TRANSFORMATION OF ADDED PHOSPHORUS
IN THREE MICHIGAN SOILS

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ABSTRACT

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Laboratory studies were performed to trace the changes in dicalcium phosphate upon its addition to three Michigan soils. Inorganic P fractions (Chang and Jackson's procedure) were compared with phase diagrams and P potentials for the untreated soils and soils to which 200 and 500 ppm P were added. The soils were incubated for two months after P additions. Periodic samples were taken for analysis throughout the incubation.

Dicalcium phosphate was found to convert readily to Al-P in both Iron River silt loam and Warsaw loam. A small quantity of the newly formed Al-P was apparently transformed to Fe-P in the Iron River soil during a two month incubation. Phosphorus phase diagrams ($pH_2PO_4^-$ vs. pH) and P potentials (pH_2PO_4 + 1/3 pAl vs. pH-1/3 pAl) indicated that Al-P or Fe-P compounds were controlling the activity of P in these soils which is consistant with P fractionation data. The P level was found to be somewhat higher in the Warsaw soil than in the Iron River soil.

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Dicalcium phosphate was not completely removed from the calcareous Wisner silty clay loam by one extraction with NH_4Cl. Thus, when Chang and Jackson's fractionation procedure was followed precisely, the added $CaHPO_4$ appeared in the Al-P fraction--a conclusion contrary to expectation and the data from P solubility diagrams. But after the $CaHPO_4$ was removed by successive extractions with NH_4Cl, little change in the Al-P fraction was noted when $CaHPO_4$ was added. This result was consistant with phase diagram and P potential ($pH_2PO_4 + \frac{1}{2}$ pCa vs. pH-$\frac{1}{2}$ pCa) data, indicating that Ca-P compounds control P activity.

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INTRODUCTION

Phosphorus was one of the first elements to be recognized as essential for plant growth. In addition, many agronomists have considered it to be the most limiting element in food production throughout the world. Consequently, much effort has been expended in studying the chemistry of soil P. But the nature of soil P has been elusive. Volumes of literature have reported a "loss" of soluble P when water soluble forms such as $Ca(H_2PO_4)_2$ are added to soils. And hypotheses have been formulated to explain this disappearance; many of which have failed to weather the test of time.

A procedure for fractionating inorganic soil P into water soluble (NH_4Cl extractable), Al-P, Fe-P and Ca-P fractions was developed by Chang and Jackson (14). This gave promise of describing the chemical transformations of P when added to soil. Volumes of data concerning P fractionation in soils have been reported. General trends in transformations of P added to soils have been summarized from these data. The fractionation procedure has not been as precise as desired, causing many researchers to propose modifications. Therefore, interpretation of the inclusion of specific P minerals in the various fractions may be approximate.

Thurlow (93) reported a major increase in the Al-P fraction of a calcareous Wisner soil when treated with P as $NH_4(H_2PO_4)$ in greenhouse studies. But this should not be expected in a calcareous soil. Sanchez (82) studied the fractions of P in Conover and Pewamo acid soils in a laboratory incubation experiment. When the soils were treated with various rates of $KHPO_4$ solution, fractionation indicated that most of the increase as a result of added P occurred in the Al-P and Fe-P fractions, with significant amounts in the water soluble fraction at the higher P levels. While these results are more plausible for the acid soils, questions may still be raised concerning their absolute accuracy.

Phase equilibrium diagrams have been used in an attempt to indicate the type of soil minerals that control P activity in solution (1,45,46,47,48,49,50,51,58,102,103). Lack of knowledge about specific P minerals in soils and possible chemical changes that may occur in the dynamic soil system has hampered interpretation of solubility data. Although this method yields only indirect evidence about the nature of soil P, it does allow for interpretation of the interactions of P and pH that have been observed in soil fertility.

This investigation was designed to study the change in soil inorganic P when P was added as $CaHPO_4$. The objectives were:

1. To compare P fractionation data with phase equilibrium data evaluating each method as it is used to trace added P in soils.
2. To study methods of removing $CaHPO_4$ from soils prior to P fractionation.

REVIEW OF LITERATURE

Fixation of Inorganic Phosphorus in Soils

Retention of P by soils has been noted for more than 100 years. According to Wild (99), Way first demonstrated this phenomenon. Since that time volumes of data concerning P in soils have been collected.

Several articles summarizing the literature concerned with the chemistry of inorganic P in soils have been published. In more recent times, reviews by Wild (99) and Dean (24) covered the retention and fixation of P in soils. Hemwall (35) termed inorganic P literature as confusion. Smith (84) presented a recent review of Al and Fe phosphates in soils, covering their reactions and availability.

The term "P fixation" will refer here to the retention of added P in soil by means of adsorption and/or precipitation.

Fe and Al phosphates have been found in abundance in acid soils and Ca phosphates in abundance in alkaline soils (9,12,15,16,19,36,52,54,56,58,64,79,82,85,93,94,98). A general relationship between synthetic soil minerals was suggested by Rathje (75):

$$\text{Ca-P's} + \begin{matrix}\text{Al}\\\text{Fe}\end{matrix}\ \text{hydroxide} \rightleftharpoons \begin{matrix}\text{Al}\\\text{Fe}\end{matrix}\ \text{phosphates} + \text{Ca(OH)}_2$$

The equilibrium would shift to the right in acid media, and to the left in alkaline media. Russell (78) stated that in acid soils P occurred in association with Fe and Al compounds.

Fixation in Acid Soils

Smith (84) suggests that four approaches have been used to study the fixation reactions of Fe and Al phosphate compounds in acid soils. First, the correlation of Fe and Al oxide content of soils with the amount of P fixed has been reported by many workers. Toth (92) demonstrated that removal of free Fe and Al oxides in soils resulted in reduced P fixation. Swenson, et al. (86) reported significant contribution to P fixation by Fe and Al oxides. Perkins, et al. (73) related high concentrations of Al and Fe oxides to high P fixation. The rate of reaction of P with the soil was greatly reduced when the extractable Fe oxides were removed, Kittrich and Jackson (42).

Upon the addition of soluble P to acid soils, increased amounts of Fe and Al phosphates have been recovered. Chang and Jackson (15) reported these increases. Saeki and Okamoto (80) recovered 60-70 percent in the form of Fe and Al phosphates. Volk and McLean (94) reported recovering almost all of the added P as Al and Fe phosphates when treating acid soil with soluble P and fractionating according to the procedure of Chang and Jackson (14).

Following the addition of Al or Fe compounds to the soil a P fixation increase was demonstrated by Larsen *et al*. (50).

A fourth approach has been the removal or inactivation of Fe and Al in solution which results in reduced P fixation. Using ferrocyanide, fulvic acid, and other agents which form compounds with Fe and Al, Leaver and Russel (53) demonstrated reduced P fixing power in soils.

Both precipitation and adsorption mechanisms have been considered in P fixation. A simplified representation of the mechanism in acid soils was proposed by Smith (84):

Adsorption

$$Al(OH)_3 + H_2PO_4^- \rightleftharpoons Al(OH)_2H_2PO_4 + OH^-$$

Precipitation

$$Al^{+3} + 2H_2O + H_2PO_4^- \rightleftharpoons Al(OH)_2H_2PO_4 + 2H^+$$

If this relationship occurs in a pure system it is easy to ascertain which mechanism is proceeding by following the concentration of H^+ or OH^- ions. But in the complex soil system other simultaneous reactions prevent such simple studies.

Rennie and McKercher (77) used the Langmuir adsorption isotherm to calculate an adsorption maximum for acid soils and found that it was a reliable indicator of the soils ability to supply P in plants. Close agreement between P fixation and Langmuir adsorption isotherm may not necessarily mean that an adsorption reaction has taken place, Hsu and Rennie (40).

Hydroxide exchange sites were reported to be associated with P fixation possibly indicating adsorption, Baker (5). Bache (4) and also Raupach (76) using pure clay and oxide mineral systems concluded that free energy surface reactions may be a better explanation for fixation than precipitation and the use of solubility products of soil minerals.

Kittrick and Jackson (42) observed under an electron microscope that Fe and Al hydroxide minerals in contact with P solution showed in a few minutes the formation of separate phase, phosphate crystals by solution precipitation. Hemwall (37) hypothesized that P is fixed by clay minerals by reacting with soluble Al which originates from the exchange sites or from lattice dissociation of the clay minerals to form a highly insoluble Al phosphate. Evidence for this occurrance is that clays support an appreciable Al concentration in solution, and there is a solubility product relationship between the Al and P concentration in clay-P suspensions.

Bache (4) reported that the ion activities in solution during sorption of P on gibbsite and hydrous ferric oxide takes place in three stages of reaction:

(a) A high energy chemisorption of small amounts of P;
(b) Precipitation of a separate P phase;
(c) A low energy sorption of P onto precipitates.

Fixation in Alkaline Soils

Eisenberger, et al. (26) reported that there exists a continuous series of solid compounds between CaO and $CaHPO_4$ in the calcareous soil system. Hemwall (36) stated that P fixation in alkaline and calcareous soils is usually attributed to the formation of Ca-phosphates. Fe and Al compounds may be responsible for some fixation in soils of higher pH; however, Ca phosphates predominate.

Ellis and Troug (27) demonstrated that Ca saturated montmorillonite treated to remove Fe and Al oxides fixed large amounts of phosphorus against water extraction. But the P was recovered with a weak acid extraction. Fixation of P by clay before and after removal of Fe and Al oxides indicated that the free oxides accounted for most of the fixation. Evidence also indicated that P fixed by Ca saturated clay is fixed as a Ca complex and not by a H_2PO_4-Ca-clay bonding as hypothesized by some workers. Clays saturated with Na, K, or Mg fixed only small amounts of P against water extraction.

Pratt and Thorne (74) reported that Ca clays fixed more P in alkaline systems than did Na clays; however, no explanation of possible mechanisms was given.

Boischott, <u>et al</u>. (6) reported on the importance of $CaCO_3$ in the fixation of P in calcareous soils. The initial reaction was indicated to be an adsorption onto the $CaCO_3$, rather than a precipitation reaction of an insoluble separate phase. The amount of P adsorbed was a function of the fineness of the $CaCO_3$ material. When the P concentration was raised to 5×10^{-5} M at pH 8.3 to 8.5, precipitation occurred. Olsen (72) also indicated that P was adsorbed on $CaCO_3$ until a concentration of 2×10^{-4} M K_2HPO_4 was reached; then precipitation took place. When the P concentration was greater than 2×10^{-4} M K_2HPO_4, precipitation began and the equilibrium concentration dropped below that found before precipitation began. Calcium phosphate crystals were noted growing on the $CaCO_3$ surface.

Fried and Shapiro (32) suggest that the two approaches to P fixation, mineralogical precipitation and adsorption, are not necessarily incompatible. Since the soil is a dynamic system, the possibility of both processes occurring is plausible, Smith (84).

Solubility Product Principle

The lack of reliable solubility information necessary for thermodynamic interpretation of soil P reactions prevented advancement for many years, Lindsay and Moreno (58). More recently much work has been done in this area.

In order to use the solubility product principle in interpreting the P status of soils, the solubility of various phosphates that occur or have been suggested to be present in the soil must be known. The following list contains many of the compounds studied and their pKsp values as obtained by different workers.

