REACTION PRODUCTS OF APPLIED ORTHOPHOSPHATES IN SOME MANITOBA SOILS AS AFFECTED BY SOIL CALCIUM AND MAGNESIUM CONTENT AND TIME OF INCUBATION

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ABSTRACT

Four soils, varying in calcium and magnesium content, were treated with KH_2PO_4 or K_2HPO_4 pellets. Crystalline phosphate reaction products were identified by means of X-ray diffraction analysis over a period of 450 days.

The addition of KH_2PO_4 resulted in the formation of DCPD in all four soils. However, DCPD formed only in two soils treated with K_2HPO_4. DMPT formed along with DCPD in soils having a water-soluble calcium to magnesium ratio of less than 1.5. OCP was a prominent reaction product in all soils. A calcium-magnesium phosphate, $Ca_3Mg_3(PO_4)_4$, previously not reported as occurring in soils, was detected in the soil containing approximately equivalent amounts of ammonium acetate-extractable calcium and magnesium. A calcium phosphate, $Ca_4P_2O_9$, also previously not reported, formed in soils high in exchangeable calcium. TMP.22H_2O, considered to be the hydrolysis product of DMPT, formed only in the high-magnesium soil. The relatively soluble reaction products, DCPD and DMPT, existed for a longer period when phosphorus was added in an acid (KH_2PO_4) rather than in an alkaline (K_2HPO_4) form.

The solubility of phosphorus in the above systems (KH_2PO_4 or K_2HPO_4 added as a pellet to each of the four soils) was determined by equilibration of the soil-fertiliser system with water. Similarly, the solubility of phosphorus was determined at intervals in each of the soils after KH_2PO_4, K_2HPO_4, DCPD or DMPT was mixed throughout the soil. The solubility of added phosphorus was near that of DCPD or DMPT when the soils were incubated for a short

period. The solubility of phosphorus decreased with time and approximated that of OCP after 12 to 15 months of incubation. Added phosphorus apparently remained more soluble when KH_2PO_4 rather than K_2HPO_4 was added in the pellet form. Mixing these carriers with the soil eliminated any differences which were evident for the pellet application. It was apparent that the addition of the actual initial reaction product (DCPD or DMPT) rather than a water-soluble phosphate (KH_2PO_4 or K_2HPO_4) did not greatly affect the solubility of phosphorus in a given system, i.e. the solubility of DCPD or DMPT added to soils was similar to that of applied KH_2PO_4 or K_2HPO_4.

INTRODUCTION

Water-soluble phosphate fertilizers, when added to soils, react with the soil constituents to form less soluble phosphates. In soils containing large amounts of calcium and in alkaline soils, it is the calcium ion that is considered to react with phosphate. Recently it has been shown that magnesium reacts with phosphate in soils containing large amounts of magnesium. Addition of a soluble phosphate to soils results in the formation of a monomolecular layer of phosphate on the surfaces of the soil particles. As more phosphate is added, this adsorption reaction is followed by precipitation of the added phosphate. Added phosphate is usually precipitated as dicalcium phosphate dihydrate and/or octacalcium phosphate in soils containing large amounts of calcium. Dimagnesium phosphate trihydrate and trimagnesium phosphate can form when phosphate is added to soils containing large amounts of magnesium. Dicalcium phosphate dihydrate and octacalcium phosphate are metastable and undergo reactions with the soil solution until an apatite is formed. Dimagnesium phosphate trihydrate is also metastable and, on dissolution, forms trimagnesium phosphate.

The solubility in water and thus the availability to plants of the calcium phosphates found in soils decreases in order: dicalcium phosphate, octacalcium phosphate, hydroxapatite. The solubility of trimagnesium phosphate is much less than that of dimagnesium phosphate. The period of time that the initial and relatively soluble phosphate reaction products exist in soils will therefore influence the value of the added phosphate as a phosphorus source to plants. Information on the rate at which the initial phosphate reaction products in base saturated soils, particularly the magnesium phosphates, change to less soluble forms is very limited.

Manitoba soils contain large amounts of calcium and magnesium in the form of carbonates or as exchangeable calcium and magnesium. Thus, a study of the phosphate reaction products formed in base saturated soils over a long period of time is essential to better understanding the phosphorus chemistry of our soils.

The objective of the work reported here was to determine the phosphate reaction products in soils incubated for periods of 15 months or less. X-ray and solubility studies were used to identify the reaction products of phosphate added to soils varying in calcium and magnesium content.

II. REVIEW OF LITERATURE

(1) Calcium and Magnesium Phosphates in Soil.

In calcareous soils, the calcium ion is primarily responsible for altering the solubility of applied water-soluble phosphates. The greater the calcium content of a soil, the greater is the possibility that calcium will play a dominating role in precipitation of fertiliser phosphorus (17). The number of calcium phosphates formed in soils is probably more extensive than our present knowledge indicates. However, the most important soil calcium phosphates are:

(i) Monocalcium phosphate monohydrate (MCP) $Ca(H_2PO_4)_2H_2O$. MCP is water soluble and is a constituent of superphosphate fertilisers. MCP is too soluble to persist in soils; consequently, the phosphorus from MCP forms less soluble products such as dicalcium phosphate or octacalcium phosphate (15). Since plants obtain most of their phosphorus from these reaction products and not from the fertiliser as such, their identification is of primary importance in understanding the behaviour of phosphorus in soils (16).

(ii) Dicalcium phosphate dihydrate (DCPD) $CaHPO_4.2H_2O$. DCPD, a calcium phosphate less soluble than MCP, is believed to be the initial reaction product when soluble phosphate is applied to calcareous soils (17). Lindsay and Stephenson (17) found that DCPD formed not only at the fertiliser placement site but also throughout the soil zone contacted by the fertiliser solution. Moreno, Lindsay and Osborn (21) equilibrated mixtures of MCP and soil with water. They found that the solution became saturated with DCPD and remained so for periods up to one month. Lindsay, Frazier and Stephenson (16) found DCPD precipitates remaining in filtrates for two months when soils were treated with saturated phosphate solutions. Larson et al. (14) found that granules equal to 10 to 20 per cent of an original application of DCPD were recovered apparently unchanged 26 months after application to soils of varying textures in pots stored in the open. All the DCPD had disappeared after 37 months of incubation.

Clark and Peech (8) state that DCPD can exist only in soils in which the concentration of soil solution phosphorus is unusually high. This suggests that it may, in fact, not exist for very long but occur as a transition product. In two basic soils treated with MCP, the final residues, identified by petrographic and X-ray methods, contained octacalcium phosphate, colloidal apatite, and only a few crystals of DCPD (15). Although DCPD is the hydrolytic precursor of octacalcium phosphate and the apatites, the formation of octacalcium phosphate and hydroxyapatite proves that these compounds are more stable than DCPD (15). These workers state that, above pH 6.5, DCPD hydrolyses to the more basic octacalcium phosphate and that this transformation is of major importance on neutral or alkaline soils.

Moreno *et al.* (23) have found the solubility product of DCPD to be 2.77×10^{-7} at twenty-five degrees centigrade.

(iii) Octacalcium phosphate trihydrate (OCP) $Ca_4H(PO_4)_3.3H_2O$.

OCP may be formed in soil systems as a result of hydrolysis of DCPD (15) or it may be formed directly as a result of adding phosphate (15). Withee and Ellis (38) found that, in two calcareous soils, a basic calcium phosphate similar in solubility to OCP controlled the amount of phosphorus in the soil solution. Weir and Soper (37) found that the solubility of phosphorus in some fertilised and unfertilised Manitoba soils approximated that of OCP. OCP, however, is metastable, and, in neutral and alkaline soils, slowly reverts to apatite with a subsequent decrease in solubility and availability to plants (17). Moreno *et al.* (22) obtained a value 1.25×10^{-47} for the solubility product of OCP at twenty-five degrees centigrade. The pK_{sp} value for OCP is reported by these workers to be 9.93. Bjerrum (3) reported pK_{sp} values of 11.8 and 9.3 depending on whether equilibration was approached by dissolution or by precipitation.

(iv) Hydroxyapatite (HA) $Ca_{10}(PO_4)_6.(OH)_2$.

Hydroxyapatite is considered to be the stable basic calcium phosphate in soils. The composition of HA has been found to vary. The composition of the surface layer can vary appreciably from that of true apatite, due to the exchange of hydronium ion $(H_3O)^+$ for calcium and possibly of the hydroxyl ion for phosphate (28)

Clark (7) verified that hydroxyapatite could exist as a compound with a fixed crystalline form and a definite solubility in pure systems. Nagelschmidt and Nixon (24) used X-ray diffraction data to show that apatite was present in soils treated with superphosphate and chalk over a long period of time.

Beaton _et al_. (2) found that HA was the major initial reaction product of a calcareous soil treated with diammonium phosphate. Clark (7) reported a value of 115.5 for pK_{sp} of hydroxyapatite at twenty-five degrees centigrade.

Although the series of reactions, MCP → DCPD → OCP → HA, can be considered to be operative in soils, it is evident that any one of the phosphates can be formed directly when a water-soluble phosphorus fertiliser is added.

Information on the compounds formed when magnesium and phosphorus interact in soils is limited. However, some orthophosphates, similar to the calcium orthophosphates previously listed, have been found in soils. Those of interest are:

(a) Struvite $MgNH_4PO_4.6H_2O$.

Lindsay and Taylor (18) found that the mineral struvite was readily formed when diammonium phosphate was applied to soils containing large amounts of magnesium. Reaction of monoammonium phosphate with a calcareous soil also caused precipitation of struvite (16). Taylor *et al*. reported a value of 7.1×10^{-14} for the solubility product of struvite at twenty-five degrees centigrade (30).

(b) Dimagnesium phosphate (DMP) $MgHPO_4.xH_2O$.

In nature, DMP has been found in the hepta-hydrate and in the tri-hydrate form (10). Natural crystals of the hepta-hydrate can be dehydrated to pseudomorphs of a lower hydrate. In the system $MgO - P_2O_5 - H_2O$ at 25 degrees centigrade, the tri-hydrate is the only stable hydrate of DMP (10).

Lindsay, Frazier and Stephenson (16) found that, with small additions of MgO to a Metastable Triple Point Solution (an aqueous solution saturated with respect to MCP and DCPD), DCPD and anhydrous DCP formed. In addition to the calcium phosphates found, DMPT was formed when large amounts of MgO were added. In dolomitic soils, precipitation of DCPD is expected to exceed that of DMPT because of the lower solubility of the calcium phosphate.

Racz and Soper (25) used X-ray diffraction analysis to identify the reaction products of water-soluble orthophosphates added to soils of varying calcium and magnesium contents. In many instances, both DCPD and DMPT formed in the same soil. Only DCPD was found in the soils with a water-soluble calcium to magnesium ratio of 1.5 or greater. Both DCPD and DMPT were usually formed in soils with a calcium to magnesium ratio of less than 1.5. These workers observed visual differences associated with the different reaction products at the phosphorus pellet site. The precipitation of DMPT was associated with the formation of small dark spots near the site of the phosphorus pellet (KH_2PO_4) application. The precipitation of DCPD was associated with the formation of a whitish ring, about 1.3 cm in radius, around the pellet site. Taylor et al. (31) reported a value of 1.5×10^{-6} for the solubility product of DMPT at twenty-five degrees centigrade.

(c) Trimagnesium phosphate (TMP) $Mg_3(PO_4)_2$.

This compound has been found to occur in the octahydrate, tetrahydrate, and twenty-two hydrate form (10),(25). Racz and Soper (25) found $Mg_3(PO_4)_2.4H_2O$ as a reaction product when soils containing large amounts of magnesium were treated with saturated orthophosphate solutions. $TMP.22H_2O$ has been shown to form as a hydrolysis product of DMPT (25). This transformation was found only in soils containing large amounts of magnesium. Taylor et al. (31) reported a value of 8.0×10^{-24} for the solubility product of $Mg_3(PO_4)_2.22H_2O$ at twenty-five degrees centigrade.

(2) Availability of the Calcium and Magnesium Orthophosphates to Plants.

The availability of phosphorus from the products formed by reaction of fertiliser with soil determines the value of the fertiliser as a source of phosphorus to plants. The availability of phosphorus from these reaction products depends upon the solubility of the reaction product and upon the period of time that the relatively soluble reaction products can exist in the soil (18). Although the initial reaction products such as DCPD are unstable under normal soil conditions, Lindsay and Taylor (18) consider that they may persist for one or more seasons in the localised environment close to the fertiliser pellet, but in time they revert to more stable and less available compounds.

According to Chin *et al*. (5), MCP, which dissolves readily to form an acid solution, is more available to crops than is DCPD. Fertilisation with MCP resulted in significantly higher yields and lower phosphorus contents of wheat than did fertilisation with DCPD. MCP was more available than DCPD to both wheat and alfalfa. Lindsay and Taylor (18) consider that, where MCP is added, sufficient calcium is present to precipitate one-half the fertiliser phosphorus as DCPD. Only small amounts of the anhydrous form occur, despite the fact that it is the more stable of the two. However, these workers consider that, in finely divided form, both the dicalcium phosphates are more available than MCP, although their value as a phosphorus fertiliser decreases markedly as particle size increases. Bouldin and Sample (4) determined that the dihydrate had greater than twice the availability of the anhydride when equal-particle size phosphates were added. This is reflected by the rates of solution of the two materials (18).

It might be expected that the dicalcium phosphates would remain available over a longer period of time than would MCP, since DCPD would dissolve more slowly. MCP, which dissolves rapidly in the soil, may have short-lived beneficial effects. MCP, however, is usually precipitated as DCPD and thus the long-term availability of MCP and DCPD may be approximately equal.

Terman, Bouldin and Lehr (32) tested the availabilities of five pure crystalline calcium phosphates to Rye grass and Sudan grass. Their results showed that DCPD was appreciably more available than the anhydride on all soils. MCP was slightly more effective than the dicalcium phosphates when added to alkaline soils. The dicalcium phosphates were a better source of phosphorus on acid soils than was MCP. OCP was less available than the dicalcium phosphates on all soils. Hydroxyapatite was found to provide plants with only very small amounts of phosphorus. Thus, on the alkaline soils, availability of phosphorus decreased in the order, MCP, DCPD, DCP(anhydrous), OCP, HA. On the acid soils, availability of phosphorus decreased in the order, DCPD, DCP(anhydrous), MCP, OCP and HA (32).

Lindsay and Taylor (18) showed that finely-divided OCP has an availability about 80 per cent that of MCP. OCP was found to undergo a slow reversion to apatite, a less available form. Racz (27) found that DCPD and DMPT supplied about equal amounts of phosphorus to plants grown on phosphorus deficient soils. The plants obtained slightly less phosphorus from DCPD and DMPT than from KH_2PO_4.

It seems from the review of literature that there is a need to further investigate the reaction products of soluble orthophosphates in soils of varying calcium and magnesium contents. Also, the solubility or availability of the added phosphorus as affected by time needs further attention.

III. MATERIALS AND METHODS

Four soils, selected for their varying calcium and magnesium content, were used throughout these investigations (Table 1). These were surface soils. A subgroup designation of the soils is given in Table 2. The analytical procedures employed in the investigations and in characterizing the soils are outlined below.

Analytical Procedures

(1) Soil pH

Soil and distilled water (1:20 w/w) were equilibrated by shaking for one hour. The pH of the supernatant above the soil was measured using a glass electrode in conjunction with a calomel half-cell on a Universal pH Meter 22.

(2) Soil Organic Matter

Soil organic matter was determined according to the method of Walkley and Black (35). Excess potassium dichromate was used to oxidize the organic matter, and the unreacted dichromate back-titrated with ferrous sulphate using barium diphenylamine sulphonate as indicator.

(3) Water Soluble Calcium and Magnesium

A ten gram sample of soil was extracted with 100 ml of distilled water for one hour. After centrifugation and filtration, the calcium and magnesium content of the filtrate was determined by EDTA titration (33).

(4) Inorganic Carbonate Content

A one gram soil sample was digested in 10% HCl for ten minutes. The

Table 1. Characteristics of the Soils Studied

		Water Soluble (meq/100 g)			Ammon.Ac.Extract. (meq/100 g)				
Soil	pH	Ca	Mg	Ca/Mg	Ca	Mg	Ca/Mg	Organic Carbon(%)	Inorganic CO_3 (%)
Darlingford	7.85	0.81	0.53	1.53	30.89	7.23	4.27	6.58	1.00
Aneda	8.20	1.02	0.60	1.70	40.23	4.02	10.00	6.85	8.40
Balmoral	8.60	0.81	1.26	0.64	21.98	21.62	1.02	6.82	27.50
Red River	7.25	3.89	10.52	0.37	19.24	33.54	0.57	6.58	0.29

Table 2. Subgroup Designation of Soils Studied

Soil Name	Subgroup
Darlingford	Orthic Black
Aneda	Thin Orthic Dark Grey
Balmoral	Carbonated Rego Humic Gleysol
Red River	Gleyed Rego Black

carbon dioxide evolved was sucked through a drying and adsorption train and absorbed on Ascarite in a Nesbitt tube. The weight of carbon dioxide absorbed on the Ascarite was determined and the carbonate content of the soil calculated.

(5) Ammonium Acetate-Extractable Calcium and Magnesium

100 ml of one normal ammonium acetate solution (pH 7) was equilibrated with ten grams of soil by shaking for one hour. The suspension was transferred to a Buchner funnel and the soil leached with ammonium acetate solution to a volume of 250 ml. The calcium and magnesium contents of the filtrate were determined by EDTA titration (33).

(6) Calcium and Magnesium in Solution

First, the total calcium and magnesium in solution was determined using EDTA as titrant and Eriochrome Black-T as indicator (33). On a separate aliquot, magnesium was precipitated quantitatively as the hydroxide by increasing the pH of the solution to approximately 12.3 using sodium hydroxide, and the calcium titrated with EDTA using Cal-Red as indicator. Magnesium was obtained by difference.

(7) Phosphorus Determination

Phosphorus was determined using a colorimetric procedure as outlined by Jackson (13). A suitable aliquot of extractant, placed into a 50 ml volumetric flask, was adjusted to pH3 with 2N H_2SO_4 or 4N Na_2CO_3 using 2,4 dinitro phenol as indicator. Two ml of 2.5 per cent ammonium molybdate-sulphuric acid solution was then added and the solution brought to volume. The phosphorus-molybdate complex was reduced by the addition of three drops of the chlorostannous acid reductant solution. Colour intensity at 660 mμ was found to be at a maximum six minutes after addition of the reductant. Thus all colour intensities were measured at 660 mμ on a Coleman Junior Spectrophotometer (Model 6A) six minutes after initiation of colour development. By comparison of the reading obtained for the extracting solutions with those obtained for a standard curve, the phosphorus contents of the extracting solutions were determined.

(8) X-Ray Procedure

The sample was finely ground ($<$300 mesh) and placed into a glass capillary tube (0.3 mm diameter) obtained from Caine Scientific Sales Company, Chicago, Illinois. The tube was then centred in a Philips cylindrical powder diffraction camera. The camera was then loaded with Kodak No-Screen Medical X-Ray Film and positioned on a Philips P.W.1010 X-Ray Generator. The X-Ray Generator was operated at 36 kv and 8 m amps and equipped with a cobalt target and an iron filter. The sample tube was rotated mechanically during exposure. Exposure time was 22 hours for all samples. After exposure, the film was removed from the camera, immersed in Kodak Rapid X-Ray Developer for five minutes, rinsed with water, and placed into Kodak X-Ray Fixer for twenty minutes. The film was again rinsed, then dried. The distances between the diffraction lines were measured on a Philips Film Illuminator and Measuring Device. Calculated d-spacings for the samples were compared to known values listed in the A.S.T.M. X-Ray Powder Data File and the Crystalline phosphate species present in the samples identified.

(9) Solubility Studies

A ten gram sample of soil was extracted with 100 ml of distilled water for 24 hours. Preliminary investigations indicated that the pH, calcium, magnesium and phosphorus content of the solutions did not change with extraction times greater than 24 hours. The suspension was centrifuged, filtered using Whatman Filter Paper No. 42, and the pH, calcium, magnesium and phosphorus contents of the filtrates determined as previously described.

Experimental Methods

(1) Reaction Products and Solubilities of K_2HPO_4 and KH_2PO_4 Added to Soils as a Pellet

Fifty grams of soil were placed in plastic cylinders (4.4 cm diameter and 5 cm high) on a large watch glass base. The soil was wetted by the addition of distilled water to the base of the column. A glass rod was used to make an opening approximately 0.6 cm deep in the centre of the soil column. 0.025 g of phosphorus as K_2HPO_4 or as KH_2PO_4 was placed into the opening. The 0.1098 g of KH_2PO_4 or 0.1450 g of K_2HPO_4 added supplied the equivalent of 50 ppm P to the soil. The samples were kept moist by the daily additions of water to the base of the columns. Samples of the reaction products and soil near the phosphorus pellet site were collected after one day, 1, 3, 6, 9, 12 and 15 months of incubation. In order to obtain sufficient soil for solubility studies, each treatment was duplicated. Duplicate samples were composited prior to analysis.

The phosphate reaction products were collected by scraping the surface of the soil near the pellet site with a sharpened spatula. The area sampled was approximately 1.3 cm. in radius. The samples were air-dried, finely ground ($<$300 mesh) in an agate mortar and pestle, and subjected to X-Ray Powder Diffraction Analysis. The d-spacing for the minerals present in the soil-reaction product mixture and in the soil without added phosphorus, were determined. Additional lines occurring in the treated soils were taken to be those of the reaction products.

Approximately ten grams of soil were taken from the site of phosphorus placement for solubility studies. The samples were air-dried and ground. The solubility of phosphorus in the soil samples was then determined.

(2) Solubility of K_2HPO_4 and KH_2PO_4 when mixed with Soils

Three hundred grams of soil were placed on plastic sheets. Phosphorus as K_2HPO_4 or as KH_2PO_4 was added to the soils in sufficient quantity to increase the phosphorus content of the soils by 100 and 400 ppm phosphorus. The phosphorus carriers were dissolved in distilled water (6.7482 g K_2HPO_4/litre and 5.2724 g KH_2PO_4/litre) and applied to the soils by the use of a pipette. One hundred ml and 25 ml of the above solutions were required for the 400 and 100 ppm phosphorus applications, respectively. The 25 ml aliquot required to increase the phosphorus content of the soil by 100 ppm was diluted to 100 ml in order that the added phosphorus could be uniformly distributed throughout the soil. The soil was then thoroughly mixed and transferred to a plastic bag (6 inches by 13 inches). Sufficient distilled water was added to wet the soils to field capacity moisture content and the bags sealed. The soils were aerated weekly by opening the bags and shaking the soils vigorously. Water was periodically added to maintain the original moisture content. Samples of soil (25 g) were removed after one day, 1, 3, 6, 9, 12 and 15 months of incubation. The samples were air-dried and ground. The solubility of the added phosphorus in the soils was then determined.

(3) Solubility of Dicalcium Phosphate Dihydrate (DCPD) and Dimagnesium Phosphate Trihydrate (DMPT) when mixed with Soils.

Dicalcium phosphate dihydrate and dimagnesium phosphate trihydrate were prepared by the method described by Racz (26). The phosphorus and calcium content of the prepared DCPD was found to be 18.18 and 23.40 per cent, respectively. The phosphorus and magnesium content of the prepared DMPT was 17.96 and 13.76 per cent, respectively. The prepared DCPD and DMPT were added in sufficient quantities to increase the phosphorus content of 300 grams of soil by 100 and 400 ppm phosphorus. 0.165 g of DCPD or 0.167 g of DMPT were used for the 100 ppm application rate. 0.660 g of DCPD or 0.668 g of DMPT were used for the 400 ppm application rate. The phosphates were thoroughly mixed throughout the soil. The soils were then placed in plastic bags and wetted and aerated as described in the previous experiment. Twenty-five gram samples of soil were removed after one day, 1, 3, 6 and 8 months of incubation. The soils were air-dried and ground. The solubility of phosphorus in the soils was then determined.

Calculation of Lime and Phosphate Potentials

The formation of a crystalline solid-phase phosphate in soil results, at equilibrium, in a fixed relationship between its component ions in the soil solution (8). The relationship between the various ions in the soil solution can be determined and the existence of crystalline phosphates in soils established by the application of such solubility criteria.

