CHEMICAL AND PHYSICAL FACTORS AFFECTING THE RELATIVE AVAILABILITY OF INORGANIC PHOSPHORUS IN SOILS

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ABSTRACT

CHEMICAL AND PHYSICAL FACTORS AFFECTING THE RELATIVE AVAILABILITY OF INORGANIC PHOSPHORUS IN SOILS

by Anthony Shiang-Ru Juo

An evaluation of the chemical and physical properties related to the availability of inorganic P compounds to plants was approached from two aspects: (a) examination of the chemical and physical properties of synthetic phosphate compounds, and (b) the distribution of the various forms of inorganic P in soil particle separates.

Synthetic colloidal ferric and aluminum phosphates were crystallized in aqueous medium to form variscite, $AlPO_4 \cdot 2H_2O$ and strengite, $FePO_4 \cdot 2H_2O$. The compounds were identified and characterized by X-ray and infrared analysis and electron micrographs. Fe phosphate crystallized at a much faster rate than Al phosphate in acidic aqueous medium under the same temperature and pressure conditions. Variscite and strengite which were crystallized at 105^oC for 40 days gave specific surface areas of 27.5 m^2g^{-1} and 1.98 m^2g^{-1}, respectively. The strengite consisted of single spherical crystals with an average diameter of 6 microns and the variscite consisted of reniform crystalline aggregates with an average diameter of 1.5 microns. In quartz-sand cultures, with Sudan grass as the indication crop, the relative availability of P from the synthetic compounds was: colloidal ferric phosphate $\approx$ colloidal aluminum phosphate $>>>$ variscite $>$ strengite.

In studying the distribution of soil inorganic P, four Michigan soil profile samples with different textural classes were selected. Inorganic P in soils was fractionated into Al-P, Fe-P and Ca-P according to the method of Chang and Jackson. Al-P and Fe-P contents are highest in the surface soils studied and decrease with the increase of depth, while the content of Ca-P generally increases with the increase of depth in the soil profiles studied. Percentage distribution curves of Al-P, Fe-P and Ca-P in the soil profiles show relationships in supporting the concept which states that the relative abundance of inorganic phosphates in soil may be used as an index for soil chemical weathering.

To determine the distribution of inorganic P in soil particle separates, a proposed procedure of dispersion using NaCl saturation and sonic vibration was developed and reported in this thesis.

Fractionation of inorganic P for each of the particle separates showed that Al-P and Fe-P was most highly concentrated in the clay fraction throughout the soil profiles studied. Ca-P tends to be highly distributed in both the silt and clay fractions in the surface horizons of the soils and becomes more highly distributed in the silt than in the clay fraction in the lower horizons of the profiles. The contents of all the three forms of inorganic P in sand are the lowest among the three particle separates.

During fixation and transformation of inorganic P, Ca-P, which is of primary origin and is present originally in the sand fraction of the soil, is brokendown chemically and physically and enters into the finer fractions of the soil. But, it still remains in high degree of crystallinity throughout the soil textural fractions. The portion of Ca-P that has been dissolved by the action of H^+ ions may reprecipitate as Al-P and/or Fe-P in the clay fraction. Also, the fixed P in soils is mainly in the form of Al-P and Fe-P and is present in the clay fraction. Al-P and Fe-P in soils can be regarded as available forms of P for plants as long as they remain in colloidal forms.

It is concluded that the degree of crystallinity is the most important factor in controlling the relative availability of inorganic P to plants. For soils under acidic and aerobic conditions, the relative availability of the native and fixed forms of inorganic P is in the order of Al-P $>$ Fe-P $>$ Ca-P.

Approved by______________________

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INTRODUCTION

Inorganic phosphorus in soils is believed to exist as sparingly soluble orthophosphates of Al, Fe and Ca. Al and Fe phosphates are the dominant forms of inorganic P in acid soils while Ca phosphates are most abundant in calcareous soils. Ca phosphate compounds, such as apatites, are the primary P-bearing minerals in soils which are further transformed to Al phosphate and Fe phosphate during the course of weathering. It is also well known that soluble P fertilizers react rapidly in soils to form insoluble phosphates bound mainly to Al and Fe. The reaction is greatly affected by the pH of the system and the sources of cations.

Since both the native and fixed forms of inorganic P in soils are present as insoluble compounds, an understanding of the factors affecting the availability of the various forms of inorganic P to plants is of great importance. To consider solubility alone would be unsatisfactory. Chemical and physical properties such as particle size, specific surface and degree of crystallinity have been brought to attention. However, a clear picture has not yet been well established.

The objectives of this investigation are:

1. To evaluate the chemical and physical properties such as particle size, specific surface, rate of crystallization and degree of crystallinity of synthetic Al and Fe phosphates as related to the relative availability of these phosphate compounds to plants.

2. To determine the distribution of various forms of inorganic P in soil particle separates of some Michigan soil profiles.

REVIEW OF LITERATURE

1. Studies on Native and Fixed Forms of Inorganic Phosphorus in Soils

Soils usually contain from 0.04 to 0.11 percent of P. Inorganic P is the preponderant form of P in mineral soils and exists almost entirely as salts of orthophosphoric acid, among which, the phosphates of Ca, Fe and Al are believed to be the most predominating forms (60,113).

Studies prior to 1953 on compounds formed during soil genesis and as a result of P fertilization in both acid and calcareous soils were reviewed by Olsen (109) and Kurtz (81).

The inorganic P content in agricultural soils is so low that attempts to study the nature of soil P compounds are beset with many difficulties. Three different approaches have been commonly employed to study the inorganic P in soils: (a) direct observations by means of X-ray diffraction, electron microscope, infrared analysis and/or differential thermal analysis; (b) the application of solubility product concepts; and (c) extraction with different acid, alkaline and complexing solutions.

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(a) Direct Observations

Several complex Fe and Al phosphates such as palmerite, taranakite and minyulite were identified by X-ray and optical methods from clay minerals, gibbsite, and geothite digested with P solutions by Haseman, et al. (57,58). By means of electron microscope, Kittrick and Jackson (77) were able to observe the progressive formation of Al phosphate crystals concurrent with the decomposition of the original kaolinite crystals. They also found that the phosphate treatment diminished the kaolinite X-ray diffraction pattern and that various Al phosphates were the end products of P induced kaolinite decomposition. Based on the results of a sequence of similar studies, Kittrick and Jackson (78,79) attempted to arrive at a unified theory of P fixation in soils and the resulting theory was merely an explanation on the basis of precipitation reactions. Beaton, et al. (14) by infra-red absorption analysis, found dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) and hydroxyapatite [$Ca_{10}(OH)_2(PO_4)_2$] to be the soil-fertilizer reaction products in a calcareous soil. With X-ray and petrographic analysis, Lindsay, et al. (93) identified about 30 crystalline P compounds of variable composition as reaction products following the addition of various fertilizer solutions to soils and soil constituents.

Due to the complexity of the soil system and the fact that most of the inorganic P compounds occur characteristically in the clay fraction and are difficult, if not impossible to separate by physical methods, the applicability of the direct means has been very limited. Furthermore, the great preponderance of nonphosphatic material serves to mask any measurable properties of the P compounds found by the various physical methods.

The identification of the native, inorganic P compounds in soils by means of the above mentioned physical techniques has not yet been reported.

(b) Phosphate Equilibria in Soils

Stelly and Pierre (137) compared the solubility versus the pH curves of soils with those of known P-bearing minerals and found that alkaline soils usually display a solubility-pH curve similar to that of apatite and acid soils usually display a solubility-pH curve similar to that of Fe-P and/or Al-P.

By applying the solubility product principles, Aslying (5) plotted the phosphate potential, ($\frac{1}{2}$pCa + pH_2PO_4), against lime potential, (pH - $\frac{1}{2}$pCa) of soils and the solubility of calcium phosphates. He found the presence or formation of octocalcium phosphate in some calcareous soils to which a large amount of superphosphate had been added. From this he concluded that dicalcium or octocalcium phosphates are formed when Ca phosphates are precipitated under condition similar to those existing in soils. But neither is stable--both are converted to a more basic calcium phosphate, presumably, hydroxyapatite, although the rate of formation of hydroxyapatite in soil may be extremely slow.

Withee and Ellis (49) equilibrated two calcareous soils with 0.01 M $CaCl_2$ and found that the P minerals that controlled the level of P in solution were basic calcium phosphates similar in solubility to octocalcium phosphate, or in other words, the equilibriated solutions were supersaturated with respect to hydroxyapatite. Rather large additions of soluble P were necessary to saturate the soils with respect to $CaHPO_4$.

Soil P solubility determinations by Clark and Peech (38) showed that neither $CaHPO_4$ nor hydroxyapatite was present in the soils or clay system studied. The solubility data of Al-P obtained in their experiment indicated the presence of variscite, $AlPO_4 \cdot 2H_2O$ in the soils studied. In a later study, Lindsay, et al. (87) treated acid soils with $Ca(H_2PO_4)_2$, and found that after 18 months of aging the soils yielded extracts that were nearly in equilibrium with variscite, indicating that variscite was the final reaction product and was governing the P concentration in these acid soils. In a more detailed study on Al-P ion products in solution equilibrated with an acid, P-deficient soil, Taylor and Gurney (141) showed that the P status of the undisturbed soil is compatible with the existence of variscite in the soil. When soil is acidified, subsequent changes in composition of the solution reflect the dissolution of $Al(OH)_3$

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and decay of clay minerals. Phosphate additions to the acidified soil are rapidly precipitated, and the final P concentration is less than would be supported by variscite under more acid conditions.

Chakravarti and Talibudeen (24) examined P equilibria in 54 acid soils from Britain and India and found that the equilibrium concentration in British soils was governed by P residues less basic than variscite and strengite. In Indian soils, both variscite and strengite are effective in controlling phosphate concentration over the pH range of 3.8-5.7.

Wada (147) found that P equilibria in some ando soils, red-yellow podzolic soils and alluvial soils in Japan were governed by Fe and Al compounds from pH 4 to 7. Below pH 5.2 P activity was apparently controlled by variscite and gibbsite or possibly with strengite and $Fe(OH)_3$. From pH 5.2 to 7.0, these compounds still persisted but alkaline hydrolysis occurred at the surface, resulting in occlusion of the P in Fe and Al oxides. This effect, together with uncertainty in estimation of unhydrolyzed metal cations, makes the use of solubility product principles difficult. Similar studies were conducted by Hernando <u>et al</u>. (61) and Mare (101).

Based upon known solubility data of the various Ca, Al, and Fe phosphate compounds that may form in soils and of other inorganic phases of the soil that furnish ions participating in soil P reactions, Lindsay and Moreno (92) presented the activity isotherms for $AlPO_4 \cdot 2H_2O$ (variscite), $FePO_4 \cdot 2H_2O$ (strengite), $Ca_{10}(PO_4)_6F_2$ (fluorapatite), $Ca_{10}(PO_4)_6(OH)_2$ (hydroxypaptite), $Ca_4H(PO_4)_3 \cdot 3H_2O$ (octocalcium phosphate), and $CaHPO_4 \cdot 2H_2O$ (dicalcium phosphate dihydrate) on a single solubility diagram in which a function of P activity in solution was plotted against pH. This generalized plot is considered to be useful for assessing relative stabilities of these P compounds and for predicting their transformations in soils upon the application of fertilizer or lime.

In a sequence of studies on the nature of the reactions of $Ca(H_2PO_4)_2 \cdot H_2O$ in soils, Lindsay, et al. (88,89, 90,91) also found the formation of complex P compounds similar to those reported by Haseman (57,58). But they pointed out that these complex phosphates are unstable in soil suspension where the equilibrium activities of component ions are much lower than those in equilibrium with the complex phosphates. They also stated that in arable soils, especially when leached in the presence of growing plants, the complex phosphates very soon revert to phosphates whose equilibrium ion activities are of the same order as those for the variscite-strengite group.

Wild (148) on the basis of solubility product principle, calculated the P concentrations to be expected in the presence of variscite and various calcium phosphates at different pH values and compared his results with the P concentrations in several soil extracts as by other workers. In the pH range 4.5 to 6.0 none of the phosphates considered could explain the level of P found in solution.

Solubility product concept has been widely used by many workers in recent years in an attempt to identify the inorganic P compounds in soils. But, due to the complex nature of the soil and the limitations of the solubility product principle itself in describing precipitation and dissolution phenomena, the results obtained by many workers may show the possibility of the existence of certain phosphate compounds in soils, but do not show explicately which form of the phosphates will control the concentration in the soil solution-solid system.

Taylor and Gurney (141) pointed out that there are several reactions that may reduce the P concentration to the desired level in the soil solution; therefore, the finding of Al-P ion products similar to the solubility product of variscite is not a satisfactory criterion for the existence of the mineral in soils.

Larsen and Court (83) examined the solubility data of a great number of British soils with or without P applications with respect to the solubilities of calcium phosphates assumed to form in soils. A scattered distribution of the points on the solubility diagram was obtained. Although some of the points fall near the lines for a pure compounds, the over-all distribution suggested that either no definite forms of calcium phosphates can be inferred to exist in soils or that the apparent solubility relationships are being influenced by other factors.

Measurements of the chemical potential of P in soil suspensions and difficulties arising in applying solubility criteria for determining the nature of P compounds in soils have been investigated by many workers (15,47,82,83,84,85, 117,152,153). However, the application of these criteria to experimental determinations of soil P solubility has not been very successful. The results for some soils obey the relationships for pure compounds while others do not, and the proposition that these can be attributed to substances of intermediate composition is not wholly satisfactory (83).

(c) Chemical Extractions

Chang and Jackson (25) developed a soil P fractionation procedure by using different extraction solutions which enables fractionation of the soil inorganic P into discrete chemical forms, namely Al-P, Fe-P and Ca-P. The method has greatly stimulated interest in study fixation, transformation, and availability of the inorganic P in soils. By using this procedure, they fractionated a number of soils and concluded that the distribution of soil inorganic P was a measurement of the degree of chemical weathering, the weathering sequence being Ca-P, Al-P, Fe-P and occluded P (27).

Chu and Chang (36) analyzed a great number of acid and calcareous soils of Taiwan and found that there are three different phosphate distribution patterns in these soils, namely, Fe-P dominating, Ca-P dominating, and Fe-P and Ca-P dominating. Al-P was not found to be a dominating form in any of the paddy soils studied. In fractionating P from soils representing different stages of maturity in India, Geol and Agarwal (52) found that total P and organic P decreased with soil maturity. Inorganic P tends to be bound to Fe and Al in mature soils which are responsive to P fertilizers, and in the form of Ca-P in immature soils which do not respond to P application. Kaila (74) fractionated 363 mineral soil samples from Finland and showed that sandy soils were richer in NH_4F-soluble P (Al-P) and poorer in acid soluble P (Ca-P) than the other soils were, but alkali-soluble P (Fe-P) was independent in soil texture. The predominance of acid-soluble P in the organic fraction, together with low amounts of reductant soluble P, pointed to a low degree of weathering of the soils studied. The high contents of the NH_4F and alkali-soluble P in the surface sample of cultivated soils as compared with samples from virgin soils or subsoils may be due to application of P fertilizer and a higher degree of weathering. They also pointed out that variations in the NH_4F and alkali-soluble P fractions were

associated with variations in active Fe and Al rather than with a direct effect of soil pH. Serbanescu and Blanaru (130) found that degraded podzols, podzolized brown soils and acid brown mountain soils were low in mobile Al phosphates and brown forest soils were dominated by Ca phosphates.

Sen Gupta and Cornfield (128,129) studied P in calcareous soils and found that the amounts of different inorganic P fractions decreased in the order, "inert P," apatites, non-apatite, Ca phosphates, Al phosphates, Fe phosphates and easily replaceable P. None of the P forms significantly correlated with $CaCO_3$ content in the soils studied.

It is generally known that Al and Fe phosphates are abundant in acid soils and Ca phosphate in alkaline or calcareous soils (36,32,23,41,81,60,109).

Numerous works have been published on the fate of water-soluble P added to soils and transformations of the various forms of inorganic P in soils. Cecconi (22) stated that fixation of P from P solution in contact with non-calcareous soils is mainly due to the Fe and Al present. Yuan *et al*. (155) found that in three acid soils, over 80 percent of the added P was retained by the soils as Al and Fe phosphates. Prolonged alternate wetting and drying reduced the percentage of P in Al-P form, and increased the percentage distribution in Fe-P form. This transformation from Al-P to Fe-P may be due to the lower solubility product of the latter.

