Pewamo soil contained more P in this fraction. The difference between this soil and the two Conover soils became greater at the highest two levels of application of fertilizer P.

The data in Table 13 were derived from those presented in Table 12. These data show the percent recovery of fertilizer P, in the form of water soluble, aluminum, iron, and calcium phosphate. These data were calculated by taking the difference between the amounts of a particular soil phosphate fraction in the treated and untreated soil and expressed as a percent of applied P.

These data show that most of the P applied as fertilizer was recovered in the total of the four P fractions. In general, the total P recovered in the four fractions accounted for more than 70 percent of the applied P. These values are slightly less than those calculated by Laverty and McLean (54). Similar results are also presented by Yuan _et_ _al_. (86).

Most of the fertilizer P was recovered in all three soils as a part of the aluminum phosphate fraction. This was followed by the iron phosphate, and then by calcium

TABLE 13 - Percent P recovered as water soluble, aluminum, iron, and calcium phosphate in three soils after 22 weeks of incubation

ppm P Added	----Conover Loam (Ingham)----				----Conover Loam(Shiawassee)---				Pewamo Silty Clay Loam-(St.Clair)------			
	H_2O Soluble Phosphate	Al-Phosphate	Fe-Phosphate	Ca-Phosphate	H_2O Soluble Phosphate	Al-Phosphate	Fe-Phosphate	Ca-Phosphate	H_2O Soluble Phosphate	Al-Phosphate	Fe-Phosphate	Ca-Phosphate
					% P Recovery 1/							
10	Trace	50.00	24.00	2.00	Trace	30.00	44.00	2.00	Trace	44.00	5.00	21.0
20	Trace	43.00	27.00	16.50	Trace	37.00	32.00	3.50	Trace	49.00	5.00	25.0
40	14.00	40.50	22.00	8.25	Trace	32.25	40.25	24.75	Trace	47.25	36.50	13.75
80	7.75	45.25	33.00	4.88	Trace	33.00	40.00	13.50	Trace	49.63	26.63	23.38
160	13.62	49.38	32.31	2.44	7.19	39.63	35.38	7.00	5.19	49.88	16.19	15.69
320	16.56	53.63	22.97	2.66	13.53	48.19	34.13	3.72	6.59	58.25	8.81	12.00
640	18.36	41.63	15.70	2.45	16.70	45.53	26.88	2.77	9.05	52.25	28.81	6.50
1,280	18.11	49.47	13.77	1.73	17.90	49.86	22.07	2.70	11.23	63.73	14.89	3.48

1/ Average of three replications

phosphate. The water soluble phosphate tended to increase with the use of increasing rates of fertilizer P. These trends are supported by the work of others (18, 20, 24, 33, 54).

The question arises as to the relationship between the percent of fertilizer P fixed in the soil and the amount of P recovered in the aluminum, iron, and calcium phosphate forms. As described previously, the total P fixed is considered to be that which was not measured by the Bray P-1 test. The values for this, expressed on a percentage basis are shown in Table 14. As can be seen, there is no direct or well-defined relationship between the percent fixed P and that recovered with the fractionation procedure. It is possible that the P that was measured as "fixed" with these procedures was not all fixed.

There were, however, direct relationships between soil P levels as measured by the Bray P-1 test and the three fractions of P for each of the soils as can be seen in Table 15. Each of the simple correlation coefficients were very high and statistically significant to the one percent level. This seems logical because the Bray P-1 extractant is composed of hydrochloric acid which can dissolve some forms of calcium phosphate and the fluorine ion in acid solution can complex aluminum and iron ions, with consequent release of P held by these trivalent ions to the solution (23).

TABLE 14 - Percent of P fixed and the total P converted to aluminum, iron, and calcium phosphate as affected by rates of P fertilizer.

ppm P Added	Conover Loam (Ingham)		Conover Loam (Shiawassee)		Pewamo Silty Clay Loam (St. Clair)	
	P fixed %	P converted to Al-Fe-, and Ca-phosphate %	P fixed %	P converted to Al,-Fe,and Ca-Phosphate %	P fixed %	P converted to Al-,Fe-,and Ca-Phosphate %
10	89.00	76.00	90.00	76.00	98.00	70.00
20	72.50	86.50	91.50	72.50	99.50	79.00
40	67.00	70.75	84.00	97.25	77.00	97.50
80	65.00	83.13	78.00	86.50	75.00	99.64
160	59.06	84.13	73.00	82.01	72.31	81.76
320	46.78	79.26	56.18	86.04	60.13	79.06
640	41.94	59.78	51.31	75.23	57.56	87.56
1,280	34.05	64.97	37.97	74.63	61.05	82.10

TABLE 15 - Simple and partial correlation coefficients which show the relationships between soil tests (Bray P-1) and the aluminum, iron, and calcium phosphate forms in three soils that were incubated for 22 weeks.