The solubility of phosphorus in calcareous soils can be expressed by the mutually interdependent variables, pH, calcium concentration, and the concentrations of the three orthophosphate species, H_2PO_4, HPO_4, and PO_4 (9). For example, the three solid phases, $Ca(H_2PO_4)_2$, $CaHPO_4$, and $Ca_{10}(PO_4)_6(OH)_2$ contain Ca, OH, and the three orthophosphate species. The solubilities of these crystalline calcium phosphates can be represented on a single diagram, provided all the constituent ions are included as co-ordinates. The phosphate species are related to one another in a definite way by dissociation constants and by the H^+ ion activity. Thus, if the H^+ ion activity (or the OH^- ion activity) is included as a co-ordinate, it is necessary to calculate the activity of only one of the phosphate species. The solubilities of the calcium phosphates can be represented on a two co-ordinate diagram in terms of the activities of the compounds $Ca(OH)_2$ and $Ca(H_2PO_4)_2$ which are assumed to be in solution and completely dissociated (8). The following, using DCPD as an example, demonstrates how the co-ordinates of the solubility diagram are derived. A balanced equation can be written for the equilibrium formation of solid dicalcium phosphate from the molecular species $Ca(OH)_2$ and $Ca(H_2PO_4)_2$: -

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

The above equation can be written in terms of the chemical potentials of the reacting species and products, assuming that the chemical potential of water is constant and the solution dilute. Thus:

$$\mu\, Ca(OH)_2 + \mu\, Ca(H_2PO_4)_2 = 2\mu\, CaHPO_4\ (solid) \qquad (2)$$

and:

$$\left[\mu^{\circ} Ca(OH)_2 + RT\ln a Ca(OH)_2\right] + \left[\mu^{\circ} Ca(H_2PO_4)_2 + RT\ln a Ca(H_2PO_4)_2\right] = 2\mu\, CaHPO_4 (solid) \qquad (3)$$

Rearranging the above equation results in the following equation:

$$RT\ln a Ca(OH)_2 + RT\ln a Ca(H_2PO_4)_2 = 2\mu\, CaHPO_4\ (solid) - \mu^{\circ} Ca(OH)_2 - \mu^{\circ} Ca(H_2PO_4)_2 = K \qquad (4)$$

Substitution of $a_{Ca^{++}} \cdot a^{2}_{OH^-}$ for $a_{Ca(OH)_2}$ and of $a_{Ca^{++}} \cdot a^{2}_{H_2PO_4^-}$ for $a_{Ca(H_2PO_4)_2}$ into Equation (4) and dividing by 2.303RT results in the following equation:

$$\log a_{Ca^{++}} \cdot a^{2}_{OH^-} + \log a_{Ca^{++}} \cdot a^{2}_{H_2PO_4^-} = K' \tag{5}$$

The above equation can be rewritten as:

$$(pCa + 2pOH) + (pCa + 2pH_2PO_4) = -K'' \tag{6}$$

where the terms pCa, pOH, and pH_2PO_4 represent the negative logarithm of the activities of the respective ions. Substituting (14 - pH) for pOH and dividing Equation (6) by -2 gives the following:

$$\left[pH - 1/2pCa \right] - \left[pH_2PO_4 + 1/2pCa \right] = K''' \tag{7}$$

The terms (pH - 1/2Ca) and (pH_2PO_4 + 1/2pCa) are known as the "lime potential" and "phosphate potential", respectively, and are the two co-ordinates of the solubility diagram. The slope of the solubility line is given by the coefficients of these two terms, in this case -1/1 for dicalcium phosphate.

Similar equations relating the lime and the phosphate potential can be developed for octacalcium phosphate and hydroxyapatite. The co-ordinates of the solubility diagram for the magnesium phosphates are (pH - 1/2pMg) and (pH_2PO_4 + 1/2pMg). The equation relating the lime potential and phosphate potential for dimagnesium phosphate trihydrate (DMPT) is:

$$\left[pH - 1/2pMg \right] - \left[pH_2PO_4 + 1/2pMg \right] = K$$

For trimagnesium phosphate the equation is:

$$2\left[pH - 1/2pMg \right] - \left[pH_2PO_4 + 1/2pMg \right] = K$$

For octacalcium phosphate the equation is:

$$5\left[pH - 1/2pCa\right] - 3\left[pH_2PO_4 + 1/2pCa\right] = K$$

and for hydroxyapatite the equation is:

$$7\left[pH - 1/2pCa\right] - 3\left[pH_2PO_4 + 1/2pCa\right] = K$$

The values for "K" can be established experimentally by measuring the lime and phosphate potentials of the pure phosphate compounds in distilled water. A two co-ordinate diagram can then be constructed by substituting values for the lime potential in the above equations and calculating the corresponding phosphate potential or vice versa. The values of K relating the lime and phosphate potentials for DCPD, DMPT, TMP 2H_2O, TMP(anhydrous) OCP, and HA are 0.50(27), 1.55(26), 8.15(26), 8.29(26), 9.8(3), and 14.7(7), respectively. The solubility diagram can be used to establish the existence of certain solid phase phosphates in soils. The position of a solubility value on the diagram indicates the solid phase phosphate governing the concentration of phosphorus in the soil solution. For example, if a solubility value was close to the DCPD isotherm, it is probable that DCPD is present in the soil and controlling the phosphorus concentration in the soil solution. This, however, does not mean that OCP (octacalcium phosphate) and/or HA (hydroxyapatite) were not present in the soil, but that the most soluble solid phase phosphate in the soil was DCPD.

The lime and phosphate potentials of the soil extracts were calculated as follows. First, the activities of the Ca, Mg, HPO_4, and H_2PO_4 ions in the extracts were corrected for the presence of undissociated $CaHPO_4$, and $MgHPO_4$. Since the pH of the systems studied remained between pH 5 to 9, the total phosphorus concentration, $\left[P_T\right] = \left[H_2PO_4^-\right] + \left[HPO_4^=\right] + \left[MHPO_4\right]$ (1)

where $H_2PO_4^-$ and $HPO_4^=$ are phosphate ions in solution and $MHPO_4$ a soluble complex of calcium or magnesium with $HPO_4^=$ (6, 31). The dissociation constant, K_d, of the $CaHPO_4$ and $MgHPO_4$ complex has been found to be 1.75×10^{-3} (6) and 1.24×10^{-3} (31), respectively. A mean value of 1.50×10^{-3} was used when both calcium and magnesium were present in solution. Substitution of activities for concentrations,

$$\frac{(M^{2+})(HPO_4^=)}{K_d} \text{ for } \left[MHPO_4\right] \text{ and } \frac{(H^+)(HPO_4^=)}{K_2} \text{ for } \left[H_2PO_4^-\right]$$

in equation (1) results in the following expression:

$$\left[P_T\right] = (HPO_4^=) \left\{ \frac{(M^{2+})}{K_d} + \frac{(H^+)}{f^- K_2} + \frac{1}{f^{2-}} \right\} \qquad (2)$$

where (M^{2+}) represents calcium plus magnesium, f^- the activity coefficient of the $H_2PO_4^-$ ion, f^{2-} the activity coefficient of the $HPO_4^=$ ion, K_2 the second dissociation constant of phosphoric acid, the brackets concentrations and the parentheses activities. The total calcium plus magnesium in solution,

$$\left[M_T^{2+}\right] = \left[M^{2+}\right] + \left[MHPO_4\right] \qquad (3)$$

where $\left[M^{2+}\right]$ represents the concentration of calcium plus magnesium in solution and $MHPO_4$ the soluble complex of calcium or magnesium with $HPO_4^=$.

Thus,

$$\left[M_T^{2+}\right] = \frac{(M^{2+})}{f^{2+}} + \frac{(M^{2+})(HPO_4^=)}{K_d} \qquad (4)$$

$$\text{and } (M^{2+}) = \frac{\left[M_T^{2+}\right]}{\left\{\frac{1}{f^{2+}} + \frac{(HPO_4^{=})}{K_d}\right\}} \tag{5}$$

where f^{2+} represents the activity coefficient of calcium and/or magnesium. Substitution of the expression derived for (M^{2+}) in equation (5) into equation (2) results in the following quadratic equation by which the $HPO_4^{=}$ ion activity was calculated.

$$(HPO_4^{=})^2\left\{(H^+)f^{2-} + f^-K_2\right\} + (HPO_4^{=})\left\{-\left[P_T\right]f^-K_2f^{2-} + \left[M_T^{2+}\right]f^-K_2f^{2-} + \frac{K_d}{f^{2+}}\left((H^+)f^{2-} + f^-K_2\right)\right\} - \frac{\left[P_T\right]K_df^-K_2f^{2-}}{f^{2+}} = 0 \tag{6}$$

The calcium or magnesium ion activity was obtained from the following quadratic equation derived by substituting the expression for $(HPO_4^{=})$ derived from equation (2) into equation (5).

$$(M^{2+})^2\left\{f^-K_2f^{2-}\right\} + (M^{2+})\left\{(H^+)K_df^{2-} + K_df^-K_2 + \left[P_T\right]f^{2+}f^-K_2f^{2-} - \left[M_T^{2+}\right]f^{2+}f^-K_2f^{2-}\right\} - \left[M_T^{2+}\right]\left\{f^{2+}(H^+)K_df^{2-} + f^{2+}K_df^-K_2\right\} = 0 \tag{7}$$

The activity coefficients, f, were calculated from the Debye-Huchel equation, $\log_{10} f = \frac{-AZ^2\sqrt{\mu}}{1 + Bai\sqrt{\mu}}$, (19) which gives the activity coefficient of the ion as a function of the total ionic strength of the solution. A and B are constants depending on the solvent used. For water, at twenty-five degrees centigrade, the values are 0.51 and 0.33×10^8, respectively. "Z" represents the valency of the ion, and "a_i" the mean ionic diameter. Values used for a_i were: HPO_4, 4Å; H_2PO_4, 4Å; Ca, 6Å and Mg, 8Å (19). The ionic strength,

μ, was calculated from the expression: $\mu = 1/2 \sum C_i Z_i^2$ (19) where "Z_i" represents the valencies of the respective ions, and "C_i" the concentrations of these ions.

The ionic activities were calculated by a series of successive approximations, first assuming no association of ions in solution and then correcting for complexing until a constant value for the ion activity was obtained. The values for pCa, pMg, and $pHPO_4$ were then calculated by taking the negative logarithm of the ion activities. The values for pH_2PO_4 were obtained from the expression

$$pH_2PO_4 = pHPO_4 - pK_2 + pH$$

where pK_2 represents the second dissociation constant of phosphoric acid.

The solubility of the added phosphates was calculated by two methods. First, using pH, and calcium and $H_2PO_4^-$ ion activities for the calculation of the phosphate and lime potentials, and second, using the magnesium ion activity rather than the calcium ion activity for the calculation of the lime and phosphate potentials. The two methods of calculation are designated as Ca-P and Mg-P, respectively.

IV. RESULTS AND DISCUSSION

Reaction Products and Solubility of K_2HPO_4 and KH_2PO_4 Added to Soils as a Pellet

(1) X-Ray Diffraction Analysis

Six calcium and magnesium phosphates were found to form in the soils studied (Table 3). Dicalcium phosphate dihydrate formed in all soils treated with KH_2PO_4 and in the Red River and Aneda soils treated with K_2HPO_4. Dicalcium phosphate dihydrate was not detected in the Darlingford and Balmoral soils treated with K_2HPO_4. Octacalcium phosphate was formed in all soils regardless of the form of phosphate added. Dimagnesium phosphate trihydrate was found as a precipitate of both K_2HPO_4 and KH_2PO_4 in the Balmoral and Red River soils. These soils have water-soluble calcium to magnesium ratios of 0.64 and 0.37, respectively (Table 1). Racz and Soper (25) have shown that, in soils having a water-soluble calcium to magnesium ratio of less than 1.5, dimagnesium phosphate trihydrate can be expected to form along with dicalcium phosphate dihydrate. Thus, the formation of magnesium phosphates in the Balmoral and Red River soils would be expected.

Trimagnesium phosphate twenty-two hydrate, considered to be the product of hydrolysis of dimagnesium phosphate trihydrate (25), was found only in the Red River soil. This soil contained very large amounts of exchangeable magnesium. A calcium-magnesium phosphate, ($Ca_3Mg_3(PO_4)_4$), and a calcium phosphate, ($Ca_4P_2O_9$), two reaction products not previously reported as occurring in soils, were detected in some of the soils studied. $Ca_3Mg_3(PO_4)_4$ was found in the Balmoral soil treated with K_2HPO_4 or KH_2PO_4, and in the Darlingford soil treated with K_2HPO_4. $Ca_4P_2O_9$ was found as a reaction product of both

Table 3. Reaction Products in Soils Detected by X-Ray Analysis After Varying Periods of Incubation

Soil	Phosphate Added	1 month	3 months	6 months	9 months	12 months	15 months
Darlingford	K_2HPO_4	OCP	OCP	OCP	OCP	OCP	OCP
					CMP	CMP	CMP
	KH_2PO_4	DCPD					
		OCP	OCP	OCP	OCP	OCP	OCP
			CPO	CPO	CPO	CPO	CPO
Aneda	K_2HPO_4	#	DCPD	DCPD			
		#	OCP	OCP	OCP	OCP	OCP
		#	CPO	CPO	CPO	CPO	
	KH_2PO_4	DCPD	DCPD	DCPD	DCPD		
		OCP		OCP	OCP	OCP	OCP
				CPO		CPO	

\# Compound Not Detected
DCPD: Dicalcium Phosphate Dihydrate $CaHPO_4.2H_2O$
OCP : Octacalcium Phosphate $Ca_4H(PO_4)_3.3H_2O$
CPO : $Ca_4P_2O_9$
CMP : $Ca_3Mg_3(PO_4)_4$
DMPT: Dimagnesium Phosphate Trihydrate $MgHPO_4.3H_2O$
TMP : Trimagnesium Phosphate $Mg_3(PO_4)_2.22H_2O$

Table 3 continued.

Soil	Phosphate Added	1 month	3 months	6 months	9 months	12 months	15 months
Balmoral	K_2HPO_4		OCP	OCP	OCP	OCP	OCP
		DMPT					
			CMP	CMP	CMP	CMP	
	KH_2PO_4		DCPD	DCPD		DCPD	DCPD
		OCP	OCP	OCP	OCP	OCP	OCP
		DMPT	DMPT		DMPT	DMPT	
		CMP	CMP	CMP	CMP	CMP	CMP
Red River	K_2HPO_4	DCPD	DCPD	DCPD			
		OCP	OCP	OCP	OCP	OCP	OCP
		DMPT	DMPT	DMPT	DMPT	DMPT	DMPT
			TMP	TMP	TMP	TMP	TMP
	KH_2PO_4	DCPD	DCPD	DCPD	DCPD		
		OCP	OCP	OCP	OCP	OCP	OCP
		DMPT	DMPT	DMPT	DMPT	DMPT	DMPT
							TMP

K_2HPO_4 and KH_2PO_4 added to the Aneda soil and of KH_2PO_4 added to the Darlingford soil.

The period of time that the more soluble reaction products, dicalcium phosphate dihydrate and dimagnesium phosphate trihydrate, existed in the soils varied with soil type and phosphorus carrier added. Dicalcium phosphate dihydrate was found to persist in the Darlingford, Aneda, Red River and Balmoral soils for one, nine, nine, and greater than fifteen months, respectively, when phosphorus was added as KH_2PO_4. Dicalcium phosphate dihydrate persisted for only six months in the Aneda and Red River soils and was not found to occur at any sampling date in the Darlingford and Balmoral soils when K_2HPO_4 was added. Dimagnesium phosphate trihydrate, detected only in the Balmoral and Red River soils, persisted for twelve months in the Balmoral soil and for the entire sampling period (fifteen months) in the Red River soil when phosphorus was added as KH_2PO_4. This phosphate was detected at the one month sampling period only in the Balmoral soil but persisted for fifteen months in the Red River soil when K_2HPO_4 was added. Octacalcium phosphate was present in all soils at all sampling dates and for both carriers, except when K_2HPO_4 was added to the Aneda and Balmoral soils where octacalcium phosphate was not detected at the one month sampling date. Trimagnesium phosphate twenty-two hydrate was detected in the Red River soil at the three month sampling date and persisted for the remainder of the sampling period when K_2HPO_4 was added. Trimagnesium phosphate twenty-two hydrate was not detected in the Red River soil until the final sampling date (fifteen months) when KH_2PO_4 was added. Racz and Soper (25) reported the formation of trimagnesium phosphate twenty-two hydrate after ninety days incubation of dimagnesium phosphate trihydrate in a soil with a water soluble calcium to magnesium ratio of 0.69. These workers suggest that a phosphorus carrier acid in reaction (KH_2PO_4) will react with the soil to form dimagnesium phosphate trihydrate and dicalcium phosphate dihydrate while the less soluble trimagnesium phosphates and/or octacalcium phosphate will be more readily formed when an alkaline carrier (K_2HPO_4) is added. In the present study, the more insoluble trimagnesium phosphate did form more readily when K_2HPO_4 rather than KH_2PO_4 was added to the Red River soil.

The rate at which dicalcium phosphate dihydrate and dimagnesium phosphate trihydrate are converted to the less soluble forms (octacalcium phosphate, hydroxyapatite or trimagnesium phosphates) will affect the long-term availability of applied phosphorus fertiliser. Since dicalcium phosphate dihydrate and/or dimagnesium phosphate trihydrate persisted in the soils for a longer period of time when KH_2PO_4 rather than K_2HPO_4 was added, phosphorus from KH_2PO_4 would have a greater long-term availability than would phosphorus from K_2HPO_4.

Literature on the solubility or availability of the calcium-magnesium phosphate, $Ca_3Mg_3(PO_4)_4$, was not found. Thus, its solubility or availability compared to that of the calcium or magnesium phosphates has yet to be determined. A similar situation exists for the calcium phosphate, $Ca_4P_2O_9$. Thus, the solubility and/or availability of these phosphates need be determined in order that the behaviour of added phosphorus in soils such as those used in this study be known.

(2) Solubility Studies

The Solubility of KH_2PO_4 and K_2HPO_4 Added as Pellets to Each of the Four Soils

The use of solubility data in determining the forms and solubility of phosphorus in soils is beset by many problems and limitations. The extremely complex nature of the soil system necessitates certain assumptions when solubility data are used to describe the reactions of fertiliser phosphate in soils. Thus, prior to discussing the results of the solubility studies conducted, several limitations of the method used are discussed.

The total phosphorus concentration measured in the equilibrium solution is assumed to consist of the three orthophosphate species, H_2PO_4, HPO_4, and PO_4. The solubility of phosphorus in a soil is represented on the solubility diagram by the values of "$pH - 1/2pCa$" and "$pH_2PO_4 + 1/2pCa$". The value of the term, pH_2PO_4, depends upon the hydrogen ion activity and is related to the other orthophosphate species by the dissociation constants of phosphoric acid. However, the total phosphorus in solution, as measured experimentally, need not consist entirely of these inorganic ionic species. It is probable that colloidal clay particles, dispersed during the twenty-four hour period of water extraction, would not be removed from the supernatant by centrifugation and filtration through No. 42 filter paper. Phosphorus can be adsorbed by the clay fraction in soils (20). Phosphorus adsorbed on colloidal material would contribute to the total phosphorus concentration as determined by the Molybdenum-Blue Method of Jackson (13). However, such phosphorus is not in true solution. Hence it cannot be considered as originating from the crystalline reaction products.

Several workers have established the role of dissolved organic matter as a complexing agent for calcium in soil extracts. Such complexation leads to an over-estimation of the ion activity of calcium in the equilibrium solution (21).

In a mixed system as complex as that of the soil, an ion product point is rarely situated on one of the solubility isotherms constructed from data for pure compounds. Thus, when the point falls between the isotherms for DCPD and OCP, the system is said to be supersaturated with respect to OCP and/or HA and undersaturated with respect to DCPD. If the point should fall on the DCPD isotherm, OCP and/or HA may or may not be present. In either case, as long as the more soluble DCPD is present and dissolving, it will mask the presence of the less soluble compounds.

On the basis of the above considerations, the use of solubility data to describe the reactions of phosphorus in soil can be criticised. Nevertheless, solubility studies properly conducted and interpreted can be useful in determining the forms and availability of phosphorus in soils.

The solubility of phosphorus in the untreated soils was between that of OCP and HA, or near that of OCP (Table 4 and Figure 1). This indicates that OCP, or a phosphate with a solubility of less than that of OCP, governs the concentration of phosphorus in the soil solution.

The solubility of phosphorus, added as KH_2PO_4 or K_2HPO_4 pellets to the various soils, is shown in Tables 5 and 6 and in Figures 2 to 9 inclusive. The concentration of phosphorus in the equilibrium solution decreased as time of incubation increased for all soils and for both forms of phosphorus added. There was a simultaneous but gradual increase in pH in all systems. Concentrations of calcium and magnesium in the equilibrium solutions generally decreased as time of incubation increased. If soils are placed in order of decreasing equilibrium phosphorus concentration, the relative position of a given soil in the series varied as the incubation progressed. The concentrations of phosphorus at the final sampling date (fifteen months) was greatest in the Red River soil and least in the Darlingford when KH_2PO_4 was added. Phosphorus concentration in solution at the fifteen month sampling period was greatest in the Red River and least in the Aneda soil when K_2HPO_4 was added. Initially,

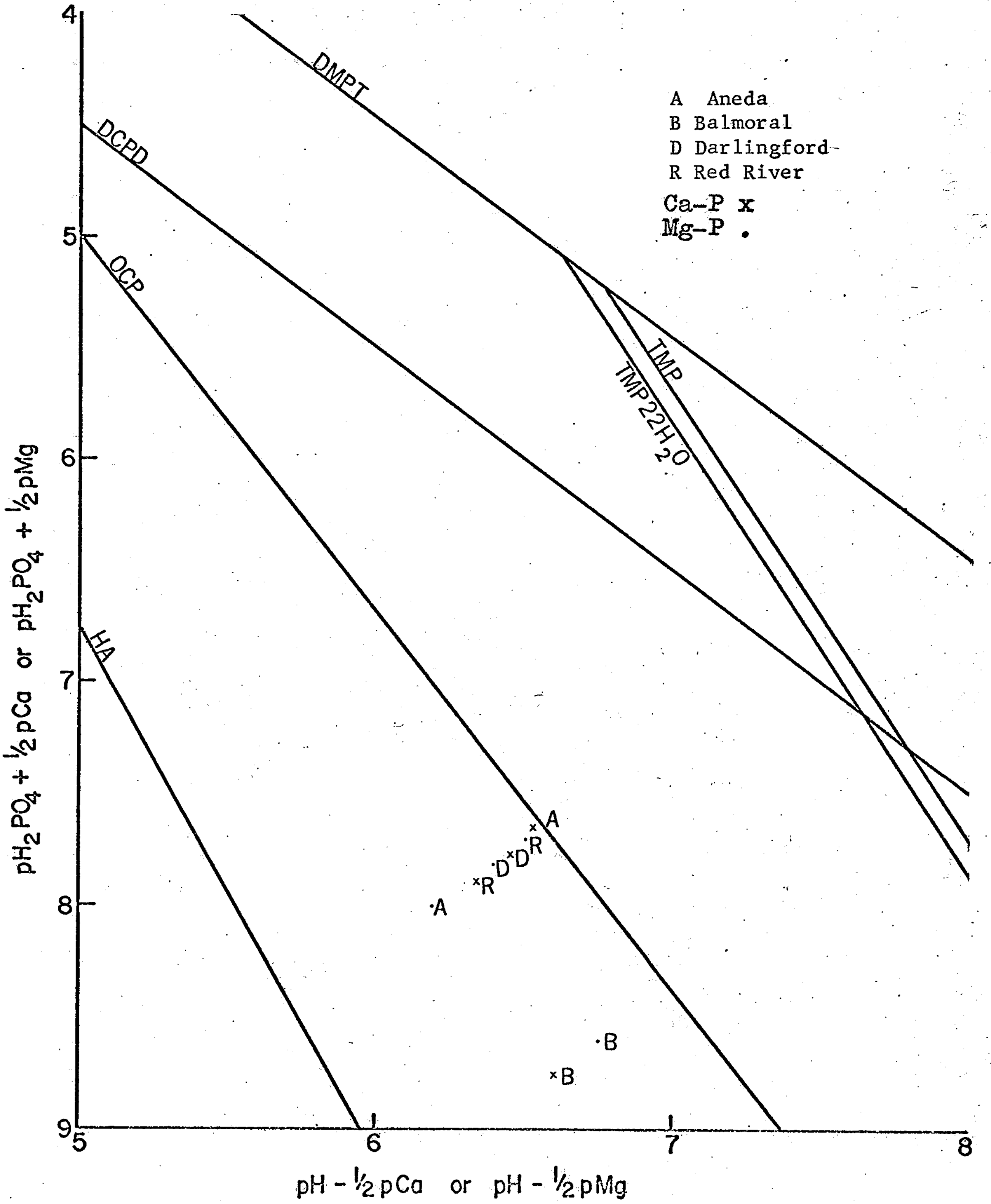

Figure 1. The Solubility of Phosphorus in Untreated Soils

Table 4. Ionic Concentrations and Activities, Lime and Phosphate Potentials of the Untreated Soils

Soil	pH	$[Ca] \times 10^3 M$	$[Mg] \times 10^3 M$	$[P] \times 10^3 M$	$\frac{1}{2}pCa$	$\frac{1}{2}pMg$	pH_2PO_4	$pH - \frac{1}{2}pCa$	$pH - \frac{1}{2}pMg$	$pH_2PO_4 + \frac{1}{2}pCa$	$pH_2PO_4 + \frac{1}{2}pMg$
Darlingford	8.05	0.788	0.606	0.009	1.60	1.66	6.15	6.44	6.38	7.75	7.81
Aneda	8.10	1.030	0.182	0.010	1.54	1.92	6.13	6.55	6.17	7.67	8.05
Balmoral	8.30	0.545	1.071	0.002	1.68	1.54	7.05	6.61	6.75	8.74	8.59
Red River	7.75	2.424	5.191	0.004	1.41	1.24	6.49	6.34	6.50	7.90	7.74

the pH of each of the treated soils was lower than the characteristic pH of the untreated soils. However, the same relative order between soils was maintained. Despite the gradual increase in pH with time, only the Red River soil treated with K_2HPO_4 regained the original pH value after fifteen months of incubation. The equilibrium phosphorus concentration at the fifteen month sampling period was lower when phosphorus was added as K_2HPO_4 rather than as KH_2PO_4 in the Aneda, Darlingford and Balmoral soils. However, in the Red River soil, the concentration of phosphorus was higher when K_2HPO_4 rather than KH_2PO_4 was added. In each of the four soils, the pH of the equilibrium system was higher when K_2HPO_4 rather than KH_2PO_4 was added. The equilibrium concentrations of calcium and magnesium were lower when K_2HPO_4 rather than KH_2PO_4 was added to the Aneda and Darlingford soils. The concentrations of calcium and magnesium did not vary greatly when K_2HPO_4 or KH_2PO_4 was added to the Balmoral soil. However, the addition of K_2HPO_4 to the Red River soil resulted in a higher equilibrium concentration of calcium and magnesium than did the addition of KH_2PO_4. The differences in the calcium and magnesium concentrations of the equilibrium solutions, noted for the two phosphate carriers added, decreased as time of incubation increased.