In working with a number of acid and calcareous soils from Taiwan, Chang and Chu (30) found that upon addition of soluble P to the soils, fixation was largely as Al-P with less as Fe-P and Ca-P after three days incubation at field capacity. During 100 days incubation under the same condition, the amount of Fe-P increased at the expense of Al-P and Ca-P. Under flooded condition for 100 days, Fe-P became the dominant form of P fixed in all soils studied. Similar results have been reported by Volk and McLean (146), and Kaila (75). Chai and Caldwell (23) reported that the P-fixing capacity of soils increased with departure from a pH near 7.0. Mackenzie and Amer (97) studying acid soils found that the Al-P fraction increased at both high and low rate of P applications, Fe-P increased only at the higher rate of P addition and Ca-P did not increase at either rate. In the alkali soils tested, Ca-P increased at both rates of added P. After removing Fe by a biological-reduction method which did not remove Al, Bromfield (20) found that the P-soprtion of three acid soils was greatly reduced. But when Al was also removed the P-sorption capacity further decreased.

Forms of inorganic P in soils after long-term continued fertilization have been investigated by many workers. Manning and Salomon (99) found that application from 65 years of superphosphate to a brown podzolic soil resulted in a large accumulation of Al-P and less accumulation of Fe-P. Application of rock phosphate increased Ca-P fraction.

Occluded and organic P fractions were not greatly affected by various levels or sources of P fertilizers. In paddy soils, it was shown that the superphosphate applied to a soil over 31 years is mostly retained in the form of Fe-P, with Al-P next, and that least is retained as Ca-P (30). Liming did not significantly change this distribution pattern.

With Loess soils, Schachtschabel and Heinemann (122) found that the Ca-P fraction increased slightly up to pH 6.5, rising sharply as soon as $CaCO_3$ occurred in the soil. Fe-P fraction decreased with increasing pH. Neither Al-P nor occluded P correlated with pH in the soils studied.

In studying a number of acid soils, Wright and Peech (154) pointed out that the results from fractionation would support the conclusion obtained from the solubility studies that some crystalline phosphate minerals of the variscite-strengite isomorphous series was the ultimate reaction product of applied P in acid soils studied.

The fractionation method of Chang and Jackson has been criticized especially with regard to the differentiation between Fe-P and Al-P (46). Also, more soluble Ca phosphates such as $CaHPO_4 \cdot 2H_2O$ or octocalcium phosphate may exist in soils under heavy P fertilization. These P compounds are readily attacked by NH_4F (88,89,90,91,104). It was also pointed out that freshly formed phosphates may have different solubility from aged crystalline compounds (86,155).

Chang (29) summarized all the criticisms and modifications and systematized the sequence of extraction in the most up-to-date form.

The fractionation procedure may not be as precise as desired. But there is no doubt, even with its shortcomings, the use of this method has broadened our knowledge of the P chemistry in soils.

2. Distribution of Inorganic Phosphorus in Soil Profiles and Particle-size Fractions

Winters and Simonson (151) reported that in soil profiles developed on uniform parent materials, the minimum P percentage usually occurs in the lower A or upper B horizon. This apparently results from the combined action of P absorption by plants and leaching. Bauwin and Tyner (13) found the profile distribution of "extractable P" (organic P + acid soluble P + "adsorbed P") in some gray-borwn podzols, brunizems, and planozols to be C horizon < A horizon < B horizon. Conversely, the relative abundance of the nonextractable P was B > A > C. A significant increase in the non-extractable P content of B horizons was found to occur with increasing soil maturity.

By dispersing the soil mechanically in water, Williams and Saunder (150) studied the distribution of organic P and inorganic P in particle-size fractions of some Scottish soils and reported that more than 85 percent of the organic P was predominating in the fine sand fractions and appeared to be largely Ca-bound. Hoyos and Garcia (64,65) found that total P in the soil particle-size fractions increased as particle-size decreased, the largest difference between silt and clay fraction. Organic P was highest in clay fraction. Most forms of P decreased with depth in all fractions. Bates et al. (12) found that in a Nigerian forest soil, inorganic P was fairly constant down the profile. Only the surface soil contained appreciable amounts of P soluble in NH_4F. Considerable amounts of P were extractable from all horizons by 0.1 N NaOH. The clay fraction of the topsoil contained a large amount of P soluble in NaOH. Goel and Agarwal (53) found that total and organic P contents decreased with the maturity of some Indian soils and the highest P concentrations were found in the clay fraction and the lowest in the sand fractions. By using a microscopic technique, Shipp and Matelshi (133) showed that in some Nebraska soil profiles, the content of apatite increased with depth.

The various forms of inorganic P contents in a soil profile were first shown by Chang and Jackson (27) to be a measure of the degree of soil chemical weathering. Their concept is that as weathering increases there is a shift in the relative abundance of the inorganic phosphates from Ca-P toward Al-P, Fe-P and occluded P. Based on this concept, Hawkins and Kunze (59) found that in nine profiles of Grumusols from Texas, the distribution percentages for Ca-P, Al-P and Fe-P served as sensitive indicators of the weathering environment.

Kaila (73) reported that podzolized virgin soils were low in all forms of inorganic P in the upper layers, especially in the A_2-horizon while their enrichment layers contained fairly high amounts of P bound to Fe and Al. The largest part of inorganic P at depth below 30-40 cm. was bound to Ca in all soils studied, except in the cultivated soil in which alkali soluble P bound to Fe predominates at all depths. Recently, the distribution of inorganic P in soil particle-size fractions has also been studied. Scheffer et al. (125) found that in the mechanically separated soil particle-size fractions, the proportion of Ca-P markedly increased with increasing particle-size and reached maximum values in the sand fraction, while a reverse, though less marked, trend in respect of Fe-P and Al-P was observed. Hanley and Murphy (56) analyzed the contents of Al-P, Fe-P, Ca-P, organic P and total P in sand, silt and clay fractions of 24 Irish surface soil samples and suggested that the Al-P and Fe-P in the clay fraction may be an important controlling factor in the relative availability of inorganic P to plants.

3. Aluminum and Iron Phosphates as Sources of Phosphorus for Plants

Having assessed the role of Fe-P and Al-P in soils, it now remains to be seen how satisfactorily these compounds are in supplying P for plant growth.

A general, but thorough review on Al-P and Fe-P in soils has been published by Smith (136).

(a) The solubility of Aluminum and Iron Phosphates

The solubility of Al and Fe phosphates is important to an understanding of the factors that control the availability of P fertilizer in soils. Huffman et al. (69), taking strengite as unity, found that the relative rate of dissolution in water of colloidal $FePO_4$ was 30. It was postulated that the great chemical similarity between strengite and colloidal phosphate was masked by the larger particle size and consequently slower rate of solution of strengite. In a latter paper, Huffman and Taylor (70), reviewing the subject of the behavior of water-soluble P in soils, gave the relative initial rates of solution of phosphates in water in terms of weight of P per unit area per unit time. Strengite was again taken as unity, colloidal $FePO_4$, colloidal $AlPO_4$, and variscite had the values of 1.3-2.4, 3-10, and 10-20 respectively. Fujiwara (50) found that the solubility of the crystalline form of Al-P and Fe-P is far less than that of their amorphous forms.

Solubility products of the various synthetic Al-P and Fe-P have been reported by many workers (26,88,45,39,78, 7, 143). The reported pKsp values are 22.5 for variscite, $AlPO_4 \cdot 2H_2O$ (143) and 35.0 for strengite based on the formula $Fe(OH)_2H_2PO_4$ (26). The value becomes 29.0 if the calculation is based on the correct formula $FePO_4 \cdot 2H_2O$.

(b) Availability of Synthetic Aluminum and Iron Phosphates to Plants

Some green-house experiments have shown that a substantial proportion of the P required by plants can be supplied by pure Fe-P and/or Al-P (139,144). But on the other hand, synthetic Al-P and Fe-P have also been reported to be relatively poor sources of P for plants (42,121). Fujiwara (50) found that synthetic Al-P and Fe-P were equally available to paddy rice, but Al-P was a better source of P than Fe-P for upland crops, such as barley. Comparison of the availabilities of the synthetic Al-P and Fe-P have also been investigated by Bartholomew et al. (10), Marais (100), Sannikova (119), Taylor, et al. (139), Lindsay and DeMent (94), Taylor, et al. (142), and Pirkl et al. (112).

Colloidal $AlPO_4$, and $FePO_4$, Ca-Fe phosphate, and K and NH_4 taranakites, all of which are believed to be formed by the action of acid solutions of fertilizers upon soil, were found to be relatively good sources of P for plants. However, variscite and strengite were almost completely unavailable to plants in acid soils (139,94,112).

Taylor, et al. (142) pointed out that the availability of the applied amorphous Al-P appeared to be controlled by its rate of hydrolysis rather than its equilibrium solubility. In calcareous soils, amorphous $AlPO_4$ and variscite were about as good sources of P for corn as $Ca(H_2PO_4)_2$. The particle size of the Al-P seemed to be the dominant factor in their availability. Huffman, et al. (69) found that the uptake of P by the plant from strengite and colloidal Fe-P was closely parallel to the rate of dissolution of these compounds in water.

(c) Availability of Soil Aluminum and Iron Bound Phosphates to Plants

Fried and Shapiro (48,49) evaluated the availability of native soil phosphorus on two factors: the amount and concentration of P in the soil solution (intensity factor) and the ability to renew the P in soil solution (capacity factor).

Chemical tests have been widely used to measure the "available" soil P. Chang and Juo (32) studied the relationships between available P determined by the various conventional chemical tests and the forms of inorganic P in soils and found Al-P and Fe-P to be the main sources of available P in the lowland, rice soils in Taiwan. Similar studies have been done by Susuki, et al. (138) on some Michigan soils. They found that the available phosphorus was highly correlated with the Al phosphate fraction in soils.

In pot experiments, significant correlations have been found between A-value P and Fe-P in paddy soils (28,33). Payne and Hanna (111) showed that the P content in millet tops was chiefly correlated with the Al-P fraction of the three acid soils studied.

Measurements in the uptake of P by plants from the various forms of inorganic P in soils have been studied. Hanley (55) grew Perennial ryegrass, white-clover and Agrostis tenuis on six soils derived from calcareous and non-calcareous parent material. The inorganic P was separated into six fractions after cropping. The Al-P extracted by NH_4F was preferred by crops, but Fe-P was important in some soils. Calcium phosphate contributed little and reductant-soluble P and occluded P were not available at all.

In similar studies, Melton (103) found that the change in Al-P during cropping was highly correlated with the initial Al-P content of the soils studied. Smith (135) found that on an acid red soil, Al-P was the preferred source of P for wheat. Alban, et al. (2) showed that the uptake of P during cropping period was significantly correlated with the decrease of NH_4F-soluble P in the soil.

In a paddy soil studied by Basak and Bhattacharya (11), it contains 847 #/A of Fe-P and Al-P which represented 47 percent of the total P at planting time in the unmanured soil. It decreased gradually to 424 #/A at post harvest time, and then increased to 521 #/A by the planting time of next season. Scheffer, et al. (126) found that the uptake of total P by plants was high from < 2 μ and 2-6 μ fractions, and decreased with increasing particle size, only to increase again from the sand fraction. The uptake of Fe-P and Al-P was highest from the < 2 μ and 2-6 μ fractions.

(d) Factors Controlling the Availability of Iron and Aluminum Phosphates

Degree of crystallinity and specific surfaces have been considered as important factors controlling the availability of the applied and native P compounds in soils. Although many of these facts have been mentioned in previous sections, a systematic and conclusive picture has not yet been established. Cecconi (22) pointed out that newly formed phosphates are generally amorphous and possess a high exchange capacity--the latter, together with the solubility, progressively decreasing with the loss of amorphous characteristics during aging. Chiang, et al. (33) suggested that under water logged conditions in soils, strengite was first changed to more soluble ferrous phosphate and the P ions were then reprecipitated by active sesquioxide to form amorphous ferric phosphate which is a source of available P for plants.

The effect of microbial activities on P mobilization in soil has been investigated (18,19,42,63,98,131,132). Changes in redox potential and pH in rice paddy soils caused by microbial activities have been observed. There was a marked increase in pH, available P, and Fe and a decrease in E_h as the time of soil kept at flooding conditions increased. Difficultly soluble Al-P and Fe-P became more soluble by being hydrolyzed or reduced (34,35,120). Bromfield (19) found that Fe-PO_4 became more soluble when incubated under water in the presence of air or N_2, while $AlPO_4$ was not dissolved under the same conditions. Ojima and Kawaguchi (107) reported that ferric and basic ferric phosphates dissolved completely in water after saturation with H_2S and subsequent aeration, and Al-P was not affected.

Liming an acid soil generally increases the available P. This may be due to the hydrolysis of Al-P and Fe-P, increase in microbial activities, and reducing the activity of the Al^{3+} in the soil solution as a result of liming (87, 98,115).

Effect of P uptake related to plant species has been studied (106). It was also found that air drying generally increased the easily soluble P content of non-calcareous soils (6). Mack and Barber (95,96) found that soil incubated at $-25^{\circ}C$ for nine months released more P when leached with water than soil incubated at $2.7^{\circ}C$. They suggested that the preconditioning temperature changes either the types of P compounds or the surface area of those present in the soil.

EVALUATION ON THE CHEMICAL AND PHYSICAL FACTORS AFFECTING THE RELATIVE AVAILABILITY OF SYNTHETIC ALUMINUM AND IRON PHOSPHATES

1. Preparation and Characterization of Samples

Pure colloidal $AlPO_4$ and variscite were prepared according to the method described by Deming and Cate (41). Colloidal $AlPO_4$ was prepared by reacting 16 g. of Al pellets in 240 ml of 50 percent H_3PO_4 while heating on a water bath. Crystalline $AlPO_4$ was prepared by digesting the colloidal material in one liter of distilled water at 105°C in an autoclave. The pH of the suspension was adjusted daily to 3.2 (measured at 25°C) by adding 0.02 N H_3PO_4 or distilled water. After 40 days of digestion, the completion of crystallization was observed under a microscope. The crystallized material was then air dried at room temperature. Colloidal $FePO_4$ was synthesized by the same procedure as for the colloidal $AlPO_4$ using iron powder and, 35 percent H_2O_2 was added to complete the oxidation of the system to ferric ion. Crystallization of $FePO_4$ was carried out at the same temperature, pressure and pH conditions and the same digestion period as for $AlPO_4$. The synthetic phosphate materials were characterized by infrared absorption analysis, X-ray diffraction and electron microscopy.

X-ray Diffraction

X-ray diffraction of the compounds was conducted using the powder technique. A thin layer of the sample was deposited on a porous ceramic plate, which was rotated with respect to an X-ray beam produced by copper ratiation. The reflections were recorded with a scanning goniometer, utilizing a Geiger-Muller counter tube in conjugation with a scale-ratio meter with an automatic recorder. A Philips electronic powder diffraction camera was also employed in other studies. The interplaner spacings were calculated using a wave length of 1.5418 Å (Cu K-λaverage). The radiation was nickle filtered.

The colloidal $AlPO_4$ and $FePO_4$ were amorphous to X-ray diffraction. The crystalline Al and Fe phosphates prepared under the same environmental conditions were identified by X-ray powder diffraction to be variscite, $AlPO_4 \cdot 2H_2O$, and strengite, $FePO_4 \cdot 2H_2O$, respectively (Table 1).

Infrared Absorption Analysis

For infrared analysis, samples were examined as fine powders mulled in vaseline between salt windows and recorded on a Beckman IR-7 Spectrometer. The films were mounted at right angles to the infrared beam and scanned from 600 to 4000 cm^{-1}.

Table 1. X-ray powder diffraction data for synthetic Al and Fe phosphates crystals.

Syn. Al phosphate (Variscite, $AlPO_4 \cdot 2H_2O$)		Syn. Fe phosphate (Strengite, $FePO_4 \cdot 2H_2O$)	
d (Å)	I*	d (Å)	I*
5.40	vs	5.43	s
4.85	s	4.96	w
4.31	vs	4.91	m
3.91	s	4.36	vs
3.64	w	3.97	m
3.27	m	3.91	w
3.08	vs	3.64	w
2.93	ms	3.27	w
2.80	ms	3.11	s
2.64	m	3.00	m
2.47	m	2.92	m
		2.54	w
		2.53	m
		2.44	w

*Intensity: vs = very strong, s = strong, ms = medium strong, m = medium, w = weak.

The infrared absorption spectra of the colloidal and crystalline Al phosphates within the frequency range of 600 to 4000 cm^{-1} are given in Figure 1. The crystalline Al phosphate was identified as variscite by comparing its spectra with the reported I.R. spectra for natural variscite (4,40).

