

REACTION PRODUCTS OF ORTHOPHOSPHATES IN SOILS
CONTAINING VARYING AMOUNTS OF
CALCIUM AND MAGNESIUM

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ABSTRACT

Some soils occurring in Manitoba contain appreciable quantities of magnesium as exchangeable magnesium or in the form of dolomite. In order to study the effect of magnesium on the reaction products of orthophosphate, soils varying in calcium and magnesium content were selected and the reaction products of added phosphate determined. Addition of granular KH_2PO_4 (pellet) resulted in the formation of dicalcium phosphate dihydrate in the soils which were predominantly calcium saturated. The phosphorus passing into solution precipitated as dicalcium phosphate dihydrate and as dimagnesium phosphate trihydrate in the soils having a water soluble calcium to magnesium ratio of approximately 1.5 or less.

Reaction of two dolomitic soils with saturated solutions of KH_2PO_4 , K_2HPO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ resulted in the formation of dicalcium phosphate dihydrate and dimagnesium phosphate trihydrate with the acid carriers and octacalcium phosphate trihydrate and trimagnesium phosphate tetrahydrate with the alkaline carriers. Addition of the orthophosphates as a pellet to a soil with a water soluble calcium to magnesium ratio of 0.70 resulted in the formation of dimagnesium phosphate trihydrate in all instances except with $\text{NH}_4\text{H}_2\text{PO}_4$ where dicalcium phosphate dihydrate was formed as well. The orthophosphates were precipitated as dicalcium phosphate dihydrate and dimagnesium phosphate trihydrate in a soil with a water soluble calcium to magnesium ratio of approximately 2.0.

Dimagnesium phosphate trihydrate, upon reaction with a soil containing large amounts of magnesium was found to dissolve incongruently

leaving a residue of trimagnesium phosphate twenty-two hydrate.

The solubilities of dicalcium phosphate dihydrate, dimagnesium phosphate trihydrate, trimagnesium phosphate twenty-two hydrate and anhydrous trimagnesium phosphate were determined. The constant derived for the equation, $(\text{pH} - \frac{1}{2}\text{pCa}) - (\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pCa})$, was found to be 0.52 for dicalcium phosphate dihydrate at 25±1 deg. C. The constant derived for the equation, $(\text{pH} - \frac{1}{2}\text{pMg}) - \text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pMg}$, was found to be 1.82 for dimagnesium phosphate trihydrate. The hydrated trimagnesium phosphate was found to be considerably less soluble than dicalcium phosphate dihydrate or dimagnesium phosphate trihydrate. The constant derived for the equation, $2(\text{pH} - \frac{1}{2}\text{pMg}) - (\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pMg})$, was found to be 8.31 for the hydrated trimagnesium phosphate and 8.55 for the anhydrous form. Addition of CaCl_2 , MgCl_2 , KCl , CaSO_4 , MgSO_4 , and K_2SO_4 increased the solubility of dicalcium phosphate dihydrate. Similar trends were observed when the salts were added to dimagnesium phosphate trihydrate with the exception of the calcium salts where a decrease in phosphate solubility occurred at high salt concentrations.

The solubility of phosphorus remained between that of dicalcium phosphate dihydrate and dimagnesium phosphate trihydrate for soils treated with varying amounts of KH_2PO_4 . Similar results were obtained when the soils were equilibrated with a 0.01 M H_3PO_4 solution or with K_2HPO_4 . The solubility of the added phosphate was greater in the soils containing large amounts of magnesium than in the soils containing large amounts of calcium.

Magnesium saturated montmorillonite clay held phosphate more tightly than did a calcium saturated clay. The adsorption maximum of the calcium saturated clay was higher than that of the magnesium saturated clay. The solubility of phosphate added to the clays was found to increase as the rate of phosphate added was increased. At low rates of added phosphate, a phosphate on soil adsorption reaction was operative, while at high levels of added phosphate a precipitation reaction was evidenced.

Dicalcium phosphate dihydrate and dimagnesium phosphate trihydrate were found to be about equally effective in supplying growing plants with phosphorus on phosphate deficient soils. The growing plants obtained slightly less phosphorus from added dicalcium phosphate dihydrate and dimagnesium phosphate trihydrate than from KH_2PO_4 .

A large proportion of phosphate added to soils was extracted by NH_4Cl or NaHCO_3 indicating that phosphate added to Manitoba soils is fixed initially in readily soluble compounds.

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I. INTRODUCTION

The mechanisms by which soils hold phosphate are not clearly understood. In acid soils iron and aluminum are considered the dominant cations which hold phosphate. In soils containing large amounts of calcium carbonate, it is the calcium ion that is considered to react with phosphate. Addition of a soluble phosphate to soils results in the formation of a monomolecular layer of phosphorus on the surfaces of the soil particles. As more phosphorus is added, this adsorption reaction is followed by precipitation of the added phosphate. In acid soils compounds such as variscite, vivianite, sturrtite and taranakite are formed as a result of adding phosphate. Added phosphate is usually precipitated as dicalcium phosphate dihydrate or as octacalcium phosphate trihydrate in soils containing large amounts of calcium. These calcium phosphates are metastable and undergo further reactions with the soil solution until an apatite is formed. The information regarding the role of magnesium in phosphate fixation is extremely limited and contradictory. To date, the existence of magnesium phosphates in soils have not been reported or was not found in the literature.

It is estimated that greater than one-half of the soils in the Red River Valley contain large amounts of magnesium. The magnesium is present in the form of dolomite or as exchangeable magnesium. Since some soils in Manitoba contain large amounts of magnesium and since the role of magnesium in phosphate fixation has received little attention, a comprehensive study of the mechanisms by which magnesium can fix

phosphate is essential to better understand the phosphate chemistry of our soils.

The objectives of the work reported were to determine:

- (a) the phosphate minerals formed when various orthophosphates are added to soils containing large amounts of magnesium.
- (b) the solubility and plant availability of the products formed.
- (c) the effect of various salts on the solubility of some of the minerals formed.