All soil systems were apparently undersaturated with respect to dimagnesium phosphate trihydrate (Figures 2 to 9). This compound, therefore, could theoretically play no dominant part in controlling the phosphorus levels in the soil solution. If the magnesium phosphates were present, (and X-ray data indicate that this was so), they were probably present in too small a quantity to exert their characteristic solubilities in the systems, despite the

Table 5. Ionic Concentrations and Activities, Lime and Phosphate Potentials of Soils Treated With a KH_2PO_4 Pellet

Soil	Incubation Period	pH	[Ca] $x10^3M$	[Mg] $x10^3M$	[P] $x10^3M$	½pCa	½pMg	pH_2PO_4	pH-½pCa	pH-½pMg	pH_2PO_4 +½pCa	pH_2PO_4 +½pMg
Aneda	1 day	7.55	0.990	0.323	1.038	1.58	1.82	3.64	5.96	5.72	5.22	5.47
	1 month	7.50	1.309	-▽	0.746	1.51	-	3.75	5.98	-	5.26	-
	3 months	7.50	1.076	-	0.575	1.54	-	3.85	5.95	-	5.40	-
	6 months	7.45	1.096	-	0.652	1.54	-	3.76	5.90	-	5.30	-
	9 months	7.75	0.812	0.103	0.386	1.60	2.05	4.21	6.14	5.69	5.81	6.26
	12 months	7.70	0.639	0.112	0.393	1.65	2.03	4.14	6.04	5.66	5.79	6.17
	15 months	7.65	1.050	0.344	0.393	1.55	1.79	4.15	6.09	5.85	5.71	5.95
Darlingford	1 day	7.40	0.646	0.566	1.257	1.67	1.70	3.44	5.72	5.69	5.12	5.15
	1 month	7.30	1.120	-	0.929	1.54	-	3.50	5.75	-	5.05	-
	3 months	7.36	1.000	-	0.801	1.56	-	3.60	5.79	-	5.17	-
	6 months	7.30	0.721	0.110	0.652	1.63	2.04	3.64	5.67	5.26	5.27	5.68
	9 months	7.65	0.650	0.060	0.334	1.64	2.16	4.17	6.00	5.48	5.81	6.33
	12 months	7.75	0.481	0.182	0.308	1.70	1.92	4.28	6.04	5.82	5.99	6.20
	15 months	7.60	0.525	0.344	0.284	1.69	1.78	4.22	5.90	5.81	5.91	6.00

▽ No Mg Detected

Table 5 continued.

Soil	Incubation Period	pH	$[Ca]$ $\times10^3$M	$[Mg]$ $\times10^3$M	$[P]$ $\times10^3$M	$\frac{1}{2}$pCa	$\frac{1}{2}$pMg	pH_2PO_4	pH-$\frac{1}{2}$pCa	pH-$\frac{1}{2}$pMg	pH_2PO_4 +$\frac{1}{2}$pCa	pH_2PO_4 +$\frac{1}{2}$pMg
Balmoral	1 day	7.95	0.747	1.293	1.386	1.66	1.54	3.90	6.28	6.40	5.56	5.44
	1 month	7.90	0.974	0.893	0.949	1.59	1.61	4.01	6.30	6.28	5.60	5.62
	3 months	7.98	0.944	0.315	0.526	1.58	1.82	4.30	6.40	6.16	5.88	6.12
	6 months	8.05	0.944	0.193	0.424	1.57	1.92	4.45	6.47	6.12	6.02	6.37
	9 months	8.25	0.741	0.254	0.323	1.62	1.85	4.74	6.62	6.39	6.36	6.59
	12 months	8.05	0.599	0.345	0.314	1.66	1.78	4.56	6.38	6.26	6.23	6.35
	15 months	7.90	0.646	0.909	0.314	1.66	1.58	4.48	6.24	6.31	6.14	6.06
Red River	1 day	6.95	3.232	6.444	1.597	1.36	1.21	3.29	5.58	5.73	4.66	4.51
	1 month	7.20	5.900	4.500	0.855	1.23	1.29	3.75	5.96	5.90	4.99	5.04
	3 months	7.23	3.100	2.500	0.484	1.35	1.39	3.92	5.87	5.83	5.27	5.32
	6 months	7.30	1.100	1.000	0.718	1.55	1.57	3.67	5.74	5.72	5.23	5.25
	9 months	7.50	0.530	0.510	0.497	1.69	1.70	3.91	5.80	5.79	5.61	5.62
	12 months	7.55	0.487	0.528	0.535	1.71	1.70	3.91	5.83	5.84	5.63	5.61
	15 months	7.50	0.202	1.151	0.584	1.91	1.53	3.86	5.58	5.96	5.78	5.40

Table 6. Ionic Concentrations and Activities, Lime and Phosphate Potentials of Soils Treated With a K_2HPO_4 Pellet

Soil	Incubation Period	pH	$[Ca] \times 10^3 M$	$[Mg] \times 10^3 M$	$[P] \times 10^3 M$	$\frac{1}{2}pCa$	$\frac{1}{2}pMg$	pH_2PO_4	$pH-\frac{1}{2}pCa$	$pH-\frac{1}{2}pMg$	$pH_2PO_4+\frac{1}{2}pCa$	$pH_2PO_4+\frac{1}{2}pMg$
Aneda	1 day	7.80	0.586	0.404	0.851	1.69	1.77	3.91	6.11	6.02	5.60	5.68
	1 month	7.65	0.893	0.061	0.452	1.58	2.16	4.06	6.06	5.48	5.64	6.23
	3 months	7.75	0.822	-▽	0.159	1.59	-	4.58	6.15	-	6.18	-
	6 months	7.75	0.802	0.050	0.179	1.59	2.20	4.54	6.15	5.54	6.13	6.74
	9 months	8.00	0.731	0.142	0.116	1.61	1.97	4.94	6.38	6.02	6.56	6.92
	12 months	7.85	0.467	0.244	0.112	1.71	1.85	4.81	6.14	5.99	6.52	6.66
	15 months	7.75	0.687	0.788	0.126	1.64	1.61	4.74	6.11	6.14	6.38	6.35
Darlingford	1 day	7.55	0.505	0.424	1.492	1.73	1.77	3.46	5.81	5.77	5.20	5.24
	1 month	7.50	0.924	-	0.884	1.58	-	3.65	5.91	-	5.23	-
	3 months	7.55	0.770	-	0.439	1.61	-	3.98	5.93	-	5.59	-
	6 months	7.55	0.751	-	0.386	1.61	-	4.03	5.93	-	5.65	-
	9 months	7.75	0.650	-	0.303	1.64	-	4.29	6.10	-	5.93	-
	12 months	7.80	0.538	0.131	0.247	1.68	1.99	4.42	6.11	5.81	6.10	6.41
	15 months	7.60	0.485	0.363	0.241	1.70	1.77	4.29	5.89	5.82	5.99	6.06

▽ No Mg Detected

Table 6 continued.

Soil	Incubation Period	pH	[Ca] x10^3M	[Mg] x10^3M	[P] x10^3M	$\frac{1}{2}$pCa	$\frac{1}{2}$pMg	pH_2PO_4	pH-$\frac{1}{2}$pCa	pH-$\frac{1}{2}$pMg	pH_2PO_4 +$\frac{1}{2}$pCa	pH_2PO_4 +$\frac{1}{2}$pMg
Balmoral	1 day	8.10	0.889	0.687	1.159	1.61	1.67	4.08	6.48	6.42	5.70	5.76
	1 month	8.05	0.863	0.812	0.684	1.61	1.62	4.28	6.44	6.42	5.89	5.90
	3 months	8.10	0.903	0.244	0.412	1.58	1.87	4.51	6.51	6.22	6.09	6.38
	6 months	7.85	0.985	0.477	0.387	1.56	1.72	4.33	6.28	6.12	5.90	6.06
	9 months	8.25	0.873	0.203	0.323	1.58	1.90	4.75	6.66	6.34	6.33	6.65
	12 months	8.10	0.548	0.437	0.320	1.68	1.73	4.60	6.41	6.36	6.29	6.34
	15 months	7.95	0.586	0.666	0.296	1.67	1.64	4.52	6.27	6.30	6.20	6.17
Red River	1 day	7.45	2.646	5.232	1.411	1.41	1.26	3.67	6.03	6.19	5.08	4.93
	1 month	7.40	6.900	3.000	1.162	1.20	1.38	3.76	6.19	6.01	4.97	5.15
	3 months	7.42	2.900	1.800	0.730	1.36	1.47	3.85	6.05	5.95	5.22	5.32
	6 months	7.30	1.200	0.500	0.750	1.53	1.72	3.63	5.76	5.57	5.16	5.36
	9 months	7.50	0.770	0.550	0.968	1.63	1.70	3.64	5.86	5.79	5.27	5.34
	12 months	7.70	0.467	0.650	1.018	1.74	1.67	3.76	5.95	6.02	5.50	5.43
	15 months	7.75	0.545	0.627	0.936	1.71	1.67	3.84	6.04	6.07	5.55	5.52

fact that, in pure systems, they are more soluble than the corresponding calcium phosphates. However, it is probable that the apparent undersaturation with respect to DMPT was the result of a secondary precipitation, phosphorus from DMPT being precipitated by soil calcium as a calcium phosphate (26).

All soil systems were supersaturated with respect to DCPD at the initial sampling periods. This situation existed for varying periods of time, depending upon the soil type and the phosphorus carrier added. This apparent supersaturation with respect to DCPD suggests that some other compound, more soluble than DCPD, may have been controlling the level of phosphorus in the soil solution. This may have been due to the presence of DMPT in some of the soils and/or to a partial complexing of calcium by soil organic matter (21). It is also possible that phosphorus from sources other than the crystalline solid phase phosphates was present (20).

The Darlingford soil was supersaturated with respect to DCPD for three months and one month, respectively, when KH_2PO_4 and K_2HPO_4 were added (Figures 2 and 3). Supersaturation with respect to DCPD was still evident in the Aneda soil at the six months sampling period when KH_2PO_4 was added, but was apparent at the one day sampling period only when K_2HPO_4 was added (Figures 4 and 5). It is evident that, immediately after treatment with either KH_2PO_4 or K_2HPO_4, the Balmoral soil yielded extracts which appear supersaturated with respect to DCPD (Figures 6 and 7). After three months of incubation, the system to which KH_2PO_4 was added was in equilibrium with DCPD. However, at this stage, the system to which K_2HPO_4 was added was already undersaturated with respect to DCPD. Supersaturation with

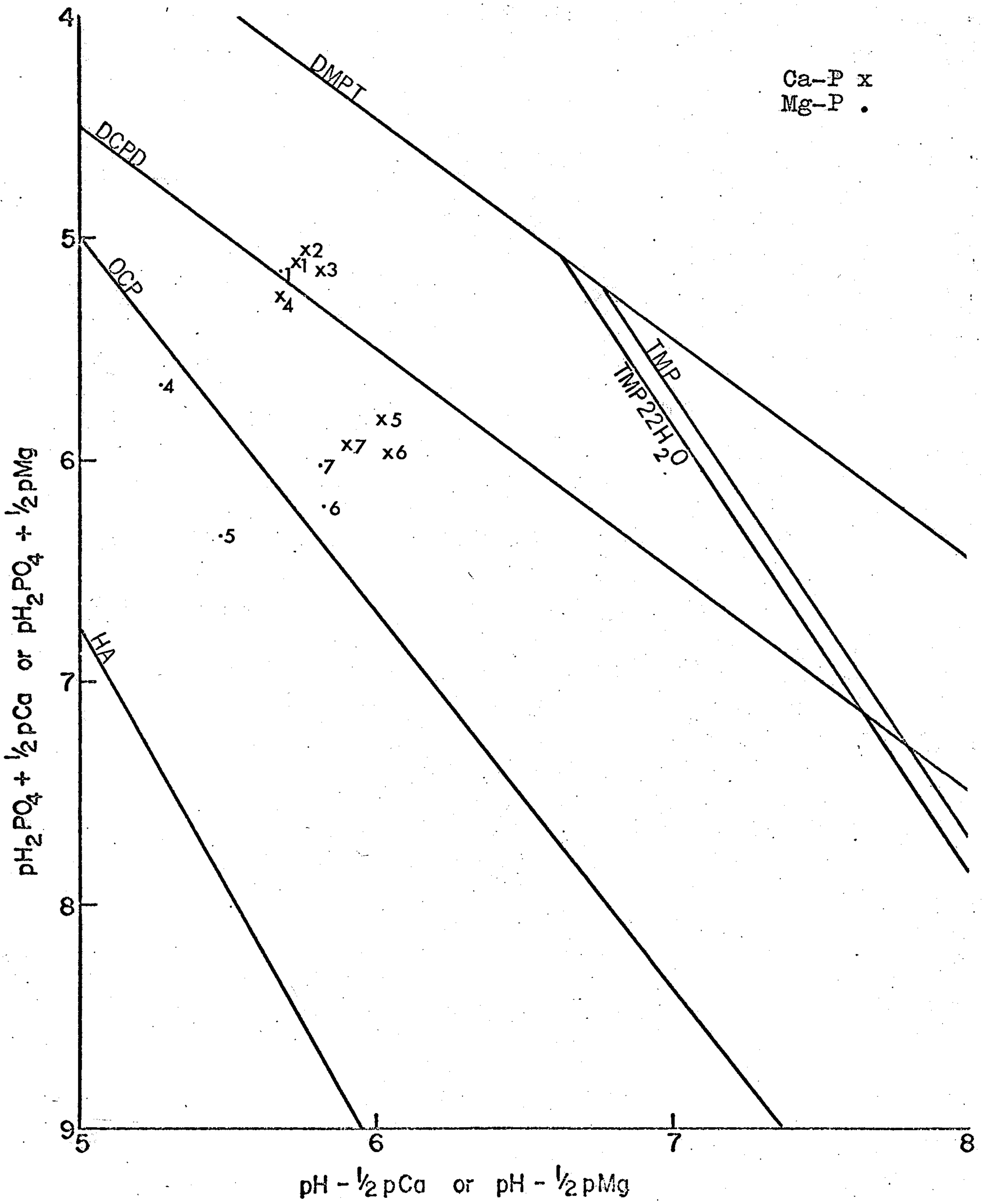

Figure 2. Solubility of KH_2PO_4 Added As a Pellet to the Darlingford Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

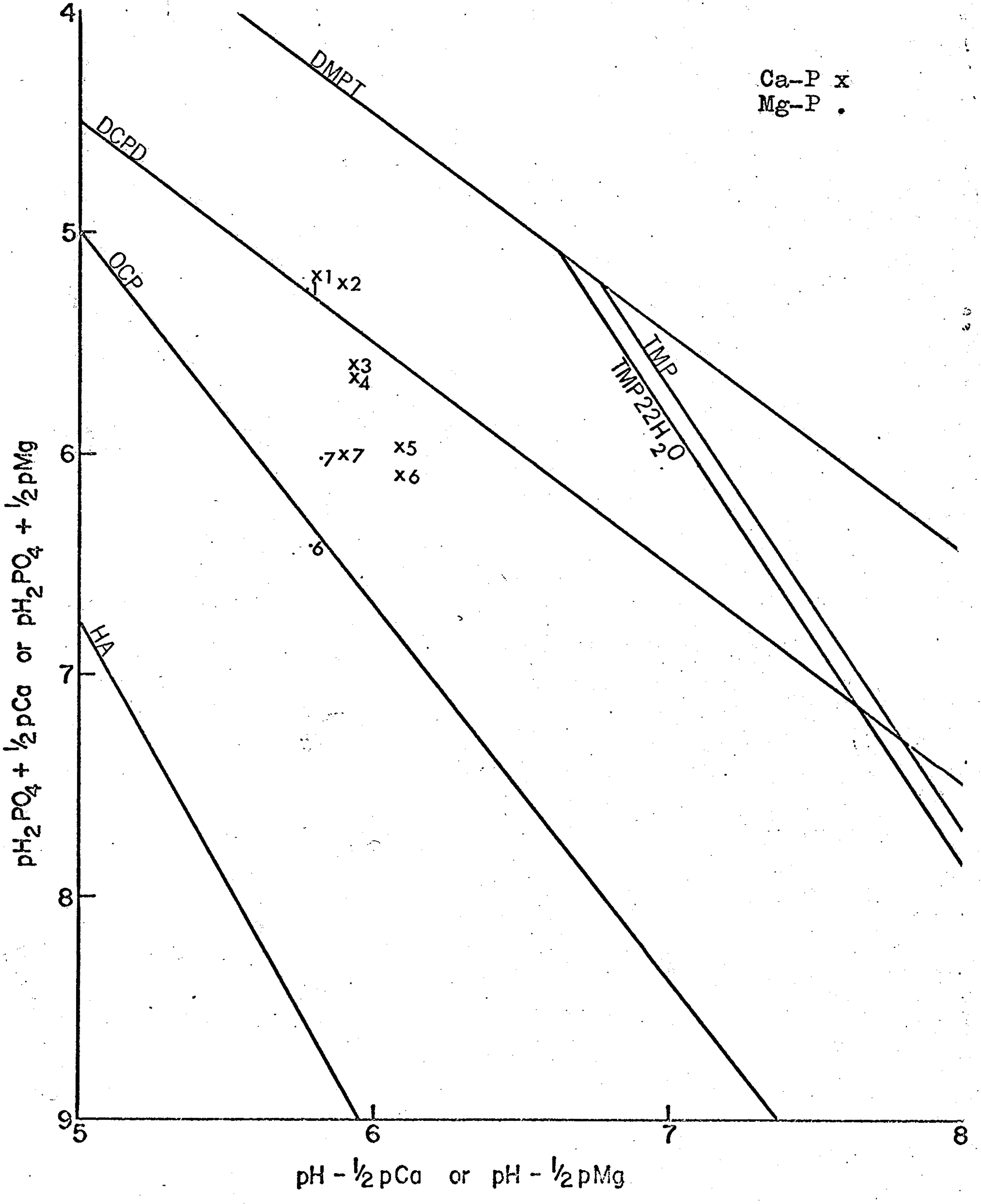

Figure 3. Solubility of K_2HPO_4 Added As a Pellet to the Darlingford Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

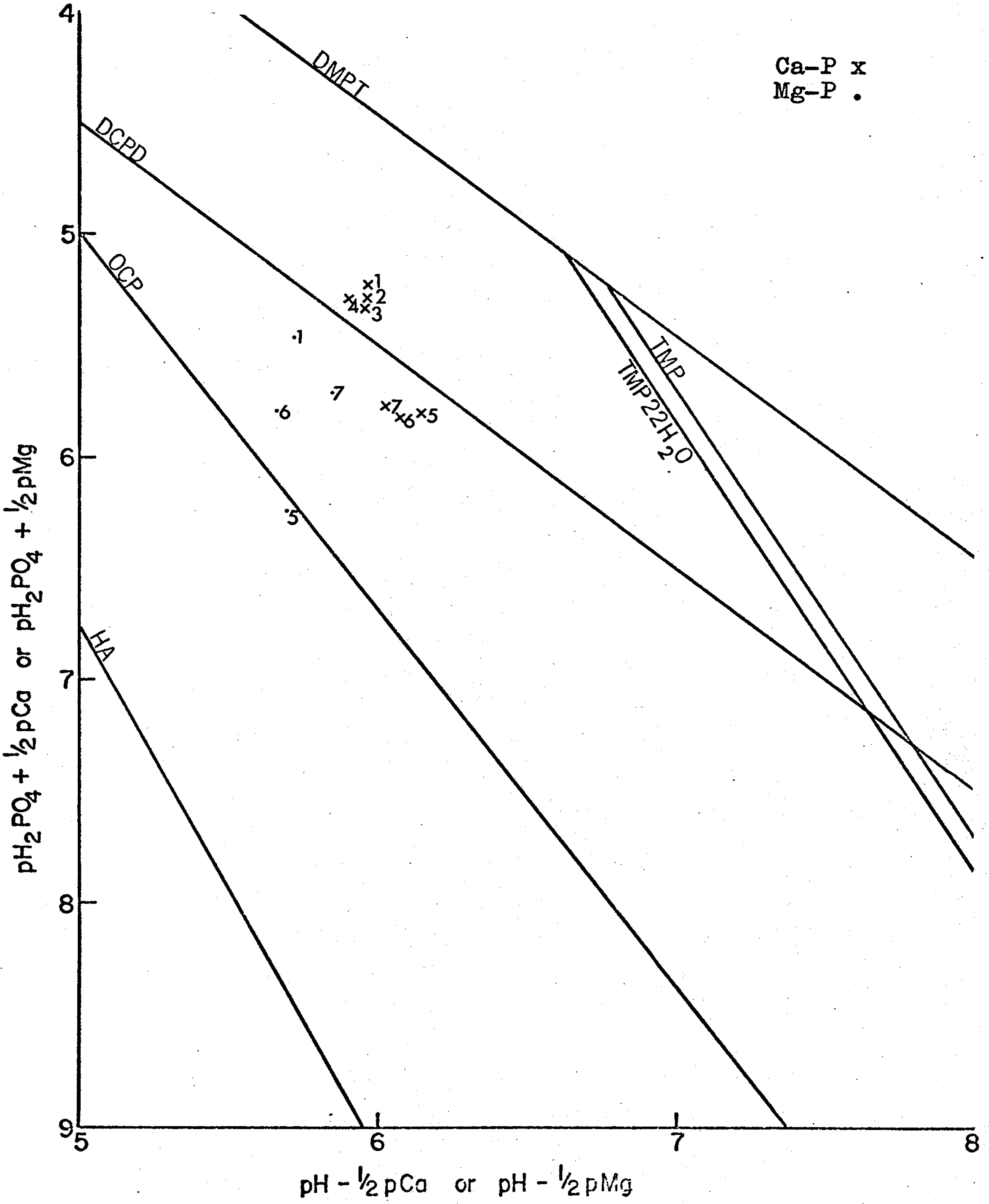

Figure 4. Solubility of KH_2PO_4 Added As a Pellet to the Aneda Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

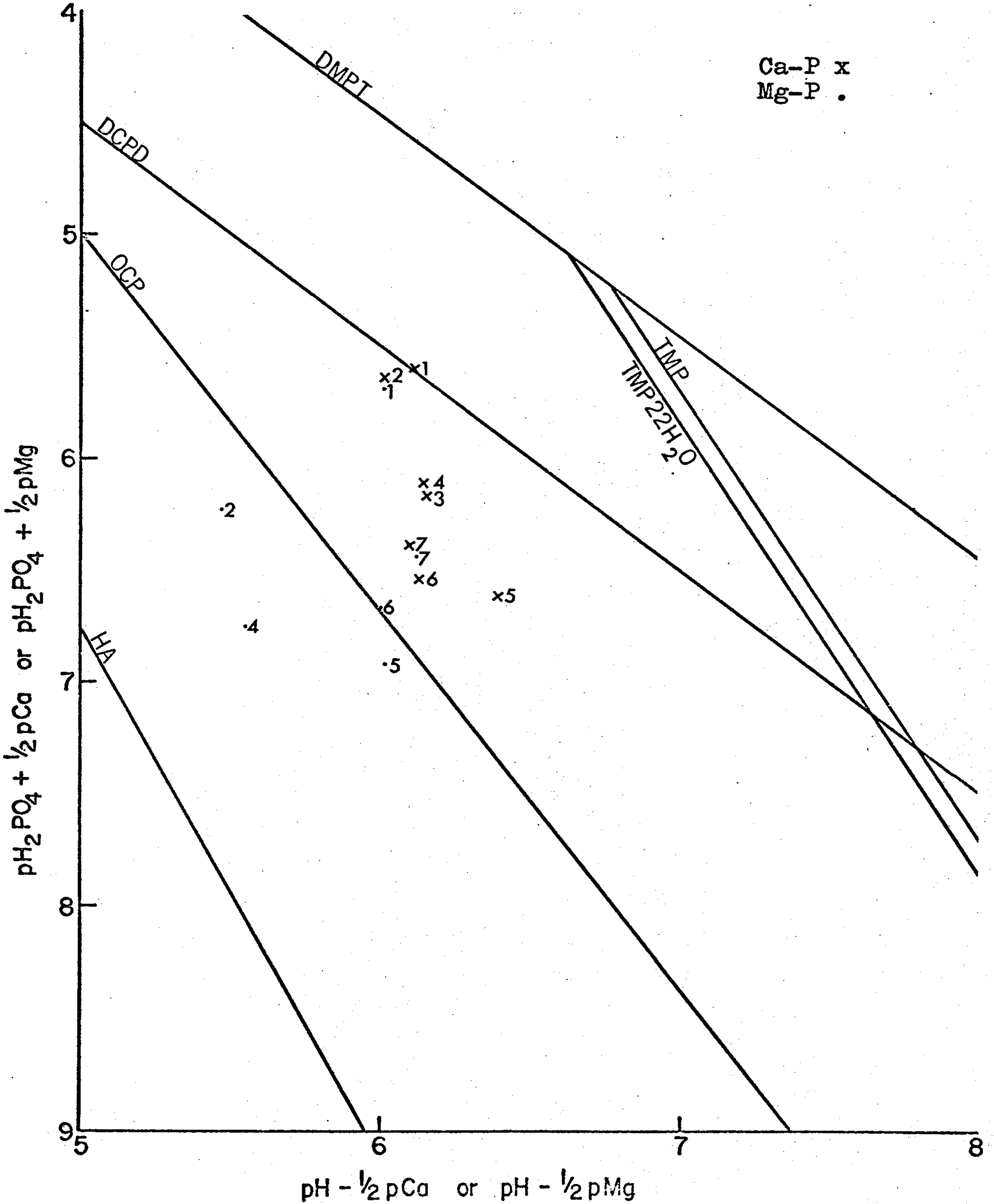

Figure 5. Solubility of K_2HPO_4 Added As a Pellet to the Aneda Soil at 1 day (1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