According to Corbridge and Lowe (40), the strong absorption between 1000 and 1200 cm^{-1} in the variscite spectra represents the ionic P-O stretching band of neutral orthophosphate. The two strong bands at 1050 and 1075 cm^{-1} in the P-O stretching region are characteristic of variscite. The medium bands at 935 and 1160 cm^{-1} represent other modes of P-O stretching. The broad band near 1600 cm^{-1} is due to OH bending of the hydrated water and the absorption at 3580 cm^{-1} is due to the OH stretching of hydrates. This sharp band at 3580 cm^{-1} indicates that the water of crystallization of variscite is probably loosely held through hydrogen bonding with the oxygen of the phosphate anion in the structure.

After heating the variscite sample at 65°C for 12 hours, the hydrated water bands of variscite at 1600 and 3580 cm^{-1} disappeared and the anhydrous form of the phosphate was obtained (Figure 1-C). The spectra also shows that the P-O stretching band shifted to higher frequencies upon dehydration. The P-O stretching bands occurred at lower frequencies in variscite as compared to its dehydrated form or the colloidal form. This is because of hydrogen bonding of the

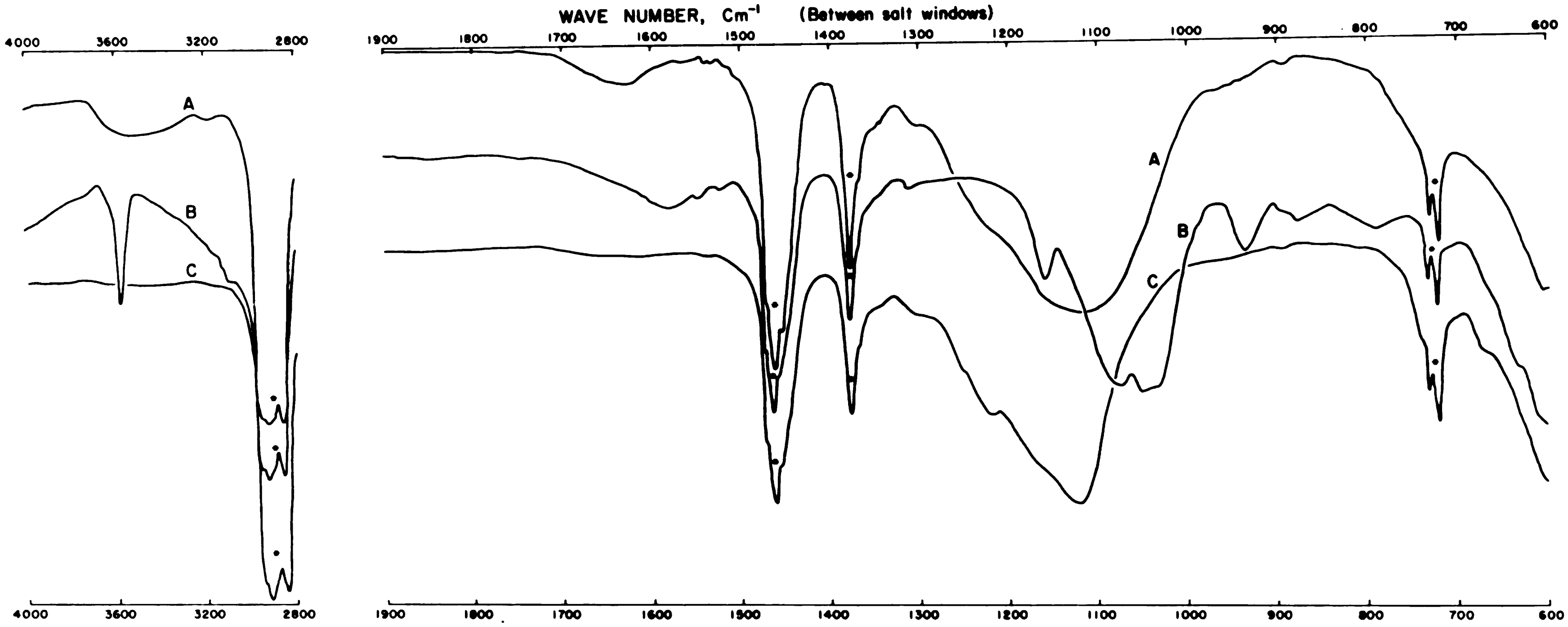

Figure 1. Infrared absorption spectra of synthetic **Al** phosphates: (A) colloidal $AlPO_4$, (B) crystalline **Al** phosphate (variscite, $AlPO_4 \cdot 2H_2O$), (C) crystalline **Al** phosphate heated at 65°C for 12 hours. *Bands due to vaseline.

hydrated water molecules to the oxygen in the phosphate anion (40).

Infrared spectra of the synthetic ferric phosphates are given in Figure 2. The Fe phosphate which was crystallized under the same conditions as variscite gave spectra (Figure 2-b) which shows strong P-O stretching bands between 900 and 1200 cm^{-1}. The water deformation band is near 1600 cm^{-1} and the sharp OH stretching band at 3560 cm^{-1} also indicates the loosely held water of crystallization. The spectra of the crystalline Fe phosphate was similar to that obtained by Corbridge and Lowe (40) for $FePO_4 \cdot 2H_2O$, but differences in the shape of the P-O stretching bands were noted when compared with the spectra reported by Arlidge, et al. (4) for strengite. The P-O bands given in Figure 2-b indicate that neutral orthophosphate ion containing PO_4^{3-} is the only ion present in the crystal.

Heating the crystalline Fe phosphate at 65°C for 12 hours resulted in partial loss of the hydrated water as shown in Figure 2-c. Hydrated water bands at 1600 and 3560 cm^{-1} still persisted after heating but the intensities were considerably less. After further heating at 130°C for 12 hours, the crystalline Fe phosphate was converted to an anhydrous material (Figure 2-d).

The loss of hydrated water from strengite at a higher temperature than from variscite may be because of the larger particle size of strengite, or because the hydrated water was more strongly held in the strengite structure.

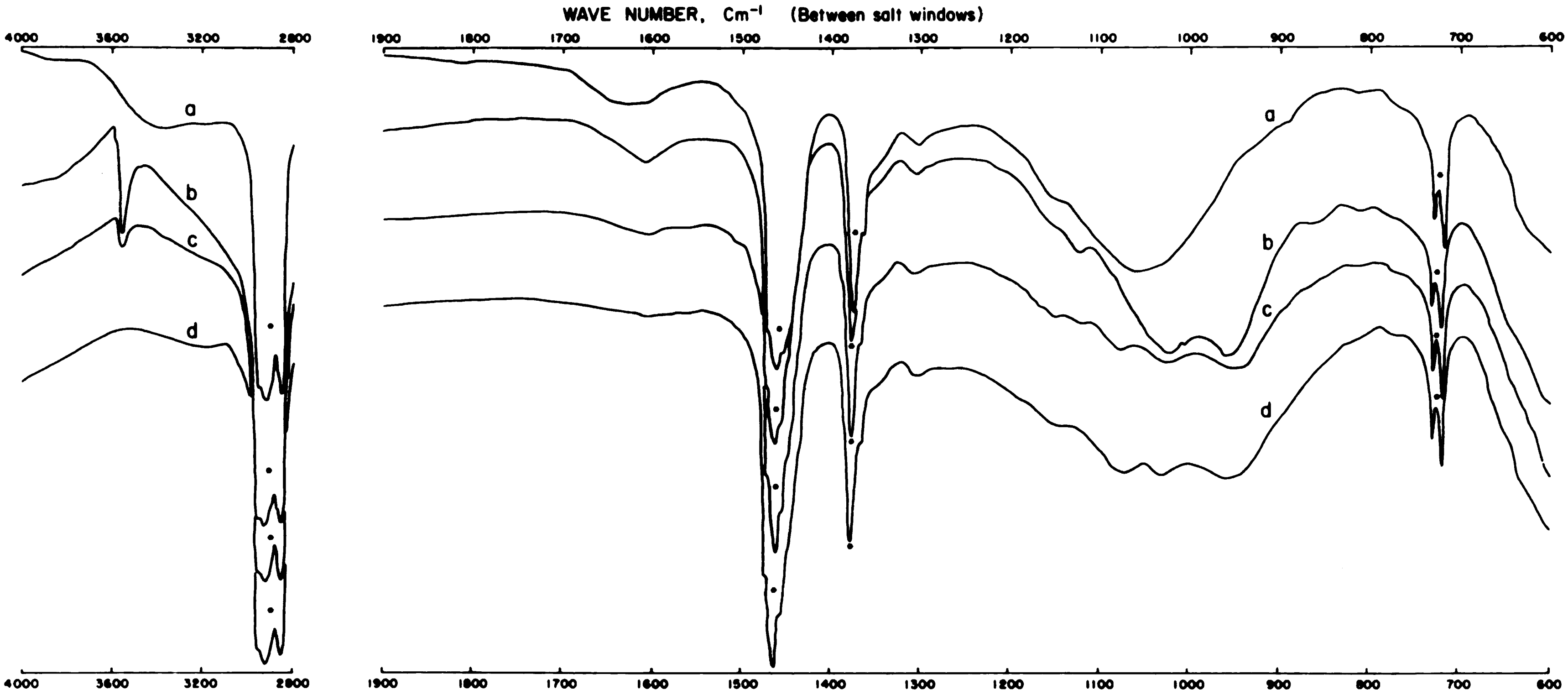

Figure 2. Infrared absorption spectra of synthetic Fe phosphates: (a) colloidal $FePO_4$, (b) crystalline Fe phosphate (strengite, $FePO_4 \cdot 2H_2O$), (c) crystalline Fe phosphate heated at 65°C for 12 hours, (d) crystalline Fe phosphate heated at 130°C for 12 hours. *Bands due to vaseline.

2. Particle Size and Specific Surface

Electron Microscopic Observations

By means of electron microscope, the particle size and the shape of the synthetic colloidal and crystalline phosphates were observed using the parlodion film and the metal vapor shadowing techniques.

Chromium shadowed electron micrographs of colloidal $AlPO_4$ and colloidal $FePO_4$ show that the individual particles of the colloidal $FePO_4$ are smaller than the particles of $AlPO_4$ (Figure 3, Plates 1 and 3); however, both are less than a half micron in average diameter. Since the hydrated water in the variscite and strengite crystals is loosely held in the structure (40), the crystalline surfaces may be damaged during the process of metal vapor casting under high vacuum. Therefore, electron micrographs of the two crystalline materials were taken using the parlodion film technique in which the sample film is prepared under room temperature and atmospheric pressure. Much larger particles were formed after the two colloidal phosphates were crystallized at 105° C in water to form variscite and strengite (Figure 3, Plates 2 and 4). The variscite crystals shown in Figure 3, Plate 2 are reniform aggregates with an average diameter of about 1.5 microns. The strengite crystallized under the same conditions seem to form large, single, spherical crystals

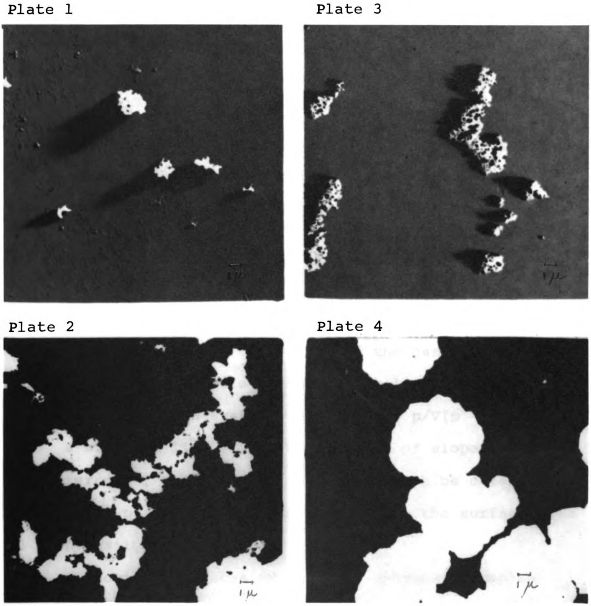

Figure 3. Electron micrographs of synthetic Al and Fe phosphates: Plate 1, newly precipitated colloidal $AlPO_4$, Cr shadowed; Plate 2, colloidal $AlPO_4$ digested at 105°C for 40 days to form variscite, parlodion film; Plate 3, newly precipitated colloidal $FePO_4$, Cr shadowed; Plate 4, colloidal $FePO_4$ digested at 105°C for 40 days to form strengite, parlodion film.

(Figure 3, Plate 4 and Figure 4, Plate 1) with an average diameter of about 6 microns. The high degree of crystallinity and the distinctive crystalline surfaces are also illustrated (Figure 4, Plate 2).

B.E.T. Surface Area

Surface area of the four P materials was measured by N_2-adsorption at $-195^{o}C$ with a Perkin-Elmer-Shell sorptometer. Samples were degassed in a flow of He gas at room temperature for 48 hours before measurements. Surface area of the sample was then calculated according to the B.E.T. equation:

$$\frac{p}{V(p^{o}-p)} = \frac{1}{V_m\ c} + \frac{(c-1)p}{V_m\ c\ p^{o}}$$

Where, p is the equilibrium vapor pressure, p^{o} the saturation vapor pressure, V the volume of the gas adsorbed, V_m the volume adsorbed for a monomolecular layer and c is a constant for a given system. By plotting $p/V(p^{o}-p)$ against p/p^{o}, a straight line should be obtained of slope $(c-1)/V_m c$ and intercept $1/V_m c$. Thus V_m and c can both be determined. If the area per gaseous molecule is known, the surface area is then easily calculated (102).

Specific surfaces of the four phosphate samples measured by the B.E.T. method (Table 2) agree well with electron microscopic observations. The surface area of 27.5 m^2g^{-1} colloidal Fe phosphate decreases sharply to 1.98 m^2g^{-1} after crystallization to strengite. The greater surface

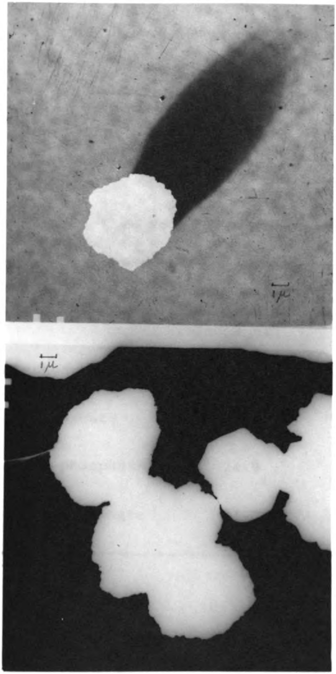

Plate 1

Plate 2

Figure 4. Electron micrographs of synthetic strengite: Plate 1, Cr shadowed strengite; Plate 2, parlodion film supported strengite.

Table 2. B.E.T. surface area of synthetic phosphate compounds.

Material	Surface Area	Notes
	m^2g^{-1}	
Colloidal Al-phosphate	10.5	Freshly precipitated
Colloidal Fe-phosphate	27.5	Freshly precipitated
Crystallized Al-phosphate (variscite)	24.9	Crystallized at 105°C, 40 days
Crystallized Fe-phosphate (strengite)	1.98	Crystallized at 105°C, 40 days

area of the variscite (24.9 m^2g^{-1}) particles as compared to colloidal Al phosphate (10.5 m^2g^{-1}) is apparently due to the irregular aggregated crystalline surfaces of variscite as shown in the electron microscopic observations (Figure 3, Plate 2). These results suggest that specific surface and degree of crystallinity are the important factors that govern the relative availability of Al and Fe-phosphates in acid soils.

3. Rate of Crystallization

To determine the rate crystallization of colloidal $AlPO_4$ and $FePO_4$ in aqueous medium, a set of colloidal $AlPO_4$ water suspensions, each consisting of 5 g. of one material and 500 ml of distilled water, were digested in an autoclave at 105°C. The pH of the suspensions was adjusted to 3.2 daily with 0.02 N H_3PO_4 or distilled water. Samples were removed after 12 hours, 72 hours, and 40 days, and were air dried for X-ray analysis for crystallinity.

Another set of colloidal $AlPO_4$ and colloidal $FePO_4$ water suspensions were crystallized at 35°C in a constant temperature incubator under atmospheric pressure. The pH of the suspensions were also adjusted to 3.2 daily. After 9 months, these samples were air dried for X-ray diffraction analysis and microscopic observations.