	Compound	Chemical formula	pKsp	Author
1.	Gibbsite	$Al(OH)_3$	33.8	Lindsay and Moreno (58)
2.	Variscite	$Al(OH)_2H_2PO_4$	30.5	Lindsay, *et al*. (58)
	Variscite	$Al(OH)_2H_2PO_4$	29.5	Cole and Jackson (21)
	Variscite	$Al(OH)_2H_2PO_4$	30.5	Bache (3)
	Variscite	$Al(OH)_2H_2PO_4$	30.6-31.7	Wright and Peech (103)
	Variscite	$Al(OH)_2H_2PO_4$	28.4-27.7	Kittrick and Jackson (42)
	Variscite	$AlPO_4 \cdot 2H_2O$	22.5	Taylor and Gurney (88)
3.	Strengite	$Fe(OH)_2H_2PO_4$	33.6-35.0	Chang and Jackson (13)
	Strengite	$Fe(OH)_2H_2PO_4$	34.3	Bache (3)
	Strengite	$Fe(OH)_2H_2PO_4$	34.7	Wright and Peech (103)
	Strengite	$Fe(OH)_2H_2PO_4$	35.3	Huffman and Taylor (39)

Compound	Chemical formula	pKsp	Author
strengite	$Fe(OH)_2H_2PO_4$	34.6	Egan, *et al*. (25)
4. Colloidal iron phosphate		33.3	Egan, *et al*. (25)
5. Ferric hydroxide	FeOOH	38.1	Lamb and Jacques (24)
6. Dicalcium phosphate dihydrate	$CaHPO_4 \cdot 2H_2O$	6.56	Moreno, *et al*. (68)
7. Dicalcium phosphate anhydrate	$CaHPO_4$	6.66	Lindsay and Moreno (58)
8. Octacalcium phosphate	$Ca_4H(PO_4)_3 \cdot 3H_2O$	46.9	Moreno, *et al*. (68)
9. Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	113.7	Lindsay and Moreno (58)
10. Fluorapatite	$Ca_{10}(PO_4)_6(F)_2$	118.4	Lindsay and Moreno (58)

The pK values for variscite were redetermined by Taylor and Gurney (88), who showed that the pKsp for variscite was 22.5 when equilibrated with dilute HCl and 21.5 when equilibrated with dilute H_3PO_4. The dissociation reaction for variscite was given to be $AlPO_4 = Al + PO_4$ with corresponding $pKsp = pAl + pH_2PO_4 - 2pH + pK_2K_3$, rather than $pKsp = pAl + 2POH + pH_2PO_4$ as reported by earlier workers. The difference in pKsp determined in the dilute HCl system compared to the dilute H_3PO_4 system was probably due to calculations of ionic activity affecting one set of data more than another. A lack of information about complex ions in dilute H_3PO_4 solutions and resultant dissociation has prevented the determination of a true solubility product for variscite.

The pKsp values for P minerals which represents the various minerals evolved in P reactions may be only approximate. Methods used to determine these values must be considered when interpreting accurate solubility product measures, Smith (84).

Phosphate Phase Equilibrium

Lindsay and Moreno (58) presented the activity isotherms for $Al(OH)_2H_2PO_4$ (Variscite), $Fe(OH)_2H_2PO_4$ (strengite), $Ca_{10}(PO_4)_6F_2$ (fluorapatite), $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite), $Ca_4H(PO_4)_3 \cdot 3H_2O$ (octacalcium phosphate), and $CaHPO_4 \cdot 2H_2O$ (dicalcium phosphate dihydrate) on a single solubility diagram in which $H_2PO_4^-$ activity was plotted as a function of pH. The diagram was proposed for predicting the formation and stability of various Al, Fe and Ca phosphate compounds that may be present in natural soils or form in soils upon fertilization. Generally, only the most soluble phosphate compounds dissolve or precipitate fast enough in soils to govern phosphate activity in solution. Dicalcium phosphate, possibly octacalcium phosphate, and the more soluble alkali or ammonium Fe and Al phosphates slowly dissolve as insoluble forms like hydroxyapatite, fluorapatite, strengite, and variscite precipitate. Amorphous, freshly precipitated phosphates of Fe and Al will have greater activities than crystalline strengite or variscite.

An example of use of the solubility diagram was presented by Lindsay and Moreno (58):

> If lime is added to an acid soil in equilibrium with gibbsite and variscite at pH 4.0 ($pH_2PO_4=6.7$) until pH 7.0 is obtained, there would be a tendency to precipitate gibbsite and dissolve variscite until $pH_2PO_4=3.7$ is reached. The resulting increase in phosphorus in solution could also result in supersaturation of calcium phosphates, and thus the precipitation of $CaHPO_4 \longrightarrow$ Octa-Ca-P with possibly eventual formation of hydroxyapatite. If this occurred pH_2PO_4 would go from 3.7 to 8.8.

Lehr and Brown (54) placed granules of $CaHPO_4 \cdot 2H_2O$ in Hartsell fine sandy loam limed to pH 7.2 and 7.8, and cropped the soil with ryegrass. They observed by X-ray analysis a mixture of octacalcium phosphate and smaller amounts of apatite occurring in the residue of the root zone. Only a few crystals of $CaHPO_4$ remained under the alkaline conditions. In three acid Hartsell soils studied, 95 percent of the residue was a mixture of $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$.

Lindsay and Stephenson (59) studied solutions of $Ca(H_2PO_4)_2 \cdot H_2O$ and the reactions of bands of $Ca(H_2PO_4)_2 \cdot H_2O$ with soil. Excess $Ca(H_2PO_4)_2 \cdot H_2O$ dissolved in water, a

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attained metastable-triple-point-solution (4.50 M P, 1.35M Ca, pH 1.00) equilibrium in one hour and remained near that point for 24 hours. The solution then approached a triple-point-solution (3.98M P, 1.44M Ca, pH 1.48) at three days until it was attained at 17 days. The reactions are represented below.

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

(2) $Ca(H_2PO_4)_2 \cdot H_2O + X\ H_2O \rightleftharpoons CaHPO_4 \cdot 2H_2O + MTPS$

(3) $Ca(H_2PO_4)_2 \cdot H_2O + X\ H_2O \rightleftharpoons CaHPO_4 + TPS$

The $Ca(H_2PO_4)_2 \cdot H_2O$ band in the Hartsell soil attained a composition in the soil solution similar to metastable-triple-point solution. Upon dissolution of $Ca(H_2PO_4)_2 \cdot H_2O$ in the band a very low pH was attained. This highly concentrated solution dissolved Fe, Al, Mn and other soil constituents. As the pH increased gradually, precipitation of Fe, Al, and Ca compounds followed. Dicalcium phosphate was noted to precipitate most abundantly at the advancing concentration front. $Ca(H_2PO_4)_2 \cdot H_2O$ had completely dissolved after eight days. It was noted that the greater the Ca content, the greater possibility that Ca will have a dominating role in precipitation of fertilizer P. Fe and Al were readily dissolved from the acid Hartsell soil, and will likely predominate in initial precipitation of P leaving the granule.

Bouldin, et al. (7) noted that the fraction of added P that remained as a residue at the granule site varied from

92 percent when $Ca(H_2PO_4)_2 \cdot H_2O$ was mixed with $CaCO_3$, to two percent when mixed with NH_4SO_4.

Moreno, <u>et al</u>. (69) leached a column of $CaHPO_4 \cdot 2H_2O$ with six liters of water and noted the formation of octacalcium phosphate in the upper column as determined by X-ray and petrographic analysis, indicating possible occurrence in soil.

Studies of the reactions of P solution with acid soils, with Al and Fe oxides, and with silicate clays (38, 42), show that when crystalline products are detected they are usually simple Al, Fe phosphates related to variscite or alkali Al and Fe phosphates related to taranakite $(H_6K_3Al_5(PO_4) \cdot 18H_2O)$. Fairly concentrated acid solutions must be used in order to detect crystals. Therefore alterations of oxide and clay minerals may occur.

Bache (3) studying the effects of time of reaction, pH of solution and solid to solution ratio concluded that variscite can be in equilibrium with the surface and solution phase only in the most acid soils, and strengite is never likely to be in equilibrium. Further, thermodynamic constants for variscite and strengite are only maintained at low pH. At higher pH's surface hydrolysis reactions occur releasing P ions into solution and forming more basic insoluble metal P. Taylor and Gurney (88) also noted incongruent dissolution of variscite as the pH was increased, a result which could not be explained as precipitation of

$Al(OH)_3$ as their system was undersaturated with respect to gibbsite.

Wada (95) indicated that solubility equilibrium of variscite and gibbsite might be established below pH 5.2, but apparently not higher on the ando, alluvial, and red yellow podzolic soils studied. Taylor, et al. (90) using a Ca-P solution in the pressence of gibbstie and goethite noted the principle precipitation was from $Al(OH)_3$ and concluded that unless large amounts of reactive Fe are present, most P will precipitate as Al phosphate.

Phosphate Potentials

Schofield (83) suggested $CaCl_2$ as an electrolyte to determine the chemical potentials of soil P. Phosphate potential is measured as an approximation to chemical potential (100). The chemical potential of P in the solid phase is a measure of its ease of removal. Since nearly all labile inorganic soil P is held by the solid portion of soil, the availability and release must be determined by the amount and form held by the solid phase. Schofield (83) first used P potential ($\frac{1}{2}pCa + pH_2PO_4$) versus lime potential ($pH-\frac{1}{2}pCa$) as proposed by Aslying (1) to identify mineral forms of P in calcareous soils. The solubilities of Ca phosphates may be represented on a single solubility diagram in which the functions of chemical potentials for $Ca(OH)_2$ and $Ca(H_2PO_4)_2$ are used as coordinates. Balanced equations can be written and a solubility line represented on the diagram. Equations for $CaHPO_4$ and hydroxyapatite are given below.

dicalcium phosphate

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

hydroxyapatite

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

Similar basic solubility relationships were used in Lindsay and Moreno's phase diagrams (58).

For the general case Clark and Peech (19) represented the formation of a hypothetical calcium phosphate as:

$$M\ Ca(OH)_2 + N\ Ca(H_2PO_4)_2 \rightleftharpoons \text{solid} + Z\ H_2O$$

where M and N represent reacting moles of $Ca(OH)_2$ and $Ca\ (H_2PO_4)_2$ forming one mole of solid + Z H_2O. Based on the assumption that the reactants are completely dissociated the linear plot of $\frac{1}{2}$p Ca + pH_2PO_4 (P potential) versus pH $-\frac{1}{2}$p Ca (lime potential) should have a slope of M/N characteristic of the solid species. For example, octacalcium phosphate $Ca_4H(PO_4)_3$ would be 5/3 = 1.67 slope.

Similar solubility diagrams may be constructed for $Al(OH)_3$-$AlPO_4$, and $Fe(OH)_3$-$FePO_4$ systems. Taylor and Gurney (89) equilibrated acid soil in dilute $CaCl_2$ and plotted pH + pH_2PO_4 as a function of pH -1/3pAl. Points for the untreated soil fell on the variscite line. The variscite ion product was written as:

$$pAl + pH_2PO_4 + 2pOH \rightleftharpoons (pH + pH_2PO_4) -3 (pH-1/3pAl)$$

Taylor and Gurney concluded that the results do not necessarily mean that variscite controls the composition of the solution.

Chakrovarti and Tablibudeen (10) examined 54 British and Indian soils plotting Fe potentials ($pH -1/3Fe^{+3}$) and Al potentials ($pH -1/3Al^{+3}$) as a function of P potential [$1/3p\ (Al^{+3}\ Fe^{+3}) + pH_2PO_4^-$]. For the determination 5 gram samples of soil were shaken in 100 ml of 0.02 M KCl for eight days. Results were interpreted as related to soils grouped according to pH. The temperate soils in pH range 3.8 - 4.2 corresponded to compounds approximating to the composition of strengite. Tropical soils pH 3.8 - 6.7 indicated strengite coexisting with hydrated Fe oxides. Variscite type compounds controlled P concentration in temperate climate soils up to pH 4.7. Above 4.7 non-stoichiometric P: hydroxide adsorption complexes may be controlling. Tropical soils in the range of pH 4.3 - 5.8 indicated that the system was controlled by compounds similar to variscite.