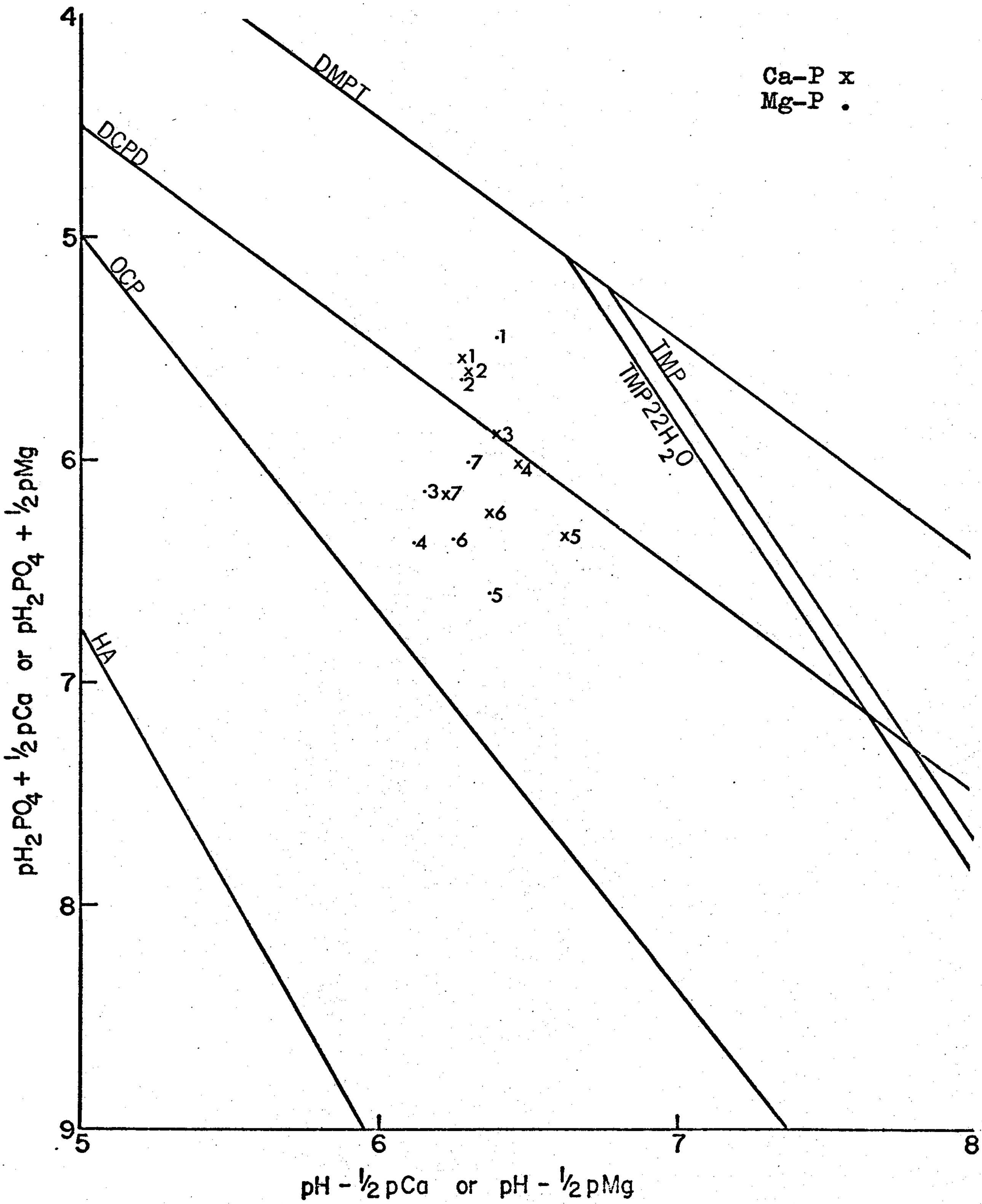

Figure 6. Solubility of KH_2PO_4 Added As a Pellet to the Balmoral Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

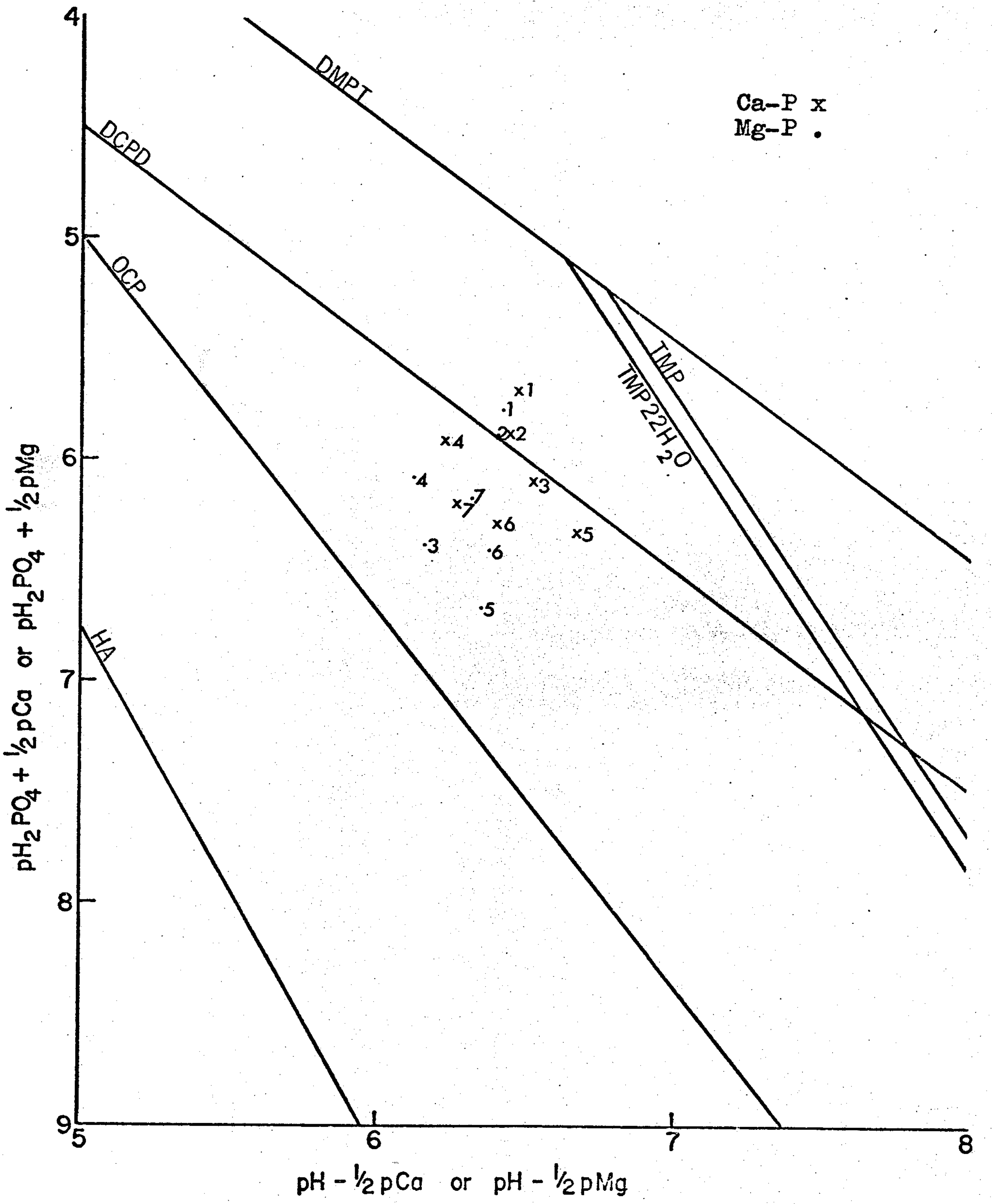

Figure 7. Solubility of K_2HPO_4 Added As a Pellet to the Balmoral Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

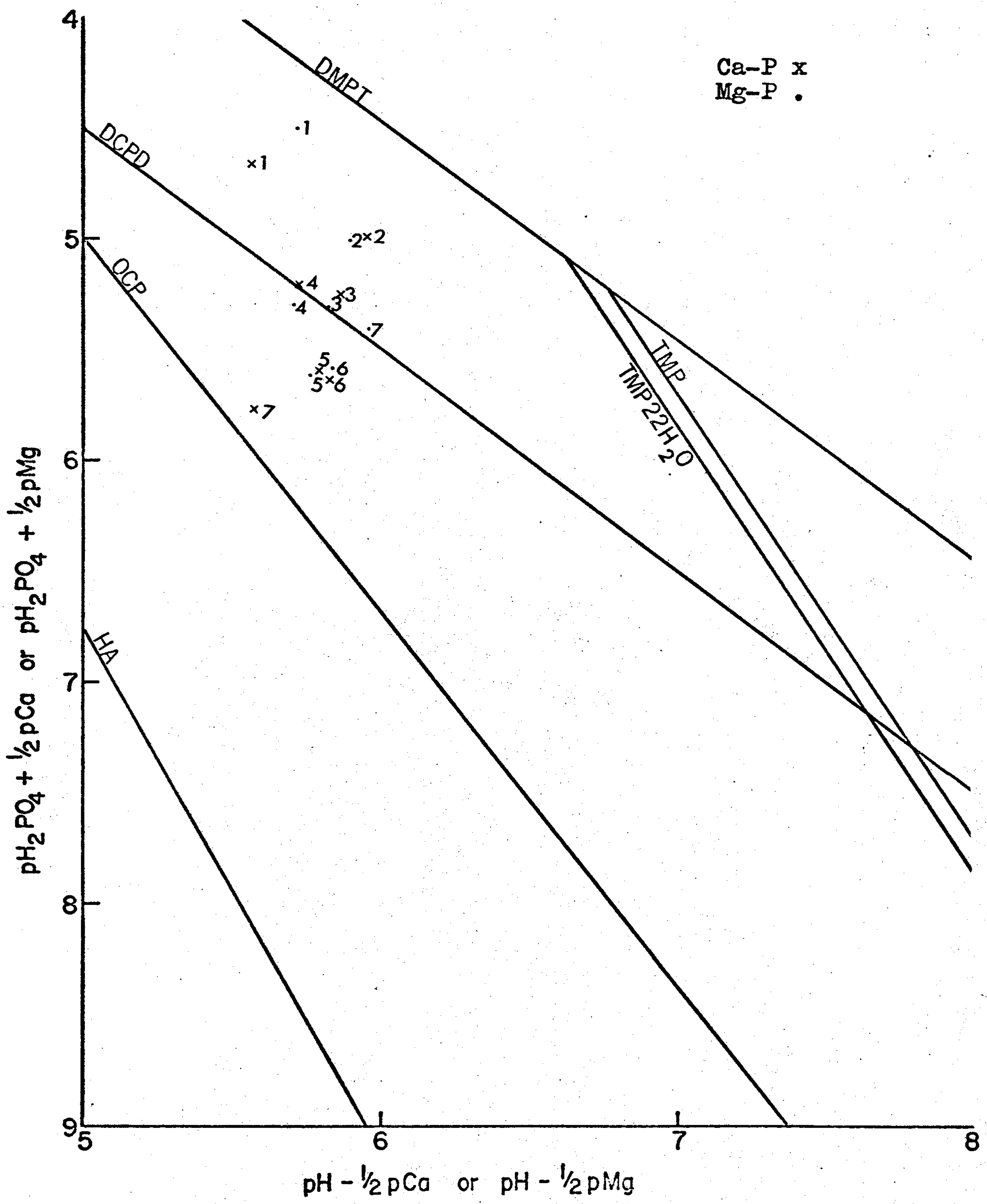

Figure 8. Solubility of KH_2PO_4 Added As a Pellet to the Red River Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

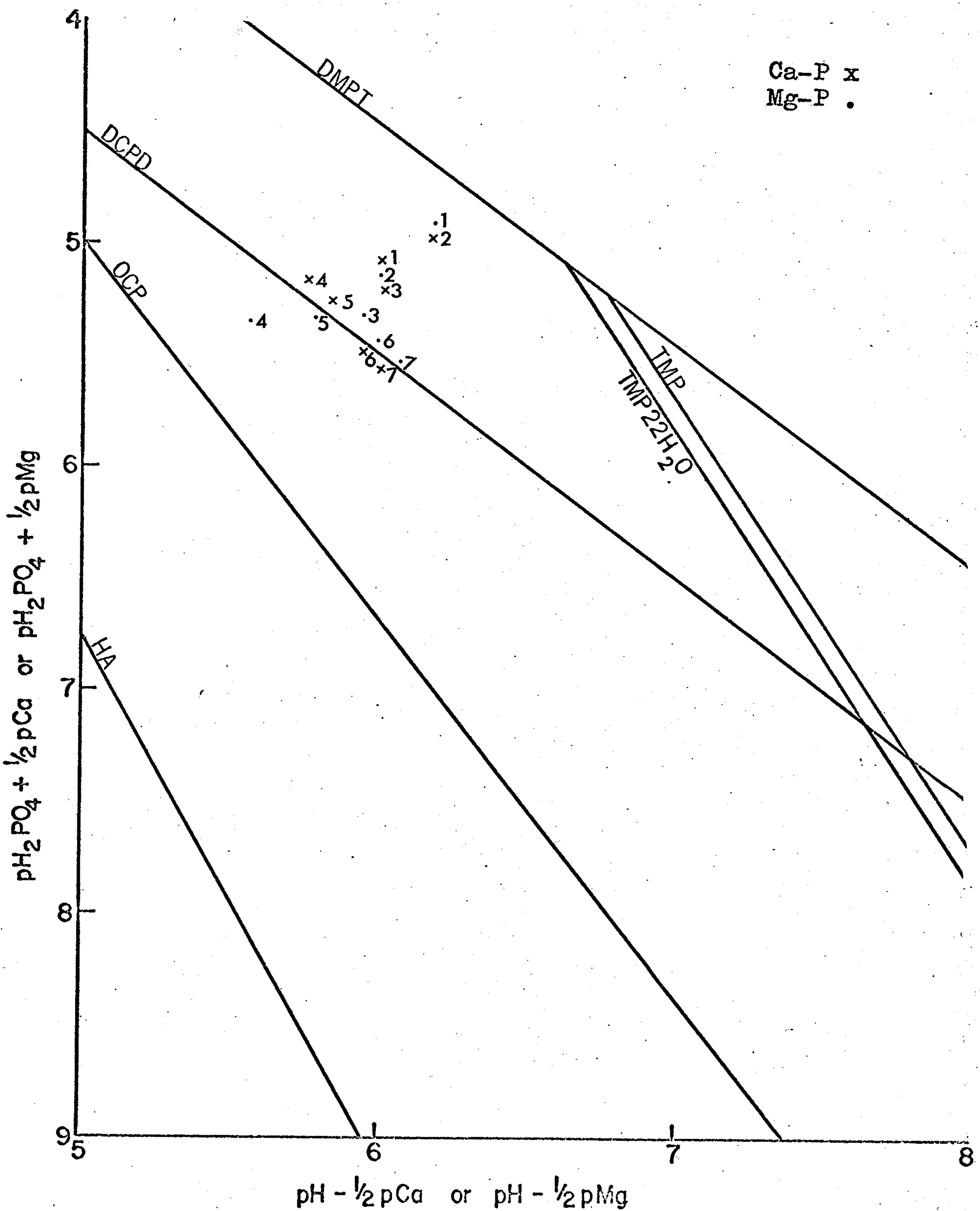

Figure 9. Solubility of K_2HPO_4 Added As a Pellet to the Red River Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

respect to DCPD existed in the Red River soil for a period of nine months when K_2HPO_4 was added. The soil solution was in equilibrium with DCPD at the six months sampling period when KH_2PO_4 was added (Figures 8 and 9). It appears that, in this soil, K_2HPO_4 yielded products which are more soluble than those produced by the addition of KH_2PO_4. This is in contrast to the behaviour exhibited by these carriers in the soils previously discussed, where, in general, phosphorus remained more soluble when added as KH_2PO_4 rather than as K_2HPO_4. This difference in behaviour between phosphorus carriers in the Red River soil was previously evident from consideration of the equilibrium phosphorus concentrations.

Since the Red River soil had a water-soluble calcium to magnesium ratio of 0.37, the magnesium ion products might be expected to be of greater significance in the Red River soil than in the other three soils. The solubility values for the magnesium ion products were relatively close to the DMPT isotherm for the samples taken one day and one month after the addition of KH_2PO_4 or K_2HPO_4. Therefore, while saturation with DMPT was not achieved, it is evident that DMPT may be greatly influencing the solubility of phosphorus in this soil. X-ray data showed that DMPT was present in the soil throughout the entire sampling period when K_2HPO_4 and KH_2PO_4 were added. Thus, in soils such as the Red River, the role of magnesium phosphates in governing the concentration of phosphorus in the soil solution cannot be ignored.

The subsequent solubility values for all soil systems indicated that the solubility of added phosphorus remained between that of DCPD and OCP for the remainder of the sampling period. Lindsay and Taylor (18) suggest that localized mixtures of DCPD and OCP, derived from the original fertiliser, may persist in the soil for months or even years. These workers have shown that finely-divided OCP has an availability of about eighty percent of that of monocalcium phosphate.

Huffman (12) suggests that the highly insoluble phosphates, such as OCP, attain equilibrium with solution extremely slowly. OCP is metastable with respect to the apatites and hydroxyapatite (HA) is generally considered to be the end-product of hydrolysis of phosphate fertiliser in neutral and alkaline soils. However, in this study, all systems were still supersaturated with respect to OCP. Even after incubation for fifteen months, the solubility of the added phosphorus was much greater than that of the untreated soils. This would indicate that phosphorus added in pellet form as KH_2PO_4 or as K_2HPO_4 to soils such as those used in this study would remain available for a long period of time.

The Solubility of KH_2PO_4 and K_2HPO_4 Added in Solution and Mixed with Each of the Four Soils

The solubility of KH_2PO_4 and K_2HPO_4 when added in solution form and mixed with the four soils is given in Tables 7 to 10 and Figures 10 to 17, inclusive.

The concentration of phosphorus in the soil solution increased with increased rate of phosphorus added and decreased with time of incubation. For a particular soil, and for a particular rate of phosphorus added, the concentrations of phosphorus in the equilibrium solutions were very similar whether phosphorus was added as KH_2PO_4 or as K_2HPO_4. The concentrations of calcium and magnesium in the soil solution did not vary greatly as time of incubation progressed. For a particular soil, the concentrations of calcium and magnesium in the soil solution were quite similar regardless of the amount of phosphorus added. Therefore, the amounts of calcium and magnesium with respect to phosphorus in the equilibrium solution when 100 ppm phosphorus was added was greater than when 400 ppm phosphorus was added. This indicates that the phosphorus compounds controlling the system when 100 ppm phosphorus was added were probably richer in calcium and/or magnesium than the compounds formed when 400 ppm phosphorus was added. The pH values of the soils treated with K_2HPO_4 and KH_2PO_4 were very similar. This is in contrast to the results obtained when these phosphates were added as pellets where the pH of the soils treated with K_2HPO_4 were slightly higher than those for the soils treated with KH_2PO_4. Adding the phosphate in pellet form results in a very large amount of phosphorus in a small volume of soil, thus the phosphate added changes the pH of the soil within that small volume. However, mixing the 100 or 400 ppm phosphorus throughout the soil as KH_2PO_4 or K_2HPO_4 was insufficient to alter the soil pH. There were noticeable changes in pH of the equilibrium solutions for several of the soils with time of incubation. A clear trend for the soils, however, was not evident. The fluctuations in the pH of the equilibrating solutions were probably due to changes in the carbon dioxide content of the soils during incubation.

The solubility of phosphorus did not approach that of DCPD in any soil system when 100 ppm phosphorus was added (Figures 10 to 17). The solubility of phosphorus added either as K_2HPO_4 or as KH_2PO_4 (100 ppm P) remained between that of OCP and DCPD for the entire sampling period in the Darlingford and Aneda soils. The systems were in equilibrium with OCP at the twelve months sampling period when KH_2PO_4 or K_2HPO_4 was added to the Balmoral

Table 7. Ionic Concentrations and Activities, Lime and Phosphate Potentials of the Darlingford Soil Mixed With Solutions of KH_2PO_4 and K_2HPO_4

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] x10^{3}M	[Mg] x10^{3}M	[P] x10^{3}M	$\frac{1}{2}$pCa	$\frac{1}{2}$pMg	pH_2PO_4	pH-$\frac{1}{2}$pCa	pH-$\frac{1}{2}$pMg	pH_2PO_4 +$\frac{1}{2}$pCa	pH_2PO_4 +$\frac{1}{2}$pMg
K_2HPO_4	100	1 day	8.05	0.914	-[▽]	0.093	1.56	-	5.09	6.48	-	6.66	-
		1 month	8.00	0.995	0.030	0.136	1.55	2.31	4.89	6.44	5.68	6.44	7.20
		3 months	7.95	0.903	0.030	0.064	1.56	2.30	5.16	6.38	5.64	6.73	7.47
		6 months	8.15	1.035	0.021	0.053	1.54	2.38	5.44	6.60	5.76	6.98	7.83
		9 months	7.10	0.914	0.060	0.053	1.56	2.15	4.62	5.53	4.94	6.19	6.78
		12 months	7.75	0.842	0.173	0.061	1.58	1.93	5.02	6.16	5.82	6.60	6.95
		15 months	7.70	0.889	0.303	0.056	1.57	1.81	5.03	6.12	5.88	6.61	6.84
	400	1 day	7.85	0.914	0.081	0.592	1.58	2.11	4.11	6.26	5.73	5.70	6.22
		1 month	7.85	0.873	0.315	0.497	1.59	1.81	4.20	6.25	6.03	5.80	6.02
		3 months	7.70	0.995	-	0.360	1.55	-	4.20	6.14	-	5.76	-
		6 months	7.90	0.974	-	0.293	1.56	-	4.46	6.33	-	6.02	-
		9 months	6.90	0.822	0.193	0.237	1.59	1.90	3.88	5.30	4.99	5.47	5.79
		12 months	7.60	0.741	0.233	0.365	1.62	1.87	4.12	5.97	5.72	5.74	5.99
		15 months	7.65	0.747	0.283	0.290	1.61	1.83	4.26	6.03	5.82	5.88	6.09

[▽] No Mg Detected

Table 7 continued.

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] x10^3M	[Mg] x10^3M	[P] x10^3M	½pCa	½pMg	pH_2PO_4	pH-½pCa	pH-½pMg	pH_2PO_4 +½pCa	pH_2PO_4 +½pMg
KH_2PO_4	100	1 day	8.00	0.832	0.041	0.102	1.58	2.24	5.00	6.41	5.75	6.59	7.24
		1 month	7.80	1.035	0.142	0.075	1.54	1.97	4.98	6.25	5.82	6.53	6.96
		3 months	8.15	1.035	0.020	0.066	1.54	2.40	5.34	6.60	5.75	6.88	7.74
		6 months	8.05	1.035	-▽	0.056	1.54	-	5.32	6.50	-	6.86	-
		9 months	7.50	0.853	0.223	0.054	1.58	1.87	4.88	5.91	5.62	6.46	6.75
		12 months	7.70	0.893	0.061	0.056	1.57	2.15	5.01	6.12	5.54	6.58	7.16
		15 months	7.70	0.747	0.425	0.057	1.61	1.73	5.02	6.08	5.96	6.63	6.76
	400	1 day	7.75	0.934	0.020	0.608	1.57	2.41	4.01	6.17	5.33	5.59	6.43
		1 month	7.60	0.893	0.193	0.460	1.58	1.92	4.02	6.01	5.68	5.61	5.94
		3 months	8.00	1.015	-	0.425	1.55	-	4.39	6.42	-	5.95	-
		6 months	7.85	1.015	-	0.231	1.55	-	4.52	6.29	-	6.08	-
		9 months	7.05	0.914	0.142	0.292	1.57	1.97	3.86	5.47	5.07	5.43	5.84
		12 months	7.60	0.903	0.153	0.259	1.57	1.96	4.27	6.02	5.63	5.85	6.23
		15 months	7.55	0.828	0.283	0.259	1.59	1.83	4.24	5.95	5.72	5.83	6.07

▽No Mg Detected

Table 8. Ionic Concentrations and Activities, Lime and Phosphate Potentials of the Aneda Soil Mixed With Solutions of KH_2PO_4 and K_2HPO_4

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] $\times 10^3$M	[Mg] $\times 10^3$M	[P] $\times 10^3$M	$\frac{1}{2}$pCa	$\frac{1}{2}$pMg	pH_2PO_4	pH-$\frac{1}{2}$pCa	pH-$\frac{1}{2}$pMg	pH_2PO_4 +$\frac{1}{2}$pCa	pH_2PO_4 +$\frac{1}{2}$pMg
K_2HPO_4	100	1 day	8.00	0.974	-▽	0.044	1.55	-	5.37	6.44	-	6.93	-
		1 month	8.15	1.340	-	0.024	1.49	-	5.81	6.66	-	7.30	-
		3 months	8.05	1.117	-	0.022	1.52	-	5.73	6.52	-	7.26	-
		6 months	8.10	1.238	-	0.025	1.50	-	5.74	6.59	-	7.24	-
		9 months	7.95	1.030	0.112	0.028	1.54	2.02	5.54	6.40	5.92	7.09	7.57
		12 months	7.90	0.974	0.143	0.042	1.55	1.97	5.32	6.34	5.92	6.87	7.29
		15 months	7.90	0.808	0.242	0.033	1.59	1.85	5.42	6.30	6.04	7.01	7.27
	400	1 day	7.85	1.577	-	0.271	1.46	-	4.50	6.38	-	5.96	-
		1 month	8.05	1.096	0.081	0.200	1.53	2.10	4.78	6.51	5.94	6.31	6.88
		3 months	7.90	1.117	-	0.142	1.52	-	4.79	6.37	-	6.32	-
		6 months	8.05	1.076	-	0.138	1.53	-	4.93	6.51	-	6.47	-
		9 months	7.55	1.015	0.041	0.154	1.54	2.24	4.46	6.00	5.30	6.01	6.71
		12 months	7.85	0.944	0.010	0.149	1.56	2.55	4.71	6.28	5.29	6.27	7.26
		15 months	7.90	0.727	0.263	0.161	1.62	1.84	4.72	6.27	6.05	6.34	6.56

▽ No Mg Detected

Table 8 continued.