As shown in Figure 5, after digesting the colloidal $AlPO_4$ for 72 hours, the material still remained amorphous to

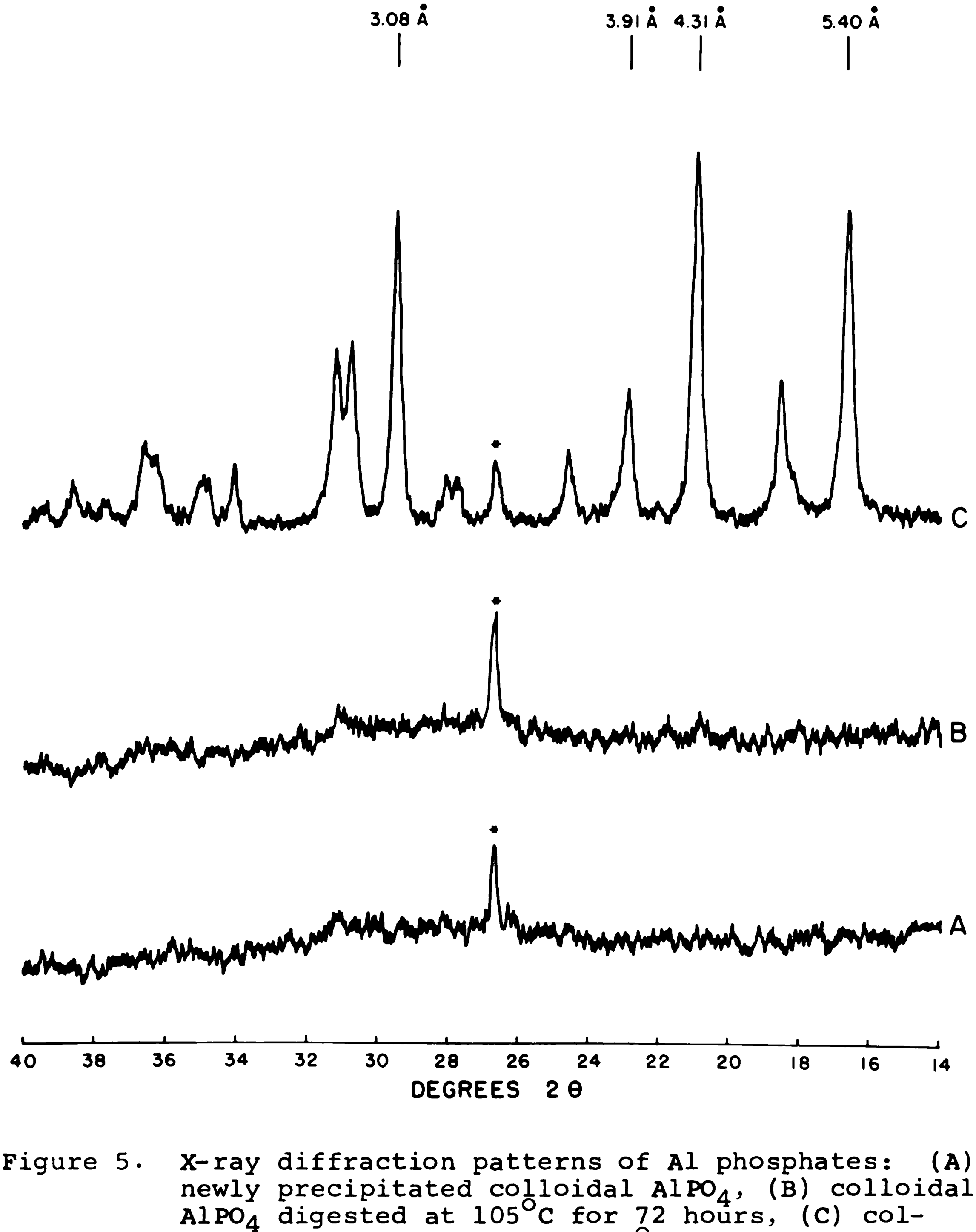

Figure 5. X-ray diffraction patterns of Al phosphates: (A) newly precipitated colloidal $AlPO_4$, (B) colloidal $AlPO_4$ digested at 105°C for 72 hours, (C) colloidal $AlPO_4$ digested at 105°C for 40 days. *Peaks due to quartz in the ceramic plates.

X-ray diffraction. But after 40 days of digestion, an X-ray diffraction pattern for pure variscite, $AlPO_4 \cdot 2H_2O$ was obtained.

By employing the same technique to study the crystallization of colloidal $FePO_4$ under the same temperature and pressure conditions as that for the $AlPO_4$, it was found that the $FePO_4$ crystallized at a much faster rate than the $AlPO_4$. Microscopic observations indicated that the crystallization was almost complete after 12 hours of digestion. X-ray diffraction of the material gave a pattern of pure strengite, $FePO_4 \cdot 2H_2O$ (Figure 6) at that time.

Crystallization of colloidal $FePO_4$ in water at 35^oC was also observed under electron microscope after 9 months of incubation. However, the material was still amorphous to X-ray. $AlPO_4$ remained essentially colloidal throughout the 9 months incubation at 35^oC.

The above results indicate that $FePO_4$ crystallizes at a much faster rate than $AlPO_4$ under the same enrivonmental conditions. This may also be true during P fixation and transformation in soils under natural conditions. In addition to temperature and pressure, the rate of crystallization of Al and Fe phosphates in aqueous media may also be greatly influenced by the pH of the medium and the presence of other ionic species. Further investigations are needed with regard to these points.

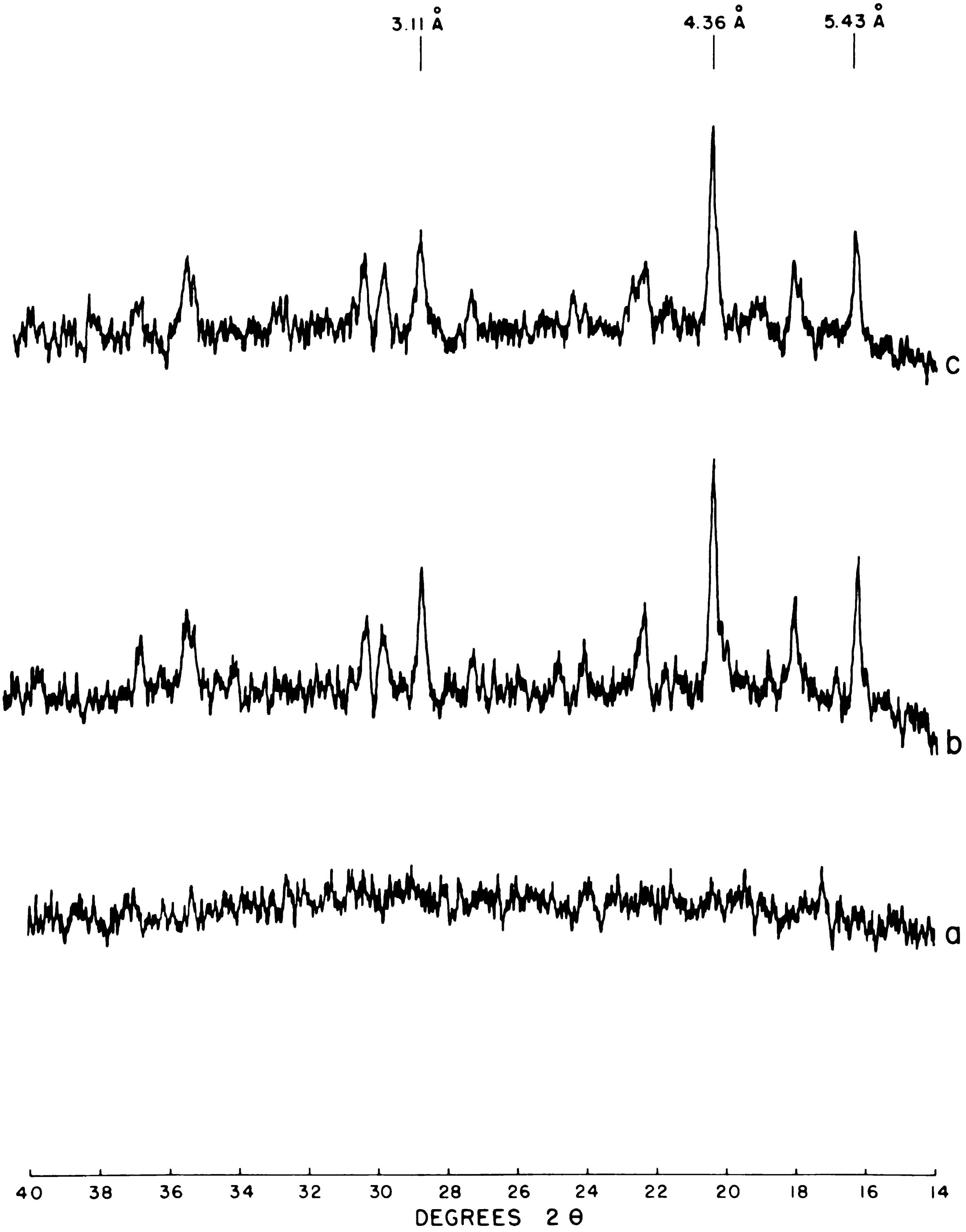

Figure 6. X-ray diffraction patterns of Fe phosphates: (a) newly precipitated colloidal $FePO_4$, (b) colloidal $FePO_4$ digested at 105°C for 12 hours, (c) colloidal $FePO_4$ digested at 105°C for 40 days.

4. Relative Availability

A quartz-sand culture experiment with two replications was conducted in a growth chamber by using Sudan grass seedlings as the indication crop, to compare the relative availability of the colloidal $AlPO_4$, colloidal $FePO_4$, variscite and strengite as sources of P for plant. The latter two minerals were synthesized under the same temperature, pressure and digesting period. The two colloidal phosphates were applied at the levels of 80 and 200 mg P per pot and the two crystalline phosphates were applied at the levels of 80 mg P per pot. A control was included which received no P. The phosphates were mixed thoroughly with 400 g of acid-washed fine quartz-sand, and the mixture was placed in a card-board paper cup. Four Sudan grass seedlings, two-weeks old, were transplanted into each plot. Hoagland solution minus P and/or distilled water were added through a side tube attached inside the cup as required. The moisture content of the quartz-sand was maintained at its field moisture capacity. Growth differences due to treatments were noted during the incubation period of 30 days as shown in Figure 7.

After 30 days, the above-ground portions of plants of each pot were clipped, dried at 65°C, weighed, and ground. The P content was determined by dry ashing in the presence of an alcoholic solution of $Mg(NO_3)_2$ and the P dissolved in dilute HCl solution was then determined colorimetrically (71).

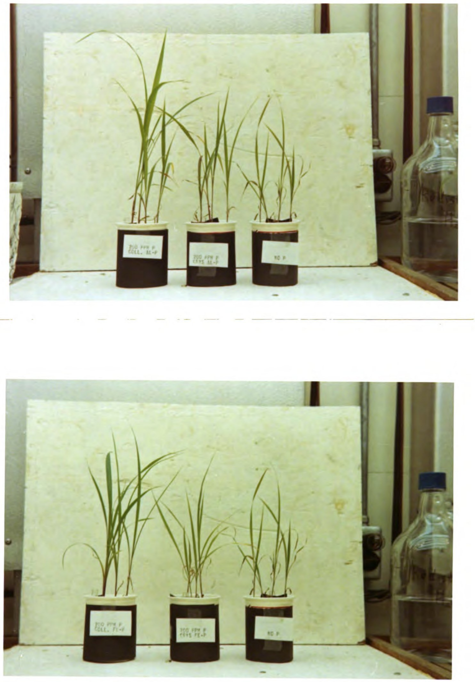

Figure 7. One month old Sudan grass seedlings with P applied as different P minerals.

The yield of tops and the P uptake indicate that colloidal $AlPO_4$ and $FePO_4$ were about equally available and were much better sources of P for the plant than their crystallized forms (Table 3). The P in the crystalline ferric phosphate form (strengite) seemed to be completely unavailable during the 30 days of cropping. The P in the form of crystalline Al phosphate (variscite) seemed to be slightly more available than strengite although both were shown to be very poor sources of P for the Sudan grass seedlings in the slightly acidic sand-cultural medium.

As also indicated in Table 3, higher rates of colloidal $AlPO_4$ and $FePO_4$ (500 ppm P or 200 mg P per pot) increased the P uptake significantly. However, increasing the rate of P applications did not effectively increase yield, probably because of some other limiting factors.

Results obtained in these experiments agree well with those reported previously by Taylor, et al. (139,142) and Lindsay and DeMent (94). In their greenhouse experiments, availability of various Al and Fe phosphates were compared by growing corn on P-deficient acid soils using $Ca(H_2PO_4)_2$ as a standard P source. After three successive crops of corn grown on a acid soil of pH 4.8, the total P uptake from colloidal $AlPO_4$ was considerably higher than that from colloidal $FePO_4$ (139). This may be because of the faster rate of crystallization of $FePO_4$. In other words, during the time required for three successive crops of corn,

Table 3. Yield and P uptake by Sudan grass after 30 days growth.

Source of P	Rate of Application	Yield of Tops	P Uptake in Tops
	mg P/Pot	g Dry wt/Pot	mg P/Pot
No P	0	0.13	0.08
Crystallized Fe-P	80	0.15	0.08
Crystallized Al-P	80	0.23	0.14
Colloidal Fe-P	80	0.47	0.64
Colloidal Fe-P	200	0.55	0.85
Colloidal Al-P	80	0.49	0.60
Colloidal Al-P	200	0.47	1.00
LSD (0.01)		0.12	0.26
LSD (0.05)		0.08	0.17

a considerable portion of the colloidal $FePO_4$ may crystallize under the acidic conditions and concurrently increase in lattice energy and particle-size while specific surface is greatly reduced. Meantime, Al phosphate may still remain highly colloidal during the entire cropping period.

The effect of pH on the availability of Fe and Al phosphates is also critical. The rate of crystallization of colloidal $AlPO_4$ and $FePO_4$ in aqueous media may be greatly influenced by the pH of the media. The fact that on a calcareous soil with pH 8.5 colloidal $AlPO_4$ and variscite as reported by Taylor, et al. (142) to be equally available clearly suggested that a rapid hydrolytic reaction of the Al phosphate compounds at alkaline pH had taken place which readily dissolved the Al-P compounds. Under this circumstance, the hydrolytic reaction greatly overwhelms the properties such as specific surface, particle size and degree of crystallinity which are the important factors that control the relative availability of Al-P and Fe-P under acidic environments.

Soil Al-P fraction determined by Chang and Jackson's procedure (25) has also been reported by many workers (55, 103,135,2) to be a more preferable form of P for upland crops than the Fe-P fraction. The findings seemed to suggest that the Fe-P fraction may exist in higher degree of crystallinity than the Al-P fraction in the acid soils studied. It is the degree of crystallinity, not the specific surface or particle size that is the factor most responsible for controlling the availability of Al-P and Fe-P in acid soils.

5. Conclusion

Based on the results obtained in this investigation and those reported by other investigators, chemical and physical factors controlling the relative availability of Al-P and Fe-P during P fixation and transformation in acid upland soils are summarized and presented diagrammatically in Figure 8.

When applying soluble P to acid upland soils, or, when soil Ca-P is dissolved during the process of chemical weathering, the soluble P is believed to precipitate rapidly to form colloidal $AlPO_4$ and $FePO_4$. Because of their smaller particle sizes, greater surface area and amorphous structure, the colloidal form of $AlPO_4$ and $FePO_4$ are readily available to plants. But these colloidal phosphates tend to crystallize readily to form hydrated compounds such as variscite and strengite which are much less available for plant growth. Thereby, as shown in the diagram, during the first stage of P fixation, the rate of crystallization is the factor controlling the relative availability of these two forms of phosphates in acid soils.

As time goes on, crystallization takes place under favorable environmental conditions. Since $FePO_4$ crystallizes at a much faster rate than $AlPO_4$, at the second stage the degree of crystallinity, or in other words, the relative proportion of the colloidal form to the crystalline form is the factor controlling the availability of Al-P and Fe-P in acid soils. Most of the arable, acid soils in the upland cropping region should fall into this category. In acid upland soils, under natural conditions, the crystallization of $AlPO_4$ may take many years while that of $FePO_4$ may only require a few years. These assumptions may be employed to explain the findings reported by many workers that in acid upland soils, the native Al-P fraction seemed always to be more available to plants than the Fe-P fraction.

In the final stage, when both forms of phosphates have completely crystallized, specific surface and crystal structure may become more important in controlling the availability of the phosphates, although both are very poor sources of P for plants in acidic, well-aerated soils. In calcareous soils and lowland soils, such as rice paddies, different mechanisms involving hydrolytic reactions and changes in redox potentials in the soil have to be considered.