SOIL	Simple Correlation coefficients			Partial correlation coefficients		
	Al-P	Fe-P	Ca-P	Al-P	Fe-P	Ca-P
Conover Loam (Ingham)	0.997**	0.964**	0.956**	0.969**	0.653**	0.504
Conover loam (Shiawassee)	0.996**	0.963**	0.918**	0.994**	0.929**	0.343
Pewamo Silty Clay loam (St. Clair)	0.992**	0.986**	0.728**	0.836**	0.806**	0.410

** Significant at the 0.01 level

The highest coefficients involved the aluminum fraction and the lowest the calcium phosphate fractions. This was especially evident in the Pewamo silty clay loam.

The relationship of the three fractions to the Bray P-1 test can be defined as follows:

Ingham county soil

$$\text{Bray P-1 Test} = -77.03 + 1.54(\text{Al-P}) - 1.28(\text{Fe-P}) + 4.97(\text{Ca-P})$$

Shiawassee county soil

$$\text{Bray P-1 test} = 30.16 + 1.72(\text{Al-P}) - 1.18(\text{Fe-P}) + 0.79(\text{Ca-P})$$

St. Clari county soil

$$\text{Bray P-1 test} = -59.94 + 0.33(\text{Al-P}) + 0.94(\text{Fe-P}) - 0.53(\text{Ca-P})$$

The partial correlation coefficients of the three factors associated with the different phosphate fractions in these equations are also shown in Table 15. For all three soils, the aluminum and iron phosphate correlation coefficients were highly significant. None of the coefficients for calcium phosphate were statistically significant. These data indicate that most of the variation in the Bray P-1 test is primarily attributed to aluminum phosphate and then to iron phosphate, and very little to calcium phosphate. This would show that the P removed from the soil by the Bray P-1 test is derived mainly from the aluminum phosphate fraction, followed by the iron phosphate and then by the calcium phosphate, when these three P fractions are considered together as a function of the Bray P-1 test.

V. GENERAL DISCUSSION

The Chang and Jackson procedure (17) used in this research to fractionate the soil P into discrete phosphate compounds, must be viewed with some reservations. Thus, the relative importance of the calcium phosphate fraction with respect to other P forms may have been masked by the fact that some dicalcium phosphate may have been dissolved in the neutral 0.5 N NH_4F, used to extract the aluminum phosphate. This would be expected when the phosphate in the soil solution is unusually high (21), especially when the water soluble fraction becomes measurable. Rinkenberger [1/] found that neutral NH_4F was more effective than water in dissolving pure dicalcium phosphate. P in this study was applied to the soils as KH_2PO_4. Since this form is very soluble in soils it rapidly converts to the less soluble $CaHPO_4$ (56). Therefore, it is expected that most of the P extracted by the NH_4Cl came from the dicalcium phosphate, which is the most soluble form of the possible intermediate P compounds when P fertilizer is added to the soils.

[1/] Rinkenberger, G. Soil Science Department, Michigan State University. Personal communication.

In spite of the above facts, the amount of P extracted by the NH_4Cl from the soils incubated with different rates of P, was relatively small as compared with the P extracted by pure NH_4F, NaOH or H_2SO_4 solutions. Consequently, the error in extracting some dicalcium phosphate in the water soluble fraction does not affect immediately the calcium phosphate fraction. It is recognized that larger error may result from the dissolution of dicaclium phosphate by the NH_4F extracting solution. However, the evaluation of this error needs future research. In addition, due to differences in solubilities between freshly formed aluminum, iron and calcium phosphates and the more aged, crystalline compounds, some degree of error would likely result from attempts to use this method for determining the amounts of the particular compounds formed from applied soluble phosphates. Although the errors given above are recognized, the extraction procedure suggested by Chang and Jackson may be used empirically as a method for determining changes produced in the phosphate fractions by addition of soluble P.