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] x10^{3}M	[Mg] x10^{3}M	[P] x10^{3}M	½pCa	½pMg	pH$_2$PO$_4$	pH-½pCa	pH-½pMg	pH$_2$PO$_4$ +½pCa	pH$_2$PO$_4$ +½pMg
KH$_2$PO$_4$	100	1 day	8.05	1.157	0.041	0.042	1.52	2.24	5.46	6.53	5.80	6.98	7.71
		1 month	8.00	1.269	0.111	0.031	1.50	2.03	5.56	6.49	5.96	7.06	7.59
		3 months	7.90	1.543	-▽	0.022	1.46	-	5.63	6.43	-	7.10	-
		6 months	8.15	1.096	-	0.023	1.52	-	5.81	6.62	-	7.33	-
		9 months	7.60	1.096	0.021	0.027	1.52	2.38	5.26	6.07	5.21	6.79	7.65
		12 months	7.75	1.035	-	0.030	1.54	-	5.33	6.20	-	6.87	-
		15 months	7.90	0.929	0.162	0.035	1.56	1.94	5.40	6.33	5.95	6.96	7.34
	400	1 day	7.70	1.567	0.057	0.360	1.46	2.19	4.25	6.23	5.51	5.72	6.44
		1 month	8.00	1.248	0.031	0.221	1.51	2.31	4.70	6.49	5.68	6.21	7.01
		3 months	8.10	1.259	-	0.129	1.50	-	5.02	6.59	-	6.53	-
		6 months	8.10	0.995	-	0.125	1.55	-	5.01	6.54	-	6.57	-
		9 months	7.55	1.096	-	0.143	1.53	-	4.49	6.01	-	6.03	-
		12 months	7.70	0.944	0.071	0.141	1.56	2.12	4.61	6.13	5.57	6.18	6.74
		15 months	7.90	0.747	0.283	0.145	1.61	1.82	4.77	6.28	6.07	6.39	6.60

▽No Mg Detected

Table 9. Ionic Concentrations and Activities, Lime and Phosphate Potentials of the Balmoral Soil

Mixed With Solutions of KH_2PO_4 and K_2HPO_4

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] $x10^3$M	[Mg] $x10^3$M	[P] $x10^3$M	½pCa	½pMg	pH_2PO_4	pH-½pCa	pH-½pMg	pH_2PO_4 +½pCa	pH_2PO_4 +½pMg
K_2HPO_4	100	1 day	8.20	0.924	0.456	0.027	1.57	1.72	5.81	6.62	6.47	7.38	7.53
		1 month	8.20	0.934	0.436	0.019	1.56	1.73	5.96	6.63	6.46	7.53	7.69
		3 months	8.25	0.914	0.710	0.016	1.57	1.63	6.10	6.67	6.61	7.68	7.73
		6 months	8.35	1.096	0.345	0.026	1.53	1.78	5.97	6.81	6.56	7.51	7.76
		9 months	7.70	0.974	0.711	0.016	1.56	1.63	5.61	6.13	6.06	7.17	7.24
		12 months	8.10	0.731	0.954	0.023	1.62	1.56	5.81	6.47	6.53	7.43	7.38
		15 months	8.20	0.646	0.990	0.017	1.65	1.56	6.03	6.54	6.64	7.68	7.59
	400	1 day	8.20	1.340	0.345	0.276	1.50	1.79	4.82	6.69	6.40	6.32	6.62
		1 month	8.05	0.893	0.437	0.211	1.58	1.73	4.77	6.46	6.31	6.35	6.51
		3 months	8.25	1.025	0.498	0.156	1.55	1.71	5.10	6.69	6.53	6.66	6.81
		6 months	8.35	0.741	0.538	0.180	1.62	1.69	5.11	6.72	6.65	6.74	6.81
		9 months	7.60	0.873	0.629	0.156	1.58	1.66	4.52	6.01	5.94	6.11	6.18
		12 months	8.20	0.761	0.822	0.173	1.62	1.60	5.01	6.57	6.59	6.64	6.62
		15 months	8.15	0.485	0.949	0.145	1.71	1.57	5.03	6.43	6.58	6.75	6.60

Table 9 continued.

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] $\times 10^3$M	[Mg] $\times 10^3$M	[P] $\times 10^3$M	$\frac{1}{2}$pCa	$\frac{1}{2}$pMg	pH_2PO_4	pH-$\frac{1}{2}$pCa	pH-$\frac{1}{2}$pMg	pH_2PO_4 +$\frac{1}{2}$pCa	pH_2PO_4 +$\frac{1}{2}$pMg
KH_2PO_4	100	1 day	8.20	0.984	0.538	0.024	1.56	1.69	5.87	6.64	6.50	7.43	7.56
		1 month	8.25	1.188	0.558	0.025	1.52	1.68	5.92	6.72	6.56	7.44	7.60
		3 months	8.35	0.903	0.538	0.013	1.57	1.68	6.27	6.77	6.66	7.85	7.96
		6 months	8.35	1.056	0.324	0.016	1.54	1.79	6.18	6.80	6.55	7.72	7.97
		9 months	7.70	1.066	0.639	0.014	1.54	1.65	5.67	6.15	6.04	7.21	7.32
		12 months	8.00	0.761	0.802	0.021	1.61	1.60	5.75	6.38	6.39	7.36	7.35
		15 months	8.20	0.525	0.889	0.017	1.69	1.58	6.01	6.50	6.62	7.70	7.59
	400	1 day	8.10	1.472	0.436	0.253	1.48	1.74	4.78	6.61	6.35	6.26	6.53
		1 month	8.20	1.411	0.355	0.186	1.48	1.79	5.00	6.71	6.41	6.48	6.79
		3 months	8.35	0.985	0.395	0.145	1.56	1.76	5.22	6.78	6.59	6.78	6.98
		6 months	8.30	0.903	0.518	0.104	1.57	1.70	5.32	6.72	6.60	6.90	7.02
		9 months	7.60	0.670	0.731	0.195	1.64	1.62	4.42	5.95	5.97	6.07	6.05
		12 months	8.05	0.761	0.944	0.145	1.62	1.57	4.96	6.42	6.47	6.58	6.54
		15 months	8.10	0.646	0.899	0.127	1.65	1.58	5.05	6.44	6.51	6.71	6.64

Table 10. Ionic Concentrations and Activities, Lime and Phosphate Potentials of the Red River Soil Mixed With Solutions of KH_2PO_4 and K_2HPO_4

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] $\times 10^3$M	[Mg] $\times 10^3$M	[P] $\times 10^3$M	$\frac{1}{2}$pCa	$\frac{1}{2}$pMg	pH_2PO_4	pH-$\frac{1}{2}$pCa	pH-$\frac{1}{2}$pMg	pH_2PO_4 +$\frac{1}{2}$pCa	pH_2PO_4 +$\frac{1}{2}$pMg
K_2HPO_4	100	1 day	7.80	2.801	4.030	0.044	1.37	1.29	5.47	6.42	6.50	6.85	6.77
		1 month	7.70	2.791	4.273	0.035	1.37	1.28	5.49	6.32	6.41	6.87	6.77
		3 months	7.65	2.385	4.578	0.029	1.41	1.26	5.52	6.23	6.38	6.93	6.79
		6 months	7.75	3.086	5.318	0.029	1.36	1.24	5.65	6.38	6.50	7.01	6.89
		9 months	7.55	1.989	4.609	0.035	1.44	1.26	5.34	6.10	6.28	6.79	6.61
		12 months	7.50	2.192	4.730	0.056	1.42	1.26	5.11	6.07	6.23	6.53	6.37
		15 months	7.40	1.980	4.949	0.047	1.45	1.25	5.10	5.94	6.14	6.55	6.35
	400	1 day	7.80	3.329	3.451	0.474	1.34	1.33	4.43	6.45	6.46	5.78	5.77
		1 month	7.50	3.167	4.009	0.244	1.35	1.30	4.47	6.14	6.19	5.82	5.77
		3 months	7.55	3.045	3.593	0.211	1.35	1.32	4.56	6.19	6.22	5.92	5.88
		6 months	7.75	2.324	4.619	0.265	1.42	1.27	4.65	6.33	6.48	6.07	5.92
		9 months	7.05	2.426	4.314	0.276	1.40	1.28	4.07	5.64	5.76	5.48	5.35
		12 months	7.30	2.172	4.527	0.224	1.43	1.27	4.34	5.86	6.02	5.77	5.61
		15 months	7.35	1.778	4.787	0.275	1.47	1.26	4.28	5.87	6.09	5.76	5.54

Table 10 continued.

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] x10^3M	[Mg] x10^3M	[P] x10^3M	$\frac{1}{2}$pCa	$\frac{1}{2}$pMg	pH_2PO_4	pH-$\frac{1}{2}$pCa	pH-$\frac{1}{2}$pMg	pH_2PO_4 +$\frac{1}{2}$pCa	pH_2PO_4 +$\frac{1}{2}$pMg
KH_2PO_4	100	1 day	7.70	2.944	4.070	0.045	1.36	1.29	5.38	6.33	6.40	6.74	6.67
		1 month	7.65	2.132	4.872	0.030	1.43	1.25	5.51	6.21	6.39	6.94	6.77
		3 months	7.75	2.101	4.700	0.033	1.43	1.26	5.55	6.31	6.48	6.99	6.81
		6 months	7.80	2.669	4.375	0.032	1.38	1.27	5.62	6.41	6.52	7.00	6.90
		9 months	7.30	2.172	4.913	0.031	1.43	1.25	5.21	5.86	6.04	6.64	6.46
		12 months	7.40	2.192	4.486	0.037	1.42	1.27	5.20	5.97	6.12	6.63	6.47
		15 months	7.35	2.182	5.393	0.044	1.43	1.23	5.10	5.91	6.11	6.54	6.34
	400	1 day	7.55	4.080	2.924	0.439	1.30	1.37	4.25	6.25	6.17	5.55	5.62
		1 month	7.35	3.147	3.897	0.360	1.35	1.30	4.18	5.99	6.04	5.53	5.48
		3 months	7.65	2.142	4.821	0.254	1.43	1.26	4.58	6.21	6.38	6.02	5.84
		6 months	7.65	3.593	3.471	0 231	1.32	1.33	4.62	6.32	6.31	5.95	5.95
		9 months	6.95	2.395	4.548	0.287	1.41	1.27	3.99	5.53	5.67	5.40	5.26
		12 months	7.30	2.030	4.649	0.206	1.44	1.26	4.37	5.85	6.03	5.82	5.64
		15 months	7.35	1.838	4.707	0.275	1.46	1.26	4.28	6.08	6.08	5.75	5.54

soil. At the final sampling date (fifteen months) these systems were undersaturated with respect to OCP. The addition of KH_2PO_4 to the Red River soil resulted in the system being in equilibrium with OCP at the twelve and fifteen months sampling periods. The system to which K_2HPO_4 was added was at all times supersaturated with respect to OCP.

The solubility of K_2HPO_4 and KH_2PO_4 added at the rate of 400 ppm phosphorus was much greater than that added at the rate of 100 ppm phosphorus. Supersaturation with respect to DCPD existed only at the one day sampling period in the Darlingford soil when KH_2PO_4 or K_2HPO_4 was added (Figures 10 and 11). The solubility of phosphorus in the soil samples taken at periods up to six months was slightly less than that of DCPD. The solubility of phosphorus, whether added as KH_2PO_4 or as K_2HPO_4, remained between that of DCPD and that of OCP for the remainder of the sampling period.

The ion product points for the nine months sampling period do not follow the general trend of the data, but exhibit lower than normal lime and phosphate potentials. The displacement of these points is evident for both carriers on all four soils. Webber (36) suggested that, if regular aeration of samples is omitted, accumulation of carbon dioxide would cause a decrease in pH. This in turn results in a shift in the equilibrium. Webber found that subsequent regular aeration increased pH values to their original levels. It is possible that lack of sufficient aeration prior to the nine month sampling could have caused displacement of these points.

Supersaturation with respect to DCPD was not apparent in the calcareous Aneda soil when phosphorus was added at the rate of 400 ppm as KH_2PO_4 or K_2HPO_4 (Figures 12 and 13). The ion product point for the one day sampling

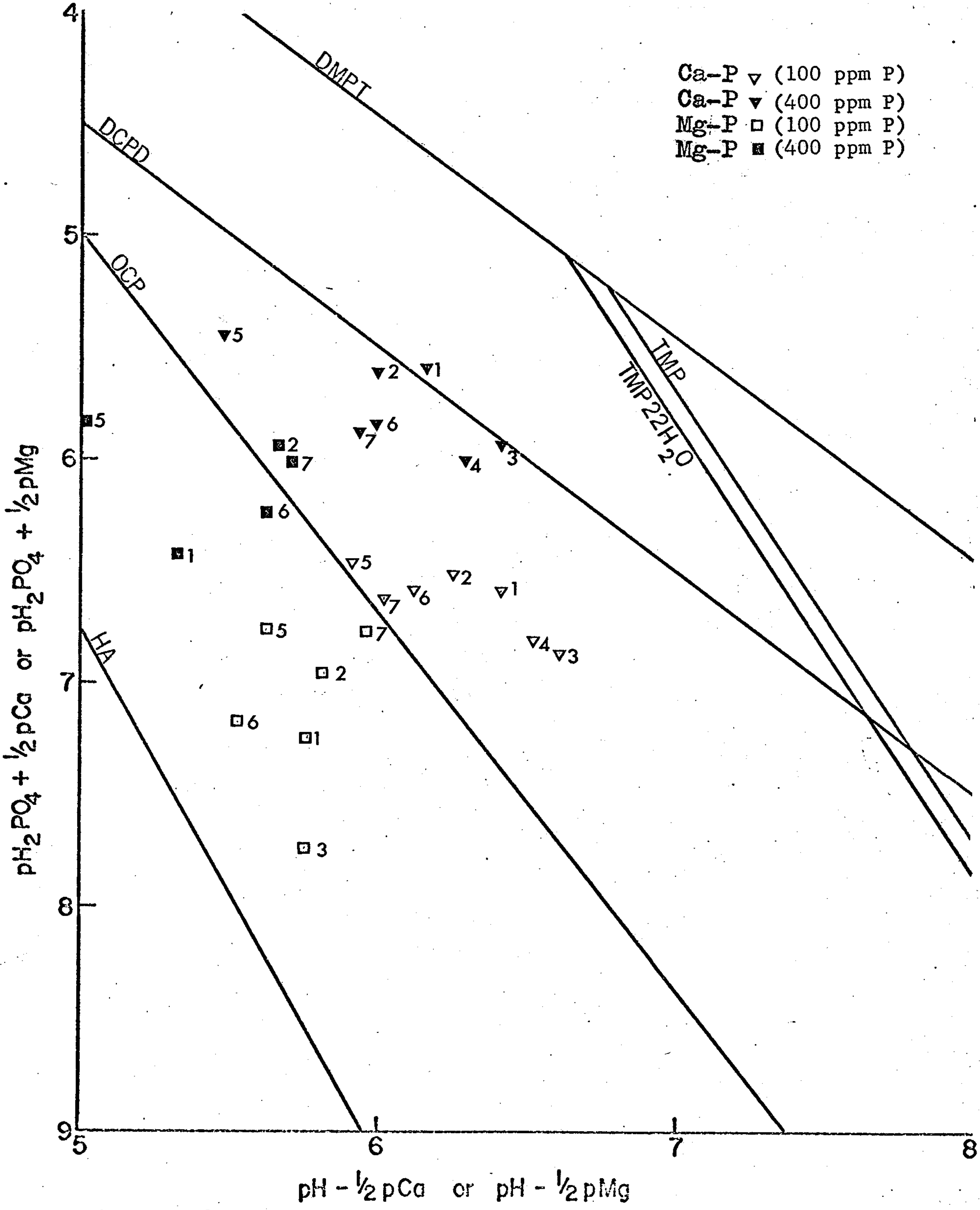

Figure 10. Solubility of KH_2PO_4 Mixed With the Darlingford Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months of incubation.

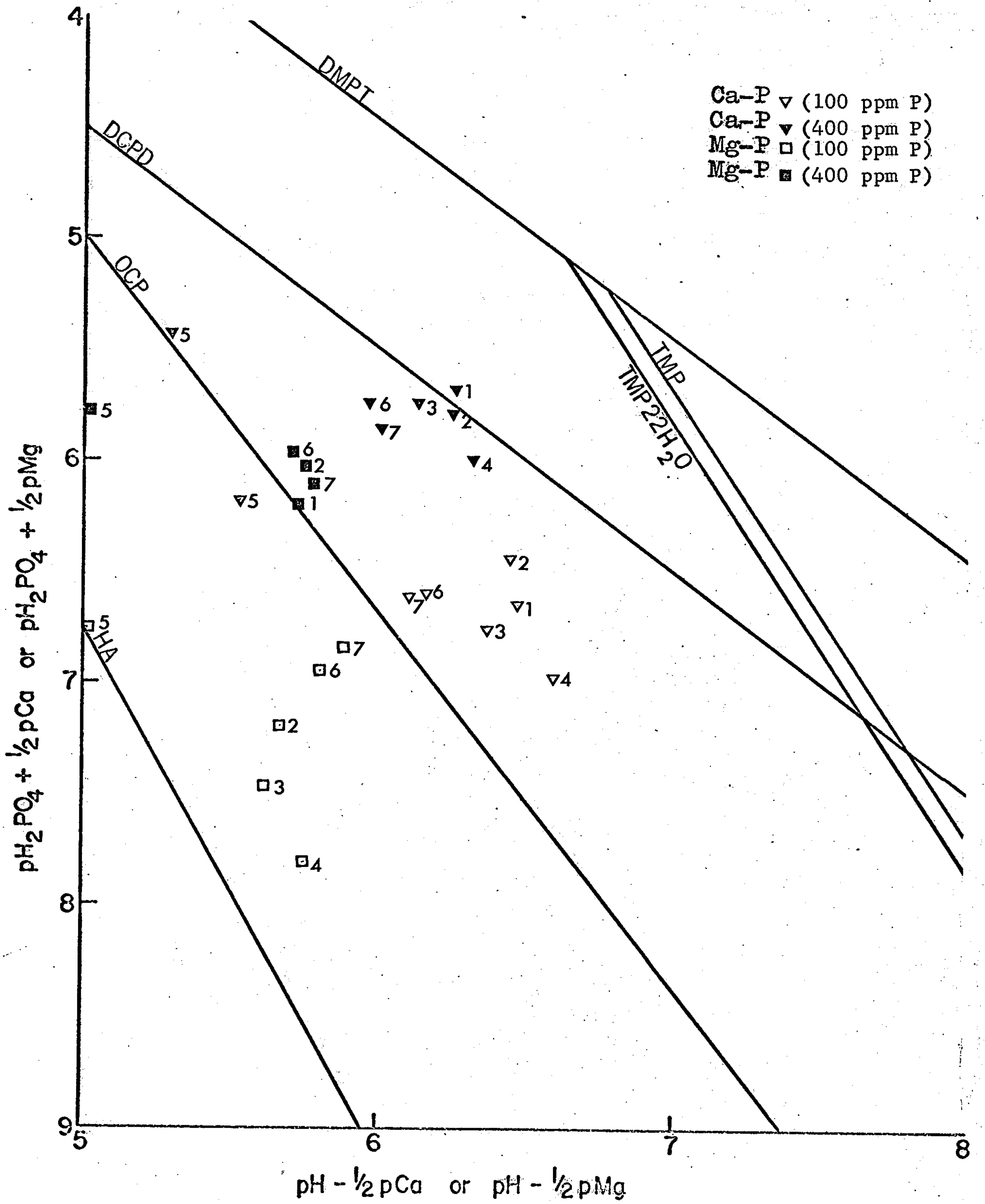

Figure 11. Solubility of K_2HPO_4 Mixed With the Darlingford Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

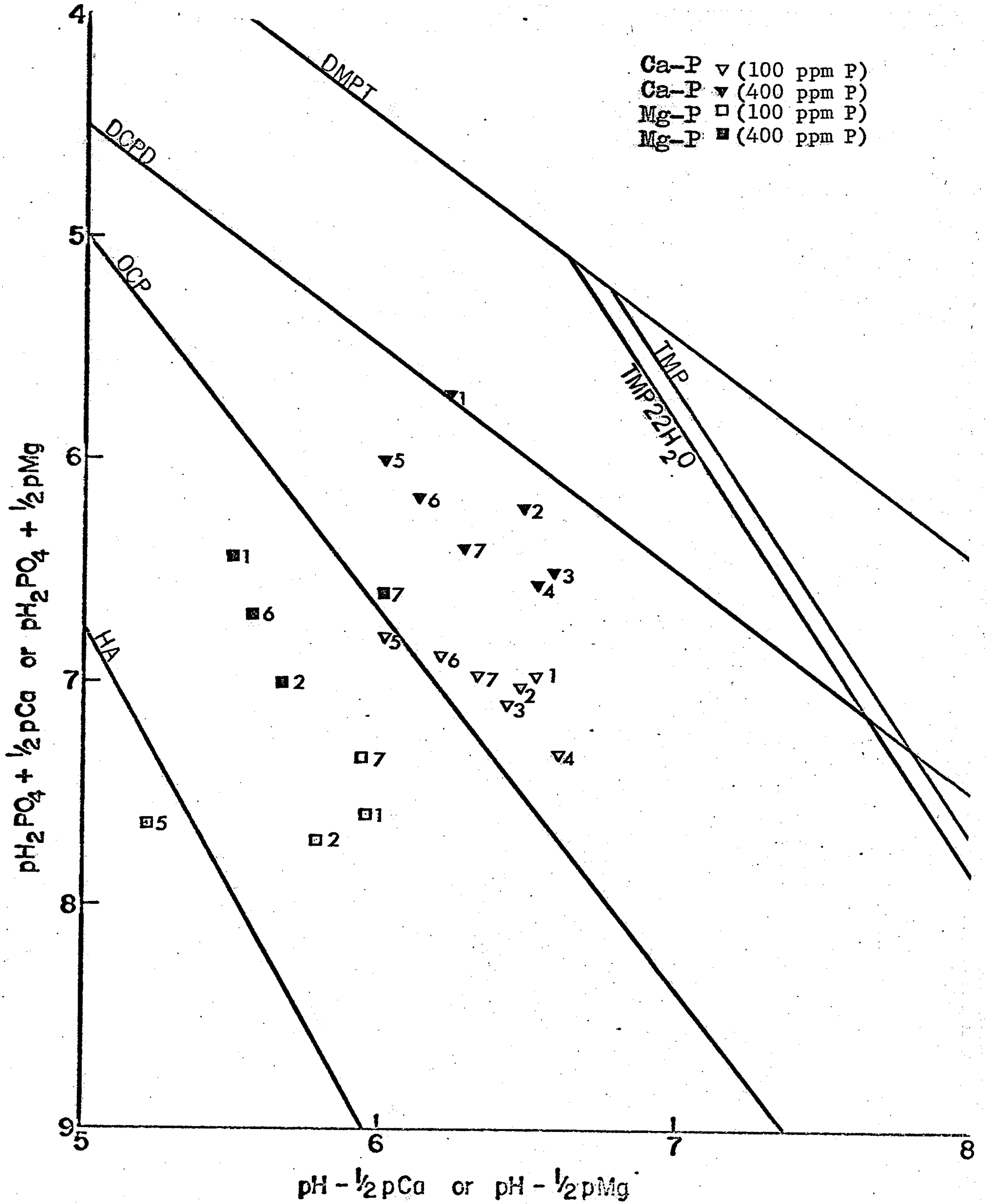

Figure 12. Solubility of KH_2PO_4 Mixed With the Aneda Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