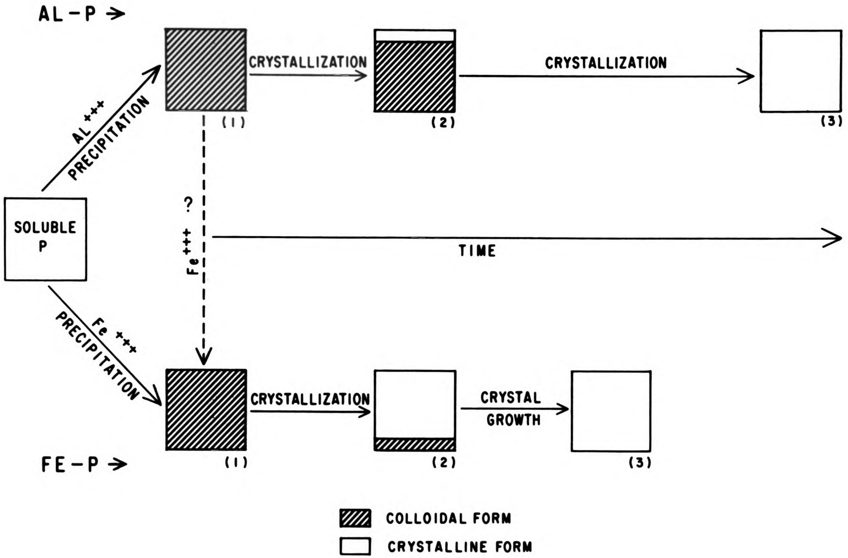

Figure 8. Transformation of soluble P into less available forms.

DISTRIBUTION OF ALUMINUM, IRON AND CALCIUM PHOSPHATES IN SOME MICHIGAN SOIL PROFILES AND THEIR PARTICLE SEPARATES

Rate of crystallization has been shown in the previous part of this investigation to be the most important factor in controlling the relative availability of Al-P and Fe-P with synthetic systems. However, with extended periods of time, as with natural soils, the degree of crystallinity and growth of crystals or crystal size of P minerals in soils may also be important. It is of great importance, therefore, to study the distribution of P minerals within textural size fractions of natural soils.

Four Michigan soils were selected to use in the development of methods that will allow for such a study. These soils were selected to give a range in textural classes and to allow for correlation with P field studies being conducted by other persons.[1]

1. Description of Soil Samples

The four Michigan soil profile samples used for this investigation have been extensively cropped, therefore, the

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[1] Field experiments are being conducted by E. C. Doll, D. R. Christenson, R. P. White and G. R. Rinkenberger.

surface horizons of the soils have been disturbed. Descriptions of the soils are stated as follows:

(1) Pewamo clay loam

a. Characteristics: It is a poorly drained, Humic Gley soil in the Gray Brown Podzolic Region. It developed in calcareous silty clay or clay loam till.

b. Sample location: Shirkey Farm, St. Clair County, Columbus Township, Memphis, Michigan. T5N-R15E NW corner of Section 6.

c. Sampling date: Fall, 1964.

d. Previous P fertilization: Received 300# 12-12-12 (36# P_2O_5/A) in 1962. No P was applied in 1963 and 1964.

(2) Karlin sandy loam

a. Characteristics: The soil is a well-drained Podzol developed in loamy fine sand to fine sandy loam overlying sand. The A2 horizon is absent in this cultivated soil and the Ap rests directly on the B2hir horizon.

b. Sample location: Estelle Farm, Antrim County, Star Township, Michigan. T 30 N--R 5 W, Section 1.

c. Sampling date: Fall, 1964.

d. Previous P fertilization: Received 800# 5-10-20 (80# P_2O_5/A) in 1963, 200# 5-10-20 (20# P_2O_5/A) in 1964.

(3) Onaway loam

a. Characteristics: It is a well drained soil with a Podzol upper sequum and a Gray-Wooded lower sequum. It developed in calcareous loam or silt loam till.

b. Sample location: Misiak Farm, Presque Isle County, Posen Township, Michigan. T 33 N - R 6 E, Section 24.

c. Sampling date: Fall, 1964.

d. Previous P fertilization: Received 200# 0-54-0 (108# P_2O_5) in 1963. No P was applied in 1964.

(4) Sims clay loam

a. Characteristics: It is a poorly drained Humic-Gley soil developed in calcareous clay loam till.

b. Sample location: Ferden Farm, Saginaw County, Chesaning Township, Michigan. T 9 N - R 3 E, Section 33.

c. Sampling date: Fall, 1964.

d. Previous P fertilization: No P has been applied for 9 years.

2. Distribution of Al-P, Fe-P and Ca-P in Soil Profiles

The amounts of Al-P, Fe-P and Ca-P in the soil samples were determined by the procedure of Chang and Jackson (25, 29,31). Total P content in soil was determined by the method of sodium carbonate fusion as stated in Jackson's "Soil Chemical Analysis" (71).

Total P, Al-P, Fe-P and Ca-P contents and pH of the soil profiles are presented in Table 4. The pH of the Pewamo and Karlin profiles are acidic throughout except for the change to neutral in the Cl horizon of the Pewamo profile. The pH of the Onaway profile varies with depth from neutral to slightly alkaline and for the Sims profile, it varies from slightly acidic to slightly alkaline from surface to subsoil.

The higher contents of total P in all surface soils are apparently due to the higher organic P contents in the surface horizons. The occluded form of Al and Fe-P was not determined. The contents of P soluble in neutral NH_4Cl (water soluble P) are negligible in all cases.

As shown in Table 4, Ca-P is the predominating form of inorganic P in the profiles of Pewamo, Onaway and Sims. In the case of Karlin, the three forms of inorganic P are about equally distributed throughout the profile except for the surface 9 inches which is highest in Al-P due to recent P application. In all cases, the contents of Al-P and Fe-P are higher in the surface horizons.

The Ca-P content increases with depth for the two calcareous soils (Onaway and Sims). With Pewamo and Karlin soils, the same trend holds in the lower part of the profile, but the surface 10 inches layer is considerably higher in Ca-P than its underlying horizon.

The percentage distribution of Al-P, Fe-P and Ca-P in the soil profiles was calculated and presented in Table 5

Table 4. Total P and inorganic P fractions of soil profile samples.

Soil No.	Horizon	Depth	pH*	Total P	Inorganic P Fractions				(Al + Fe + Ca) - P	
					Water Soluble	Al-P	Fe-P	Ca-P	Sum	Fraction of Total P
		in.				----------------ppm----------------			ppm	%
Pewamo										
1a	Ap	0-6	5.6	615	Trace	34	65	102	201	33
1b	A12	6-10	6.0	579	0.4	32	63	112	207	36
1c	B12g	10-19	5.7	405	Trace	11	36	94	141	35
1d	B22g	19-27	5.9	359	Trace	8	38	50	96	27
1e	B22g,Cl	27-42	6.9	390	Trace	20	40	150	210	51
Karlin										
2a	Ap	0-9	6.0	313	3.2	104	56	55	215	69
2b	B2hir	9-20	6.2	169	Trace	21	24	14	59	35
2c	Dl	20-29	5.4	86	Trace	20	16	20	56	65
2d	D2	29-37	5.3	129	Trace	20	19	27	66	51
Onaway										
3a	Ap	0-7	6.9	415	1.4	45	37	99	181	44
3b	A2	7-9	7.2	369	3.2	16	19	87	122	33
3c	Bhir	9-16	7.3	602	1.3	20	12	96	128	21
3d	A2	16-17	7.6	295	0.6	11	8	124	143	49
3e	B2t	17-30	7.9	132	Trace	2	0	136	138	100
Sims										
4a	Ap	0-9	6.0	672	Trace	47	55	129	231	34
4b	B21g	9-16	6.3	628	Trace	38	46	139	223	36
4c	B22g	16-27	7.1	436	Trace	9	10	124	143	33
4d	Cg	27-34	7.3	441	Trace	10	11	166	187	42

*1:1 soil/water ratio.

Table 5. Percentage distribution of Al, Fe and Ca-P in soil profiles.*

Soil No.	Horizon	Al-P	Fe-P	Ca-P
		%	%	%
Pewamo				
1a	Ap	16.9	32.3	50.7
1b	A12	15.5	30.4	54.1
1c	B12g	7.8	25.5	66.7
1d	B22g	8.3	39.6	52.1
1e	B22g,C1	9.5	19.1	71.4
Karlin				
2a	Ap	48.4	26.0	25.6
2b	B2hir	35.6	40.7	23.7
2c	D1	35.7	28.6	35.7
2d	D2	30.3	28.8	40.9
Onaway				
3a	Ap	24.9	20.4	54.7
3b	A2	13.1	15.6	71.3
3c	Bhir	15.6	9.4	75.0
3d	A2	7.7	5.6	86.7
3e	B2t	1.4	0	98.6
Sims				
4a	Ap	20.3	23.8	55.8
4b	B21g	17.0	20.6	62.3
4c	B22g	6.3	7.0	86.7
4d	Cg	5.3	5.9	88.8

*Calculated as:

$$\frac{\text{ppm P of Al or Fe or Ca-P in soil}}{\text{Sum of (Al+Fe+Ca)-P in ppm P in soil}} \times 100$$

and Figures 9 and 10. The percentage distributions of Ca-P and Fe-P for the Pewamo soil profile are essentially of mirror images of each other--Fe-P decreases with depth and Ca-P increases with depth. Al-P never exceeds 17 percent of the three fractions and remains relatively constant throughout the B and C horizons. The relative distribution of inorganic P in a soil profile has been shown by Chang and Jackson (27) to be a measure of the degree of soil chemical weathering. Their concept is that as weathering progresses there is a shift in relative abundance of the inorganic phosphates from Ca-P toward Al-P, Fe-P and occluded P. The Ca-P is believed to be of primary origin and exists in the form of apatites. According to this concept, the percentage distributions of inorganic P for the Pewamo soil profile indicates that weathering within the profile has been relatively uniform. The remarkably high percentage of Fe-P and correspondingly low percentage of Ca-P in the B22g horizon (19-27") is apparently due to the strongly reduced condition in this horizon of this poorly drained, Humic-Gley soil which brings Fe as ferrous ion into the solution phase and at the same time results in a more acidic environment that favors the dissolution of Ca-P. Consequently, when the soil is brought to a more oxidized environment, the P in the solution phase precipitates instantaneously as Fe-P with the ferric ion which has been oxidized from the ferrous form. The content of Al-P in the Pewamo soil indicates that under this

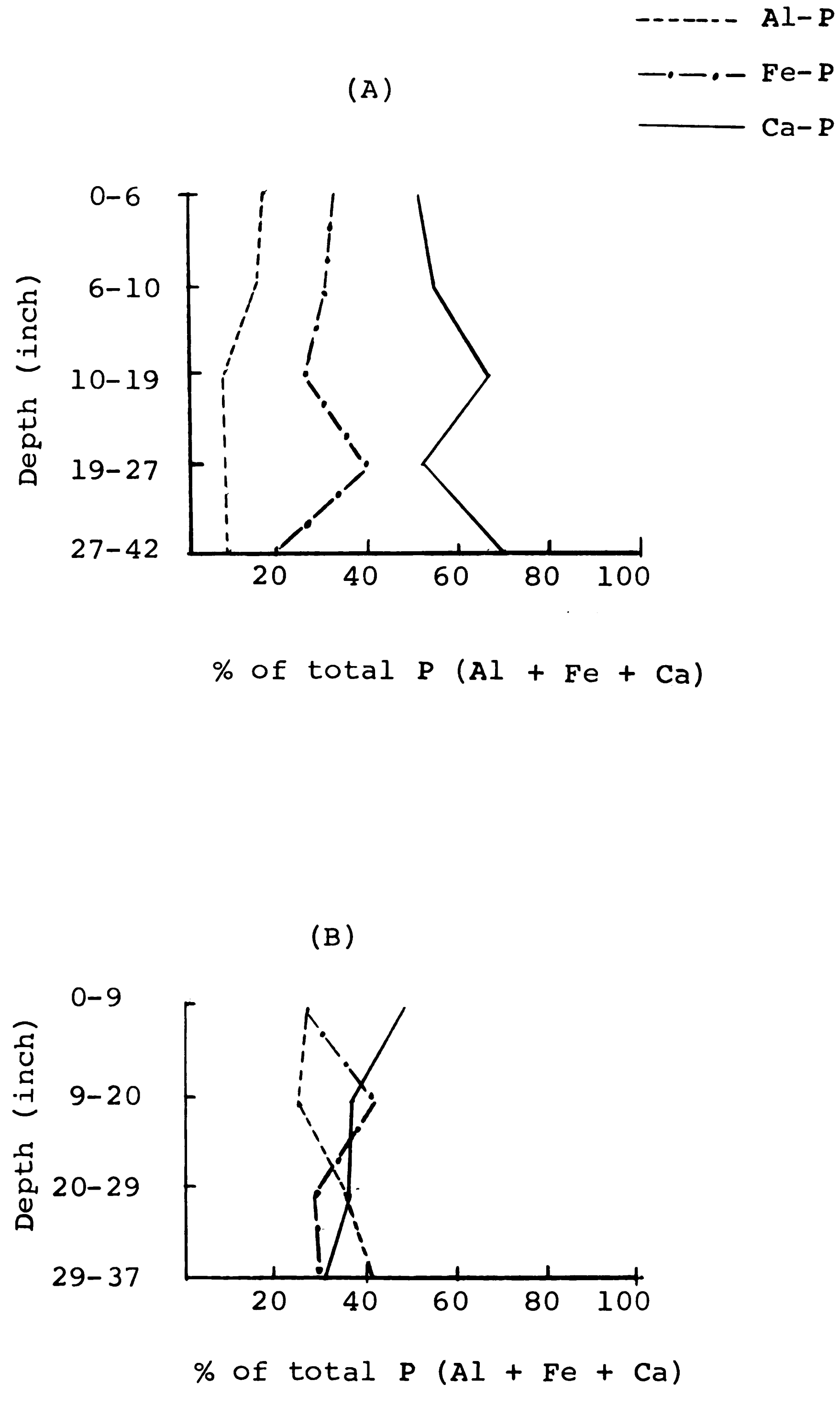

Figure 9. Percentage distribution of Al-P, Fe-P and Ca-P in profiles of (A) Pewamo clay loam, (B) Karlin sandy loam.

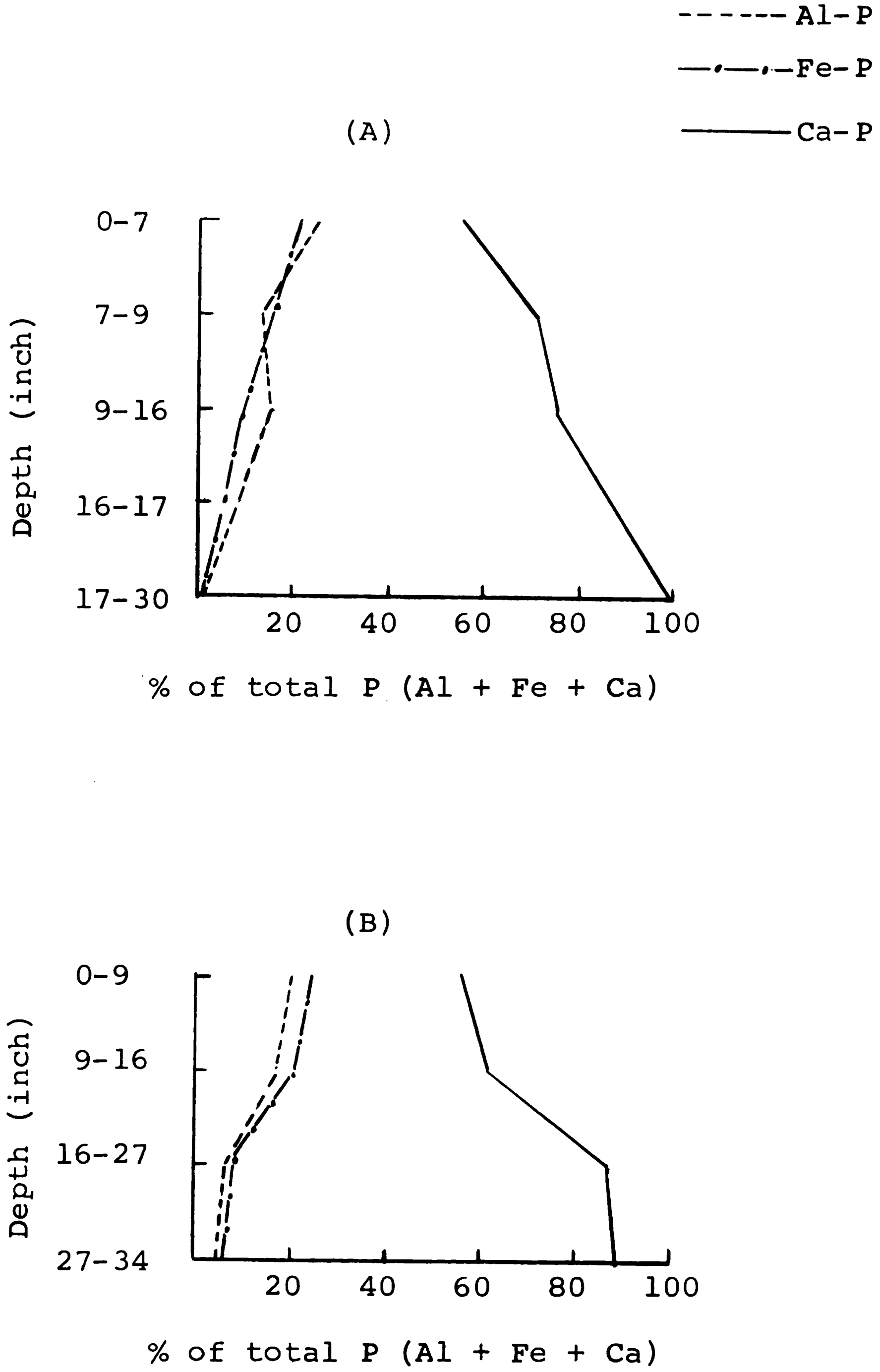

Figure 10. Percentage distribution of Al-P, Fe-P and Ca-P in profiles of (A) Onaway loam, (B) Sims clay loam.

environment, it serves either as a transitional phase for the decreasing Ca-P and increasing Fe-P fractions (27,59) or as an initial phase of P fixation in the surface soil as a result of fertilization (30,97,118).