II. REVIEW OF LITERATURE

The calcium ion plays a dominant role in fixing phosphate in soils containing large amounts of calcium carbonate. The source of the calcium ion may be the exchange complex, the soil solution, or the calcium ions on the surfaces of calcium carbonate particles.

Calcium phosphates exist in several forms, the most important in soils are:

- (1) Monocalcium phosphate monohydrate (MCPM) - $\text{Ca} (\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. MCPM is water soluble and is a constituent of superphosphate fertilizers. MCPM cannot persist in soils if added as a fertilizer. It is converted to some other form (7, 4).
- (2) Dicalcium phosphate dihydrate (DCPD) - $\text{Ca H PO}_4 \cdot 2\text{H}_2\text{O}$. This form is only slightly water soluble, metastable, and is believed to be the initial reaction product formed when soluble phosphatic fertilizers, acid in reaction, are added to soils containing large amounts of calcium (4) . DCPD may be formed at the site of phosphorus application due to hydrolysis of MCPM or in the soil surrounding the site (21). DCPD can exist only in soils in which the phosphorus concentration in solution is unusually high. Due to the low concentration of phosphorus in most soil solutions DCPD undergoes a slow change to the more basic octacalcium phosphate trihydrate (19). When water is added to DCPD, it forms free phosphoric acid plus a more alkaline phosphate, octacalcium phosphate trihydrate (33). Moreno et al. (22) have found the

solubility product of DCPD to be 2.77×10^{-7} at 25 deg. C.

(3) Octacalcium phosphate trihydrate (OCP) $\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$.

OCP may be formed in soil systems as a result of hydrolysis of DCPD (19) or it may be formed directly under suitable conditions as a result of adding phosphate (19).

Bjerrum (5) reported pK_{sp} values for OCP of 11.8 and 9.3 depending on whether equilibrium was approached by dissolution or by precipitation. Moreno et al. (23) defined the solubility product constant for OCP by the expression:

$4\text{pCa} + 3\text{pHPO}_4 - 2\text{pH} = \text{pK}_{\text{sp}}$ in which p denotes the negative logarithms of ionic activities. They obtained a value of 9.93 for pK_{sp} at 25 deg. C.

(4) Hydroxyapatite (HA.) - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. HA. is considered the predominant solid phase phosphate in neutral and alkaline soils. It occurs as a result of hydrolysis of the more soluble calcium phosphates (33, 24). It is also formed as a result of adding phosphates, alkaline in reaction, to calcareous soils (4, 6).

Clark (7) defined the pK_{sp} of HA. according to the following equation:

$$10\text{pCa} + 6\text{pPO}_4 + 2\text{pOH} = \text{pK}_{\text{sp}}$$

and reported a value of 115.5 for pK_{sp} at 25 deg. C.

The effects of calcium in phosphate fixation in soils is fairly well understood, but little is known about the effects of magnesium on phosphate fixation. Perkins (27) found that up to a pH of 4.5,

magnesium ions were about as effective as calcium ions in precipitating phosphate added to 100 mesh kaolin. At higher pHs magnesium ions were far less effective than calcium ions. He concluded that precipitation of phosphorus by magnesium was not important in agricultural soils.

Hibbard (12) studied the effect of various cations on the solubility of phosphate. He found the solubility of phosphate increased in the order calcium, magnesium potassium, sodium, ammonium. He also found that calcium carbonate depressed the solubility of phosphate more than did magnesium carbonate but that both greatly reduced the solubility of phosphate. Hibbard (12) also observed that below a pH of 7.0 added calcium and magnesium markedly depressed the solubility of phosphate and above a pH of 7.0 the phosphates were nearly insoluble.

Halstead et al. (11) found that the application of calcium carbonate to acid soils resulted in higher amounts of NaHCO_3 - soluble phosphorus than were obtained with magnesium carbonate. The carbonates of calcium tended to be more effective than that of magnesium in increasing the phosphorus content of the plants.

Although there are a few reports on the effect of magnesium on phosphate solubility, the compounds formed when magnesium and phosphorus interact in soils have not been reported or were not found in the literature. Magnesium orthophosphates, similar to the calcium orthophosphates previously listed, have been found in nature or have been prepared from aqueous systems. Those of interest are:

(1) Monomagnesium phosphate (MMP) - $\text{Mg}(\text{H}_2\text{PO}_4)_2$. MMP is similar to MCPM

in that it is soluble in water. In instances it has been used as a phosphate fertilizer.

(2) Dimagnesium phosphate (DMP) - $MgHPO_4$.

This form of phosphate has been found in both the trihydrate (Newberyite) and heptahydrate (phosphorroesslerite) form (8). The seven hydrate form (DMPH) can be obtained by precipitation of a magnesium sulfate solution by phosphate ions at room temperature (8). This form can then be dehydrated to give the trihydrate form (DMPT).

(3) Trimagnesium phosphate (TMP) - $Mg_3(PO_4)_2$.

Trimagnesium phosphate has been found to occur in the four (TMP.4H₂O), eight (TMP.8H₂O) and twenty-two (TMP.22H₂O) hydrate form (33, 9). The eight hydrate form has been prepared by slow precipitation of a magnesium sulfate solution by a solution of Na_2HPO_4 and $NaHCO_3$ (9).

(4) Wagnerite - $Mg_2(PO_4)F$

Wagnerite has been found to occur in nature and therefore could possibly exist in soils.

Mono and dimagnesium orthophosphates decompose in contact with water to form free phosphoric acid and a more alkaline phosphate essentially in the same manner as the calcium orthophosphates (33). It was shown that poorly soluble phosphates (DMP and TMP) hydrolyzed when suspended in water into free phosphoric acid and a more basic phosphate (10). A review of the literature indicates that the magnesium orthophosphates tend to be more soluble than the calcium orthophosphates. However, solubility products for the magnesium orthophosphates were not found in the literature.

It seems from the review of literature that there is a need for identifying the phosphorus compounds formed in soils containing large amounts of magnesium. The solubility and plant availability of these phosphates also need be determined.