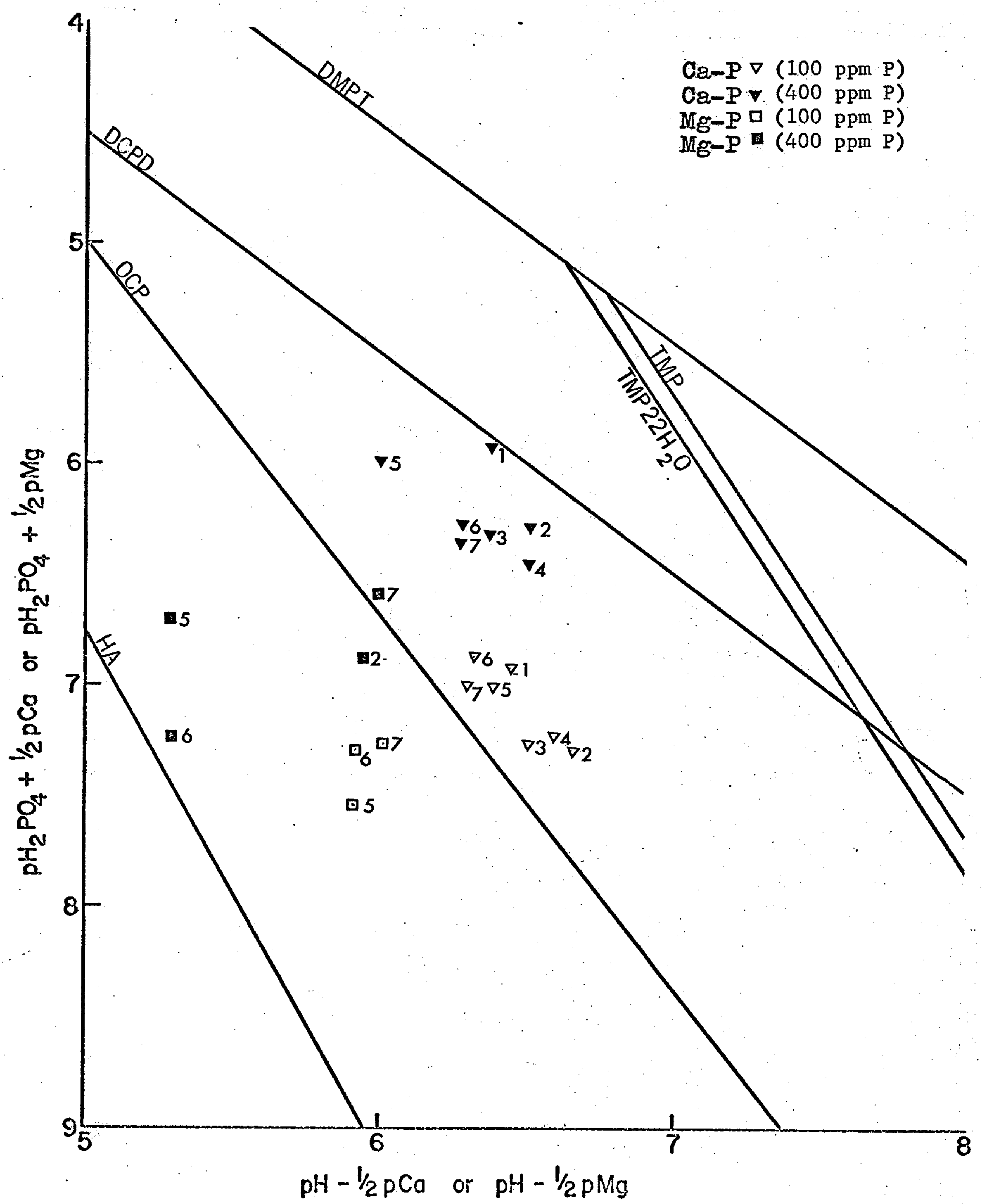

Figure 13. Solubility of K_2HPO_4 Mixed With the Aneda Soil at 1 day (1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

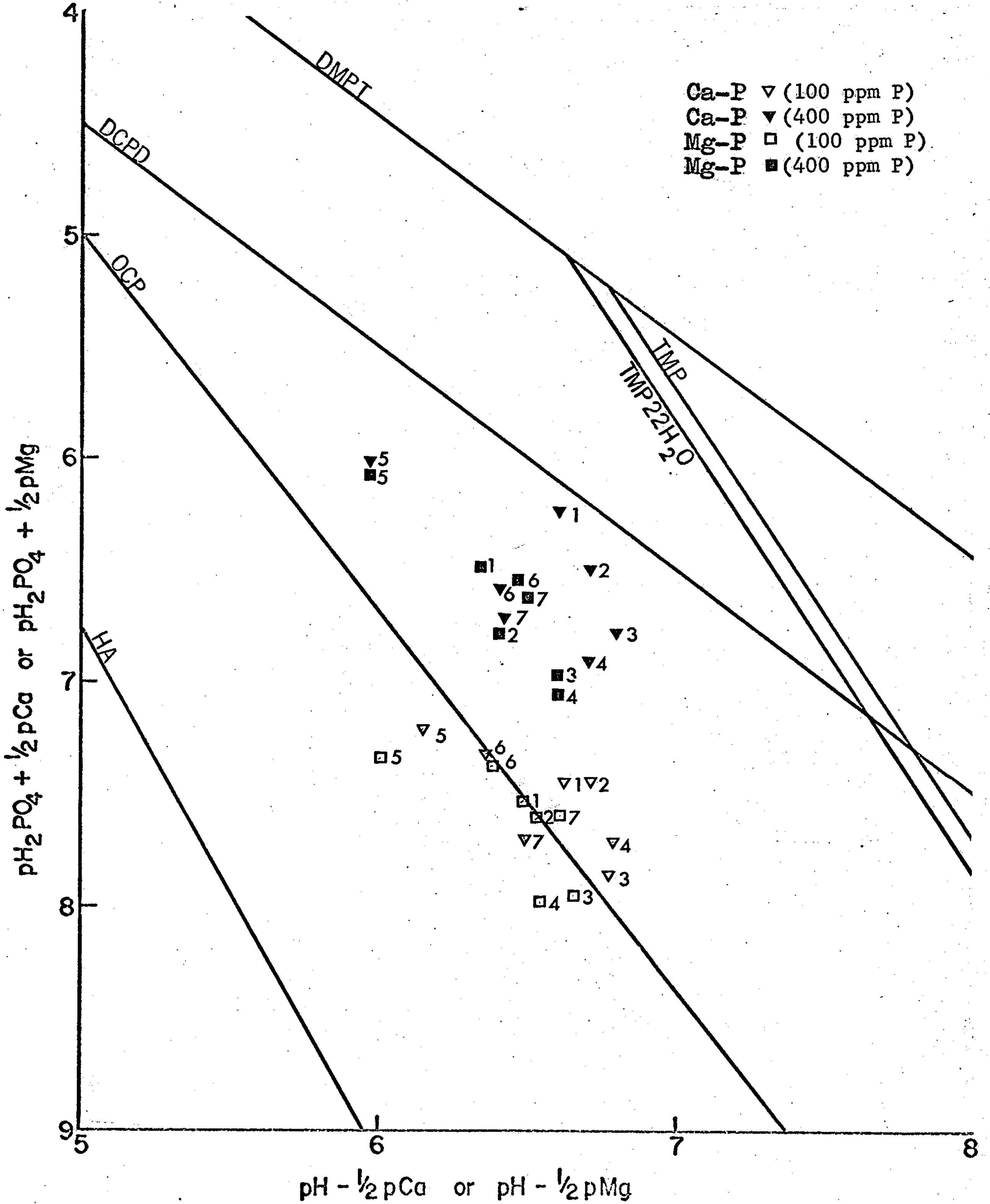

Figure 14. Solubility of KH_2PO_4 Mixed With the Balmoral Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

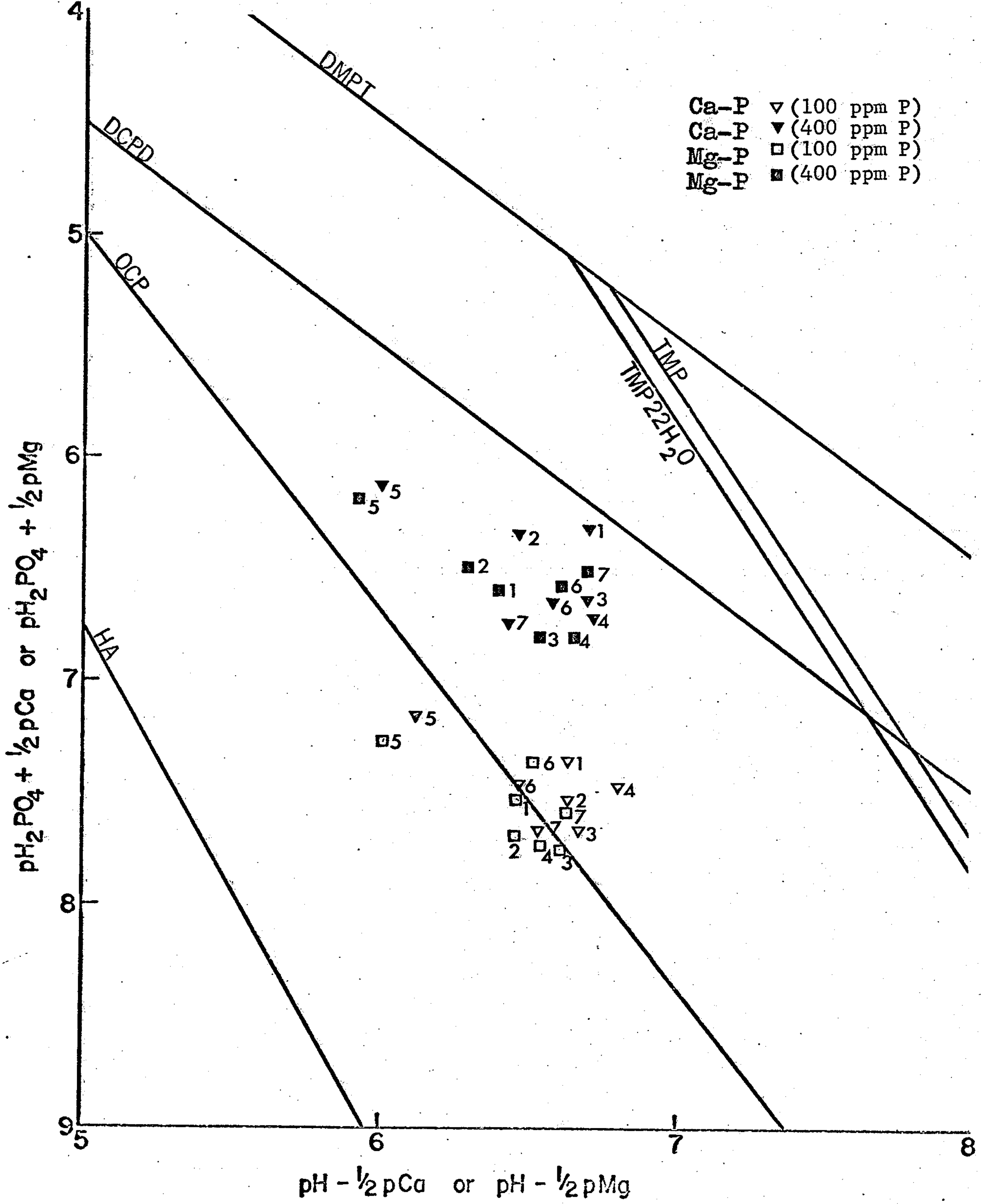

Figure 15. Solubility of K_2HPO_4 Mixed With the Balmoral Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

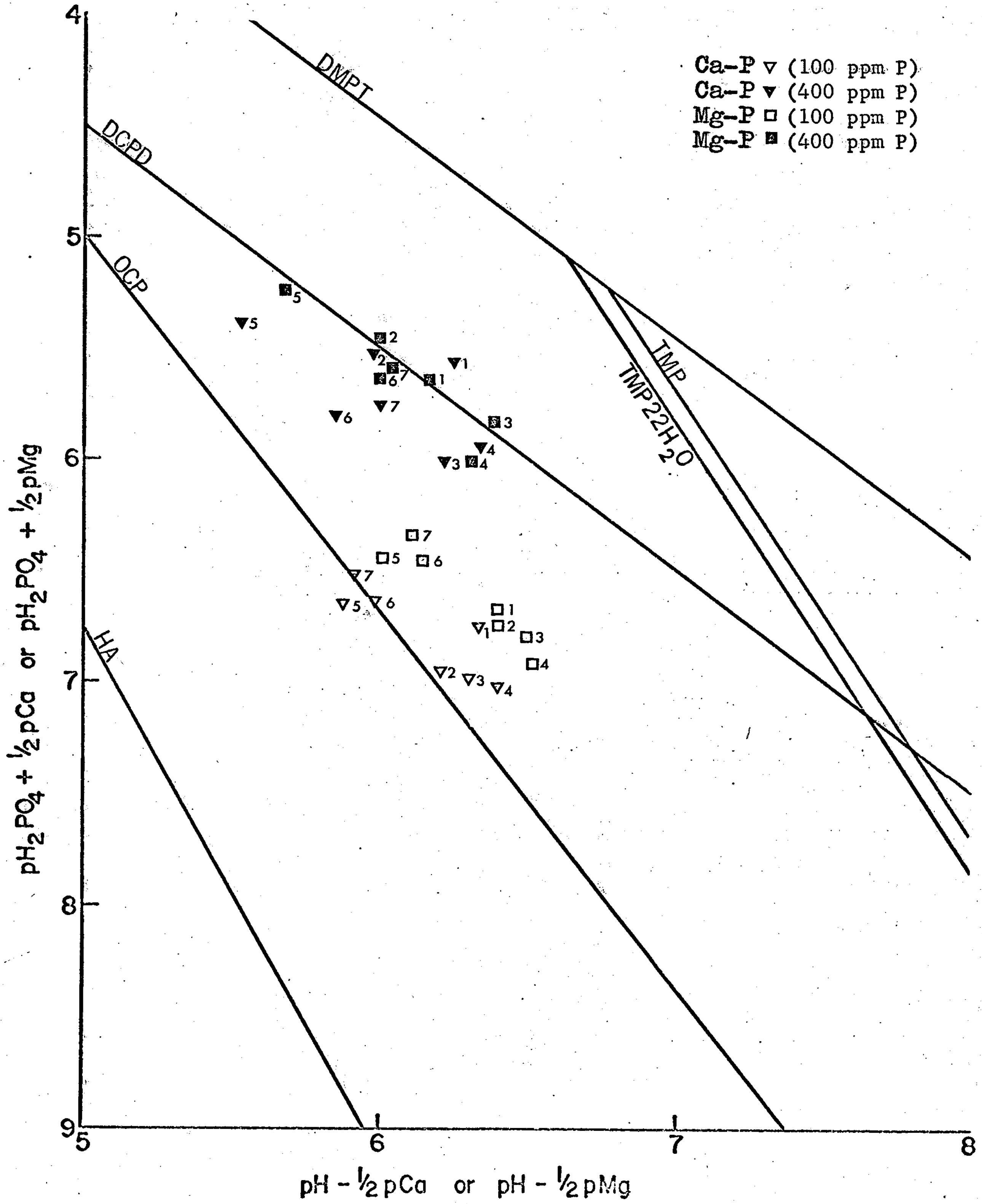

Figure 16. Solubility of KH_2PO_4 Mixed With the Red River Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

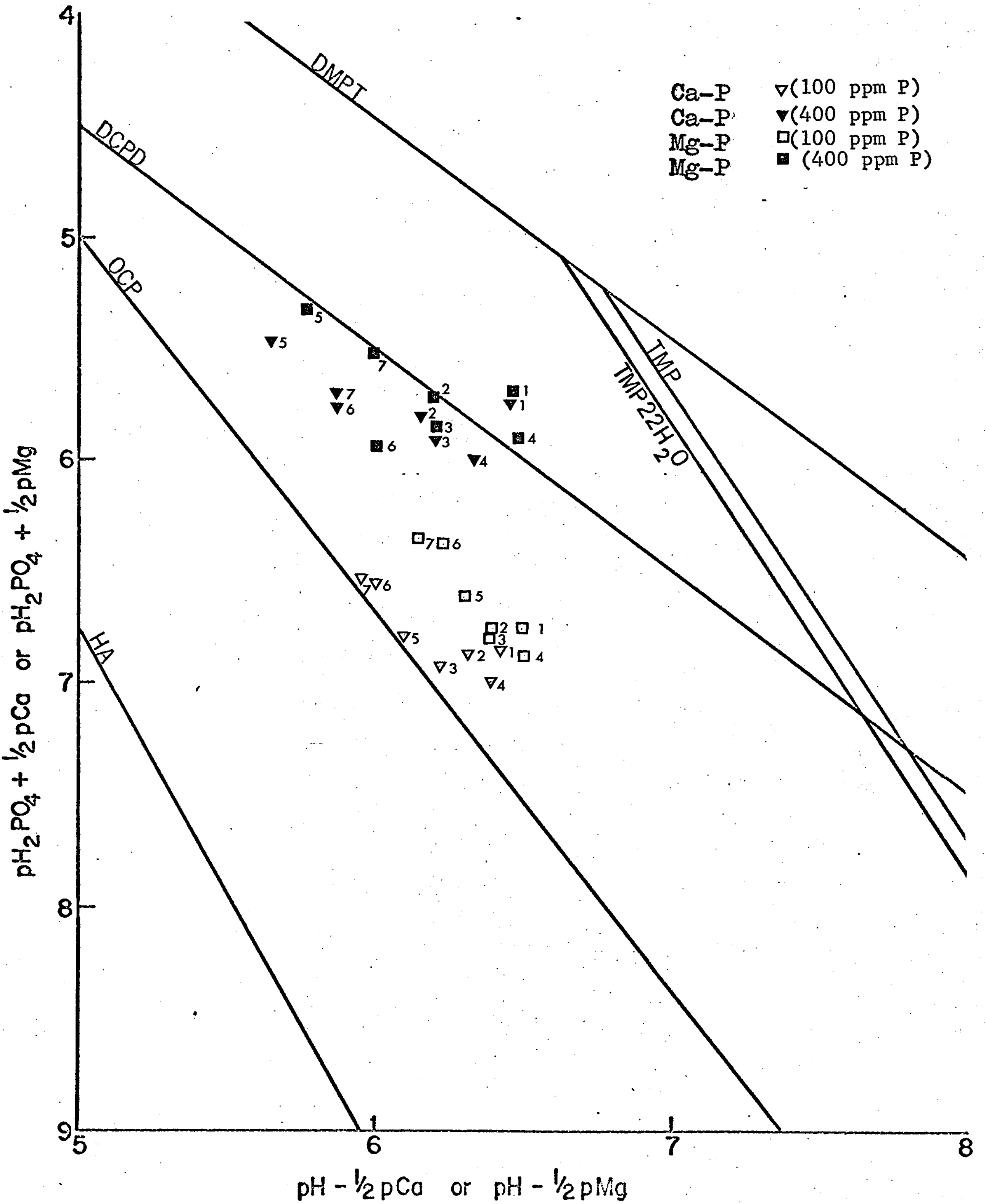

Figure 17. Solubility of K_2HPO_4 Mixed With the Red River Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4), 9 months(5), 12 months(6) and 15 months(7) of incubation.

was on the DCPD isotherm when phosphorus was added as KH_2PO_4. This indicates that the system was in equilibrium with DCPD. In a mixed system such as the soil, it is not often that an ion product determined experimentally will correspond to a point on a given isotherm since the data from which the isotherms are constructed are obtained in pure systems. Samples taken after one day of incubation from the K_2HPO_4-treated soils indicate that the system was already undersaturated with respect to DCPD. Subsequent points for both carriers indicate that the solubility of the added phosphorus was between that of DCPD and OCP. The solubilities of K_2HPO_4 and KH_2PO_4 differed only when samples were taken after one day of incubation. The solubility values obtained after nine months of incubation are probably in error due to lack of aeration.

Supersaturation with respect to DCPD was not apparent at any stage when 400 ppm phosphorus as KH_2PO_4 or K_2HPO_4 was mixed with the Balmoral soil (Figures 14 and 15). The solubility of phosphorus approached that of DCPD when the soils were sampled after one day of incubation. The soils were supersaturated with respect to OCP for the entire sampling period. The solubility values obtained for the Balmoral soil may have been influenced by the presence of the calcium-magnesium phosphate, $Ca_3Mg_3(PO_4)_4$. X-ray data indicated that this compound was present for the entire sampling period when KH_2PO_4 was added to the Balmoral soil and for a period of three months to twelve months when K_2HPO_4 was added. As previously pointed out, no information regarding the solubility of this phosphate has been sighted. The soil samples obtained after nine months of incubation probably indicate an artefact due to irregular aeration of samples during incubation as was the case in the Darlingford and Aneda soils.

Four hundred ppm phosphorus added either as KH_2PO_4 or as K_2HPO_4 to the Red River soil caused the systems to appear supersaturated with respect to DCPD at the initial (one day) sampling period. Subsequent points indicated that the solubility of phosphorus in the Red River soil remained between that of DCPD and OCP for the remainder of the incubation period. The displacement of the ion product point for the nine months sampling period is most probably indicative of irregular aeration as previously discussed.

Differences in solubility between phosphorus carriers which were evident when the phosphates were added in pelleted form were not apparent when the carriers (KH_2PO_4 or K_2HPO_4) were mixed with the soil. Since the soil pH was very similar when K_2HPO_4 and KH_2PO_4 was mixed with the soil, it would be expected that the solubility of the added phosphorus would be similar regardless of source of added phosphorus. Addition of the phosphates in pellet form resulted in differences in soil pH near the pellet and thus differences in the solubility of the added phosphate. The solubility of phosphorus in the soils treated at the rate of 400 ppm phosphorus decreased in the order:

Red River, Darlingford, Aneda, Balmoral.

The above is also the order of increasing inorganic carbonate content of the four soils. Total inorganic carbonate ranged from 0.29 percent in the Red River to 27.5 percent in the Balmoral soil. Work published by Racz and Soper (25) however, showed that the formation of the initial reaction products (DCPD and/or DMPT) are not affected by whether or not the soil is calcareous. Also, the order of decreasing phosphorus solubility with increasing carbonate content of the soil did not hold when phosphorus was added in the pellet form.

The solubility of the added KH_2PO_4 and K_2HPO_4 was greatest in the Red River soil. This is probably due to the formation of a magnesium phosphate more soluble than the calcium phosphates formed in the Aneda or Darlingford soils. The presence of DMPT was verified by X-ray data when KH_2PO_4 and K_2HPO_4 were added in pellet form to the Red River soil. The solubility of the added phosphorus generally decreased with time of incubation for all soils. This decrease in solubility, however, was not very great and the solubility of added phosphorus after fifteen months of incubation was still much greater than that obtained for the untreated soils.

The Solubility of Dicalcium Phosphate Dihydrate and Dimagnesium Phosphate Trihydrate Mixed with Each of the Four Soils

Most of the phosphates that form readily from water soluble phosphates in soils are metastable products (12). These intermediate products may persist in the soil for varying periods of time, depending upon conditions that exist in the reaction zone. Dicalcium phosphate dihydrate (DCPD) is one of the major initial products formed when water soluble phosphates such as monocalcium phosphate are added to calcareous soils (18). In dolomitic soils, and soils high in exchangeable magnesium, dimagnesium phosphate trihydrate (DMPT), as well as DCPD, has been found to occur (25). The results of a study in which DCPD and DMPT were added to soils and incubated for periods of eight months or less are discussed in the following section.

The concentration of phosphorus in the equilibrium soil solutions decreased only very slightly with increased time of incubation when DCPD or DMPT were mixed with each of the four soils (Tables 11 - 14). There was a simultaneous slight decrease in the pH of the systems. This decrease was most marked in the Red River soil. Fluctuations in pH could have been due to accumulation of carbon dioxide in the soil during incubation. The concentrations of calcium and magnesium in the equilibrium solutions varied only slightly as the incubation progressed. At the final sampling period (eight months) there did appear to be an increase in magnesium content of the equilibrium solution and this was most noticeable in the Aneda, Darlingford and Balmoral soils. The Red River soil had large amounts of magnesium in solution at all stages during the incubation.

The addition of DCPD rather than DMPT did not result in any large differences in phosphorus concentration of the soil solution although concentration of phosphorus was slightly greater when DCPD rather than DMPT was added to the Aneda soil. The pH of the systems was initially higher when DMPT rather than DCPD was added to each of the four soils. These differences were most marked at the one month sampling period. After three months of incubation these differences were no longer apparent. The addition of DCPD rather than DMPT did not consistently affect the concentration of calcium and magnesium in the equilibrium solutions. The concentration of phosphorus in solution was greater when 400 ppm phosphorus rather than 100 ppm was added as DCPD or DMPT. However, the pH of the systems did not vary with rate of phosphorus added.