The distributions of the Ca-P and Fe-P for the Karlin loamy sand soil from 9 to 37 inches of depth show a mirror image relationship similar to that of the Pewamo clay loam profile although Fe-P is the dominant fraction in the 9 to 20 inches layer indicating a relatively greater degree of transformation of inorganic P within this horizon. Al-P remains essentially constant throughout the profile between 9 to 37 inches of depth and the difference between Al-P and Fe-P is less than for the Pewamo soil. But, in the top nine inches, Al-P is a predominating fraction which is easily accounted for by the recent P application to the soil (97,118).

In the calcareous Onaway soil profile, which is comprised of a Podzol upper sequum and a Gray-Wooded lower sequum, the percentage distributions of Ca-P and Fe-P also show a mirror image relationship. The Al-P decreases with depth and the difference between Al-P and Fe-P is also less. However, the percentage of Al-P exceeds that of Fe-P in the surface (0-7 inches) layer which may be attributed mainly to the heavy P fertilization during the previous year. The same relationship observed in the lower sequum of the profile may indicate a lower degree of weathering. Ca-P is the most abundant form among the three forms of P throughout the profile and it increases from 55 to 99 percent from surface to 30 inches of depth. Neither Al-P nor Fe-P exceeds 25 percent. These relationships indicate a much lesser amount of weathering for the Onaway profile as compared with the profiles of Pewamo and Karlin providing the distribution of inorganic P does serve as an indicator of chemical weathering.

The distribution curves of Ca-P and Fe-P for the Sims clay loam profile are also mirror images of each other. Again, Ca-P, the predominating component, increases with depth, while the content of Fe-P never exceeds 24 percent and decreases with depth. However, the Al-P and Ca-P distribution curves also show mirror image relationship between each other; nevertheless, the content of Al-P never exceeds that of Fe-P throughout the profile.

The inorganic P distribution curves of the four soil profiles studied seem to indicate the progressive dissolution of Ca-P, followed by the subsequent precipitation as Al-P and/or Fe-P in soils during the course of weathering. The degree of chemical weathering is generally greater for the acid soils than that for the calcareous soils with regard to the relative abundance of the inorganic P forms. As also shown in the distribution curves, Al-P seems to serve as a transitional phase for the decreasing Ca-P and increasing Fe-P fractions within the profile. The relationship is particularly pronounced in the case of Pewamo soil profile.

3. A Proposed Procedure for the Separation of Soil Particle-size Fractions for Nutrients Analysis

Methods developed by Soil Physicists (16) to disperse soil samples prior to mechanical analysis generally include acid treatment (final pH about 4.0) and neutralization with NaOH to pH about 9.5. It is likely that the acid treatment will dissolve Ca-P, particularly that in the clay fraction, and the dissolved P may reprecipitate as Al-P and/or Fe-P. The alkaline treatment undoubtedly results in the dissolution of Fe-P and Al-P. Therefore, the original distribution of the soil P compounds is greatly disturbed. The use of Na_2CO_3 as a dispersing agent will again hydrolyze Fe-P in soils. Also, the use of sodium hexametaphosphate (Calgon) will not be satisfactory because of the content of P in the compound and the high pH value of the solution. Mechanically shaking the soil in distilled water for an extended period of time also does not seem to be satisfactory, particularly with soils of heavy texture or with high organic matter content.

For the analysis of inorganic P and/or other mineral nutrients contents in soil particle separates, it seems that none of the commonly used dispersion procedures would satisfactorily serve the purpose of obtaining a complete separation of the soil particles without causing drastic disturbance of the original distribution of P and other mineral nutrients in the solid phase of the soil. Therefore, a proposed procedure involving NaCl treatment and sonic vibration was developed during this investigation.

Procedure

Sample pretreatment.--Hand-sieve the air-dried soil sample through a 2 mm sieve. Use a mortar and rubber-tipped pestle to break the aggregate which are larger than 2 mm.

Dispersion of the soil sample.--To 50 g of soil (passed 2 mm sieve) in a 250-ml beaker, add 150 ml of 5 percent NaCl solution. After 20 minutes soaking, disperse the suspension with the supersonic dispersion apparatus (Bronwill Biosonik) for 2-5 minutes. After standing overnight, remove the excess NaCl solution first by decantation or by the suction filtration apparatus (16). After most of the excess NaCl solution has been removed, add an additional 100 ml of distilled water and transfer the suspension into a dialysis bag. Wash the beaker thoroughly in order to transfer all the soil particles by using an additional 100 ml of distilled water. A few drops of sulphanilamide is then added to the suspension to suppress growth of microorganisms. Dialyze the suspension for 5 to 10 days by putting each five bags in a 20-liter container filled with distilled water. The water is changed daily. Transfer the suspension back into a 600-ml beaker. Further disperse 100 mls increments of the soil suspension by the supersonic disperser for 2-5 minutes.

<u>Separation of clay from the silt and sand fractions by siphoning</u> (16).--Transfer the dispersed soil suspension completely into a 1-liter graduate cylinder. Add distilled water to bring up to mark that gives a 5 percent suspension. Allow it to settle under constant temperature. Record the temperature of the suspension and determine from Stokes' equation the time required for a 2 μ particle to fall through a definite height, equal to 80 percent of the depth of the suspension. Insert a siphon tube to the predetermined depth at the proper time, and siphon the suspension into a sample jar, proceeding very slowly to reduce disturbance. Continue the siphoning until the supernatant liquid has been removed to the desired depth. Remove the siphon, add distilled water again to the original level, mix the suspension thoroughly as before, and repeat the sedimentation and siphoning. While the second period sedimentation is in progress, use the filtration apparatus (16) to concentrate the clay that has been collected in the sample jar. When a coherent layer of the clay has formed on the surface of the filter candle, disconnect the vacuum and apply air pressure to the interior of the filter by squeezing the rubber bulb attached to it. Continue the filtration until no free water remains. Collect all the siphonings of the clay fraction in the same jar, and repeat the operation until the yield becomes negligible. The clay is then air dried, ground and stored.

Separation of silt and sand fractions by wet-sieving (16).--Inspect the 300-mesh (47μ) sieve for cleanliness and mechanical condition. Moisten both sides with water and place it in a wide-mouth funnel which is supported by a ring supporter over a 1-liter cylinder. Without shaking or swirling the mixture, pour the suspended portion of the sample into the sieve. Add more water to the residue in the cylinder. Swirl the mixture and allow to settle for 2 minutes. Decant the suspended portion into the sieve as before. Repeat the operation several times until most of the fine material has been transferred. Tilt the cylinder downward over the sieve. Direct a jet of water upward into it, sweeping the soil particles downward into the sieve by the force of the effluent stream. Do not rub the screen at any time. When the transfer has been completed, agitate the residue on the sieve with a jet of water and obtain as complete a separation as possible. Air dry the sand fraction. Dry sieve the sand into further fractions if needed. Remove the water in the silt fraction by vacuum filtration. The silt is then air dried, ground and stored. The air-dried samples of the soil particle-size fractions are then ready for P fractionation and other mineral nutrients analysis.

Notes: (a). In light of the rise of pH during dialysis, complete removal of the excess Na and Cl ions from the Na-saturated soil system by dialysis is not necessary;

however, the concentration of the salt in the solution phase of the system should be low enough to maintain the soil in a well dispersed condition. (b) Excessive dialysis against distilled water will cause Donnan hydrolysis which may produce reflocculation of the system (102). (c) Time of treatment under sonic vibration should be carefully controlled in order to prevent undesired breakdown of soil particles into finer ones. (d) The procedure may not be found satisfactory for soils high in $CaCO_3$ or sesquioxides.

Efficiency of the Procedure

Efficiency of the proposed procedure was compared with that of the common procedure of sodium hexametaphosphate (Calgon) dispersion by using the Hydrometer method for soil mechanical analysis (17). Results are listed in Table 6a. Mechanical analysis of six soil samples showed that the two dispersion procedures were in good agreement and the proposed procedure of dispersion can thus be regarded as comparable to Calgon dispersion.

The change in pH of the NaCl-soil suspension before and after dialysis was also measured and is presented in Table 6b. The final pH values of the four acid soils are near neutral, while for the two alkaline soils, the pH has increased about 0.8 unit after removal of the Cl ions from the system. The results indicate that the change in pH will not be sufficient to cause hydrolysis or dissolution of the

Table 6a. Comparison of the proposed sonic and the calgon methods of dispersion.*

Soil No.	Soil	Particle-size Composition (USDA)					
		Sonic Dispersed			Calgon Dispersed		
		Sand	Silt	Clay	Sand	Silt	Clay
		--------%-------			--------%-------		
1	Pewamo, surface	36.0	31.7	32.2	34.8	31.7	33.5
2	Pewamo, subsoil	30.0	30.3	39.7	30.0	29.1	40.9
3	Karlin, surface	83.2	12.3	4.5	82.0	12.5	5.5
4	Karlin, subsoil	93.2	4.5	2.3	93.2	3.7	3.0
5	Onaway, surface	61.2	30.6	8.2	61.2	29.4	9.4
6	Onaway, subsoil	59.4	25.1	15.6	59.4	23.8	16.8

*Particle-size composition was determined by the Hydrometer Method.

Table 6b. Change in pH of NaCl-soil suspension before and after dialysis against distilled water.

Soil No.	Soil Reaction	
	Before Dialysis	After Dialysis
	------------------pH------------------	
1	5.8	6.8
2	5.4	7.0
3	5.6	6.6
4	4.5	6.6
5	7.1	7.9
6	7.6	8.4

inorganic P. However, excessive dialysis does bring the pH of the acid soil systems to the vicinity of 8.5 and under this circumstance, considerable hydrolysis of Fe-P may occur. Therefore, the pH of the dialyzed soil suspension should be carefully controlled in order to achieve high dispersion with the least disturbance of the original P distribution of the soil.

The proposed procedure of dispersion is considered to be a satisfactory method for the purpose of studying the particle-size distribution of inorganic P as well as other water-insoluble mineral nutrients in the soil on the basis of the following advantages:

(a) It does not cause drastic change in pH of the system.

(b) The homogeneous sonic vibration treatment has less tendency to cause the mechanical breakdown of the original soil particles than might occur when a motor mixer is used.

4. Distribution of Al-P, Fe-P and Ca-P in Soil Particle Separates

Particle-size fractions of the soil samples were separated according to the proposed procedures of dispersion and separation. Particle-size composition of the soil samples based on large-scale separation is given in Table 7. Al-P, Fe-P and Ca-P contents in the soil particle separates were determined according to the method of Chang and

Table 7. Particle-size composition of soil profile samples based on large-scale separation.

Soil No.	Horizon	Depth in.	Particle-size Composition*			Texture
			Sand	Silt	Clay	
			----------%----------			
Pewamo						
1a	Ap	0-6	20.6	42.9	37.1	CL
1b	A12	6-10	20.0	44.6	35.4	CL
1c	B12g	10-19	18.2	41.5	40.3	SiC
1d	B22g	19-27	18.8	40.7	40.5	SiC
1e	B22g,C1	27-42	18.4	41.1	40.5	SiC
Karlin						
2b	B2hir	9-20	78.9	17.0	4.1	LS
2c	D1	20-29	78.6	16.9	4.5	LS
2d	D2	29-37	87.3	4.9	7.9	S
Onaway						
3a	Ap	0-7	39.2	43.2	17.6	L
3b	A2	7-9	38.5	36.5	25.0	L
3c	Bhir	9-16	40.9	32.3	26.8	L
3d	A2	16-17	71.1	21.0	7.9	LS
3e	B2t	17-30	53.0	33.7	13.2	SL
Sims						
4c	B22g	16-27	36.4	30.5	33.1	CL
4d	Cg	27-34	34.9	30.9	32.2	CL

*(1) According to USDA classification of soil particles.

(2) Calculated from the actual weights of the sand and silt fractions obtained in the large-scale separation. The clay content is obtained by subtraction.

(3) % air-dried basis.

Jackson (25) and the results are given in Table 8. Due to the presence of certain organic compounds and/or microbial activity in the Karlin and Sims surface soils, the dialyzing bags disintegrated and these surface soil samples were lost.

For all soil profile samples studied, Al-P and Fe-P seem to be highly concentrated in the clay fraction; whereas, the Ca-P has a tendency to be equally distributed in the silt and clay fractions in the upper horizons and higher in the silt fraction than in the clay in the lower horizons indicating that Ca-P in soil is of primary origin. The sand fraction contains less inorganic P than other separates.

The contents of Al-P, Fe-P and Ca-P in each of the particle separates throughout the soil profile are in the following orders: in the sand fraction, the order is Ca-P $>$ Fe-P $>$ Al-P for Pewamo, Onaway and Sims soil profiles; and Ca-P $\approx$ Fe-P $\approx$ Al-P for the Karlin profile. In the silt fraction, the order is Ca-P $\gg$ Fe-P $>$ Al-P for the Pewamo profile and Sims subsoil; Fe-P $\approx$ Al-P $\approx$ Ca-P for Karlin; and Ca-P $\gg$ Al-P $>$ Fe-P for the Onaway profile. In the clay fraction, the order is Ca-P $>$ Fe-P $\approx$ Al-P for Pewamo, Onaway and Sims profiles. It becomes Fe-P $>$ Al-P $\approx$ Ca-P in the case of Karlin.

The above results indicate differences in the degree of weathering of inorganic P within the soil profiles. The fact that all three forms of inorganic P are more concentrated in the finer fractions of the soil suggests that

Table 8. Al-, Fe- and Ca-P contents in soil particle-size fractions.

		ppm P in particle-size fraction								
		Al-P			Fe-P			Ca-P		
Soil No.	Horizon	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
	Pewamo									
1a	Ap	12	26	51	25	34	80	75	137	156
1b	A12	10	25	45	20	31	59	88	138	191
1c	B12g	6	6	14	16	16	20	64	133	59
1d	B21g	6	9	14	36	23	24	41	71	54
1e	B22g,Cl	10	9	68	21	18	52	60	200	106
	Karlin									
2b	B2hir	14	30	92	8	50	205	13	23	70
2c	Dl	14	39	98	9	41	164	16	39	70
2d	D2	14	56	98	10	79	70	20	83	123
	Onaway									
3a	Ap	9	37	99	8	16	66	58	105	323
3b	A2	8	22	46	7	9	21	40	70	218
3c	Bhir	10	25	56	6	6	19	61	131	232
3d	A2	8	20	60	3	3	18	73	261	334
3e	B2t	5	3	8	2	1	0	52	204	397
	Sims									
4c	B22g	7	7	26	3	6	6	75	251	170
4d	Cg	5	6	36	4	7	12	79	259	169

specific surface and/or particle size are not likely to be the factors controlling the relative availability of the various forms of inorganic P in soils.

To obtain a clearer picture of the distribution of the various forms of inorganic P in the soil, the percentage distribution of Al-P, Fe-P and Ca-P in sand, silt and clay, and the distribution of Al-P, Fe-P and Ca-P within soil separates were calculated.