Taylor and Gurney (88) reported that upon acidification of a potential system, the points moved parallel to the variscite isotherm and not toward it as if variscite were dissolving. The movement was due almost entirely to pH and Al content change, probably associated with clays. Wright and Peech (103) made five successive extractions with 200 ml

0.01 M $CaCl_2$ plus 2g soil shaking for 72 hours. The constantcy of ion product of variscite was maintained. Moreno, et al. (70) placed one gram of $Ca(H_2PO_4)_2 \cdot H_2O$ in 50 g of Hartsell acid soil shaking in 100 ml of water. After one hour and at 30 days the system, represented by lime potential versus P potential, was still on the $CaHPO_4 \cdot 2H_2O$ isotherm. In a similar experiment with the acid Hartsell, after 20 days of shaking in 100 ml of water, 0.1 grams of $CaHPO_4 \cdot 2H_2O$ in soil resulted in points below the apatite isotherm, 0.3 grams of $CaHPO_4 \cdot 2H_2O$ in soil was on the apatite isotherm, 1.2 grams of $CaHPO_4 \cdot 2H_2O$ in soil was on $CaHPO_4 \cdot 2H_2O$ isotherm, and 5.0 grams of $CaHPO_4 \cdot 2H_2O$ in soil was above the $CaHPO_4 \cdot 2H_2O$ isotherm.

Weir and Soper (98) studied P and lime potentials in calcareous Manitoba soils. Using 20 grams of soil in 50 ml 0.01 M $CaCl_2$ and shaking 12 hours they noted that all soils were supersaturated with respect to hydroxapatite. Fertilized soils fell in a region closer to the octacalcium phosphate isotherm, with P activity seemingly governed by octacalcium phosphate and $CaHPO_4 \cdot 2H_2O$. Withee and Ellis (102) treated two calcareous soils with 200 and 500 ppm P as H_3PO_4 and noted equilibrium at the 200 ppm level with octacalcium phosphate, and equilibrium at 500 ppm level similar to $CaHPO_4 \cdot 2H_2O$.

Procedures for measuring phosphate potentials have received much attention recently. Nethsinghe (71) noted that air drying of soils caused a change in chemical potentials of soil P not reversable upon rewetting. Larsen and Court (48) reported that P enrichment has an effect on potential varying markedly with soil to solution ratio. Several possible reasons for this variance were proposed.

(a) An energy effect in which mean bonding energies change as P is removed;

(b) The mechanism of adsorption may be dependent on a unit weight of soil;

(c) Incongruent dissolution of solids may occur;

(d) Solutions of ions related to a definite solubility product may cause a shift in the equilibrium;

(e) P of indefinite forms may be unexplainable;

(f) Soil organic matter reactions are probably not a factor in 0.01 $CaCl_2$ solution;

(g) Variation in the cation balance in the system is not probable, as a 10% change in 0.01 $CaCl_2$ solution results in only 1% change in potential.

Lindsay et al. (57) concluded that pH-1/3pAl (aluminum potential) for 100 grams of soil in 200 ml of $CaCl_2$ varying from 0.01 M to 0.10 M remained constant. Frink and Peech (33) reported that equilibrium of gibbsite and $Al(Cl)_3$ solution was attained slowly (i.e., 1-3 months). Limed acid soils, one gram in 200 ml 0.01 M $CaCl_2$, were not in equilibrium in one month; however, unlimed soils were in equilibrium.

Larsen and Widdowson (51) studied the production of CO_2 at different soil to solution ratios concluding that it seemed to explain the variation in pH. A reduction in pH and an increase in P concentration (decreased P potential) was noted with increasing weight of soil in the suspension. Ten grams of four soils were shaken for 16 hours in 50 ml of $CaCl_2$, Larsen (45). The lime potential was independent of the $CaCl_2$ concentration between 0.002 to 0.05 M. The P potential of neutral and alkaline soils decreased with increased molarity of $CaCl_2$. If allowance was made for the formation of a $CaHPO_4$ complex, P potential was also independent of $CaCl_2$ molarity in the pH range 5 to 8. Larsen (46) noted higher lime potentials when calcareous soils were shaken in a $CaCl_2$ solution in stoppered bottles as a result of CO_2 pressure not present in bottles open to the atmosphere. White and Beckett (99) also reported that aeration was critical in determining potentials.

Limitation in the use of the Solubility Product Principle

Lewin (55) pointed out limitations in the use of the solubility product principle. There is a neglect of any possible variations in the activities of solvent molecules and the solid phase in determining activity products.

Equilibrium conditions may not be present in most precipitation reactions. The equilibrium of a soil with an extracting solution requires equilibrium between difficulty soluble compounds and its constituent ions adsorbed by the clay. Adsorbed ions obtain equilibrium rapidly. But difficulty soluble compounds are probably rate controlling, Frink and Peech (33). This implies that assessments of P ion activity in soil solution based on the solubility product principle are bound to be approximate. No exact definite relationship between pH and $H_2PO_4^-$ was noted in arable soils studied by Wada (95), as would exist if $H_2PO_4^-$ activity in the soil solution was governed by simple phosphates and related compounds. Results indicated that operative ranges of simple solubility are rather limited for interpreting P transformations. P fertilizer application is small in comparison with amounts of aluminosilicates, iron oxide minerals, and calcium compounds present in soils, and therefore P fertilizers may not increase P in soil solution very much, Kittrick and Jackson (42).

Fractionation of Inorganic Soil Phosphates

Chang and Jackson (14) proposed a fractionation procedure to separate soil inorganic P into water soluble Ca, Al, Fe and reductant soluble P removed after the first four forms. Since its development the procedure has been widely used. Fractionation of fertilized acid soils, Wright and Peech (103), showed an increase mainly as Fe-P, although two soils increased in Al-P. The Ca-P fraction was affected little. In acid Taiwan soils after three days incubation most of the 200 ppm P added was fixed in the Al-P fraction. Some Fe-P and Ca-P were indicated, Chang and Chu (12). After one-hundred days however, the percent recovery was more variable with a noticeable increase in Fe-P and a decrease in Al-P. In two latosols studied there was more of an increase in the Fe-P fraction in comparison to the Al-P fraction.

Eight soils from Ontario, Canada, (six alkaline, one acid, one slightly acid) were equilibrated with p^{32} and 0.01 M $CaCl_2$ for 120 hours, MacKenzie (63). A comparison of P solubility with the various fractions removed by Chang and Jackson's procedure indicated that upon removal of Al-P the solubility (micrograms P per gram of soil) dropped considerably except in the case of an Fe-P, Ca-P dominant soil. Al-P appeared to supply most of the soluble fraction. Specific activities of P^{32} for Fe-P were one-third those for Al-P, while Ca-P were very low. Chang and Juo (16) studied twenty-six Tiawan soils (latosols, sandstone, shale, slate, mudstone, and alluvial) finding eleven soils dominant in Fe-P, eight soils dominant in Fe-P and Ca-P, and seven soils dominant in Ca-P.

Volk and McLean (94) studied four Ohio acid soils pH 4.5-5.3 and concluded that if high P fixing acid soils were treated with P there was a decrease in the availability of native P, and a tendency to recover more than half as Fe-P. In the low P fixing soils added P increased available native P, and there was a tendency to recover more than half as Al-P. Almost all the added P was recovered as Al-P and Fe-P. The forms of P in a Bridgehampton silt loam (Brown Podzolic) after 65 years of superphosphate and rock phosphate treatments resulted in recovery of most P in the rock phosphate treatment as Ca-P, while the superphosphate treatment resulted in a greater increase in the Al-P fraction, Manning and Solomon(66).

In a recent review of soil P literature Smith (84) stated that many workers have noted an equal if not greater importance of Fe compared to Al in P fixation. A number of workers have reported the reverse. Many factors such as soil type, type of fertilizer used, method of application and sampling, and time between application and sampling may affect the importance of interpretation of the role of Fe and Al in P fixation.

Modified Fractionation Procedure

The fractionation procedure described by Chang and Jackson (14) for soil inorganic P has been criticized for lack of a good separation between P forms. The procedure will be described here briefly. One gram of soil is placed in 50 ml of 1 N NH_4Cl shaking 30 minutes to remove exchangeable Ca and readily soluble P such as $Ca(H_2PO_4)_2$ and $CaHPO_4$ in the soil. One-half normal NH_4F, pH 7.0 is then employed (one hour shaking time) to remove Al-P (Fe-P dissolves slightly). Chang and Jackson (14) proposed a second one hour NH_4F extraction to determine the amount of Fe-P removed by the NH_4F. Tenth normal NaOH is then employed with a seventeen hour shaking period to remove Fe-P. Next, Ca-P is removed by shaking one hour in 50 ml of 0.5 $\underline{N}$ H_2SO_4. Reductant soluble and occluded P may then be removed if desired.

Fife (28,29,30,31) studied the separation of Al-P and Fe-P and suggested use of 1 $\underline{N}$ NH_4F pH 8.5 for 16 hours, to reduce the amount of Fe-P removed. Chang (11) states that a longer extraction time may completely dissolve Al-P whose solubility decreases above pH 7.0; however, alkaline hydrolysis of Fe-P must also be considered. Dependent on the soil it would be difficult to predict whether an increase or decrease of P extracted would result from a longer extraction period at pH 8.5. Chang and Liaw (17), studied representative Tiawan soils and concluded that the pH of 1 $\underline{N}$ NH_4F ranging from 7.0 to 8.5, made little difference in dissolution of iron phosphate. Khin and Leeper (43) suggested that P may be adsorbed by ferric oxide during the extraction period and thus recorded as Fe-P. The enhanced solubility of Al-P in NH_4F may result in the shift from Al-P to Fe-P of some P, a process which occurs slowly in nature.

Extending the reaction time may enhance such a shift. Chang and Liaw (17) noted that in neutral NH_4F solutions a reprecipitation of some P released from Al-P occurred on the Fe-oxides. Thus the Fe-P fraction increased at the expense of the Al-P fraction. The dissolution of Fe-P by NH_4F has reverse effect, increasing the Al-P fraction. A correction may not be necessary if these two amounts are about the same.

Chang and Jackson (14) noted that some reductant soluble Fe-P which is dissolved in sodium dithionite-citrate, and occuluded Al-P may be dissolved in 0.5N H_2SO_4. Khin and Leeper (43) suggested dissolved amounts of occluded P could be considerable. Glen, et al., cited by Chang (11) suggested the extraction of occluded Fe and Al-P be done after the 0.1 N NaOH, before 0.5 N H_2SO_4.

Questions as to the solubility of $Ca(HPO_4) \cdot 2H_2O$ in NH_4F and NaOH have been raised. Igawa, cited by Chang (11), suggested the use of 2.5 percent acetic acid to separate Ca-P before separation of Al-P and Fe-P. No mention as to the acids affect on the other fractions was made. Saeki (79) used 2 N $(NH_4)_2SO_4$ leaching soil placed on filter paper with four 50 ml portions. Dicalcium phosphate was added to the soils at 250 and 500 ppm P. Recovery of P added as $CaHPO_4$ was 18 percent for the 500 ppm level and 28 percent for the 250 ppm level when leaching with two 50 ml portions of $(NH_4)_2SO_4$ solution immediately after adding the material.

Forty-three percent of the P added as $CaHPO_4$ was recovered when four 50 ml leachings were employed. Additional increments of leaching recovered only small amounts of P. Chang (11) states that, "Since the concentration of P in soil solutions is usually only a fraction of a ppm, there should not exist any appreciable amount of the more soluble P such as $CaHPO_4$ in common soils."

Chang (11) proposed a modified procedure for the fractionation of soil inorganic phosphates. He suggested the use of pH 7, 0.5 N NH_4F shake one hour for paddy soils, and pH 8.2, NH_4F shake one hour for upland soils for removal of Al-P. Chang also suggested removing reductable soluble Fe-P and removal of occluded Fe-P and Al-P after the 0.1 N NaOH Fe-P fraction, and prior to the 0.5 N H_2SO_4 Ca-P fraction.

MATERIALS AND METHODS

Three Michigan surface soils were selected on the basis of their dominant inorganic phosphate fraction. Iron River was selected because of its' iron phosphate dominance. Warsaw was selected as a dominant aluminum phosphate soil, and Wisner as a calcium phosphate dominant calcareous soil. The locations from which the soils were sampled are listed below.