The solubility of phosphorus, as indicated by the calcium ion products, remained relatively high during the entire sampling period when DCPD or DMPT was added to the Darlingford soil at a rate of 400 ppm phosphorus (Figure 18). Supersaturation with respect to DCPD occurred in the Darlingford

Table 11. Ionic Concentrations and Activities, Lime and Phosphate Potentials of the Darlingford Soil Mixed With DCPD△ and DMPT▲

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] $\times 10^3$M	[Mg] $\times 10^3$M	[P] $\times 10^3$M	$\frac{1}{2}$pCa	$\frac{1}{2}$pMg	pH_2PO_4	pH-$\frac{1}{2}$pCa	pH-$\frac{1}{2}$pMg	pH_2PO_4 +$\frac{1}{2}$pCa	pH_2PO_4 +$\frac{1}{2}$pMg
DCPD	100	1 day	8.10	0.883	0.183	0.093	1.57	1.92	5.15	6.52	6.18	6.73	7.07
		1 month	7.60	1.015	0.061	0.061	1.54	2.15	4.90	6.05	5.44	6.45	7.06
		3 months	7.80	1.167	0.092	0.047	1.51	2.07	5.19	6.28	5.72	6.71	7.27
		6 months	7.80	1.117	0.060	0.069	1.52	2.16	5.02	6.27	5.63	6.55	7.18
		8 months	7.60	0.667	0.424	0.058	1.63	1.73	4.93	5.96	5.86	6.56	6.66
	400	1 day	8.00	1.076	0.274	0.565	1.55	1.85	4.29	6.44	6.14	5.85	6.15
		1 month	7.45	0.995	0.101	0.360	1.55	2.05	4.02	5.89	5.39	5.58	6.07
		3 months	7.65	0.934	0.162	0.341	1.57	1.95	4.19	6.07	5.69	5.77	6.15
		6 months	7.65	0.934	0.162	0.464	1.57	1.95	4.06	6.07	5.69	5.64	6.02
		8 months	7.45	0.747	0.384	0.312	1.62	1.76	4.08	5.83	5.68	5.70	5.85
DMPT	100	1 day	8.10	1.005	0.020	0.108	1.54	2.40	5.08	6.55	5.69	6.63	7.48
		1 month	8.00	0.995	0.040	0.067	1.55	2.24	5.20	6.45	5.75	6.75	7.45
		3 months	7.70	1.106	0.112	0.058	1.53	2.02	5.02	6.17	5.67	6.55	7.04
		6 months	7.80	0.995	0.142	0.076	1.55	1.97	4.98	6.24	5.82	6.53	6.95
		8 months	7.65	0.707	0.485	0.058	1.62	1.70	4.97	6.02	5.94	6.60	6.68
	400	1 day	7.80	1.025	0.264	0.360	1.55	1.85	4.31	6.24	5.94	5.87	6.16
		1 month	7.75	1.056	0.041	0.412	1.54	2.25	4.19	6.20	5.49	5.74	6.45
		3 months	7.70	0.883	0.193	0.282	1.58	1.91	4.32	6.11	5.78	5.90	6.23
		6 months	7.55	0.924	0.233	0.379	1.57	1.87	4.07	5.97	5.67	5.65	5.95
		8 months	7.55	0.768	0.484	0.283	1.61	1.71	4.21	5.93	5.83	5.82	5.93

△DCPD: Dicalcium Phosphate Dihydrate
▲DMPT: Dimagnesium Phosphate Trihydrate

Table 12. Ionic Concentrations and Activities, Lime and Phosphate Potentials of the Aneda Soil Mixed With DCPD△ and DMPT▲

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] x10^{3}M	[Mg] x10^{3}M	[P] x10^{3}M	½pCa	½pMg	pH_2PO_4	pH-½pCa	pH-½pMg	pH_2PO_4 +½pCa	pH_2PO_4 +½pMg
DCPD	100	1 day	8.10	1.045	0.143	0.046	1.54	1.97	5.47	6.55	6.12	7.01	7.44
		1 month	7.65	1.096	-▽	0.041	1.53	-	5.12	6.12	-	6.65	-
		3 months	7.85	1.218	0.020	0.037	1.50	2.40	5.34	6.34	5.44	6.85	7.74
		6 months	7.90	1.035	0.081	0.041	1.54	2.09	5.33	6.35	5.80	6.87	7.43
		8 months	7.85	0.828	0.323	0.045	1.59	1.79	5.25	6.25	6.05	6.84	7.04
	400	1 day	8.15	1.086	0.233	0.347	1.54	1.88	4.64	6.60	6.26	6.19	6.52
		1 month	7.50	1.198	-	0.200	1.51	-	4.32	5.98	-	5.83	-
		3 months	7.80	0.974	0.143	0.189	1.56	1.97	4.58	6.24	5.83	6.14	6.55
		6 months	7.70	1.096	-	0.182	1.53	-	4.51	6.16	-	6.04	-
		8 months	7.75	0.929	0.263	0.190	1.57	1.84	4.54	6.17	5.90	6.11	6.38
DMPT	100	1 day	8.10	1.137	-	0.050	1.52	-	5.42	6.57	-	6.95	-
		1 month	8.15	0.995	-	0.030	1.54	-	5.68	6.60	-	7.23	-
		3 months	7.85	1.127	0.132	0.028	1.52	1.99	5.46	6.32	5.85	6.99	7.45
		6 months	7.95	1.066	0.050	0.039	1.53	2.20	5.40	6.41	5.74	6.93	7.60
		8 months	7.85	0.768	0.363	0.041	1.60	1.77	5.29	6.24	6.08	6.89	7.06
	400	1 day	7.90	0.842	0.487	0.299	1.59	1.71	4.48	6.30	6.18	6.08	6.20
		1 month	8.00	1.076	-	0.140	1.53	-	4.88	6.46	-	6.42	-
		3 months	7.90	0.934	0.162	0.132	1.56	1.94	4.82	6.33	5.95	6.39	6.77
		6 months	7.90	1.096	0.020	0.185	1.53	2.40	4.67	6.36	5.49	6.21	7.08
		8 months	7.80	0.959	0.233	0.175	1.56	1.87	4.62	6.23	5.92	6.18	6.49

△DCPD: Dicalcium Phosphate Dihydrate
▲DMPT: Dimagnesium Phosphate Trihydrate
▽ No Mg Detected

Table 13. Ionic Concentrations and Activities, Lime and Phosphate Potentials of the Balmoral Soil Mixed With DCPD△ and DMPT▲

Phosphate Added	Rate ppmP	Incubation Period	pH	[Ca] x10^3M	[Mg] x10^3M	[P] x10^3M	$\frac{1}{2}$pCa	$\frac{1}{2}$pMg	pH_2PO_4	pH-$\frac{1}{2}$pCa	pH-$\frac{1}{2}$pMg	pH_2PO_4 +$\frac{1}{2}$pCa	pH_2PO_4 +$\frac{1}{2}$pMg
DCPD	100	1 day	8.20	0.751	0.782	0.022	1.61	1.61	5.91	6.58	6.59	7.53	7.52
		1 month	7.90	0.853	0.690	0.016	1.59	1.63	5.77	6.30	6.26	7.36	7.41
		3 months	8.05	0.954	0.995	0.037	1.57	1.56	5.57	6.47	6.48	7.14	7.14
		6 months	8.10	0.802	0.619	0.022	1.60	1.65	5.81	6.49	6.44	7.41	7.46
		8 months	8.15	0.566	1.090	0.021	1.68	1.53	5.89	6.46	6.61	7.57	7.43
	400	1 day	8.00	0.924	0.832	0.237	1.58	1.60	4.70	6.41	6.39	6.29	6.31
		1 month	7.80	0.782	0.639	0.126	1.61	1.65	4.78	6.18	6.14	6.39	6.43
		3 months	8.15	0.609	0.853	0.141	1.66	1.59	5.05	6.48	6.55	6.71	6.64
		6 months	7.95	0.812	0.568	0.143	1.60	1.68	4.85	6.34	6.26	6.45	6.53
		8 months	8.05	0.707	1.071	0.149	1.63	1.54	4.95	6.41	6.50	6.59	6.50
DMPT	100	1 day	8.10	1.066	0.599	0.032	1.54	1.67	5.66	6.55	6.43	7.21	7.33
		1 month	8.30	0.802	0.538	0.014	1.60	1.68	6.18	6.69	6.61	7.78	7.87
		3 months	8.10	0.822	0.863	0.019	1.60	1.59	5.89	6.49	6.51	7.49	7.48
		6 months	8.10	0.822	0.599	0.024	1.59	1.66	5.77	6.50	6.43	7.36	7.43
		8 months	8.15	0.566	0.929	0.024	1.67	1.57	5.82	6.47	6.57	7.50	7.39
	400	1 day	8.15	1.045	0.721	0.244	1.55	1.63	4.83	6.59	6.51	6.39	6.47
		1 month	8.25	0.853	0.730	0.150	1.59	1.62	5.12	6.65	6.62	6.72	6.75
		3 months	8.10	0.650	0.913	0.165	1.65	1.58	4.94	6.44	6.51	6.59	6.52
		6 months	8.00	0.721	0.618	0.159	1.62	1.66	4.85	6.37	6.33	6.48	6.51
		8 months	8.10	0.667	0.848	0.145	1.64	1.59	4.99	6.45	6.50	6.64	6.59

△ DCPD: Dicalcium Phosphate Dihydrate
▲ DMPT: Dimagnesium Phosphate Trihydrate

Table 14. Ionic Concentrations and Activities, Lime and Phosphate Potentials of the Red River Soil Mixed With DCPD△ and DMPT▲

Phosphate Added	Rate ppmP	Incubation Period	n	pH	[Ca] x10^3M	[Mg] x10^3M	[P] x10^3M	$\frac{1}{2}$pCa	$\frac{1}{2}$pMg	pH_2PO_4	pH-$\frac{1}{2}$pCa	pH-$\frac{1}{2}$pMg	pH_2PO_4 +$\frac{1}{2}$pCa	pH_2PO_4 +$\frac{1}{2}$pMg
DCPD	100	1 day		7.90	3.370	4.019	0.029	1.33	1.29	5.76	6.56	6.60	7.10	7.06
		1 month		7.30	2.517	4.852	0.035	1.40	1.25	5.16	5.89	6.04	6.56	6.42
		3 months		7.50	2.741	5.075	0.050	1.38	1.25	5.18	6.11	6.24	6.56	6.43
		6 months		7.35	2.426	5.207	0.051	1.41	1.24	5.04	5.93	6.10	6.45	6.29
		8 months		7.35	2.464	5.757	0.046	1.41	1.22	5.10	5.94	6.12	6.51	6.32
	400	1 day		7.80	3.867	4.152	0.334	1.31	1.29	4.62	6.48	6.50	5.94	5.92
		1 month		7.30	3.410	3.979	0.253	1.33	1.30	4.30	5.96	5.99	5.64	5.60
		3 months		7.55	2.426	4.902	0.260	1.41	1.25	4.49	6.13	6.29	5.90	5.75
		6 months		7.35	2.416	5.034	0.302	1.41	1.25	4.26	5.93	6.09	5.68	5.52
		8 months		7.45	2.222	5.212	0.231	1.43	1.24	4.46	6.01	6.20	5.89	5.70
DMPT	100	1 day		7.65	2.243	5.512	0.048	1.42	1.23	5.32	6.22	6.41	6.75	6.56
		1 month		7.80	3.147	4.303	0.036	1.35	1.28	5.58	6.44	6.51	6.93	6.86
		3 months		7.50	2.192	5.015	0.039	1.43	1.25	5.27	6.07	6.24	6.70	6.52
		6 months		7.40	2.253	5.096	0.058	1.42	1.24	5.02	5.97	6.15	6.44	6.27
		8 months		7.40	2.141	5.252	0.031	1.43	1.24	5.29	5.96	6.15	6.73	6.53
	400	1 day		7.80	2.690	5.430	0.271	1.39	1.24	4.72	6.40	6.56	6.11	5.96
		1 month		7.65	3.278	4.395	0.211	1.34	1.28	4.68	6.30	6.36	6.03	5.96
		3 months		7.55	2.233	5.380	0.265	1.43	1.24	4.49	6.11	6.31	5.92	5.73
		6 months		7.35	2.456	5.380	0.326	1.41	1.24	4.24	5.93	6.10	5.65	5.48
		8 months		7.35	2.565	5.818	0.267	1.40	1.22	4.34	5.94	6.12	5.74	5.56

△ DCPD: Dicalcium Phosphate Dihydrate
▲ DMPT: Dimagnesium Phosphate Dihydrate

soil incubated for one day when DCPD was added at the rate of 400 ppm phosphorus. The soil was undersaturated with respect to DCPD for the remainder of the incubation period, but the solubility of the added DCPD or DMPT did not decrease to that of OCP. Moreno, Lindsay and Osborn (21) equilibrated DCPD with soil and found that systems reached equilibrium with respect to DCPD and remained so for considerable periods of time. These workers suggest that the formation of OCP, expected in DCPD-saturated solutions at pH values above 6.4, is reduced by the presence of organic matter. All the calcium ion products indicate undersaturation with respect to DCPD but supersaturation with respect to OCP when DMPT was added (Figure 19). In general, this system closely approximated that to which DCPD was added except for the sample taken after one day of incubation. The solubility of phosphorus was between that of DCPD and OCP when DCPD or DMPT was added at the rate of 100 ppm phosphorus. The systems are close to equilibrium with OCP eight months after the phosphorus was added.

Supersaturation with respect to DCPD did not occur when 400 ppm phosphorus as DCPD or DMPT was added to the Aneda soil (Figures 20 and 21). The solubility of DCPD and DMPT, added at a rate of 400 ppm phosphorus, was near that of DCPD after one day of incubation and decreased slightly with time of incubation. The solutility of the added DMPT or DCPD was between that of OCP and DCPD after eight months of incubation. The soils treated with DMPT behaved similarly to the soils treated with DCPD. However, the phosphorus concentrations in the soil solution were slightly greater when DCPD rather than DMPT was added (Table 12). DCPD and DMPT, added at the

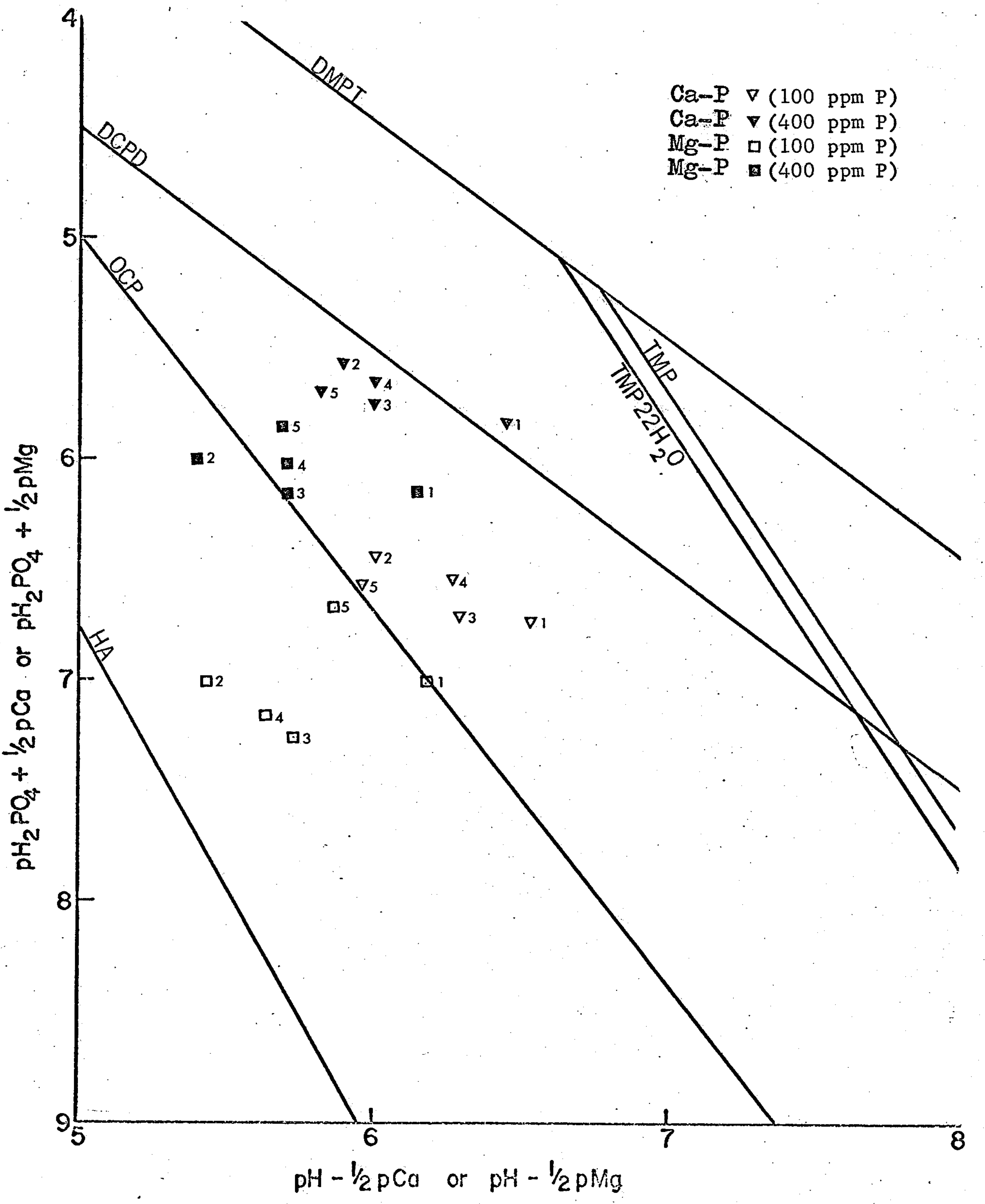

Figure 18. Solubility of DCPD Mixed With the Darlingford Soil at 1 day(1), 1 month(2) 3 months(3), 6 months(4) and 8 months(5) of incubation.

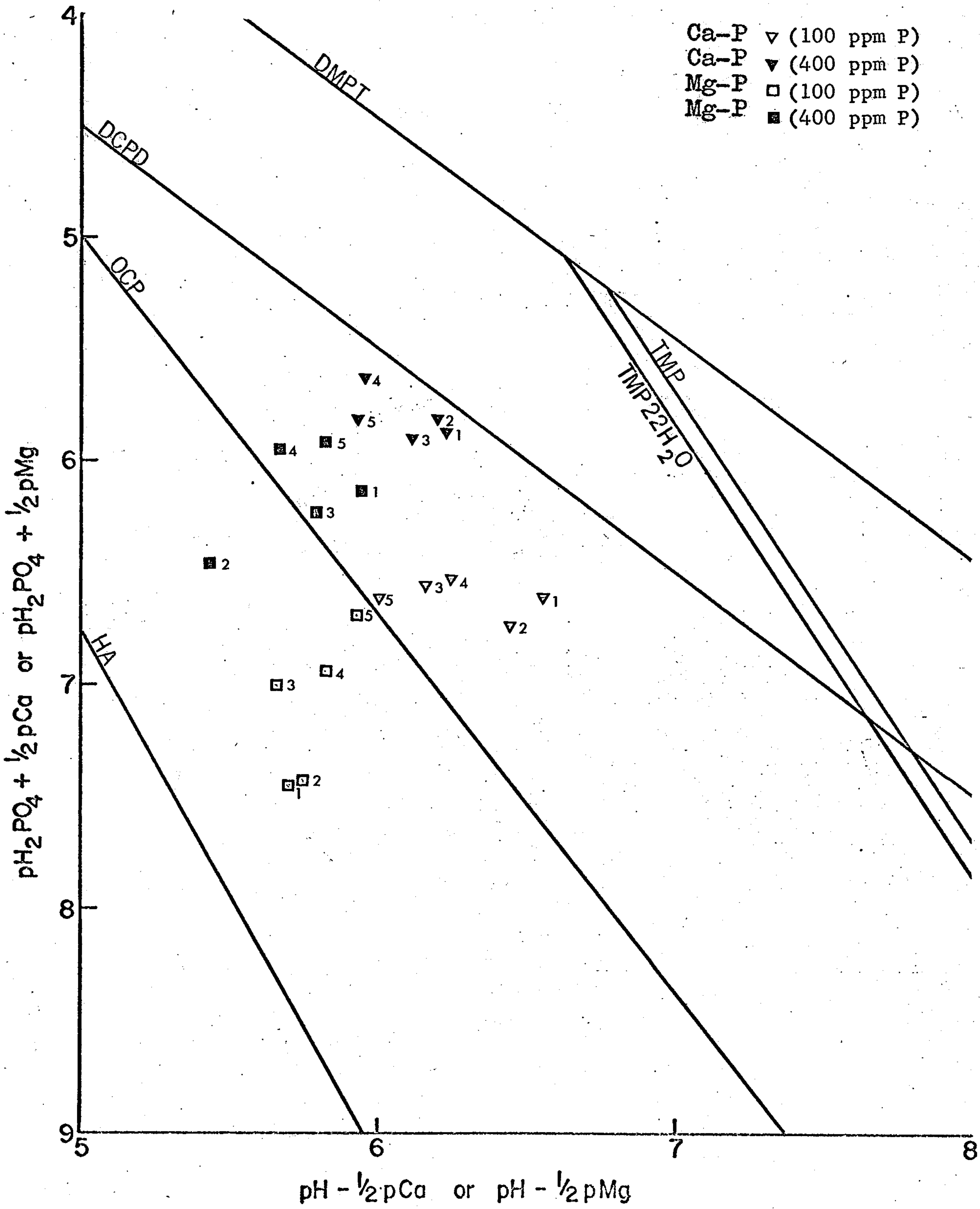

Figure 19. Solubility of DMPT Mixed With the Darlingford Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4) and 8 months(5) of incubation.

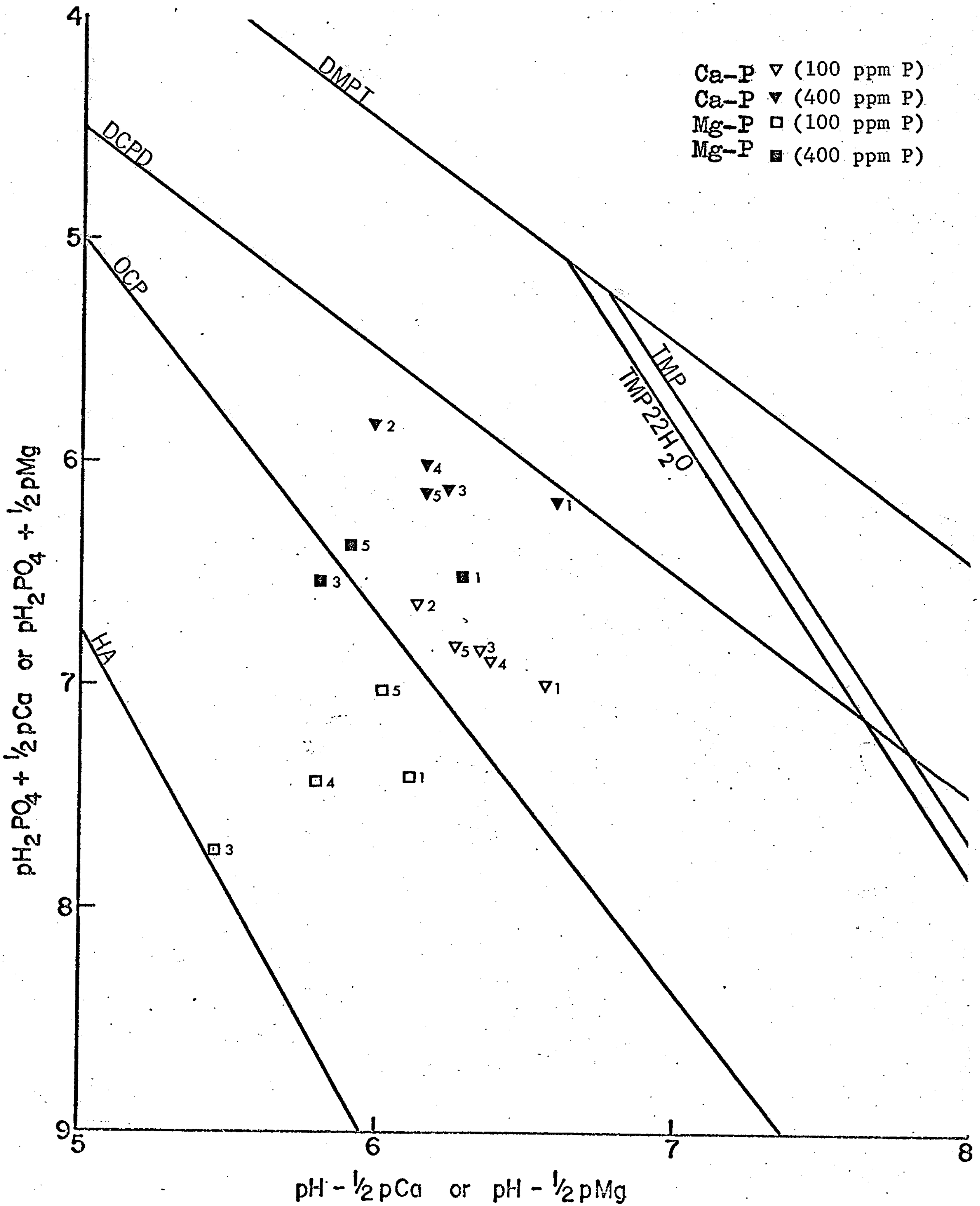

Figure 20. Solubility of DCPD Mixed With the Aneda Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4) and 8 months(5) of incubation.