Percentage Distributions of Al-P, Fe-P and Ca-P in soil Particle Separates

The percentage distribution of Al-P, Fe-P and Ca-P in sand, silt and clay fractions was calculated by:

$$\frac{\text{ppm P of Al-P (or Fe-P or Ca-P) in a certain particle-size fraction}}{\text{ppm P of (Al + Fe + Ca)-P in the same particle-size fraction}} \times 100.$$

The results are listed in Table 9 and Figures 11, 12 and 13.

For the Pewamo clay loam, the percentage distribution curves (Figure 11) of Ca-P and Fe-P show excellent mirror image relationships in the sand and silt fractions. The Al-P remains fairly constant throughout the profile in the sand faction, but it decreases somewhat with depth in the silt fraction. Ca-P predominates in this soil and the Al-P is the least abundant form. The difference between the Fe-P and Al-P in the sand fraction is greater than that in the silt fraction indicating the particle-size

Table 9. Percentage distribution of inorganic P in sand, silt and clay fractions.*

Soil No.	Horizon	Sand Fraction			Silt Fraction			Clay Fraction		
		Al-P	Fe-P	Ca-P	Al-P	Fe-P	Ca-P	Al-P	Fe-P	Ca-P
		%	%	%	%	%	%	%	%	%
Pewamo										
1a	Ap	10.7	22.3	67.0	13.2	17.3	69.5	17.8	27.9	54.3
1b	A12	8.5	16.9	74.6	12.9	16.0	71.1	15.3	20.0	64.7
1c	B12g	7.0	18.6	74.4	3.9	10.3	85.8	15.1	21.5	63.4
1d	B22g	7.1	41.9	50.0	8.7	22.3	68.9	15.2	26.1	58.7
1e	B22g,Cl	11.0	23.1	65.9	4.0	7.9	88.1	30.1	23.1	46.9
Karlin										
2b	B2hir	40.0	22.9	37.1	29.1	48.5	22.3	25.1	55.8	19.1
2c	D1	36.0	23.0	41.0	32.8	34.5	32.3	29.5	49.4	21.1
2d	D2	31.8	22.7	45.5	25.7	36.2	38.1	33.7	24.1	42.2
Onaway										
3a	Ap	12.0	10.7	77.3	23.8	10.1	66.5	20.3	13.5	66.2
3b	A2	14.5	12.7	72.7	21.8	8.9	69.3	16.1	7.4	76.5
3c	Bhir	13.0	7.8	79.2	15.4	3.7	80.9	18.2	6.2	75.6
3d	A2	9.5	3.6	86.9	7.0	1.1	91.9	14.6	4.4	81.0
3e	B2t	8.5	3.4	88.1	1.4	0.5	98.1	2.0	0	98.0
Sims										
4c	B22g	8.2	3.5	88.3	2.7	2.3	95.0	12.9	3.0	84.1
4d	Cg	5.7	4.5	89.8	2.2	2.6	95.2	16.6	5.5	77.9

*Obtained by:

$$\frac{(\text{one of the three inorganic P in a certain particle-size fraction in ppm P})}{(\text{Sum of Al-, Fe- and Ca-P in the same particle-size fraction in ppm P})} \times 100$$

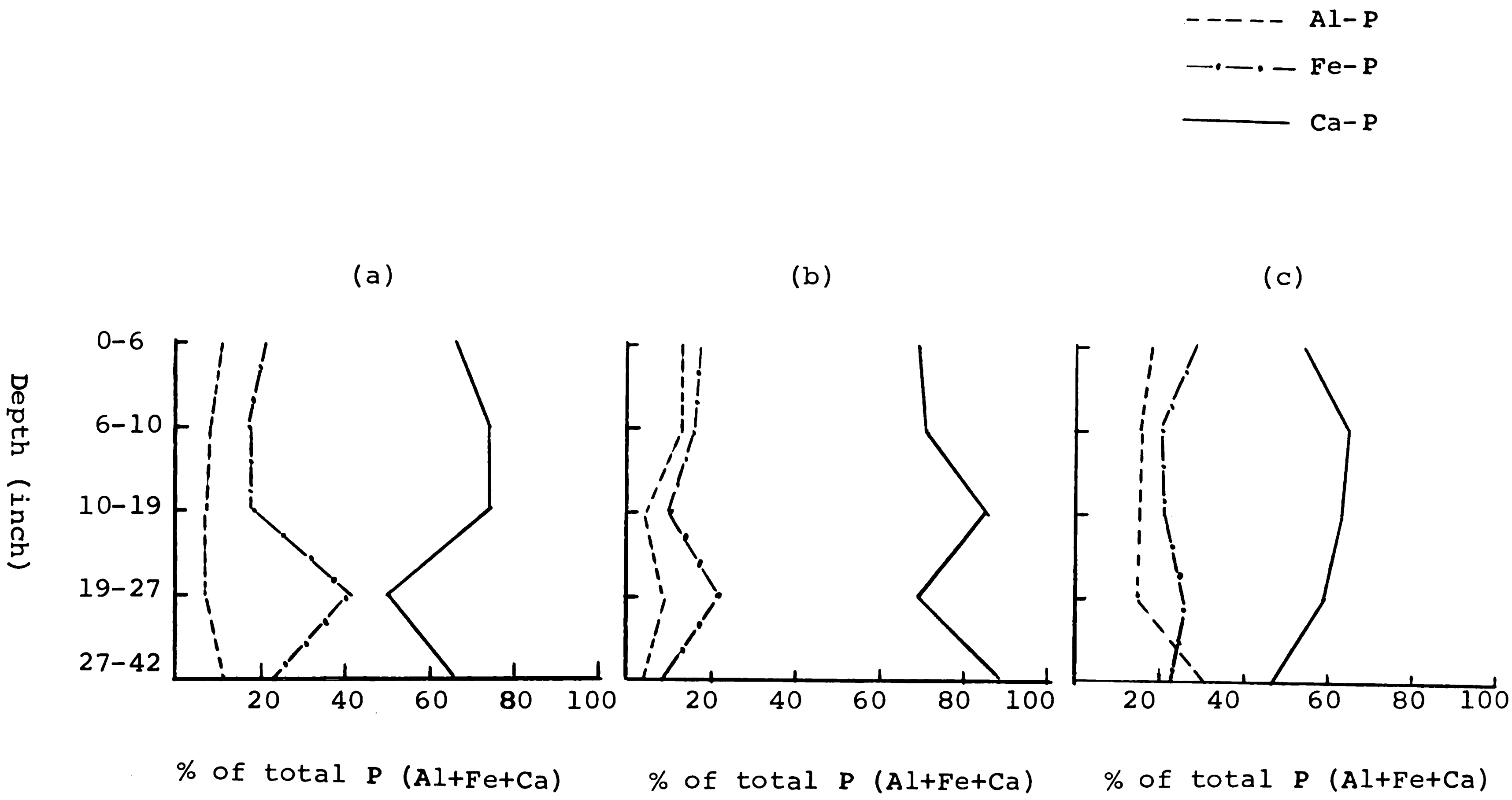

Figure 11. Percentage distribution of Al-P, Fe-P and Ca-P in particle separates of Pewamo profile: (a) sand fraction, (b) silt fraction and (c) clay fraction.

relationship between the two phosphate compounds. In the clay fraction of the Pewamo soil, the distribution curves of Ca-P and Fe-P show mirror image relationships from the surface to 27 inches of depth but the difference between the two curves is relatively smaller than those for the sand and silt fractions. The Al-P remains constant and is the least abundant form of P from 0 to 27 inches of depth. However, in the layer of 27 to 42 inches, Al-P exceeds Fe-P and becomes the second most abundant form of P in the clay fraction. This change of status may indicate that the chemical weathering and transformation of the inorganic P remains in a more transitional stage in the clay fraction than in the surface horizons of the Pewamo soil.

In the case of Karlin loamy sand (Figure 12), Fe-P is the least abundant form in the sand fraction, and remains constant in the three horizons, while Al-P decreases with depth and Ca-P increases with depth. Ca-P predominates in the lower horizons. The differences in the three P distribution curves in the sand fraction is probably not significant since the contents of Al-P, Fe-P and Ca-P (Table 8) are so low that experimental errors and the sensitivity of the analytical procedure may influence the shape of the curves. In the silt fraction, the relative abundance of the three forms of P is Fe-P $>$ Al-P $>$ Ca-P in the B2hir horizon (9-20 inches), Fe-P $\approx$ Al-P $\approx$ Ca-P in the D1 horizon (20-29 inches), and Ca-P $\approx$ Fe-P $>$ Al-P in the D2 horizon (29-34 inches). In

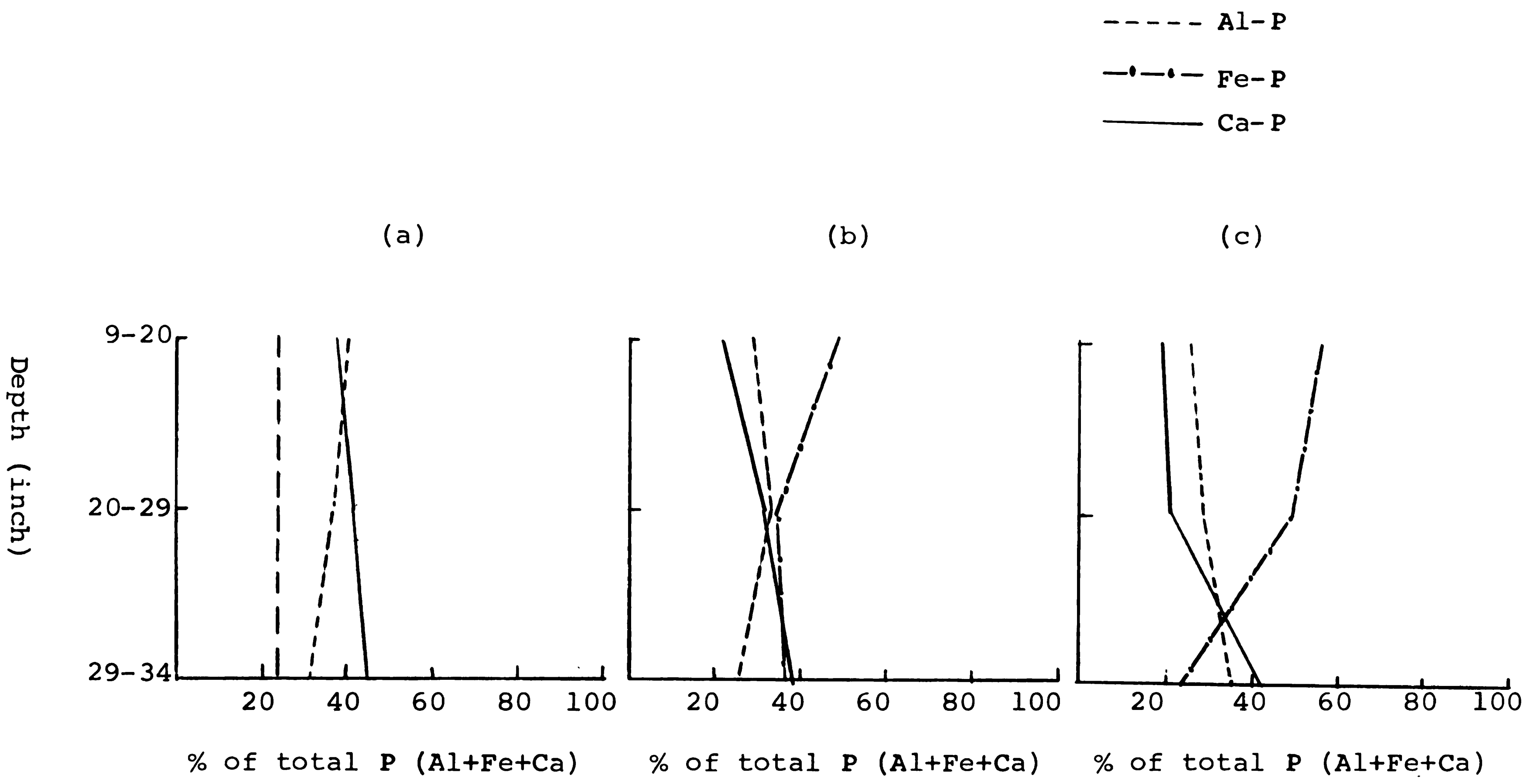

Figure 12. Percentage distribution of Al-P, Fe-P and Ca-P in particle separates of Karlin profile: (a) sand fraction, (b) silt fraction and (c) clay fraction.

the clay fraction, a good mirror image relationship is seen between Fe-P and Ca-P distribution curves. It is also shown that Fe-P is the most abundant form of P in the upper horizons and Ca-P becomes predominating in the clay fraction of the lower horizon of this acid, sandy soil. Al-P remains second in abundance throughout the profile from 9 to 34 inches of depth.

In the case of the Onaway loam, the relative abundance of the three forms of P is in the order of Ca-P >> Al-P > Fe-P for sand, silt and clay fractions throughout the profile (Figure 13). In all three soil particle fractions, both Al-P and Fe-P distribution curves are essentially mirror images of the Ca-P curves, although the best relationship is seen between Al-P and Ca-P. The difference between the Al-P and Fe-P curves is greater for the clay and silt fractions than for the sand fraction. All these relationships indicate that within the calcarous Onaway soil profile, the degree of inorganic phosphate weathering and transformation is less than that in the Pewamo and Karlin soil profiles, and that a greater degree of P transformation has occurred in the finer fractions than in the coarse fraction within the surface horizons.

In the lower horizons of Sims clay loam, Ca-P is the dominating form of P in all three soil particle fractions. The differences between Al-P and Fe-P contents are very

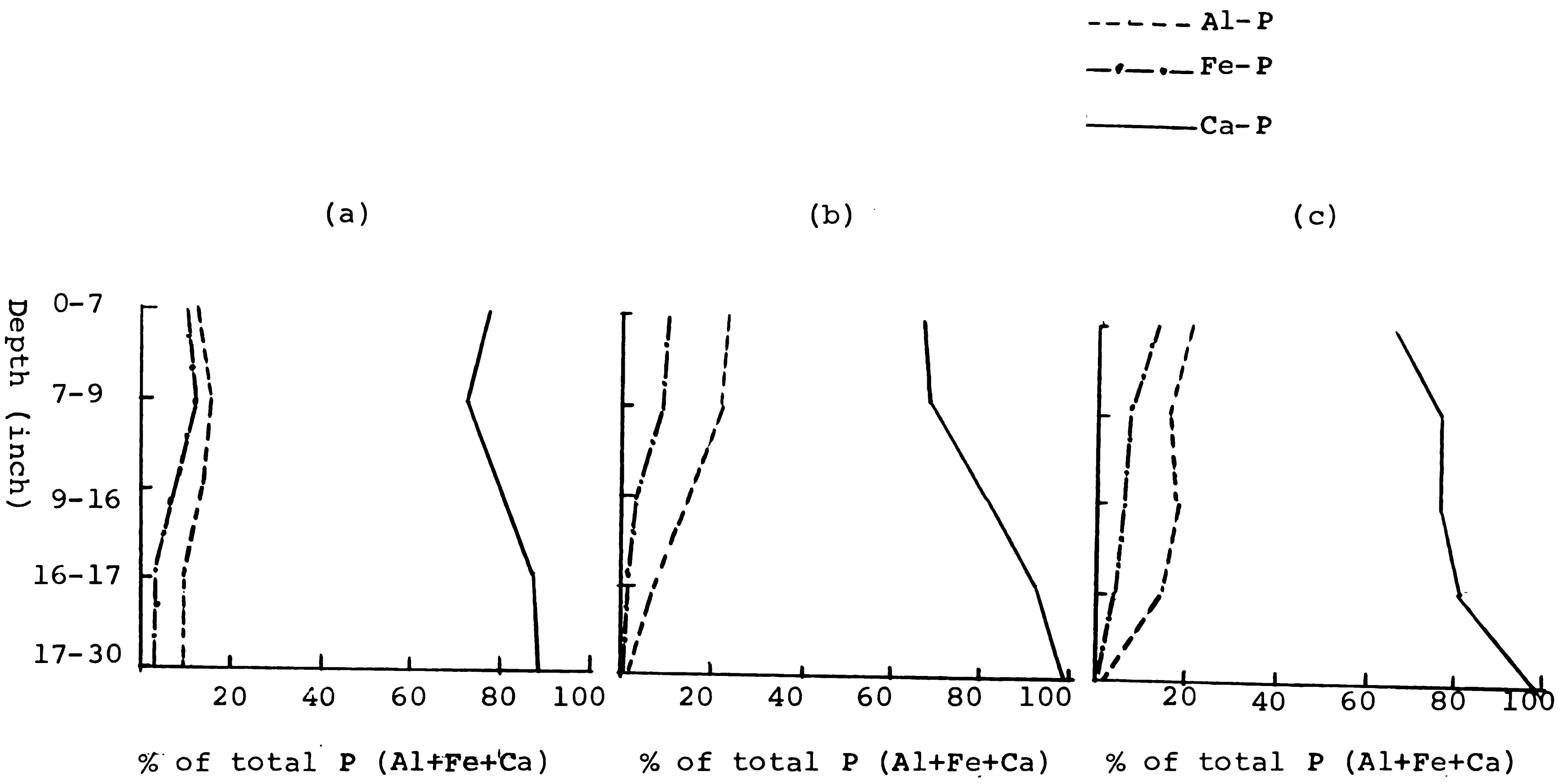

Figure 13. Percentage distribution of Al-P, Fe-P and Ca-P in particle separates of Onaway profile: (a) sand fraction, (b) silt fraction and (c) clay fraction.

small in the sand and silt fractions while the Al-P content is greater than that of Fe-P in the clay fraction.