Warsaw Loam - Surface - Lee Rhoda, RFD, Schoolcraft, Michigan. One mile south of Schoolcraft on west side of road. SE ¼ SW¼ Sec. 19 T 4S R 11 W. Samples taken in old garden area directly south of house.

Iron River Silt Loam - Surface - Raiko Petroff, RFD 3, Iron River. SE ¼ NE ¼ Sec. 14 R 35W T 42N. Upper peninsula, Michigan.

Wisner Silty Clay Loam - Surface - No Zn, No P treatment, tier B, Monitor Sugar Co. plots, Bay City, Michigan, 1965.

One-thousand gram portions of air dry soil that had been passed through a .7 mm sieve were placed in a tumbling mixer. Treatments of 200 and 500 ppm P as $CaHPO_4$ were mixed with the soils, tumbling for fifteen minutes. Preliminary studies indicated that adequate uniform mixtures were obtained in fifteen minutes of mixing. Six polyethelene bags of each soil; two control, and two each containing 200 and 500 ppm P as $CaHPO_4$ respectively, were incubated at eighty-five percent of the one-third atmosphere pressure moisture content. Incubation was at 30 degrees centigrade. The moisture content was maintained throughout the incubation by addition of distilled water to a given weight. Periodic samples were taken for fractionation and phosphate potential determinations. Samples were taken initially at three days, one week, two weeks, one month and two months.

Samples of five to ten grams of moist soil were dried in a vacuum oven at 40 degrees centigrade under 30 pounds vacuum. One gram samples of dry soil were fractionated into NH_4Cl (water soluble) Al-P, Fe-P, and Ca-P fractions according to the procedure of Chang and Jackson (14).

Potentials were determined by sampling a weight of moist soil equivalent to fifty grams of oven dry soil. The soils were shaken four days in 100 ml. of 0.01 M $CaCl_2$ plus one ml. of chloroform. The chloroform was employed to limit microbial activity. The pH of the soil suspension was determined with a Beckman (Model G) glass electrode pH meter. The soil suspension was then centrifuged at 2200 rpm for 15 minutes and Ca, P, Al, and Fe concentrations were determined in the clear supernatant liquid. Calcium concentration was determined using a Perkin-Elmer 303 atomic absorption spectrophotometer. Phosphorus concentration was determined by the colorimetric sulfomolybdic, stannous chloride method described by Chang and Jackson (14). Aluminum concentration was determined by the "Aluminon method" as described by Jackson (41). The Orthophenantholine method was employed to determine Fe concentration colorimetrically (41). Total P was determined in all soil samples, after two months incubation by sodium carbonate fusion, Jackson p. 175 (41).

Calcium, P, and Al activities were calculated using the Debye-Huckel Theory of interionic attraction (67). The pKsp values used for the various minerals as represented on potential diagrams and on phosphate phase diagrams were taken from Lindsay and Moreno (58), and from Taylor and Gurney (88).

The pKsp values used included strengite 35.0, variscite 30.5 and 22.5, $CaHPO_4 \cdot 2H_2O$ 6.56, $CaHPO_4$ 6.66, octacalcium phosphate 46.91, and fluorapatite 118.4.

Successive extractions of one-gram samples of Wisner and Warsaw treated with $CaHPO_4$ and also untreated samples were made with 1 $\underline{N}$ NH_4Cl pH 7.0. Each increment envolved shaking the soil with 50 ml. of solution for one-half hour. Phosphorus concentration was determined by the sulfomolybdic acid colorimetric method (14). Following the NH_4Cl

extractions, the samples were fractionated (14) into inorganic Al-P, Fe-P, and Ca-P. The successive extractions of the Wisner soil were done on the two month incubated sample. For the Warsaw soil, 200 ppm P as $CaHPO_4$ was added and immediately extracted with successive extractions on the unincubated samples.

RESULTS AND DISCUSSION

Fractionation of Inorganic Phosphates

The results of fractionation of three incubated soils at two phosphorus levels and a control are presented in tables 1, 2, and 3. The untreated, acid Iron River soil showed essentially no change in the four fractions during two months of incubation. The untreated soil contained approximately 120 ppm P in the Fe-P fraction, 30 ppm P in Al-P fraction and 50 ppm P in Ca-P fraction, with only a trace of P in the NH_4Cl (water soluble) fraction. The total P content of the soil was 740 ppm P as determined from a Na_2CO_3 fusion.

With the addition of 200 ppm P as $CaHPO_4$ increases from 31 to 155 ppm P in Al-P fraction and 119 to 178 ppm P in Fe-P fraction were noted in comparison of the initial untreated to 200 ppm P treated soil. No change in the water soluble and Ca-P fractions were noted during the two months incubation. However, a small increase in the Fe-P fraction at the expense of the Al-P fraction was indicated during the two month period.

The Ca-P fraction was the only fraction of the iron river soil unaffected at the 500 ppm P level. The initial

Table 1. Interaction of added P, inorganic P fractions in a Wisner silty clay loam and time.

		Time (days)					
P added[1]	P fraction[2]	0	3	7	14	28	56
		----------ppm P[3]----------					
None	water soluble	5	6	5	5	5	5
	Al-P	70	68	63	87	61	56
	Fe-P	36	36	33	41	37	45
	Ca-P	170	119	172	157	149	167
200 ppm P	water soluble	51	58	66	64	65	65
	Al-P	163	165	141	149	130	133
	Fe-P	43	41	43	44	47	46
	Ca-P	178	200	196	181	182	179
500 ppm P	water soluble	133	130	143	158	141	141
	Al-P	323	255	294	254	270	278
	Fe-P	36	44	48	51	49	37
	Ca-P	193	206	198	165	204	220

[1] P was added as $CaHPO_4$ at the initiation of the experiment.

[2] Chang and Jackson phosphorus Fractionation procedure (14).

[3] Each value reported is a mean of two replications.

Table 2. Interaction of added P, inorganic P fractions in a Warsaw loam and time.

		Time (days)					
P added[1]	P fraction[2]	0	3	7	14	28	56
		-----------ppm P[3]---------------					
None	water soluble	3	4	3	3	2	5
	Al-P	239	230	289	247	273	225
	Fe-P	138	150	130	135	141	129
	Ca-P	38	43	39	35	43	40
200 ppm P	water soluble	25	19	14	16	13	13
	Al-P	315	275	268	310	322	289
	Fe-P	156	169	153	151	164	163
	Ca-P	48	48	42	37	45	42
500 ppm P	water soluble	115	103	74	66	54	49
	Al-P	438	413	351	453	350	407
	Fe-P	166	175	168	161	174	173
	Ca-P	43	48	52	46	54	52

[1] P was added as $CaHPO_4$ at the initiation of the experiment.

[2] Chang and Jackson phosphorus Fractionation procedure (14).

[3] Each value reported is a mean of two replications.

Table 3. Interaction of added P, inorganic P fractions in an Iron River silt loam and time.

		Time (days)					
P added[1]	P fraction[2]	0	3	7	14	28	56
		ppm P[3]					
None	water soluble	2	3	0	0	1	0
	Al-P	31	30	35	31	31	28
	Fe-P	119	122	125	117	130	122
	Ca-P	53	51	46	51	53	47
200 ppm P	water soluble	4	5	3	0	1	3
	Al-P	155	138	146	-	139	131
	Fe-P	178	200	211	218	225	234
	Ca-P	51	54	51	50	50	52
500 ppm P	water soluble	15	14	11	1	7	6
	Al-P	310	290	328	308	276	293
	Fe-P	218	262	271	258	283	317
	Ca-P	54	54	49	52	58	53

[1] P was added as $CaHPO_4$ at the initiation of the experiment.

[2] Chang and Jackson phosphorus Fractionation procedure (14).

[3] Each value reported is a mean of two replications.

samples showed an increase from a trace to 15 ppm P in the water soluble fraction, 31 to 310 ppm P in Al-P, and 119 to 219 ppm P in Fe-P compared to the untreated soil. A decrease in the water soluble and Al-P fractions and a simultaneous increase in the Fe-P fraction over the incubation period was also noted at the 500 ppm P level. Calculation of the percent recovery of the added P showed 95 percent at the 200 ppm P level and 88 percent at the 500 ppm P level. This is well within experimental error.

The acid Warsaw soil is dominant in Al-P. Untreated samples of the Warsaw soil revealed essentially no change in the water soluble, Fe-P, and Ca-P fractions throughout the incubation; however, somewhat variable results were obtained for the Al-P fraction. This fraction was unchanged except for the one week and one month sampling dates yielding slightly higher ppm P values. Total analysis indicated 905 ppm P in the untreated soil.

A slight increase in Fe-P at the 200 ppm and 500 ppm P levels was generally noted in the Warsaw soil. The initial samples increased from 137 to 156 to 166 ppm P as Fe-P from the untreated to the 200 and 500 ppm P levels respectively. A very slight increase in Ca-P was noted at both 200 and 500 ppm P levels. Initial samples indicated the water soluble fraction to be 115 ppm P at the 500 ppm P level, 25 ppm at the 200 ppm level and 3 ppm for the untreated soil. After two months of incubation, the untreated Warsaw soil was unchanged, but the P content of the water soluble fractions in the 200 and 500 ppm P levels had decreased by half. The percent recovery of added P showed 44 percent recovered from the 200 ppm P treated soil, and 54 percent recovered from the 500 ppm P level. Other workers have reported low recovery, with no explanation as to possible reasons (15,94).

The Wisner calcareous soil is dominant in Ca-P. The P content in all four fractions of the untreated soil was unchanged at the various sampling dates. The addition of 200 and 500 ppm P caused the Al-P fraction to increase from 70 to 163 to 323 ppm P respectively. Some increases were noted in Fe-P and Ca-P fractions over the complete incubation period. But the most significant increases were in the water soluble and Al-P fractions at both 200 and 500 ppm P rates. The total P content indicated 905 ppm P to be present in the Warsaw soil. The percent recovery was 85 percent at the 200 ppm P level, and 79 percent at the 500 ppm P level.

Upon the addition of $CaHPO_4$ to the acid Iron River soil, initial rapid increases in the Fe-P and the Al-P fractions were noted at both 200 and 500 ppm P levels. An indication of a shift of some P from the Al-P fraction to the Fe-P fraction throughout the incubation period may be explained by a shift from a more soluble compound (Al-P such as variscite) to a less soluble phosphate (an Fe-P like strengite) adhering to the solubility product principle. Chang and Chu (12) reported the greatest fixation of P after three days to be in the Al-P fraction of P enriched, acid, Taiwan soils. However, after one-hundred days, most of the added P was in the Fe-P fraction. This type of shift was not noted in the acid Warsaw after two months. An increase in the Al-P fraction accounted for most of the P added as $CaHPO_4$ to the acid Warsaw soil.

Little change in the Ca-P fraction was noted in the three soils. The first of two reasons why this may occur is the fact that Ca-P's detectable in the 0.1 N NaOH extracted fraction (i.e. Hydroxyapatite) are not probable to form under very acid conditions. Secondly, the forms of Ca-P that may appear in this fraction have been noted to form very slowly, possibly taking more than a year. This consideration is especially important in interpreting calcareous soil P fractions where Ca-P formation is more probable.

The fact that a given inorganic P fraction (i.e. Al-P) indicates an increase or decrease may not necessarily mean that the forms included in the fraction are actually P of the specified type (Al-P's). It is realized that Chang and Jackson's fractionation procedure has not been acclaimed to be precise but rather a good indicator of inorganic P forms. When it was devised, the method was tested on acid soils that had not received recent application of P fertilizer. The application to calcareous soils or soils that have received recent applications of P fertilizer may result in misinterpretation. The question as to whether $CaHPO_4$ changes into Al-P and Fe-P as rapidly as indicated is paramount.