III. MATERIALS AND METHODS

The investigations reported in this manuscript include several individual studies where different procedures were used. The experimental methods used for each of these investigations are not described in a general methods section, but, for purposes of clarity, are discussed along with the results obtained, under the appropriate subsection. The analytical procedures employed in the investigations and in characterizing the soils are outlined below. A brief description of the soils studied is also included.

(1) Soils

A subgroup designation of the soils studied is given in Table I. Other soil characteristics are given in the following section along with the results obtained on the soils.

(2) Soil Organic Matter

Soil organic matter was determined according to the method outlined by Walkey and Black (35). The organic carbon was oxidized with excess potassium dichromate, followed by titration of the unreacted potassium dichromate with ferrous sulfate.

(3) Soil pH

The pH of the soil samples or solutions was determined electrometrically by the use of the glass and calomel electrodes on a Universal pH meter 22. A soil: distilled water ratio of 1:20 (W/W) was usually employed unless otherwise stated. The pH of the supernatant above the soil was measured.

Table 1.

Subgroup designation of soils studied

<u>Soil Name</u>	<u>Subgroup</u>
Balmoral	Carbonated Rego Humic Gleysol
Inwood	Gleyed Dark Grey
Aneda	Thin Orthic Dark Grey
Plum Ridge	Gleyed Carbonated Rego Black
Foley	Carbonated Rego Humic Gleysol
Scanterbury	Gleyed Black
Reinland	Gleyed Carbonated Rego Black
Darlingford	Orthic Black
Pine Valley	Gleyed Dark Grey Wooded
Frammes	Gleyed Dark Grey
Kipling	Gleyed Dark Grey
Seven Sisters	Orthic Dark Grey Wooded
Osborne	Rego Humic Gleysol
Thalberg	Solonetzic Dark Grey
Pequis	Gleyed Dark Grey
Lee River	Orthic Humic Gleysol
Red River	Gleyed Rego Black

(4) Carbonate Content

The method outlined by Ridley (29) was used. A one gram soil sample was digested in 10% HCl for 10 minutes. The CO₂ evolved was sucked through a drying and adsorption train, then absorbed by Ascarite. The weight of CO₂ absorbed was determined and expressed as percent CO₃.

(5) Water Soluble Calcium and Magnesium

Five grams of soil was shaken for one hour in 100 ml. distilled water. The suspension was centrifuged and filtered through Whatman No. 42 quantitative filter paper. The calcium and magnesium content of the filtrate was determined using EDTA.

(6) Acid Soluble Calcium and Magnesium

One hundred milliliters of 0.2 N HCl was added to a one gram soil sample and reacted near the boiling point for 2.5 hours. The suspension was filtered, brought to volume, and the calcium and magnesium content of the filtrate determined using EDTA. The calcium and magnesium contents of the samples were then calculated.

(7) Ammonium Acetate Displaceable Calcium and Magnesium

Twenty-five grams of air-dried soil was shaken in 50 ml. neutral ammonium acetate solution for one hour. The supernatant was sucked through a Buchner funnel and the soil transferred to the funnel with NH₄Ac solution. The soil was then leached with small portions of NH₄Ac to a volume of 250 ml. The calcium and magnesium contents of the filtrate were determined and the calcium and magnesium content of the soils calculated.

(8) Calcium and Magnesium in Solution

A titration procedure was used for the determination of the calcium

and magnesium contents of most extracts (32). First the total calcium plus magnesium content was obtained by titration with ethylene diamine tetraacetic acid (EDTA), using Eriochrome Black T as indicator. On a separate aliquot magnesium was precipitated as the hydroxide by adding NaOH and the calcium titrated with EDTA using Calcon as an indicator. Magnesium was obtained by difference.

(9) Phosphorus

Phosphorus was determined using a colorimetric procedure as outlined by Jackson (14). A suitable aliquot was adjusted to pH 3.0 with 4 N NH_4OH or 4 N HCl using 2-4 dinitrophenol indicator. Twenty milliliters of ammonium molybdate hydrochloric acid reagent was added, followed by 10 ml. of dilute SnCl_2 reagent. The volume was adjusted to 100 ml. and after 5 minutes the color intensity measured on a Model 6A Coleman Junior Spectrophotometer at 660 m μ . By comparison of these readings to those obtained for a standard curve, the phosphorus contents of the solutions were determined.

(10) X-Ray Technique

A small sample, ground to less than 300 mesh, was placed into a 0.3 mm. diameter glass capillary tube obtained from Caine Scientific Sales Company, Chicago, Illinois. The prepared tube was centered into a Philips cylindrical powder diffraction camera. The camera was 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 equipped with a cobalt target and iron filter. It was operated at 36 KV. and 8 ma.

in all studies. Exposure time varied from 3 to 24 hours depending upon the study and the material being X-rayed. The samples were rotated mechanically during exposure. After exposure the film was removed from the camera, placed into Kodak Rapid X-Ray Developer for 5 to 6 minutes, rinsed in water, placed into Kodak X-Ray Fixer for 20 minutes, rinsed again and then dried. The distances between diffraction lines were measured on a Philips Film Illuminator and Measuring Device. The "d" spacing corresponding to each diffraction line was calculated. The minerals present in the samples were identified by a comparison of the "d" spacings obtained to known values listed in the ASTM X-Ray Powder Data File.

(11) Preparation of DCPD, DMPT, and TMP

DCPD was prepared by slow addition of a CaCl_2 solution and a phosphorus solution ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} + \text{KH}_2\text{PO}_4$) into a phosphate solution (KH_2PO_4) maintained at pH 4 to 5 (2). When the precipitation was complete, the mother liquor was sucked from the precipitate. The precipitate was first washed with a very dilute solution of H_3PO_4 , then with ethanol and air dried.

DMPT was prepared by substituting MgCl_2 for the CaCl_2 in the above procedure. The initial pH of the reaction mixture had to be raised to a pH of 5 to 6 with KOH before precipitation would occur. A pH of 4 to 5 was maintained after precipitation was initiated.