As was reported previously, most of the P added was fixed in the form of iron phosphate in the untreated soils. However, increasing the amount of P applied to the three soils increased the aluminum phosphate fraction the most.

This may mean, as suggested by Chang and Jackson (18), that the initial stage of the reaction of applied phosphates involves mainly the formation of aluminum and calcium phosphates. The activity of the aluminum or calcium ions in the soil is relatively higher than that of the iron ions. Therefore, aluminum and calcium would be exptected to initially complex the applied phosphate. Even if the iron phosphate forms are less soluble than the other phosphate fractions, it can be postulated that, if the iron is present as "ferric hydroxide", its solution and recombination as phosphate is very slow. Ultimately, if an equilibrium could be reached, the reaction of phosphate with iron, aluminum, and calcium ions would depend only on the solubility products of the complex formed. Because this equilibrium state is never attained, the formation of iron phosphate depends, at any one time, on the solubility products of other phosphate complexes and the activity of the iron ions. More research should be performed in order to find a better delineation of the aluminum and calcium fractions, so that the relative content of these two fractions can then be determined more accurately.

VI. SUMMARY AND CONCLUSIONS

Field, greenhouse and laboratory studies were initiated in 1964 to evaluate certain chemical transformations of phosphate applied to three Michigan soils. The products of the transformations were related to "available P" as measured with the Bray P-1 soil test. A Pewamo silty clay loam from St. Clair county and two Conover loam soils from Shiawassee and Ingham counties were investigated. Six P levels, namely 0, 10, 20, 40, 80 and 160 pounds per acre, were studied in the field experiments. Corn leaf samples at three stages of growth were collected for P analysis.

Field yield results were obtained from the two Conover loam soils. Similar experiments were carried out in the greenhouse using 0, 20, 40, 80, 160 and 320 pounds of P per two million pounds of soil and corn was grown for 35 days. In another experiment, the three soils were incubated at 25°C with 0, 10, 20, 40, 80, 160, 320, 640, and 1,280 ppm P. At the end of one, two, eight and twenty-two weeks, soil samples were taken. Tests for "available P" were made with the Bray P-1 test. The soil P was fractionated by the Chang and Jackson method, at the end of 22 weeks of incubation.

The results can be summarized as follows:

(1) In both the field and the greenhouse, corn responded to the use of P fertilizer. The P response in the field was not nearly as large as that obtained in the greenhouse.

(2) In the field, in one experiment, maximum yield was obtained from the use of 80 pounds per acre of P. In another experiment, also on a Conover loam but in Shiawassee county, maximum yields were produced with 100 pounds per acre of P.

(3) Yield results from field and greenhouse studies showed essentially the same trend. Corn grown in Shiawassee county responded more to P fertilizer than that grown in Ingham county. On the Pewamo silty clay loam in St. Clair county, an intermediate response to P was obtained in the greenhouse.

(4) The P content of the leaves of corn grown in the field increased with the use of P containing fertilizer. The correlation was best early in the season. The P content of the leaves and the rates of P application were closely related to grain yields.

(5) The P uptake by corn plants and P left in the soil after the application of fertilizer accounted for only a small fraction of the total fertilizer P applied.

(6) In incubation studies the amount of P retained by the three soils was positively correlated to the amount of fertilizer P applied.

(7) The percent P fixed decreased significantly as the amount of fertilizer P increased. This was most evident on the Conover loam soil from Ingham county which contained the least colloidal material.

(8) There was a tendency for the percent P fixed by each of the soils to increase with time, especially where high fertilizer rates were used. The percent P fixed in seven days ranged between 10 to 80 percent on the Conover loam in Ingham county; from 30 to 90 percent on the Conover loam in Shiawassee county; and, from 35 to 100 percent on the Pewamo silty clay loam.

(9) The water soluble, aluminum, iron, and calcium phosphate fractions increased with rates of P fertilizer. This was most evident in the aluminum phosphate fraction.

(10) From 70 to 99 percent of the applied P was recovered in the four phosphate fractions. The aluminum phosphate fraction contributed the most to these values, followed in order by the iron, the calcium, and finally, by the water soluble phosphate fraction.

(11) The P extracted from the soil with the Bray P-1 method after the use of P containing fertilizer was predominantly aluminum phosphate, followed by iron and then by calcium phosphate.

(12) Some shortcomings of the Chang and Jackson procedure for determining changes produced in the phosphate fractions by the addition of soluble P to soils, are discussed.

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