Igawa, cited by Chang (11), suggested the use of 2.5 percent acetic acid for the removal of $CaHPO_4$ before extracting Al-P, Fe-P and Ca-P. No reference was made as to the acetic acids effect on the other forms of inorganic P in the soil. An evaluation of the use of 2.5 percent acetic acid for this purpose indicated that it was unsuccessful in removal of 200 ppm P as $CaHPO_4$ when added and immediately extracted from the acid Iron River and Warsaw soils. Successive NH_4Cl extractions of $CaHPO_4$ treated soils was used in an attempt to explain the indicated rapid change of $CaHPO_4$ to an Al-P as revealed by the fractionation procedures. The untreated and 500 ppm P treated Wisner samples were analyzed after two months incubation. Five, thirty-minute extractions with 50 ml of 1.0 $\underline{N}$ NH_4Cl pH 7.0, followed by one 50 ml extraction for one hour shaking with 0.5 $\underline{N}$ NH_4F, pH 7.0 were carried out. The results (given in Table 4 and Figure 1) for this procedure are compared with the Chang and Jackson procedure of one NH_4Cl extraction followed by the NH_4F extraction. The second increment of NH_4Cl extraction of the 500 ppm P treated Wisner removed about twice as much P as did the first. The following increments removed considerably less P until increment five which contained a level about

Table 4. Successive 1 $\underline{N}$ NH_4Cl, pH 7.0, extractions of Wisner silty clay loam, untreated and treated with 500 ppm P as $CaHPO_4$, incubated two months.

	NH_4Cl Extraction[1] No.					
P Added ppm	1	2	3	4	5	Al-P[2]
	ppm P[3]					
0	11	14	12	10	10	55
0	5	-	-	-	-	56
500	115	209	42	21	14	91
500	140	-	-	-	-	278

[1] Extracted with NH_4Cl for one-half hour shaking period.

[2] Extracted with NH_4F as described by Chang and Jackson procedure (14).

[3] Each value reported is a mean of two duplicates.

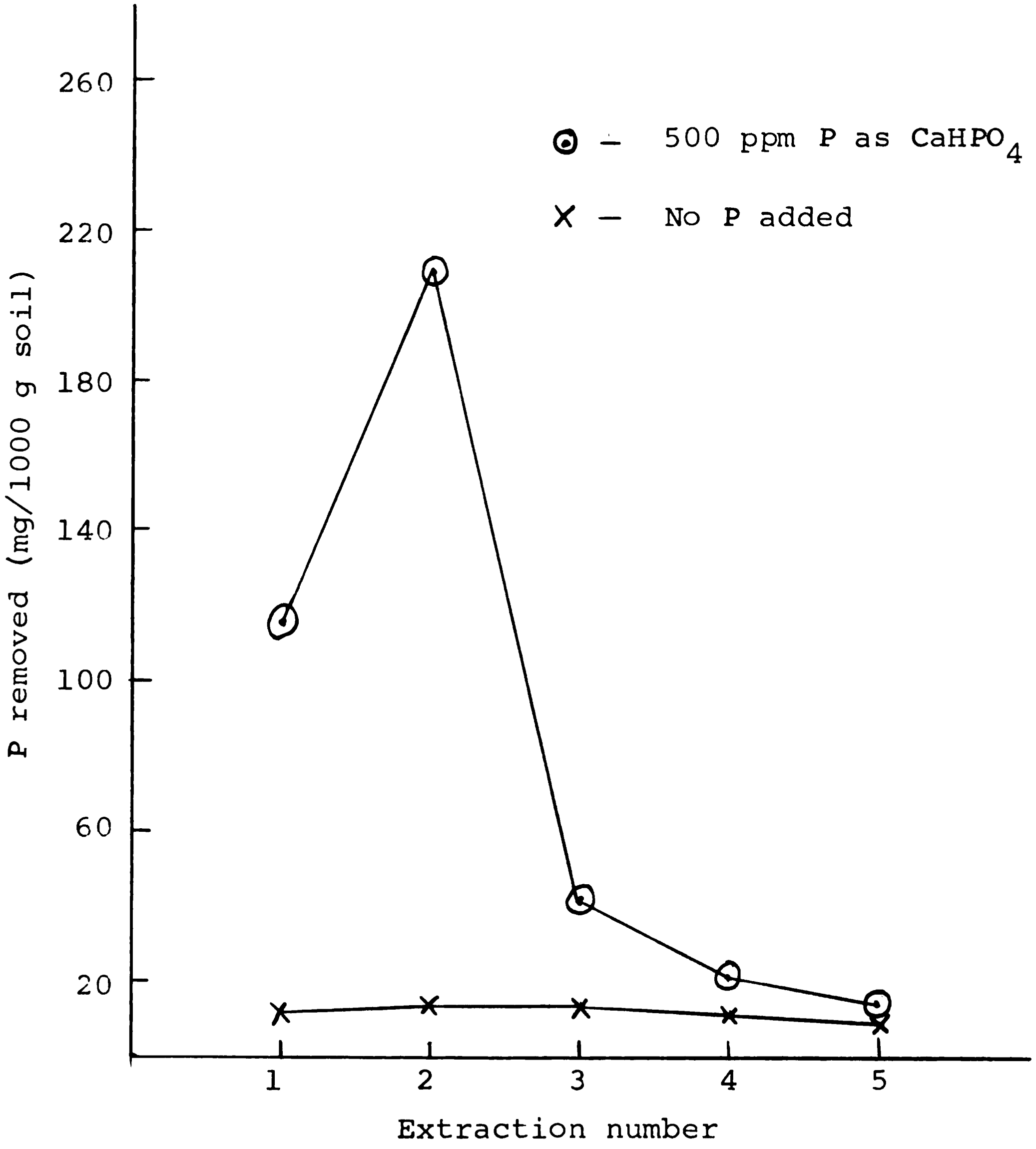

Figure 1. Phosphorus removed from Wisner silty clay loam by successive extraction with 1 N NH_4Cl. P removed vs. extraction number.

equivalent to that in each of the five extractions of the untreated soil. The NH_4F extracted Al-P fraction seemed to be unaffected following five extractions with NH_4Cl, having about the same concentration of P in the Al-P fraction after one extraction as it did after five NH_4Cl extractions. The great increase in P in the second increment of NH_4Cl indicates that one 50 ml NH_4Cl extraction may be inadequate to remove all the $CaHPO_4$ present in treated calcareous soils. If only one extraction is made, some $CaHPO_4$ may be reported as Al-P since $CaHPO_4$ is soluble in NH_4F. A probable reason for not removing more in the first increment may be the high concentration of Ca in that first extraction, and the resultant common ion effect keeping much of the $CaHPO_4$ in the solid state. With much of this Ca ion removed, more $CaHPO_4$ would go into solution during the second increment of extraction. The possibility of some of the P in the five increments being from other sources is recognized; however, freshly precipitated Fe and Al phosphates are probably not abundant in this alkaline Wisner soil. Therefore $CaHPO_4$ or some Ca-P more soluble than octacalcium phosphate is probable. Further, successive extractions with NH_4Cl did not affect the Al-P fraction in the untreated soil, and amorphous forms of $AlPO_4$ probably would be associated with the NH_4F fraction and therefore be unaffected.

One gram samples of untreated acid Warsaw soil were extracted with 50 ml portions of 1 N NH_4Cl pH 7.0 for two, three, five, and seven increments, followed by fractionation into Al-P, Fe-P, and Ca-P. Only trace amounts of P were detected in each of the increments, and the following extractions revealed essentially no change in the Al-P, Fe-P, or Ca-P fractions due to a number of NH_4Cl extractions (see Table 5). Samples of the Warsaw soil treated with 200 ppm P as $CaHPO_4$ were immediately subjected to increments of NH_4Cl extraction followed by fractionation into the remaining forms. One extraction removed about one third of the added P. About 20 ppm P was removed in each of the additional increments. The forms of P indicated by immediate fractionation of the $CaHPO_4$ treated acid Warsaw soil must be considered from the standpoint of the solution phase. Probably much of the $CaHPO_4$ added was rapidly transformed into freshly precipitated Al-P, and/or fixed by clay minerals. These processes would be speeded up when shaking in the NH_4Cl solution. Avnimelech (2) reported that P applied to soils in solution was fixed within hours to about the same degree as that applied as powder and incubated three months in moist soil.

Solubility Product Diagrams

Solubility data for thermodynamic interpretations of phosphate reactions is presented on two types of diagrams; phosphate phase diagram as described by Lindsay and Moreno (58), and phosphate potential diagrams as described by

Table 5. Successive extractions with NH_4Cl of treated (200 ppm P as $CaHPO_4$) and untreated Warsaw loam.

P added[1] ppm	NH_4Cl Extraction[2] No. 1	2	3	4	5	6	7	Total	Al-P	Fe-P	Ca-P
ppm P											
0	3	2						5	202	116	36
0	2	3	4					9	206	116	36
0	3	2	2	T	T			7	204	122	44
0	3	3	5	T	T	T	T	11	203	116	39
200	70							70	279	149	74
200	72	19						91	248	135	60
200	72	28	19					118	238	144	49
200	68	33	20	8	10			138	264	133	58

T indicates trace.

[1] Each value reported is a mean of two duplicates. The $CaHOP_4$ was added to unincubated soil and immediately extracted with NH_4Cl, and then fractionated by Chang and Jackson procedure (14).

[2] Each NH_4Cl extraction involved shaking one-half hour.

Aslying (1), and also by Wright and Peech (103). The solubility products (pKsp) for the various components of the phase equilibrium systems used in the calculation of solubility isotherms were taken from Lindsay and Moreno (58), and from Taylor and Gurney (88).

Before interpreting the results obtained on the basis of solubility diagrams, a consideration of the values used to calculate solubility products of minerals is important. Lindsay and Moreno (58) represented the dissociation of variscite in the following way:

$$Al(OH)_2H_2PO_4 \rightleftharpoons Al^{+++} + 2OH^- + H_2PO_4^-$$

$$pKsp(v) = pAl + 2pOH + pH_2PO_4$$

$$pKsp(v) = 30.5$$

More recently Taylor and Gurney describe the relationship as:

$$AlPO_4 \cdot 2H_2O \rightleftharpoons Al^{+++} + PO_4^{\equiv}$$

$$pKsp(v) = pAl + pPO_4$$

$$\text{or} \quad pKsp(v) = pAl + pH_2PO_4 - 2pH + pK_2K_3$$

$$pKsp(v) = 22.52$$

Both isotherms have the same slope on a phase diagram or a potential diagram, but differ in intercept, with Taylor and Gurney's relationship being shifted downward from the isotherm calculated by Lindsay and Moreno. These relationships have been calculated and represented on phase diagrams assuming that the Al^{+3} activity in solution is controlled by gibbsite with a pKsp(G) of 33.8. Solubility diagrams are only approximate indicators of controlling solid phases and therefore ion activity in solution. A lack of knowledge about P minerals, their solubilities, dissociation products, and modes of formation in a dynamic soil system renders interpretations difficult. For example, an amorphous form of $Al(OH)_3$ that is more soluble than gibbsite may be controlling Al^{+3} activity in the solution phase. Also, consider an amorphous $AlPO_4$ more soluble than variscite affecting P activity in solution.

1. $pKsp(G) = pAl + 3(14-pH)$
2. $pKsp(AG) = pAl + 3(14-pH)$

where: pKsp(G) = solubility products of gibbsite

pKsp(AG) = solubility products of amorphous $Al(OH)_3$ and $pKsp(G) > pKsp(AG)$

3. $pKsp(V) = pAl + PO_4$
4. $pKsp(AV) = pAl + PO_4$

where: pKsp(V) = solubility product for variscite

pKsp(AV) = solubility product for amorphous $AlPO_4$ and $pKsp(V) > pKsp(AV)$

Consider the representation of isotherms on a phase diagram where:

$$pH + pH_2PO_4 = pK(v) - pK(G) + pKw$$

pKw = pKsp for water

If an amorphous form of $Al(OH)_3$ more soluble than gibbsite is controlling Al^{+3} activity, the $AlPO_4$ isotherm would shift downward from the isotherm where gibbsite and variscite are controlling the system (Figure 2). Phosphorus activity could be controlled by an amorphous $AlPO_4$ more soluble than variscite, and if gibbsite controls Al^{+3} activity the $AlPO_4$ isotherm would shift upward. If both an amorphous $AlPO_4$ and amorphous $Al(OH)_3$ are present, or the presence of any combined participation of crystalline and amorphous forms of both variscite, or variscite-like compounds and gibbsite, the resulting isotherms may shift up or down dependent on the relative amounts of each form present.