The phosphorus and calcium or magnesium content of the prepared products was determined. Phosphorus content was determined colorimetrically

and the calcium or magnesium content determined as outlined in Kolthoff and Sandell (17). In addition, loss on ignition at 900 deg. C. was determined for each of the phosphates. The phosphorus and calcium content of the prepared DCPD was found to be 18.18 and 23.40 percent respectively. The phosphorus and magnesium content of the prepared DMPT was 17.96 and 13.76 percent respectively. Conversion of the DCPD to $\text{Ca}_2\text{P}_2\text{O}_7$ and DMPT to $\text{Mg}_2\text{P}_2\text{O}_7$ resulted in weight losses of 26.21 and 36.34 percent respectively. X-ray diffraction analysis indicated that both of the phosphates were successfully prepared.

TMP. $22\text{H}_2\text{O}$ was prepared by slow precipitation of a MgSO_4 solution by a solution of Na_2HPO_4 . Separate solutions of MgSO_4 (28.4 g in 350 ml.) and Na_2HPO_4 (36.1 g in 350 ml.) were added dropwise to distilled water stirred mechanically. The pH of the reaction mixture was maintained at pH 10 by the addition of NaOH. The precipitate was filtered, washed with distilled water and air dried.

The magnesium and phosphorus content of the prepared TMP. $22\text{H}_2\text{O}$ was found to be 11.10 and 9.35 percent respectively. Differential thermoanalysis indicated that the water of hydration was completely lost at 250 deg. C. Ignition of the TMP. $22\text{H}_2\text{O}$ at 300 deg. C. resulted in a weight loss of 60.12 percent. After ignition the phosphorus and magnesium content of the anhydrous TMP was 27.60 and 23.40 percent respectively. The "d" spacings for the hydrated form were determined as no values were found in ASTM X-Ray Powder Data File.

IV. PRESENTATION OF EXPERIMENTAL METHODS AND RESULTS

Reaction Products of KH_2PO_4 in Calcium Carbonate, Magnesium Carbonate and Soils High in Carbonates

The compounds formed when calcium and phosphorus interact in soils have been identified and reported, but, the compounds formed when magnesium and phosphorus interact in soils have not been reported or were not found in the literature. It is therefore of interest to determine if compounds containing phosphorus and magnesium could form in soils containing large amounts of magnesium.

Six soil samples, one clay (montmorillonite) and calcium and magnesium carbonates were studied. The soil samples were obtained from the A and C horizons of two Balmoral soils, the C horizon of an Inwood soil and the A horizon of an Aneda soil. The Balmoral and Inwood soil samples and the montmorillonite clay were saturated with either calcium or magnesium using solutions of 1.0 M CaCl_2 or 1.0 M MgCl_2 . The pH of the saturating solution was adjusted to coincide with the pH of the soil. Eight hundred grams of soil was shaken with two liters of solution for 3 to 4 days. The solution was then decanted and an additional two liters of solution added and shaking continued for another 3 to 4 days. The solution was withdrawn and the soil washed free of chlorides, air dried and ground. Equal portions of calcium and magnesium saturated soils were mixed to obtain a soil in which both calcium and magnesium were present. The Aneda soil was not treated with CaCl_2 or MgCl_2 . In addition to the soil samples, calcium carbonate, magnesium carbonate

and a 1:1 mixture of calcium carbonate to magnesium carbonate were studied.

Seventy-five grams of soil or carbonate were placed in a plastic cylinder (1-3/4" dia. x 2") on a large watch glass base. The soil or carbonate was wetted and a small opening made in the center of the soil column in which 0.1 gram granular KH_2PO_4 (pellet) was placed. The soils or carbonates were kept in a moist state (field capacity to saturation) for three weeks by the addition of water to the base of the column. Several days after the addition of the KH_2PO_4 , a ring formation and/or small crystals were observed on the surface of the soil columns. The products formed were collected for powder X-ray diffraction analysis 21 days after the addition of the KH_2PO_4 . The "d" spacings for the minerals present in the soil-reaction product mixture and for the soil without added phosphate were determined. Additional spacings occurring in the treated soil were taken to be those of the reaction product. A check (not treated with CaCl_2 or MgCl_2), a calcium, a magnesium, and a calcium plus magnesium system was studied for each of the Balmoral and Inwood soils. The only treatment on the Aneda soil was a check.

Acid soluble, water soluble and ammonium displaceable calcium and magnesium and pH were determined on all soil samples.

The reaction products of the added KH_2PO_4 , along with the soil characteristics are listed in Table II. The carbonate, calcium and magnesium content of all the soils were very high. Complete saturation of the samples with calcium or magnesium was not attained especially on the calcareous soils. This is indicated by the presence of both calcium and magnesium in the ammonium acetate and water extracts.

Table 11. Reaction products of KH_2PO_4 in $CaCO_3$, $MgCO_3$ and soils high in carbonates