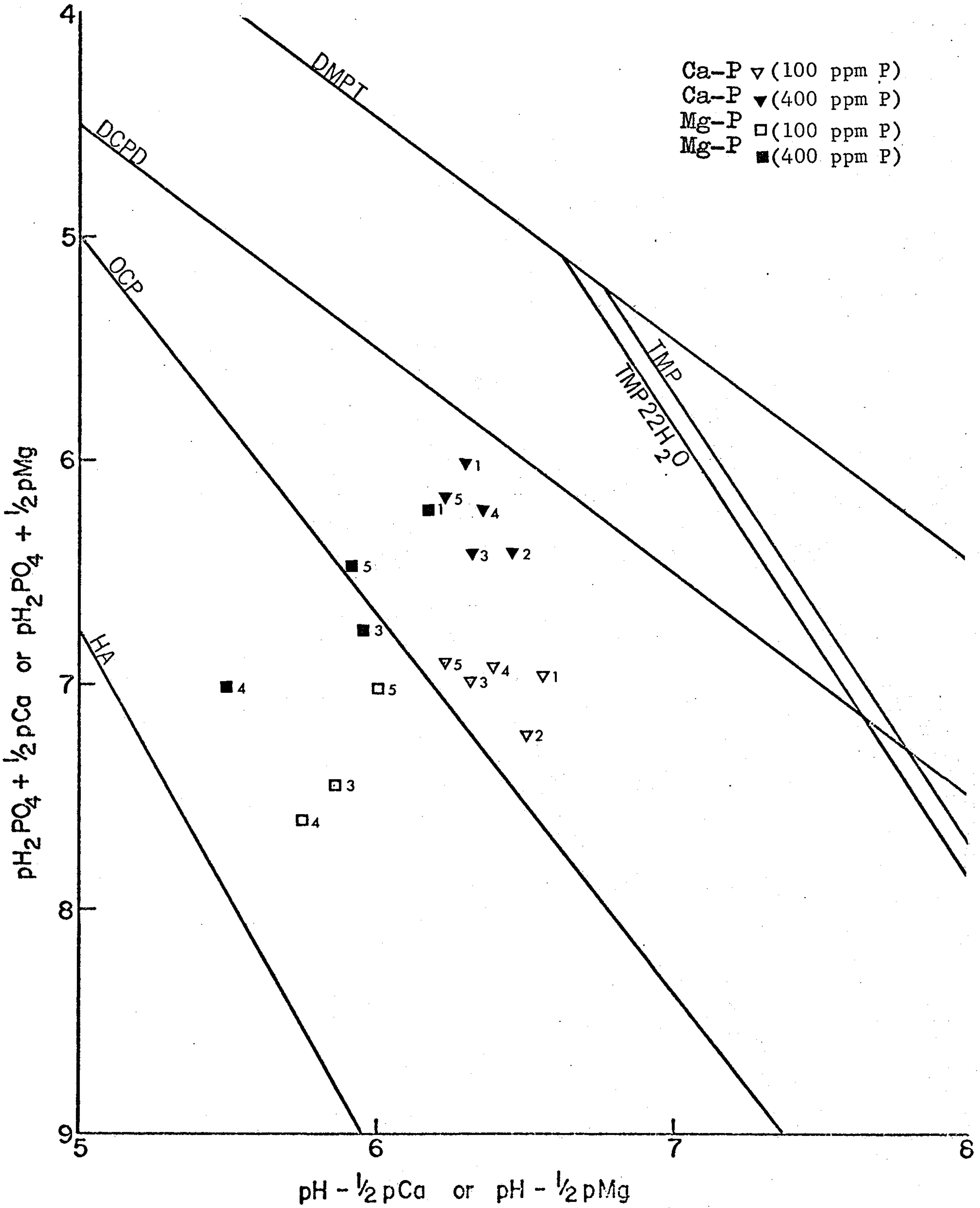

Figure 21. Solubility of DMPT Mixed With the Aneda Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4) and 8 months(5) of incubation.

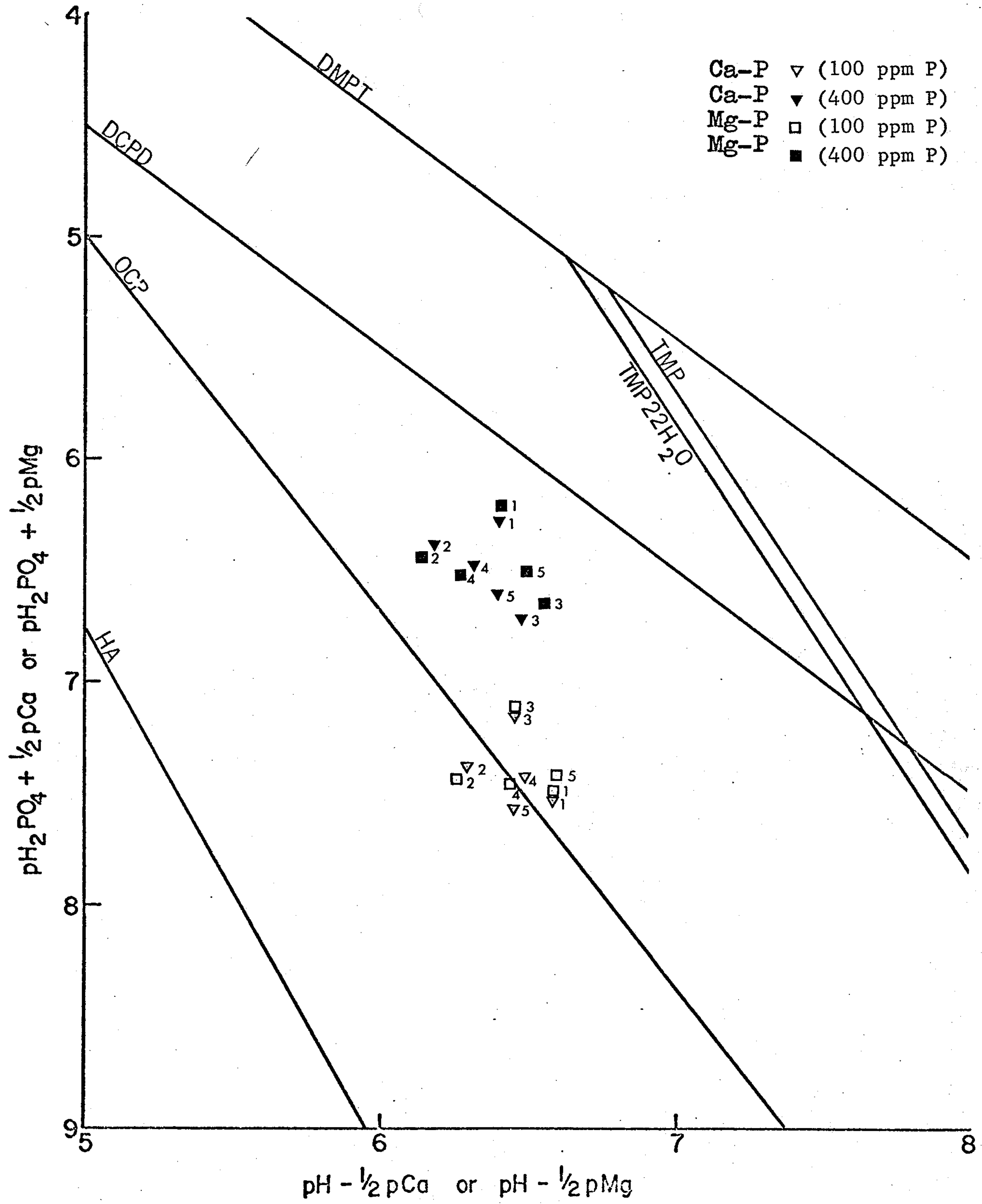

Figure 22. Solubility of DCPD Mixed With the Balmoral Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4) and 8 months(5) of incubation.

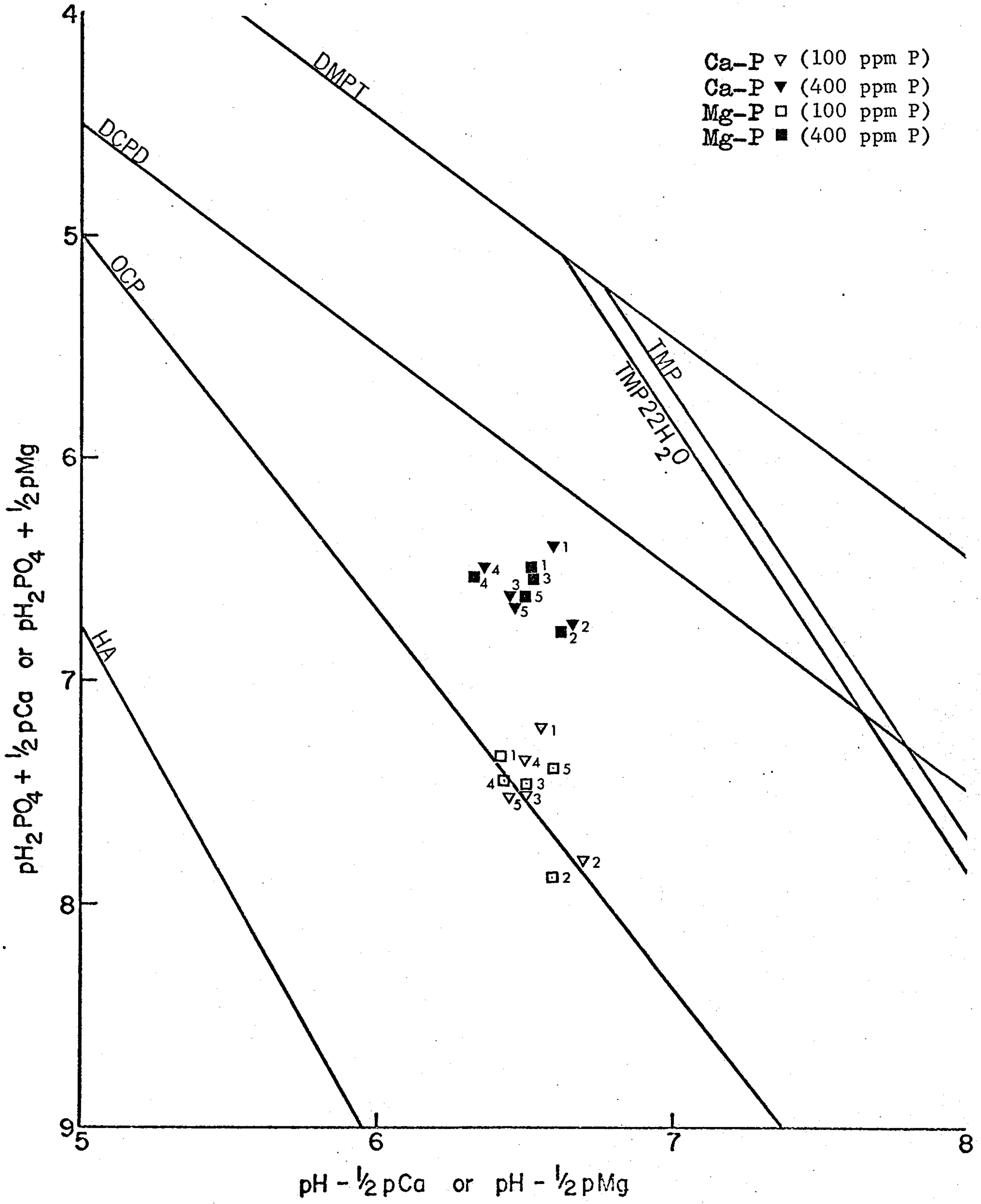

Figure 23. Solubility of DMPT Mixed With the Balmoral Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4) and 8 months(5) of incubation.

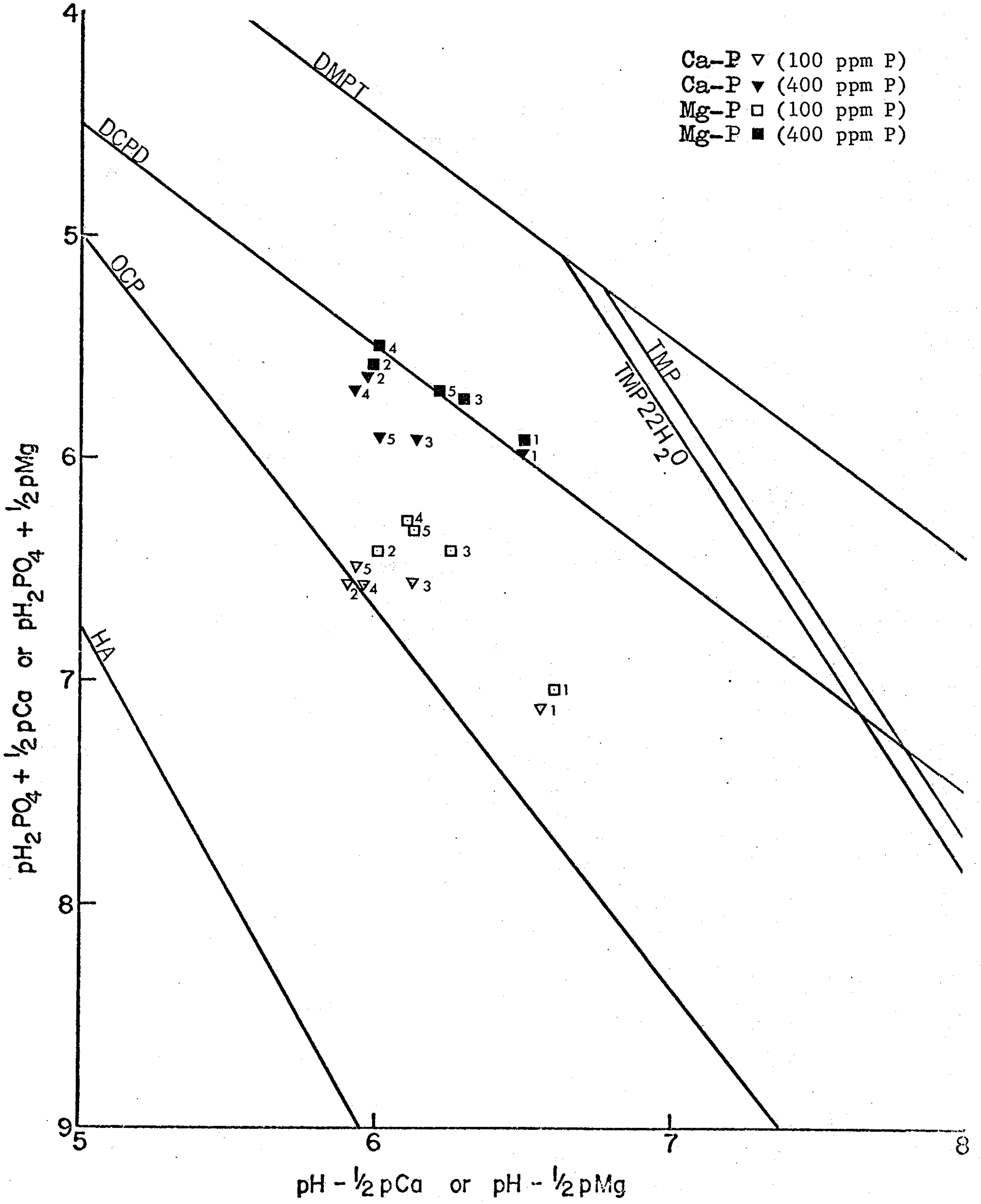

Figure 24. Solubility of DCPD Mixed With the Red River Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4) and 8 months(5) of incubation.

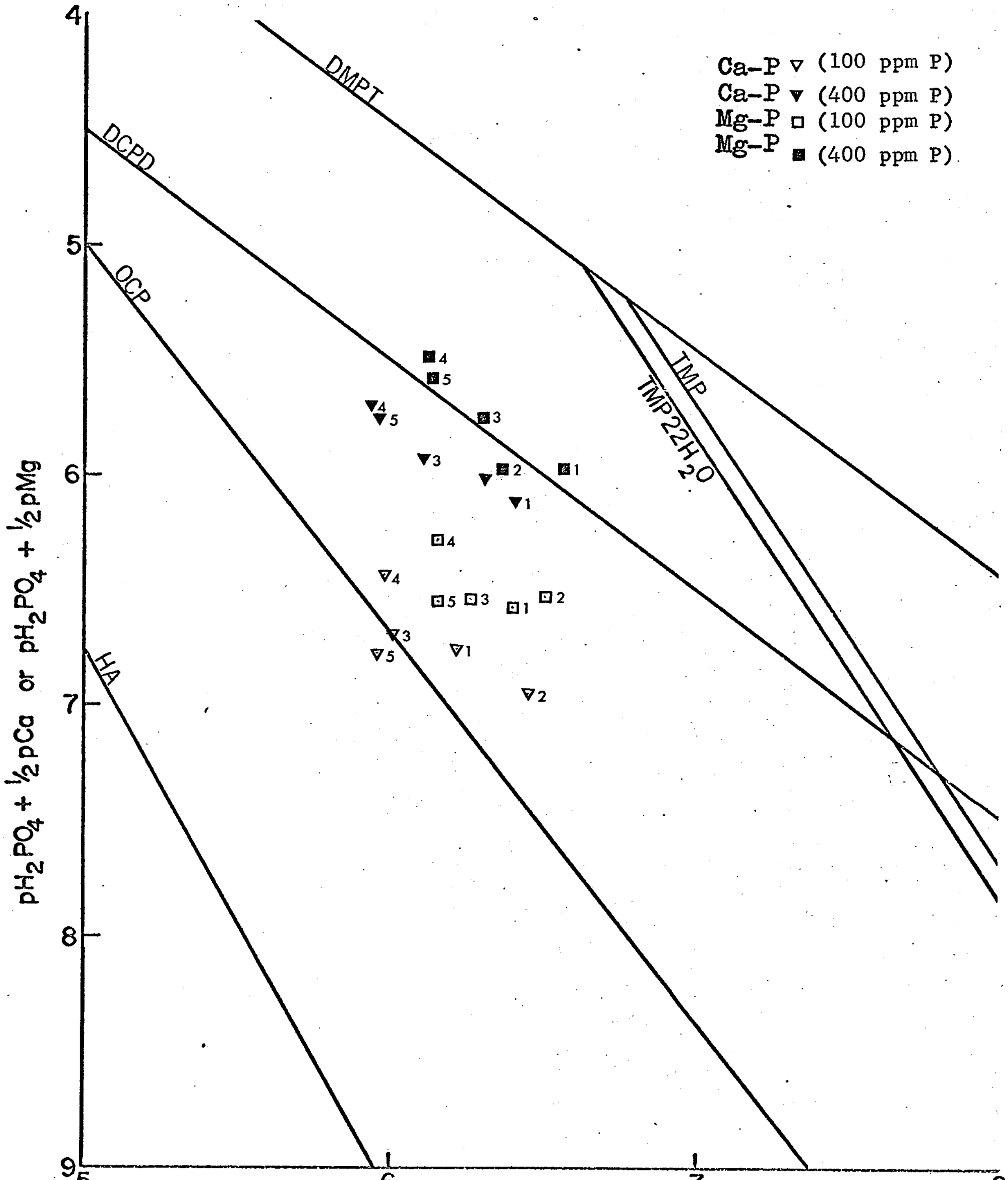

Figure 25. Solubility of DMPT Mixed With the Red River Soil at 1 day(1), 1 month(2), 3 months(3), 6 months(4) and 8 months(5) of incubation.

rate of 100 ppm phosphorus, were much less soluble than when added at the rate of 400 ppm phosphorus. The solubilities of DCPD and DMPT, added at the rate of 100 ppm phosphorus, were very similar and decreased only slightly with time of incubation.

Supersaturation with respect to DCPD did not occur when 400 ppm phosphorus as DCPD or DMPT was added to the Balmoral soil (Figures 22 and 23). The solubility of the added phosphorus was intermediate between that of DCPD and OCP for the entire sampling period. The solubility of the added phosphorus was lower when 100 ppm phosphorus was added than when 400 ppm phosphorus was added. Solubility values indicated that OCP may have been governing the phosphorus concentration in the soil solution.

DMPT and DCPD, when added to the Red River soil, remained more soluble than when added to the other three soils (Figures 24 and 25). This is probably due to the formation of magnesium phosphates in this high magnesium soil. X-ray data have shown DMPT and a trimagnesium phosphate to be present in the reaction zone when pellets of KH_2PO_4 and K_2HPO_4 were added to this soil. Supersaturation with respect to DCPD existed in the soils incubated with DCPD for one day, but did not occur for the soils treated with DMPT. Added phosphorus was rendered less soluble when added at the rate of 100 ppm than when added at the rate of 400 ppm. The majority of points indicate supersaturation with respect to OCP. Again, phosphorus added as DMPT was slightly less soluble than that added as DCPD.

The studies show that both DCPD and DMPT, although metastable, can increase the solubility of phosphorus in soils for a considerable period of time when added at rates of 100 or 400 ppm phosphorus. The solubilities of

DCPD and DMPT in the soils studied were very similar and decreased slightly with time. This would indicate that phosphorus added in this form would eventually decrease in solubility to a level near that of the native soil phosphorus. This, however, would probably take a considerable period of time.

The soils treated with 400 ppm phosphorus as DCPD and DMPT behaved very similarly to the soils mixed with 400 ppm phosphorus as KH_2PO_4 and K_2HPO_4. Therefore, it is apparent that the addition of the actual initial reaction product rather than of a water-soluble phosphate does not greatly affect the solubility of phosphorus in a given system, i.e. the solubility of DCPD or DMPT added to soils was similar to that of applied KH_2PO_4 or K_2HPO_4.

V. SUMMARY AND CONCLUSIONS

The role of the calcium ion in processes of phosphorus fixation has received much attention. Until recently, information regarding the possible role of the magnesium ion in similar processes has been limited. The formation of the magnesium phosphates has been studied only under short term incubations. Since the initial reaction products, DCPD and DMPT, undergo reaction to form less soluble phosphates, the length of time that DCPD and DMPT persist in soils will affect the long-term availability of applied phosphate fertiliser. This study was conducted in order to trace the fate of applied soluble phosphate during a prolonged incubation period (450 days) in soils varying in calcium and magnesium content.

Six calcium and magnesium phosphates were detected by X-ray analysis when KH_2PO_4 and K_2HPO_4 were added in pellet form to four soils. These phosphates were: DCPD, $CaHPO_4.2H_2O$; DMPT, $MgHPO_4.3H_2O$; OCP, $Ca_4H(PO_4)_3.3H_2O$; HA, $Ca_{10}(PO_4)_6.(OH)_2$; TMP, $Mg_3(PO_4)_2.22H_2O$; a calcium phosphate, $Ca_4P_2O_9$; and a calcium-magnesium phosphate $Ca_3Mg_3(PO_4)_4$, DCPD formed in all soils treated with KH_2PO_4 and in two soils treated with K_2HPO_4. The magnesium phosphates formed only in soils which contained large amounts of magnesium. DMPT formed along with DCPD in soils having a water-soluble calcium to magnesium ratio of less than 1.5. Octacalcium phosphate was a prominent reaction product in all soils. The calcium-magnesium phosphate, $Ca_3Mg_3(PO_4)_4$ was formed in the soil containing approximately equivalent amounts of ammonium-acetate extractable calcium and magnesium. The calcium phosphate, $Ca_4P_2O_9$ was detected in the soils containing larger amounts of calcium relative to magnesium. Neither $Ca_3Mg_3(PO_4)_4$ nor $Ca_4P_2O_9$ has previously been reported as occurring in soils. TMP.$22H_2O$, considered the hydrolysis product of DMPT formed only in the soil containing very large amounts of magnesium. This relatively insoluble magnesium phosphate tended to form less readily when phosphorus was added as KH_2PO_4 rather than as K_2HPO_4.

The period of time that the more soluble reaction products, DCPD and DMPT, existed in the soils varied with soil type and phosphorus carrier added. These initial reaction products persisted for a longer period of time when phosphorus was added as KH_2PO_4 rather than as K_2HPO_4. It is therefore probable that phosphorus added in a carrier acid in reaction will have a greater long-term availability than will phosphorus added in a carrier alkaline in reaction.

Solubility studies indicated that the solubility of phosphorus added in pellet form or mixed with the soils as KH_2PO_4 or K_2HPO_4, decreased as time of incubation increased. The solubility of phosphorus in all soils was initially near that of DCPD or DMPT and remained so for a short period of time. The solubility of added phosphorus then decreased and approximated that of OCP after 12 to 15 months of incubation. Phosphorus remained most soluble in the soil having the highest magnesium content. Phosphorus remained more soluble when added as a KH_2PO_4 pellet rather than as a K_2HPO_4 pellet. Mixing the orthophosphates with the soil apparently eliminated any differences between carriers which were operable for the pelleted source of phosphorus.

The solubility of DCPD and DMPT mixed with the soils followed the same trend as when KH_2PO_4 or K_2HPO_4 was added. It was apparent that the addition of the actual initial reaction product rather than a water-soluble phosphate does not greatly affect the solubility of phosphorus in a given system, i.e. the solubility of DCPD or DMPT added to soils was similar to that of applied KH_2PO_4 or K_2HPO_4. In all studies, the solubility of added phosphorus was much greater than the solubility of the native soil phosphorus, even after 15 months of incubation. The studies indicated that phosphorus added as KH_2PO_4 and K_2HPO_4 in pellet form, or as KH_2PO_4, K_2HPO_4, DMPT and DCPD mixed with soils, remained relatively soluble for considerable periods of time. Reaction products formed around pellet sites were relatively soluble phosphates. These results indicated that phosphorus added to soils such as those used in this investigation would probably remain available to plants over a long period of time.

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