Similar relationships should be considered for a strengite isotherm when assuming that goethite controls Fe^{+3} activity in solution.

Representing an $AlPO_4$ isotherm on a P and Al potential diagram will also be approximate. Consider the following:

$$AlPO_4 \rightleftharpoons Al + PO_4$$

$$pKsp(V) = pAl + pK_3 - pH + pK_2 - pH + pH_2PO_4$$

rewritten: $$pH_2PO_4 + 1/3\ pAl = \underset{\text{intercept}}{(pKsp(V) - pK_2K_3)} + \underset{\text{slope}}{2}(pH - 1/3pAl)$$

where: $$pK_2 = pH + pHPO_4 - pH_2PO_4 = 7.20$$

$$pK_3 = pH + pPO_4 - pHPO_4 = 12.32$$

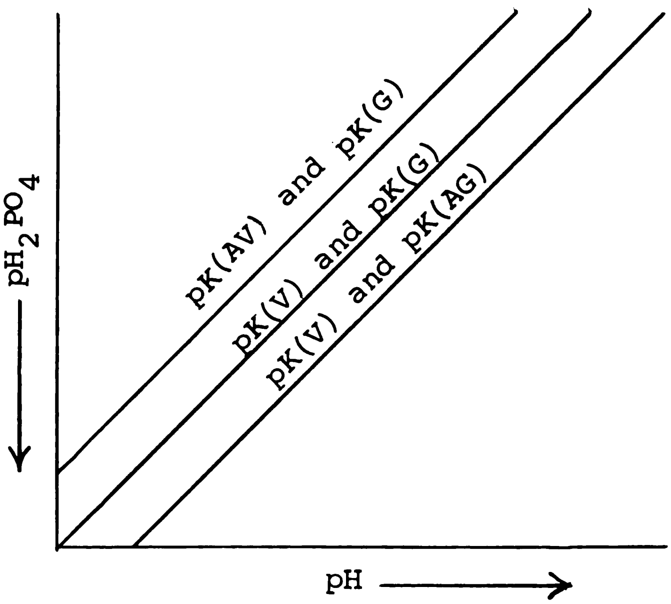

Figure 2. Theoretical Al-p isotherms as influenced by increased solubilities of amorphous variscite and/or gibbsite.

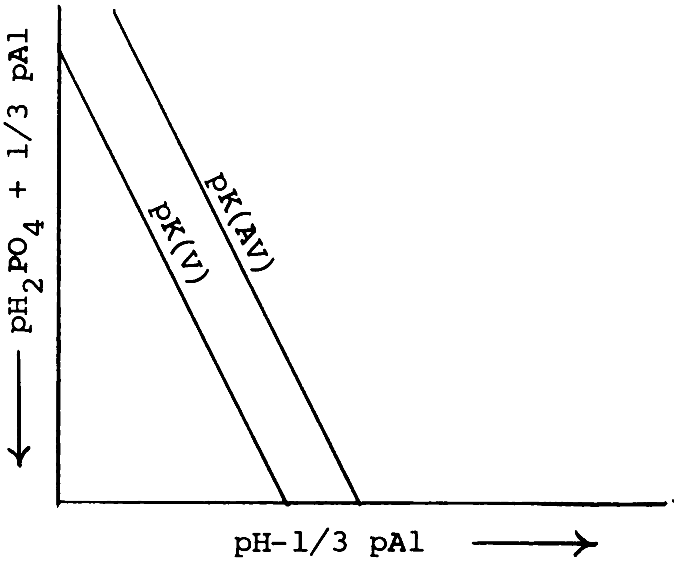

Figure 3. Theoretical aluminum vs. phosphate potentials as influenced by increased solubility of amorphous variscite.

The slope of the variscite, or variscite-like compound isotherm will be two when P potential is plotted against Al potential. The intercept will vary according to the values of pKsp(V) used. If an amorphous form of variscite is controlling the system, experimental points may be above the isotherm calculated on the basis of crystalline variscite.

Data for treated and untreated Iron River, Warsaw and Wisner soils at various sampling dates throughout the incubation period are presented on phase diagrams. The untreated Iron River appeared to indicate that variscite or strengite like compounds were controlling P solubility (Figure 4). Upon incubation the "equilibrium" points moved parallel to the variscite and strengite isotherms, with a resultant decrease in P activity in solution and a decrease in pH. With the addition of 200 ppm P as $CaHPO_4$ to the system slight increases in P activity with the points moving approximately parallel to the variscite and strengite lines occurred. At the 500 ppm P level the points moved up vertically with increased P activity in the system. Slight increase in pH were noted when the Iron River soil was treated at both P levels. The 500 ppm P level resulted in a greater increase in pH than did the 200 ppm P level. This increase in pH may be due to the dissociation of $CaPHO_4$ according to the following equations.

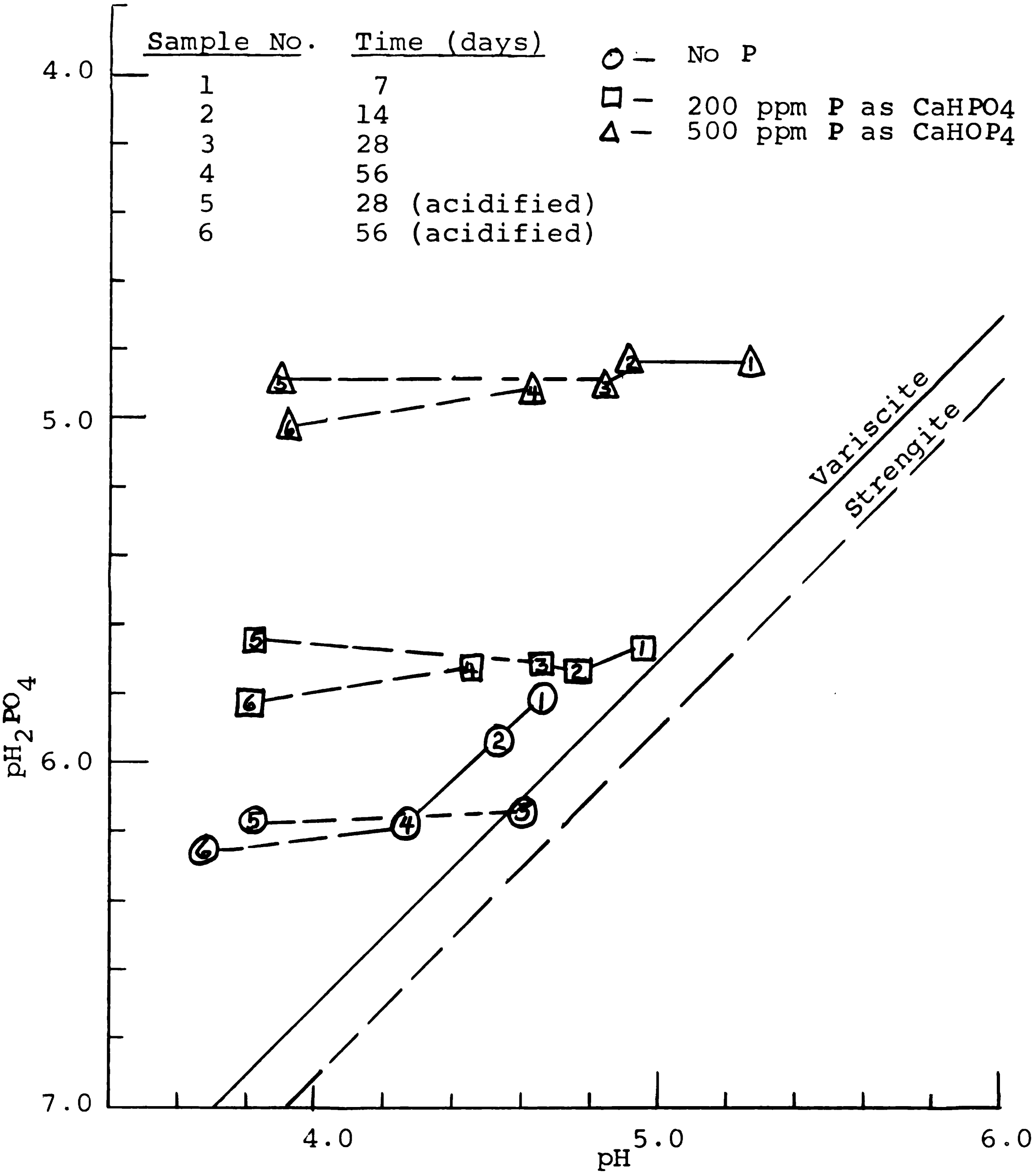

Figure 4. Solubility phase diagram, pH_2PO_4 vs. pH, for Iron River silt loam. Each point is an average of duplicate samples.

$$CaHPO_4 \rightleftharpoons Ca^{++} + HPO_4^{=}$$

$$HPO_4^{=} + H_2O \rightleftharpoons H_2PO_4^{-} + OH^{-}$$

The rise in pH may be off set somewhat since microbial activity during the shaking period produces CO_2. At both P treatment levels, the pH of the Iron River soil decreased with no apparent change in P activity. This decrease occurred continuously from the initial samples until the end of the two month incubation. When the pH of the system was reduced by acidification of the two month incubated samples, the P concentration was essentially unchanged for the treated and untreated soil. After the four day shaking period, the system may not be in equilibrium, therefore P activity would not have changed. It has been suggested by Chakravarti and Talibudeen (10) that an eight day shaking period was necessary for equilibrium in acid soils. In the Iron River acid soil it seems that variscite-like and/or strengite-like compounds control the untreated system, with possibly amorphous forms participating in the P treated systems.

The phase diagram for the acid Warsaw soil (see Figure 5) indicates compounds more soluble than those in the Iron River soil control P activity in solution. Generally, no change in treated or untreated systems were noted upon incubation. But the two month sampling of the 500 ppm P treatment indicated a lower P concentration than all the