Soil	Treat.	pH	Inorg. CO_3 (%)	NH ₄ Ac displaceable (meq./100g.)		Water soluble (meq./100g.)		Dil. HCl soluble (%)		Reaction products
				Ca	Mg	Ca	Mg	Ca	Mg	
Balmoral I, A	Check	8.20	20.1	20.0	23.4	1.25	1.55	8.12	4.40	DMPT
	Mg	8.35		12.1	31.8	0.90	2.40			DMPT
	Ca-Mg	8.15		24.4	17.9	1.70	1.30			DMPT
	Ca	8.00		36.0	4.8	2.50	0.04			DCPD
Balmoral I, C	Check	8.20	31.5	15.5	10.8	0.50	0.90	12.16	5.52	DMPT
	Mg	8.30		14.0	12.4	0.60	1.30			DMPT
	Ca-Mg	8.10		16.6	7.7	0.95	0.75			DMPT
	Ca	8.05		21.4	3.7	1.35	0.35			none detected
Balmoral II, A	Check	7.90	30.9	30.3	13.3	1.90	1.10	15.20	4.00	DCPD + DMPT
	Mg	8.20		12.1	30.6	1.40	2.40			DMPT
	Ca-Mg	8.00		25.6	16.1	1.60	1.30			DCPD + DMPT
	Ca	7.80		38.1	3.0	2.45	0.35			DCPD
Balmoral II, C	Check	8.10	29.3	20.4	13.6	1.10	1.40	13.40	4.12	DCPD + DMPT
	Mg	8.35		14.6	20.2	0.85	1.55			DMPT
	Ca-Mg	8.10		20.6	11.5	1.25	0.95			DCPD
	Ca	7.95		26.6	6.8	1.90	0.30			DCPD
Inwood C	Check	8.25	34.2	15.7	5.4	1.05	0.85	15.30	4.66	DCPD
	Mg	8.30		14.9	6.7	0.80	1.10			DCPD
	Ca-Mg	8.15		15.8	5.2	1.05	0.75			DCPD
	Ca	8.05		18.2	2.7	1.65	0.15			DCPD
Montmorillonite	Check	7.50	0.3	89.0	19.9	0.65	0.55	1.48	0.49	DCPD
	Mg	7.70		14.8	90.8	0.40	0.90			DCPD + DMPT
	Ca-Mg	7.70		61.7	46.6	0.85	0.35			DCPD
	Ca	7.85		104.2	3.3	1.10	0.30			DCPD
MgCO ₃ , CaCO ₃	-	10.20	-	-	-	-	6.10	-	-	DMPT
	-	9.70	-	-	-	0.15	5.35	-	-	DMPT
	-	8.40	-	-	-	1.00	-	-	-	DCPD
Aneda A	Check	7.20	4.57	21.5	2.8	1.62	0.44	2.44	0.90	DCPD
										2.71

It is evident that calcium replaced magnesium on the exchange complex more readily than vice versa. It is also interesting to note that the Balmoral I soil had large quantities of exchangeable magnesium prior to saturation. The pH of the soils was altered during saturation. The pH of the soils increased as the ratio of calcium to magnesium was decreased for individual soils. This was observed for all samples except the montmorillonite.

X-ray analysis of the reaction products indicate that large quantities of magnesium affects the type of phosphate compounds formed. The reaction products in the Balmoral I soils were identified as DMPT except in the calcium saturated Balmoral I, A soil where DCPD was formed. The phosphate crystals obtained in the montmorillonite and Inwood samples were identified as DCPD except in the magnesium saturated montmorillonite where both DCPD and DMPT were detected. The Balmoral II soils containing large amounts of water soluble or NH_4Ac displaceable magnesium reacted with the KH_2PO_4 to form DMPT or DMPT and DCPD. The phosphate compounds formed in the CaCO_3 , $\text{CaCO}_3\text{-MgCO}_3$ mixture and MgCO_3 were identified as DCPD, DMPT and DMPT respectively. The phosphate compound formed in the Aneda soil was identified as DCPD.

In many samples as many as 13 diffraction lines were obtained for DMPT. The largest number of diffraction lines occurring for DCPD in any one sample was eight. Table III shows the calculated "d" spacings for the DMPT and DCPD formed in the soils. The experimental values are compared to corresponding values given for DCPD and DMPT in the ASTM file. Brackets denote the relative intensity of the diffraction lines.

Table III

Experimental and ASTM "d" spacings for DMPT and DCPD (\AA)

<u>DMPT</u>		<u>DCPD</u>	
<u>ASTM</u>	<u>Experimental</u>	<u>ASTM</u>	<u>Experimental</u>
5.9 (40)	5.91	7.57 (100)	7.62
5.3 (20)	5.33	4.24 (100)	4.24
4.70 (40)	4.71	3.80 (7)	3.78
3.45 (100)	3.43	3.05 (75)	3.04
3.05 (80)	3.06	2.93 (50)	2.94
2.80 (32)	2.78	2.623 (50)	2.63
2.71 (24)	2.71	2.603 (50)	2.60
2.57 (32)	2.57	2.434 (15)	2.432
2.39 (24)	2.39		
1.92 (16)	1.93		
1.75 (4)	1.74		
1.66 (8)	1.67		
1.59 (8)	1.59		

The experimental values agree reasonably well with the given values. The most intense lines for both products were present. Since the agreement between the given and experimental values is good, it can be assumed that the products were correctly identified.

In order to verify the presence of DMPT in some of the soils, the reaction product formed in the Balmoral I,C check soil was collected, cleaned of soil, dissolved in HCl and analyzed for phosphorus, calcium and magnesium. The phosphorus content was determined colorimetrically. The calcium and magnesium content was determined as outlined in Kolthoff and Sandell (17). The phosphorus in solution was removed by means of an exchange resin before the precipitation of calcium and magnesium was initiated. The samples did not completely dissolve in the HCl due to soil impurities. The weight of the impurities was obtained and subtracted from the initial sample weight. Similar analysis was conducted on the Balmoral I,C check soil. Results are expressed as a percent of the material dissolved by cold HCl.

The percent calcium, magnesium and phosphorus contained in the reaction product was found to be 6.35, 10.17 and 10.68 respectively (Table IV). Since the soil is extremely high in calcium, it is possible that the calcium found in the reaction product may have resulted from dissolving some of the soil components adhering to the reaction products. The ratio of magnesium to phosphorus in the reaction product was approximately 1:1; that for DMPT is 1:1.27, (w/w). Since the soil impurities also contained magnesium, it is very likely that DMPT was the reaction product in the Balmoral I,C check soil.

Table IV. Chemical composition of the reaction product in the Balmoral I,C check soil and of the Balmoral I,C check soil

Sample	Ca (%)	Mg (%)	P (%)
Reaction product	6.35	10.17	10.68
Soil	22.04	11.72	0.07

The formation of the calcium and magnesium reaction products on the surface of the soil columns were markedly different. Precipitation of the KH_2PO_4 as DCPD was associated with the formation of a ring about one-half inch from the source of phosphate. Figure 1 shows the appearance of the reaction product, DCPD, formed in the Aneda soil. Precipitation of the KH_2PO_4 as DCPD and DMPT resulted in the formation of a ring and small dark crystals near the source of phosphate (Figure 2). The product formed in the ring was DCPD; the phosphate in the crystals was in the form DMPT. Figure 3 shows the presence of DMPT. The illustrations in Figures 2 and 3 were obtained from soils Balmoral II,C check and Balmoral I,C check respectively.