The percentage distribution curves of Al-P, Fe-P and Ca-P in the soil particle separates are essentially the differentiated forms of the curves obtained from the whole soil and generally in good agreement with each other in revealing the relationships of inorganic P weathering.

Particle-size Distribution of Al-P, Fe-P and Ca-P in soils

In order to evaluate the inorganic P content in each of the particle separates together with the soil textural composition, the mg of P per 1,000 g of soil was calculated by the following formula:

$$\text{mg P per 1,000 g soil} = x \cdot y \,/\, 100$$

where, x is the content of P in ppm in a particle-size fraction, and y is the percent content of a particle-size fraction of the soil. This value is essentially the same as the "F-value" introduced by Williams and Saunders (150). The percentage particle-size composition obtained from the large-scale separation (Table 7) was used for the calculation.

The relative distribution of each form of P within the particle separates was calculated as follows:

$$\frac{\text{mg M-P in a given particle-size fraction}}{\text{Total of mg of M-P in all particle-size fractions}} \times 100$$

where, M-P is Al-P, or Fe-P, or Ca-P.

The particle-size distribution of Al-P in soils is given in Table 10. In the Pewamo profile, which has a texture of clay loam in the surface 10 inches and of silt clay loam in the lower horizons, more than 50 percent of the Al-P is present in the clay fraction of the soil throughout the profile, and less than 12 percent of the Al-P is in the sand fraction. The distribution of Al-P in sand, silt and clay fractions of the soil remains fairly constant with depth from surface to 27 inches. But, in the 27 to 42 inches layer, more than 80 percent of the Al-P is present in the clay fraction.

The Karlin soil, a loamy sand topsoil changing to sand in the D2 horizon, has more than 50 percent of the Al-P in the sand fraction, with the remainder equally distributed in the silt and clay fractions in the B2 and D1 horizons.

In the calcareous Onaway profile with a loamy textured top soil and a sandy textured subsoil, the distribution of Al-P is highest in clay, medium in silt and lowest in sand in upper Podzol sequum (0-16 inches). In the lower sequum (a Gray-Wooded profile), Al-P becomes equally distributed in all particle-size fractions.

In the lower portion of the Sims profile, a clay loam, more than 65 percent of the Al-P is distributed in the clay fraction.

The particle-size distribution of Fe-P is given in Table 11. In the Pewamo profile, the Fe-P is the highest in

Table 18. [illegible] of all P in soils

Table 10. Particle-size distribution of **Al-P** in soils.

Soil No.	Horizon	Sand	Silt	Clay	Sum	% Distribution* Sand	% Distribution* Silt	% Distribution* Clay
		----mg	P / 1000	g soil----		----------	%	----------
Pewamo								
1a	Ap	2.5	11.2	18.9	32.6	7.7	34.3	58.0
1b	A12	2.0	11.5	15.9	29.4	6.8	39.1	54.1
1c	B12g	1.1	2.5	5.6	9.2	11.9	27.2	60.9
1d	B22g	1.1	3.7	5.7	10.5	10.5	35.2	54.3
1e	B22g,C1	1.8	3.7	27.5	33.0	5.5	11.2	83.3
Karlin								
2b	B2hir	11.0	5.1	3.8	19.9	55.3	25.6	19.1
2c	D1	11.0	6.6	4.4	22.0	50.0	30.0	20.0
2d	D2	12.2	2.7	7.7	22.6	54.0	11.9	34.1
Onaway								
3a	Ap	3.5	16.0	17.4	35.9	9.8	44.6	48.5
3b	A2	3.1	8.0	11.5	22.6	13.7	35.4	50.9
3c	Bhir	4.1	8.1	15.0	27.2	15.1	29.8	55.1
3d	A2	5.7	4.2	4.7	14.6	39.0	28.8	32.2
3e	B2t	2.6	1.0	1.1	4.7	55.3	21.3	23.4
Sims								
4c	B22g	2.5	2.1	8.6	13.2	18.9	15.9	65.2
4d	Cg	1.7	1.9	11.6	15.2	11.2	12.5	76.3

*% of total **Al-P** in soil.

Table 11.

Table 11. Particle-size distribution of **Fe-P** in soils.

Soil No.	Horizon	Sand	Silt	Clay	Sum	% Distribution* Sand	Silt	Clay
		----mg **P** / 1000 g soil----				--------%--------		
Pewamo								
1a	Ap	5.2	14.6	29.7	49.5	10.6	29.5	60.0
1b	A12	4.0	13.8	20.9	38.7	10.3	35.7	54.0
1c	B12g	2.9	6.6	8.1	17.6	16.5	37.5	46.0
1d	B22g	6.8	9.4	9.7	25.9	26.3	36.3	37.5
1e	B22g,C1	3.9	7.4	21.1	32.4	12.0	22.8	65.1
Karlin								
2b	B2hir	6.3	8.5	8.4	23.2	27.2	36.6	36.2
2c	D1	7.1	6.9	7.4	21.4	33.2	32.2	34.6
2d	D2	8.7	3.9	5.5	18.1	48.1	21.5	30.4
Onaway								
3a	Ap	3.1	6.9	11.6	21.6	14.4	31.9	53.7
3b	A2	2.7	3.3	5.3	11.3	23.9	29.2	46.9
3c	Bhir	2.5	1.9	5.1	9.5	26.3	20.0	53.7
3d	A2	2.1	0.6	1.4	4.1	51.2	14.6	34.2
3e	B2t	1.0	0.3	0	1.3	76.9	23.1	0
Sims								
4c	B22g	1.1	1.8	2.0	4.9	22.5	36.7	40.8
4d	Cg	1.4	2.2	3.9	7.5	18.7	29.3	52.0

*% of total **Fe-P** in soil.

the clay fraction, intermediate in the silt fraction and lowest in the sand fraction throughout the profile. The distribution pattern changes little with depth. These relationships are similar to that of Al-P for this soil.

In the Karlin profile, the Fe-P is equally distributed in the sand, silt and clay fractions throughout the profile.

Fe-P is highest in the clay fraction in the surface Ap horizon of Onaway soil and lowest in the sand fraction. It remains highest in the clay fraction but becomes equally distributed in the silt and sand fractions in the A2 and B2hir horizons of the Podzol upper sequum of the profile. The content of Fe-P is so low in the lower sequum of the profile that the percent distribution becomes less meaningful.

In the Sims subsoil, the content of Fe-P is also low, however, it appears that the distribution of Fe-P is highest in clay and lowest in sand.

The particle-size distribution of Ca-P in soils is given in Table 12. The sand fraction contains less than 14 percent of the Ca-P throughout the Pewamo profile. The rest of it is equally distributed in the silt and clay fraction in the surface horizons and becomes much higher in the silt than in the clay fraction in the lower horizons.

In the Karlin profile, about 60 percent of the Ca-P is present in the sand fraction throughout the profile.

Table 12. Particle-size distribution

Table 12. Particle-size distribution of Ca-P in soils.

Soil No.	Horizon	Sand	Silt	Clay	Sum	% Distribution* Sand	% Distribution* Silt	% Distribution* Clay
		----mg	P / 1000 g	soil----		--------%--------		
Pewamo								
1a	Ap	15.5	58.8	57.9	132.2	11.7	44.5	43.8
1b	A12	17.6	61.5	67.6	146.7	12.0	41.9	46.1
1c	B12g	11.6	55.2	23.8	90.6	12.8	60.9	26.3
1d	B22g	7.7	28.9	21.9	58.5	13.2	49.4	37.4
1e	B22g,C1	11.0	82.2	42.9	136.1	8.1	60.4	31.5
Karlin								
2b	B2hir	10.3	3.9	2.9	17.1	60.2	22.8	17.0
2c	D1	12.6	6.6	3.2	22.4	56.3	29.5	14.3
2d	D2	17.5	4.1	9.7	31.3	55.9	13.1	31.0
Onaway								
3a	Ap	22.7	45.4	56.8	124.9	18.3	36.4	45.3
3b	A2	15.4	25.6	54.5	95.5	16.1	26.8	57.1
3c	Bhir	24.9	42.3	62.2	129.4	19.2	32.7	48.1
3d	A2	51.9	54.8	26.4	133.1	39.0	41.2	19.8
3e	B2t	27.6	68.7	52.4	148.7	18.6	46.2	35.2
Sims								
4c	B22g	27.3	76.6	56.3	160.2	17.0	47.8	35.1
4d	Cg	27.6	80.0	54.4	162.0	17.0	49.4	33.6

*% of total Ca-P in soil.

There is more Ca-P in the silt than in the clay in the B2hir and D1 horizons and the reverse is true for the D2 horizon.

In the Onaway profile, the distribution of Ca-P is similar to that in the Pewamo profile. In the surface horizons, Ca-P is highest in the clay fraction, intermediate in the silt fraction and lowest in the sand fraction; while in the A2 horizon of the lower sequum (a Gray-Wooded profile), Ca-P is equally high in the silt and sand fractions and lowest in the clay fraction. In the B2t horizon, Ca-P is highest in the silt and lowest in the sand fraction.

In the Sims subsoil, Ca-P is highest in the silt fraction, intermediate in the clay and lowest in the sand fraction.

In considering the P status of a soil from the fertility point of view, the texture of the soil becomes important. Since the more available forms of P are present in the clay fraction of the soil, therefore, a soil of heavy texture contains greater amounts of available P than a soil of light texture regardless of their total P contents.

The sum of mg P per 1,000 g of soil in each particle separate for a particular form of P is generally in good agreement with the content of that form of inorganic P determined directly from P fractionation of the soil (Table 5). Errors may arise from the use of large-scale particle-size separation data for the calculation. Nevertheless, the comparison of the two sets of data did not indicate any significant loss of P during the processes of dispersion and separation. Neither did any significant breakdown of the occluded P during the sonic vibration treatment appear to have occurred.

GENERAL DISCUSSION AND SUMMARY

Inorganic P minerals in arable soils are of two origins: (a) primary P-bearing minerals, such as apatites; and (b) insoluble P compounds formed as a result of P fertilization, such as crystalline and colloidal phosphates of Al and Fe.

During the course of soil chemical weathering under acidic condition and intensive vegetation, the primary P-bearing minerals which are present in the coarse fraction of the soil are broken down into smaller particles by chemical, biological and mechanical forces, and thus are transfered into the finer fractions of the soil. The portion of P that is brought into the solution phase by the action of H^+ ions may precipitate as colloidal $AlPO_4$ and colloidal $FePO_4$ in the clay fraction of the soil. The colloidal phosphates then crystallize to form variscite ($AlPO_4 \cdot 2H_2O$) and strengite ($FePO_4 \cdot 2H_2O$) or related compounds and in an extended period of time with favorable environmental conditions, the compounds may enter into the coarser fractions of the soil as a result of crystal growth. For this reason, the relative abundance of the various forms of inorganic P in the soil has been considered as an index of the degree of chemical weathering of the soil.

It is well known that soluble P compounds added to soils as fertilizer are rapidly changed into insoluble forms. The process is commonly called fixation. Fixed forms of P are believed to be colloidal phosphates of Al and Fe and are present in the clay fraction of the soil. Again, they may crystallize to form variscite and strengite and grow into larger crystals in an extended period of time.

The extent of both the P transformation and fixation reactions in soils is greatly dependent upon factors, such as, the concentration of H^+ ion in the solution, sources of Al and Fe, and temperature and moisture conditions of the soil.

It has been shown in the first part of this investigation that colloidal $AlPO_4$ and colloidal $FePO_4$ are much better sources of P for the plant than variscite and strengite. The two colloidal phosphates are equally available and the two crystalline phosphates are almost completely unavailable to the plant. Colloidal $AlPO_4$ crystallizes at a much slower rate than the colloidal $FePO_4$ in aqueous system under the same temperature and pressure conditions. Based upon these findings, the colloidal form of Al-P and Fe-P in the clay fraction formed during the processes of P fixation and transformation can be regarded as readily available form of P for plant growth. Therefore, the "fixed form" and the "unavailable form" of P are not unanimous terms. In other words, the fixed forms of P in soils may be available for plant growth as long as they remain colloidal. Under this circumstance, the rate of crystallization of the fixed forms of P in the soil becomes the most important factor affecting their relative availability to plants.

To confirm the conclusion derived from the study of the synthetic phosphate systems, an investigation of the actual distribution of the various forms of inorganic P in the soil particle separates was carried out. Since most of the commonly used dispersion procedures for soil mechanical analysis cannot be used satisfactorily for this purpose, a method was developed and reported in this thesis which may be used to separate the textural fractions from the soil samples without alteration of the P minerals in soils. Four Michigan soil profile samples were used for this study and the results can be concluded as follows:

(a) The contents of all the three forms of inorganic P, namely, Al-P, Fe-P and Ca-P in the soil particle separates are in the order of clay > silt > sand for all surface soils studied. This indicates that particle size and/or specific surface may not be the critical factors in controlling the relative availability of the various forms of inorganic P in soils. Therefore, it is the degree of crystallinity of the various inorganic P compounds that is most responsible for their relative availability.

(b) In the lower horizons of the soil profiles studied, Ca-P tends to be most highly concentrated in the silt fraction, intermediate in the clay fraction and lowest in the sand fraction. The result provides information in supporting the conception that Ca-P in soils is of primary origin.

(c) Since clay fraction contains the major portion of the inorganic P in the agricultural soils, soil texture becomes important when the P status of a soil is considered from the fertility point of view. The amorphous or colloidal form of Al-P and Fe-P which is readily available to plants, is included in the portion of the inorganic P which is present in the clay fraction.

It has been reported by Scheffer, et al. (125) who worked on a group of surface soils from Germany, and by Hanely and Murphy (56) who studied a number of grassland surface soils from Ireland, that Ca-P in soils is highly concentrated in the sand fraction and decreases with the decrease of soil particle size. However, the results from this investigation do not provide evidence to support their conclusion. Two reasons may account for this discrepancy. First, the methods they used for the textural separation of the soil samples may dissolve certain P minerals in the soil, particularly, in the clay fraction. Second, the degree of inorganic P weathering may be greater in the acid soils used in this study.

The four soil profile samples used in this study were developed under a more acidic environment and have been under intensive cropping operations. Thus, a great portion of the Ca-P which exists as primary minerals such as apatites in the sand fraction should have been transferred into the silt and clay fractions as a result of some chemical and physical forces during the process of weathering, such as dissolution and mechanical breakdown. A major part of the dissolved P reprecipitates as Al-P and Fe-P and the reactions mainly occur in the clay fraction. Meanwhile, the added soluble P fertilizer is also fixed in the forms of Al-P and Fe-P in the clay fraction.

The fact that all the three forms of inorganic P are most concentrated in the clay fraction in the surface soils studied strongly support the conclusion from the first part of this thesis that it is the degree of crystallinity, not the specific surface or particle size that is the most important factor affecting the relative availability of the various forms of inorganic P in soils. Ca-P, due to its primary origin, exists as highly crystalline minerals throughout the textural fractions of the soil. Thus, it is the least available form of inorganic P in soils under slightly acidic to alkaline conditions. Al-P, due to its relatively slow rate of crystallization in aqueous medium, remains highly colloidal in the clay fraction, and thus, it is the most available form of inorganic P among the three. The relative availability of Fe-P in acid soils, lies between Ca-P and Al-P. Owing to its relatively faster rate of crystallization in aqueous medium, it exists in a higher degree of crystallinity in the soil as compared with that of Al-P, although the major portion of the Fe-P still remains in the clay fraction.

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