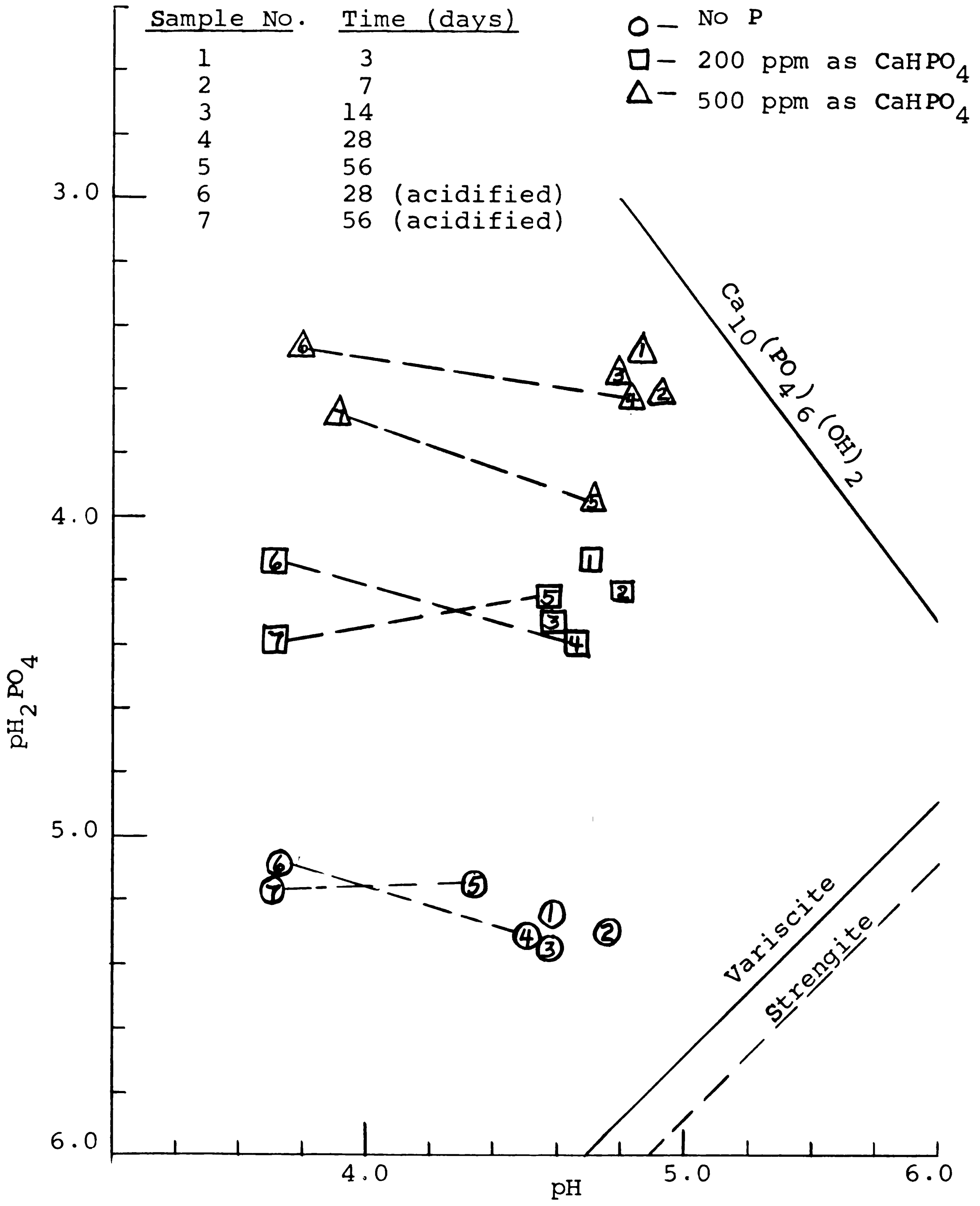

Figure 5. Solubility phase diagram, pH_2PO_4 vs. pH, for Warsaw loam. Each point is an average of duplicate samples.

previous samplings. In the acidified untreated soil, a slight increase in P concentration accompanied the decrease in pH. The acidification of the one month incubated 200 and 500 ppm P soils resulted in little change in P concentration. The 500 ppm P treated two month incubated samples had a more noticeable decrease in P activity accompanying the decreased pH. Amorphous forms of $AlPO_4$ are likely to be controlling this system. The $CaHPO_4$ probably accounts for the points being far above the variscite isotherm for the treated soils, as generally the most soluble compounds control P activity in solution. A Ca-Al phosphate or Al phosphate more soluble than variscite might control the system.

The calcareous Wisner soil is a dominant Ca-P soil. Equilibrium points for the untreated soil fell into a group half way between the octacalcium phosphate and hydroxyapatite isotherms (Figure 6). No consistent changes in the treated or in the untreated soil equilibrium points were noted when incubated for two months. The addition of 200 ppm P as $CaHPO_4$ caused a vertical shift toward the octacalcium phosphate isotherm. Essentially no change in pH was accompanied by an increase in P activity. This was also noted at 500 ppm P as the points shifted closer to the octacalcium phosphate isotherm. Dicalcium phosphate raised the P activity in solution with little change in pH. The formation of significant amounts of apatite is improbable as

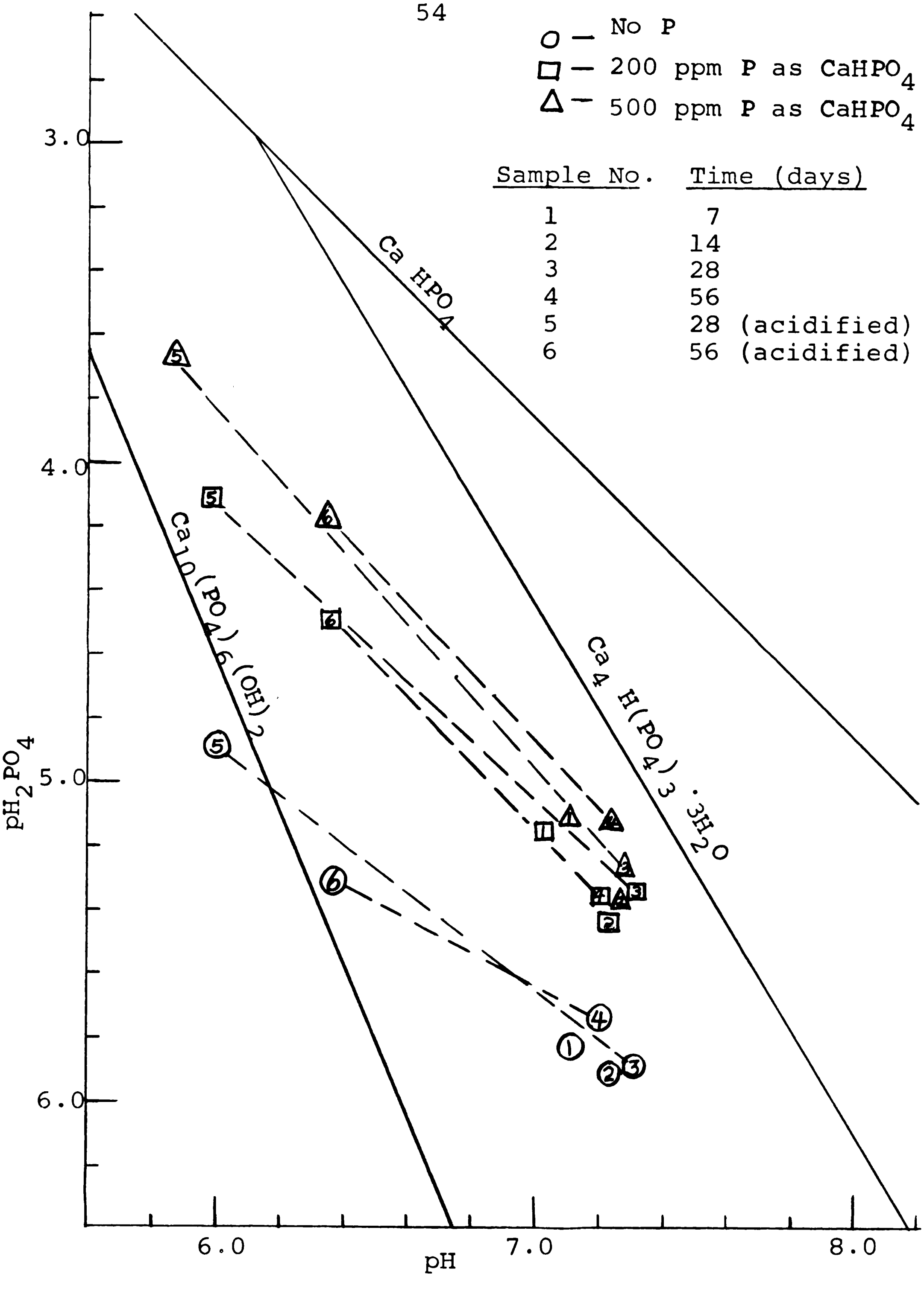

Figure 6. Solubility-phase diagram, pH_2PO_4 vs. pH for Wisner silty clay loam. Each point is an average of duplicate samples.

this mineral forms slowly. Further, the phase diagram seems to indicate that a Ca-P similar to octacalcium phosphate still remains after two months incubation as no large shift at the various sampling dates is noted. A Ca-P compound more soluble than octacalcium phosphate could be present in the treated soil, and not by revealed or a solubility diagram. This is probable as a four day shaking period in dilute $CaCl_2$ may result in its shift to more insoluble compounds such as octacalcium phosphate. Acidifying the system at the end of two months incubation caused the untreated points to move parallel to the $CaHPO_4$ line. This is evidence of a Ca-P controlled P activity in solution.

A plot of lime potential ($pH-\frac{1}{2}pCa$) versus phosphate potential ($\frac{1}{2}pCa + pH_2PO_4$) for the treated and untreated Wisner soil indicated similar results as compared to the phase diagram (Figure 7).

Aluminum potential (pH-1/3 pAl) versus phosphate potential (pH_2PO_4 + 1/3 pAl) are presented on a single solubility diagram (Figure 8). Two variscite isotherms are represented as pKsp(V) = 22.52 (88), and pKsp(V) = 30.50 (58). Results of analysis of the Warsaw and Iron River soils after two months incubation indicated similar results to the phase diagram. The untreated Iron River soil "equilibrium" points are on the pKsp(V) = 22.52 variscite line. Points on the pKsp(V) = 30.5 variscite isotherm occurred with 200 ppm P in the Iron River soil. The 500 ppm P level in

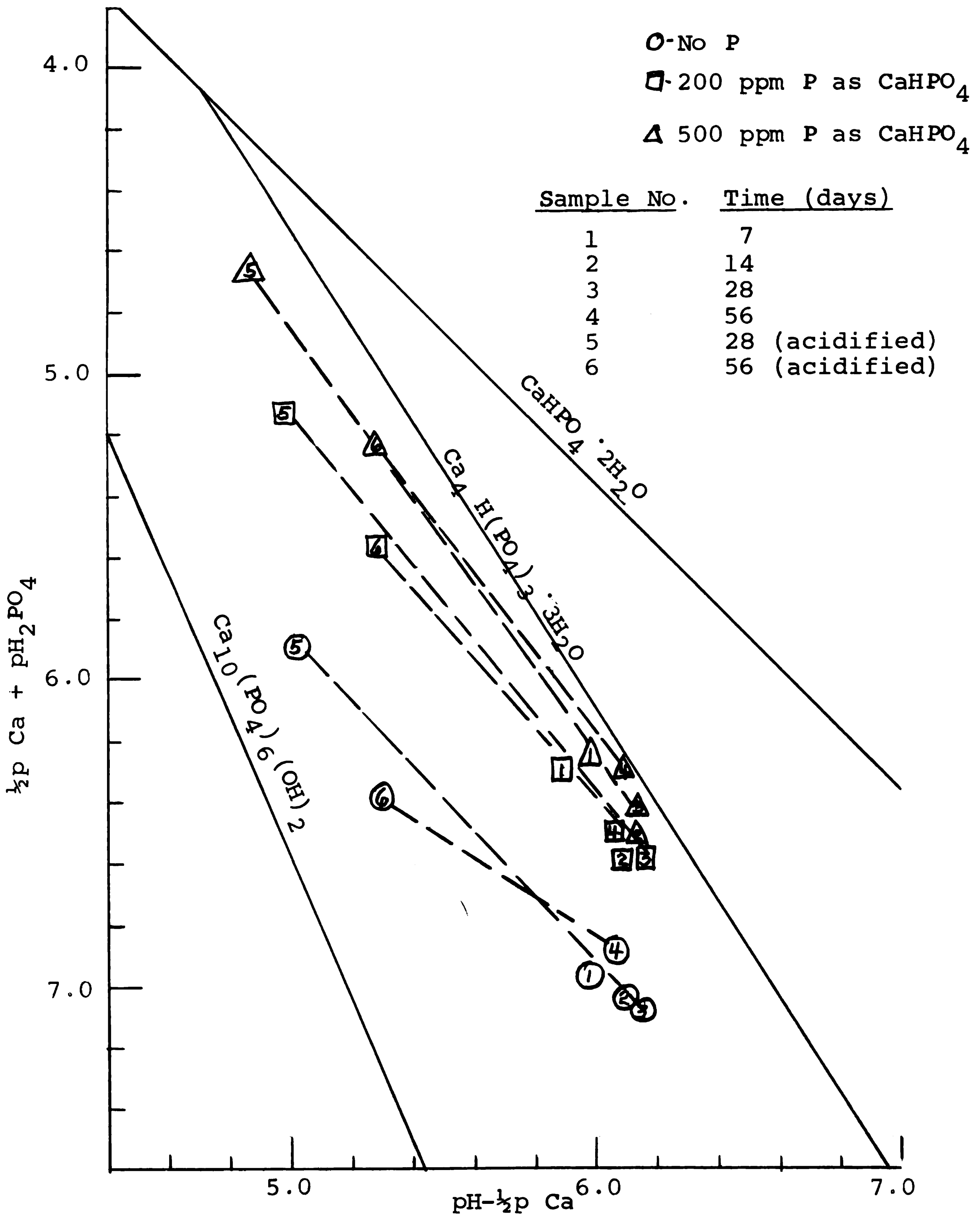

Figure 7. Lime vs. phosphate potential for Wisner silty clay loam. Each point is an average of duplicate samples.