Radioautographs were taken at intervals after the addition of KH_2PO_4 to determine the rate and extent of phosphorus movement from the placement zone into the surrounding soil. One hundred and fifty μC . P^{32} in 0.1 g. KH_2PO_4 was placed in each of Aneda, Balmoral I,C check and Balmoral II,C check soils. No-Screen Medical X-Ray Film was placed over the zone of phosphorus addition for 10 minutes. The films were processed and the radius of the darkened area on the film measured. Radioautographs were taken 1, 2, 4, 7, 10, 15 and 21 days after the

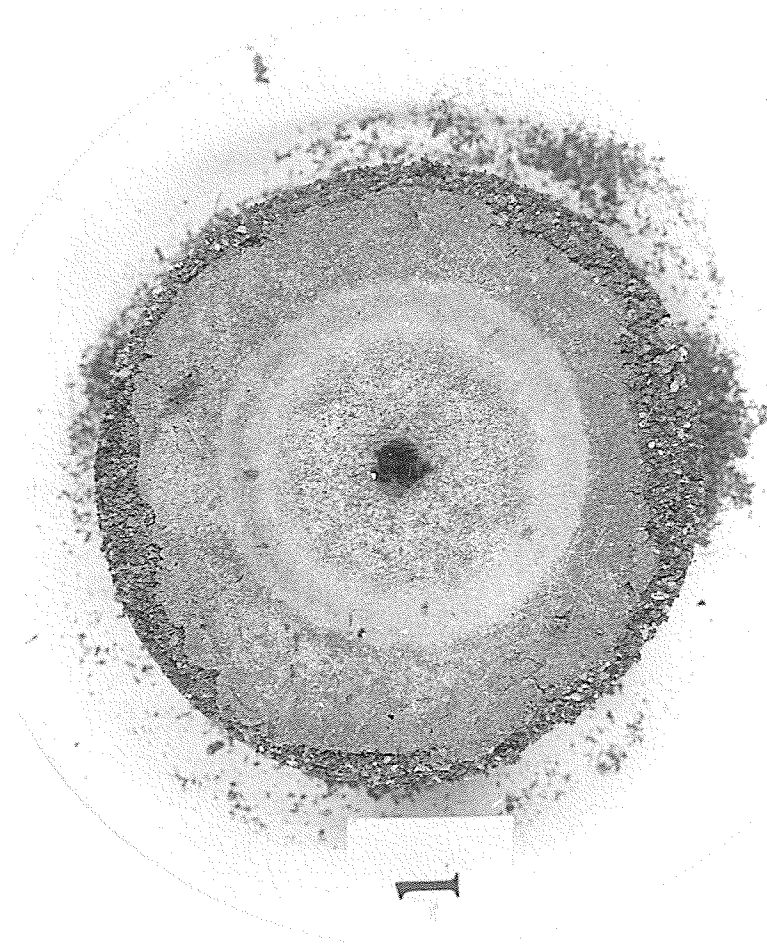


Figure 1. DCPD in Aveda soil

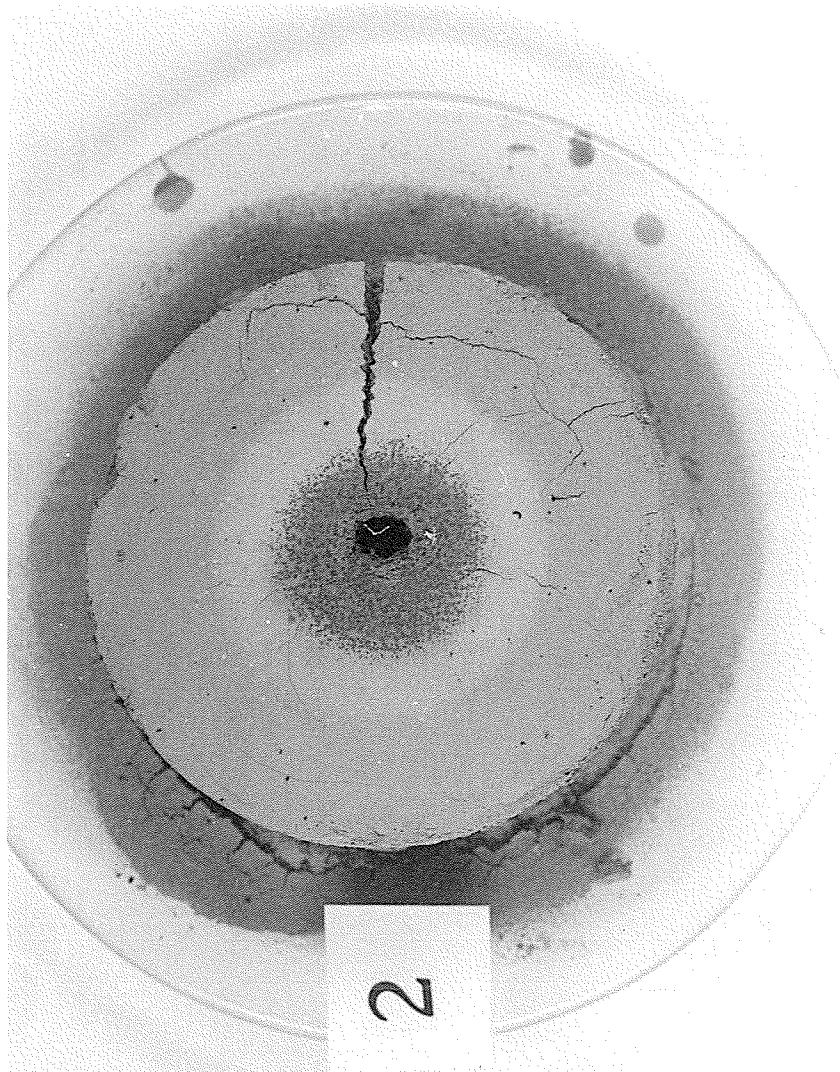


Figure 2. DCPD and DMPF in Balmoral II₂C soil

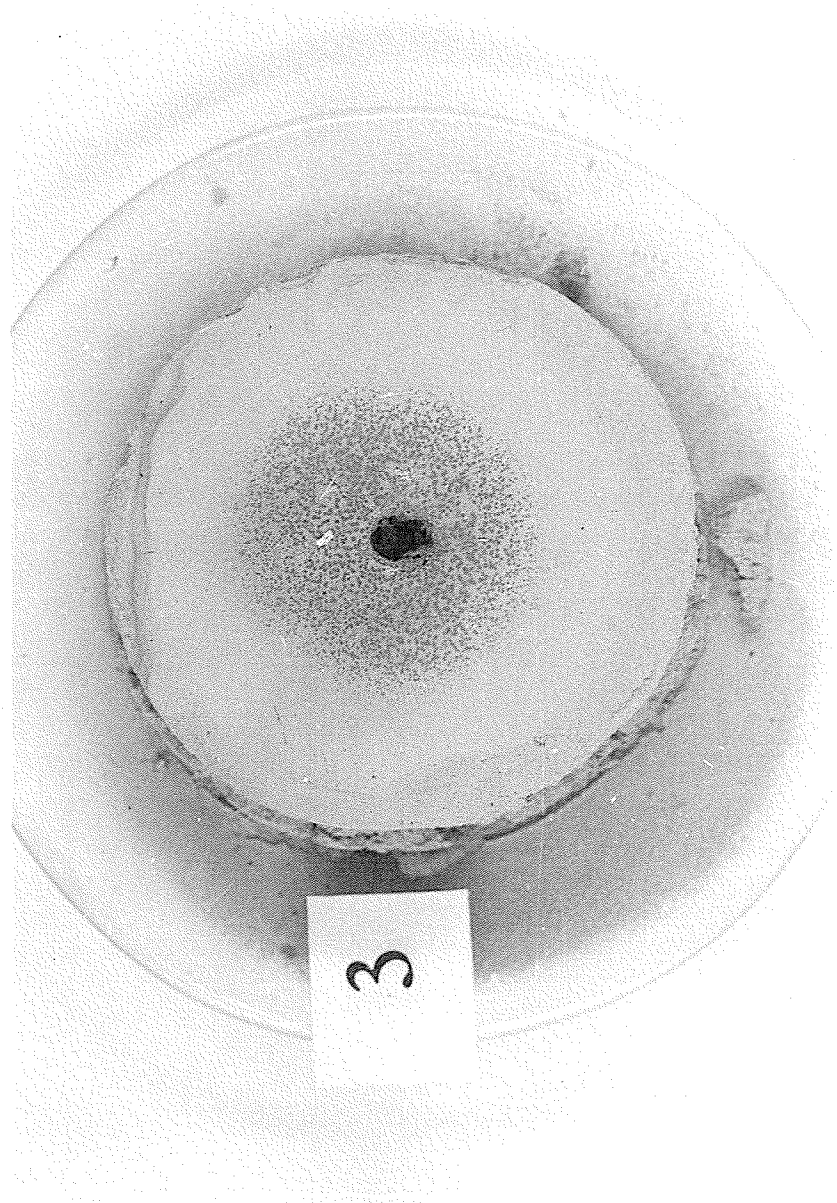


Figure 3. DMPT in Balnoral I,C soil

addition of KH_2PO_4 . The results shown in Table V indicate the distance phosphate moved from the placement zone.

Table V. Movement of phosphorus from the zone of KH_2PO_4 placement (cm.)

Soil	<u>Days after addition of KH_2PO_4</u>						
	1	2	4	7	10	15	21
Balmoral I	1.4	1.7	1.9	1.9	1.9	2.2	2.2
Balmoral II	1.3	1.4	1.4	1.6	1.6	1.6	1.6
Aneda	1.4	1.6	1.6	1.7	1.9	1.9	2.1

Rapid movement of phosphorus occurred during the first day after the addition of KH_2PO_4 (Table V). After the second day, the phosphorus moved out into the surrounding soil very slowly. The movement of phosphorus was similar in the Balmoral I and Aneda soils. In the Balmoral II soil, the diffusion of phosphorus was markedly slower than in the other two soils studied. This was probably due to the heavier texture of the Balmoral II soil. It appears from the study that in soils with moisture contents of field capacity or higher, added phosphate dissolves and moves out into the soil fairly rapidly. Since the formation of reaction products on the surface of the soil columns was first noted on about the second or third day after the addition of KH_2PO_4 , the precipitation of the added phosphate would reduce the rate of phosphorus movement.

The Effect of Varying Amounts of Soil Calcium and Magnesium on the Reaction Products of KH_2PO_4

Results reported in the preceding section indicated that soils containing large amounts of magnesium precipitate added KH_2PO_4 as DMPT, and soils containing large amounts of calcium precipitate the added phosphate as DCPD. The study, however, did not completely establish the effects of varying amounts of soil calcium and magnesium on the reaction products formed. To fulfill these needs, twenty-two soils varying in calcium and magnesium content were selected and the reaction products of added KH_2PO_4 determined.

The procedure employed in the study has been previously described in detail (page 15). NH_4Ac displaceable, water soluble and dilute HCl soluble calcium and magnesium was determined on all soil samples. The soil samples used in the study were collected from A horizons, and consisted of eleven soils containing small to not detectable amounts of carbonates and eleven soils containing large amounts of carbonates.