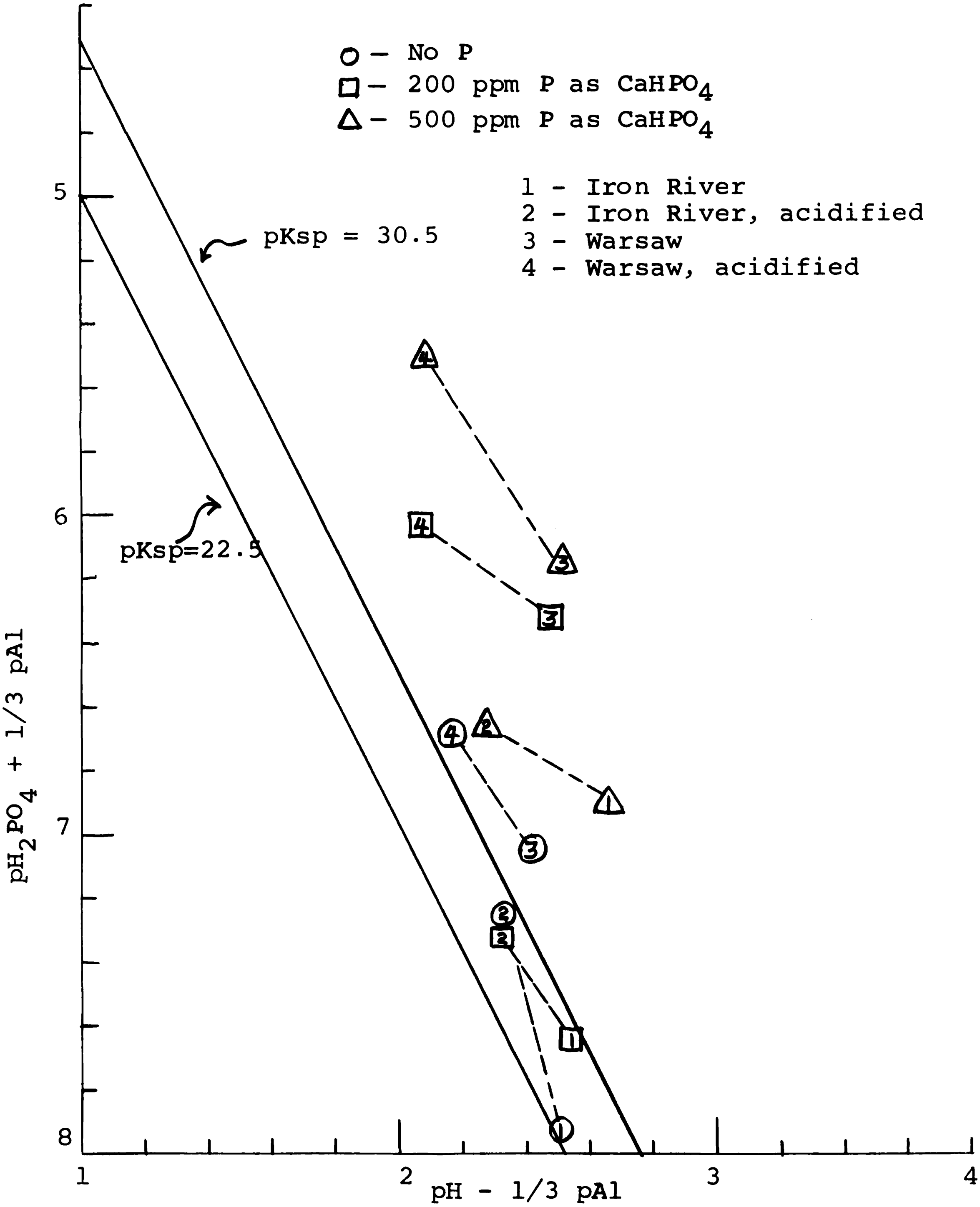

Figure 8. Aluminum vs. phosphate potential for Iron River silt loam and Warsaw loam. Each point is an average of duplicate samples.

Iron River seemed to be supersaturated with respect to variscite after two months. Upon acidification both treated and untreated points moved parallel to the isotherms indicating variscite like compounds probably control the P activity. Again, compounds more soluble than those present in the Iron River soil seemed to control P activity in the Warsaw soil. The untreated soil equilibrium points are located just above the pKsp(V) = 30.5 isotherm. The 200 and 500 ppm P treated equilibrium points were located vertically above the untreated "equilibrium" points by about one phosphate potential unit. Upon acidification the treated and untreated Warsaw points moved parallel to the variscite isotherms indicating variscite-like, possibly amorphous $AlPO_4$ compounds controlling P activity in solution.

Inorganic phosphorus fractionation results and the two types of solubility diagrams will be compared. These two procedures measure different phases of soil P. The fractionation procedure measures the amount of P in the solid phases. Solubility product diagrams are used to determine the dominant forms of mineral P which control P activity in solution.

Fractionation of untreated iron river indicated the dominance of Fe-P, and some Al-P and Ca-P. Solubility diagrams indicated that quite insoluble compounds like variscite or strengite control P activity in the soil solution. When treated with 200 or 500 ppm P as $CaHPO_4$ an increase in the Al-P fraction is immediately noted. Solubility diagrams display an increased P activity in solution as amorphous $AlPO_4$ is probably formed. After two months incubation the Fe-P fraction increased somewhat at the expense of the Al-P fraction. An indication that $CaHPO_4$ does not persist in the acid Iron River soil is evidenced by the trace of P in the water soluble fraction. Thus, both methods suggest that Al-P's control P activity over a short period of time; however, P fractions suggest that in time the newly formed Al-P may revert to Fe-P.

Fractionation of untreated Warsaw soil indicated Al-P dominance. When treated with $CaHPO_4$ the greatest increase was noted in the Al-P fraction. A smaller increase in the water soluble fraction was noted. Solubility diagrams show increased P activity in the P treated soils, with an amorphous $AlPO_4$ compound more soluble than that present in the Iron River soil, probably controlling P activity. Both methods suggest Al-P's controls P activity in the Warsaw soil.

Dicalcium phosphate does not appear to be transformed as rapidly in the acid Warsaw as in the Iron River soil. Successive NH_4Cl extractions of Warsaw soil treated with 200 ppm P as $CaHPO_4$ showed that only about one-third could be removed with one 50 ml extraction, and that only about 70 percent with five extractions. Whether the seventy percent P removed was $CaHPO_4$ or was some other form of P as a result of a transformation from $CaHPO_4$ during the extraction period is not known. Generally, only the most soluble P compounds dissolve or precipitate fast enough in soils to govern the P activity in solution (58); thus, the possibility of a shift during extraction is evident.

Fractionation of the treated Wisner soil indicated the greatest increases in the Al-P fraction, and a considerable increase in the water soluble fraction. The considerable increase in Al-P was indicated to probably be $CaHPO_4$ not removed by one NH_4Cl extraction, since successive NH_4Cl extraction removed sufficient P that no gain was shown in the Al-P fraction. Solubility diagrams indicate that Ca-P's control P activity in both treated and untreated soil. Fractionation data agrees with this only if care is exerted to remove all water-soluble P prior to fractionation.

SUMMARY AND CONCLUSIONS

Chang and Jackson's (14) procedure for fractionating soil inorganic P into water soluble, Al-P, Fe-P, and Ca-P fractions has shown large increases in the Al-P fraction when P was added to both acid and calcareous soils. These results are not expected in calcareous soils. It was thought that considerable $CaHPO_4$ was not extracted with NH_4Cl and was therefore reported as Al-P. In an attempt to verify proper separation into these fractions, two acid soils and one calcareous soil were treated with $CaHPO_4$ and incubated for two months. Fractionation data and phase equilibrium data from samples throughout the incubation period were compared. Also, successive NH_4Cl extractions were carried out to remove $CaHPO_4$ before other fractions were extracted.

One extraction of NH_4Cl was inadequate in $CaHPO_4$ removal from the treated calcareous Wisner soil. The second increment of NH_4Cl removed considerably more P than did the first, with the third, fourth, and fifth increments removing decreasing amounts of P. Possibly high Ca activity in the first increment resulting in a common ion effect kept much of the $CaHPO_4$ out of solution. One NH_4Cl extraction seemed to be adequate when employed on the untreated Wisner soil. The acid Iron River and Warsaw soils both treated and untreated seemed to be adequately extracted with one increment of NH_4Cl, thus little or no carry over of $CaHPO_4$ into the Al-P fraction would occur.

Fractionation of Wisner soil treated with 200 and 500 ppm P as $CaHPO_4$ indicated that most of the added P was present in the Al-P and water soluble (NH_4Cl) fractions. Both the P potential diagrams and the P phase solubility diagram showed Ca-P's to be controlling P activity in solution. Equilibrium points for untreated soil were located between the octacalcium phosphate and hydroxyapatite isotherms. Treated soil points were closer to the octacalcium phosphate isotherm. Upon acidification of the dilute $CaCl_2$ systems, equilibrium points shifted parallel to the $CaHPO_4$ isotherm. A large increase in the Al-P fraction as reported by fractionation is more likely to be a fairly soluble Ca-P such as $CaHPO_4$, that was not removed with one NH_4Cl extraction and was then extracted with NH_4F and reported as Al-P. Al-P's are not likely to form in large quantities in this calcareous soil. Fractionation is in agreement with solubility data when care is taken to remove all water-soluble (NH_4Cl) P prior to fractionation. Thus, Ca-P's are indicated to control P activity in the Wisner soil.

Solubility diagrams indicated that in the Iron River soil quite insoluble compounds like variscite or strengite control P activity in solution. Fractionation indicated only traces of P in the water soluble fraction, a small Ca-P fraction, and a Fe-P dominance with considerable Al-P fraction in the untreated soil. Upon the addition of $CaHPO_4$ the greatest increase was noted in the Al-P fraction with some increase in the Fe-P fraction. The water soluble and Ca-P fractions were essentially unaffected. After two months incubation the Al-P fraction decreased somewhat with an accompanied increase in the Fe-P fraction. Both methods suggest that Al-P's control P activity over a short period of time; however, P fractions suggest that in time the newly formed Al-P may revert to Fe-P.

Fractionation of Warsaw untreated soil revealed Al-P dominance. Solubility diagrams indicated that amorphous Al-P probably controls P activity in solution. Treated soils contained most of the added P in the Al-P fraction, with some in the water soluble fraction. The phase diagram indicated increased P activity in the treated soil. But upon acidification little change in P activity was noted. Phosphate potential plotted against Al potential showed movement somewhat parallel to the variscite isotherm when treated and untreated systems were acidified. More soluble compounds were indicated to control P activity in the Warsaw soil in comparison to the Iron River soil. Both methods suggest Al-P's control P activity in Warsaw soil.

Interpretation of fractionation and solubility product data is approximate, and gives only an indication as to quantities of different P solid phases present in soils. These phases control P activity in the soil solution. Much is still unknown about forms and properties of P minerals in soils. Especially complex is the problem of understanding their reactions in a dynamic soil system when P is added to the soil.

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