Table VI. shows the reaction products formed in the soils containing small amounts of carbonates. The carbonate content of the soils ranged from 0.00 to 0.70 percent and the pH of the soils varied from 5.55 to 7.95. The soils are arranged in order of decreasing water soluble calcium to magnesium ratio. A clear endpoint for the determination of calcium and magnesium by EDTA on the HCl extracts was not attained and therefore the results are not recorded. The reaction products detected in the soils were DCPD and DMPT. In many instances both products were formed in the same soil. The data show that if a soil has a water

Table VI. Reaction products of KH_2PO_4 in soils containing small amounts of carbonates

Soil	pH	Inorg. CO ₃ (%)	NH ₄ Ac displaceable (meq./100 g.)		Water soluble (meq./100 g.)		Reaction products		
			Ca	Mg	Ca	Mg			
Darlingford	7.70	0.70	31.30	8.58	3.66	0.93	0.36	2.58	DCPD
Pine Valley	6.94	0.11	17.95	4.65	3.86	0.46	0.28	1.64	DCPD
Frammes	6.10	0.67	21.64	27.80	0.78	0.45	0.30	1.50	DCPD + DMPT
Kipling	7.44	0.43	13.20	9.00	1.47	0.52	0.54	0.96	DCPD + DMPT
Seven Sisters	6.05	0.00	14.55	7.86	1.85	0.15	0.16	0.94	DCPD
Osborne	7.05	0.30	16.50	27.22	0.61	1.30	1.60	0.81	DCPD + DMPT
Thalberg I	5.55	0.00	14.08	9.39	1.50	0.25	0.34	0.74	DMPT
Thalberg II	6.60	0.53	21.78	22.75	0.96	0.45	0.70	0.64	DCPD
Pequis	6.67	0.37	17.84	28.35	0.63	0.64	0.35	0.55	DCPD + DMPT
Lee River	6.66	0.41	13.50	17.80	0.76	0.81	1.66	0.49	DCPD + DMPT
Red River	7.95	0.17	11.23	25.88	0.43	0.32	0.66	0.48	DCPD + DMPT

soluble calcium to magnesium ratio of 1.5 or less, the formation of DMPT along with DCPD can be expected in many instances when a phosphate acid in reaction is added.

Table VII shows the reaction products formed on the series of soils containing large amounts of carbonates. The carbonate content of the soils varied from 3.61 to 25.20 percent CO_3 . The pH of the soils varied from 7.20 to 8.30. The amounts of calcium and magnesium in the water extracts were higher than those recorded for the soils containing small amounts of carbonates. In many instances both DCPD and DMPT were formed in the same soil. Only on soils which were predominantly calcium saturated was DCPD formed alone. The formation of DMPT, along with DCPD in most instances, occurred at a water soluble calcium to magnesium ratio of less than 1.5. Dilute HCl soluble and NH_4Ac displaceable calcium and magnesium did not afford a good indication as to the products that would be formed in the soils.

Table VII. Reaction products of KH_2PO_4 in soils containing large amounts of carbonates

Soil	pH	Inorg. CO_3 (%)		NH ₄ Ac displaceable (meq./100 g.)		Water soluble (meq./100 g.)		Dil. HCl soluble (%)		Reaction products	
		Ca	Mg	Ca/Mg	Ca	Mg	Ca/Mg	Ca	Mg		Ca/Mg
Aneda	7.20	4.57	2.81	7.64	1.62	0.44	3.68	2.44	0.90	2.71	DCPD
Balmoral II	8.10	25.20	14.24	3.00	1.70	0.80	2.12	13.52	3.16	4.28	DCPD
Plum Ridge	7.65	12.31	9.41	1.85	1.06	0.56	1.89	5.24	2.50	2.10	DCPD
Balmoral III	7.70	9.70	9.04	2.85	1.20	0.80	1.50	4.15	2.08	2.00	DCPD
Balmoral IV.	7.80	22.73	11.81	1.43	2.14	1.70	1.26	9.18	4.19	2.19	DCPD+DMPT
Balmoral V	7.75	6.73	26.58	20.27	1.07	0.92	1.16	2.99	1.58	1.89	DCPD+DMPT
Foley	7.95	7.38	9.09	12.03	1.08	1.02	1.06	3.56	1.42	2.51	DCPD+DMPT
Scanterbury	7.45	2.17	22.55	20.85	1.03	0.98	1.05	1.56	2.34	0.67	DCPD+DMPT
Lakeland	8.00	16.70	12.60	7.64	0.88	1.16	0.76	6.54	3.31	1.98	DCPD+DMPT
Balmoral I	8.30	16.50	13.00	16.24	1.00	1.44	0.69	6.76	3.91	1.73	DMPT
Reinland	8.30	3.61	14.20	10.40	0.59	1.08	0.55	1.44	1.20	1.20	DCPD+DMPT

Reaction Products of KH_2PO_4 , K_2HPO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ and
 $(\text{NH}_4)_2\text{HPO}_4$ in CaCO_3 , MgCO_3 and in Soils High in Carbonates

In the preceding investigations the reaction products of an orthophosphate acid in reaction have been studied. Since the pH of the added orthophosphate also determines the reaction product formed, the reaction products of orthophosphates acid in reaction and orthophosphates alkaline in reaction were determined in soils, CaCO_3 and MgCO_3 .

Two experiments were conducted. The first experiment was designed to determine the reaction products of the various phosphate carriers when added in granular form as a pellet to soils placed in columns. The procedure employed is described in detail on page 15. The pH of the soil near the zone of phosphate addition was measured for all carriers. Soil samples were taken $1/4$, $1/3$, $1/2$ and $3/4$ inches from the zone of phosphate addition to a depth of $1/4$ inch into the column after three weeks of incubation. Two grams of soil was placed into 20 ml. distilled water, shaken for one hour and the pH of the suspension measured.

The second experiment was designed to determine the reaction products of various carriers when added in solution to soils. The procedure employed was similar to that of Lindsay and Stephenson (20). Saturated solutions of KH_2PO_4 (MKP), K_2HPO_4 (DKP), $\text{NH}_4\text{H}_2\text{PO}_4$ (MAP) and $(\text{NH}_4)_2\text{HPO}_4$ (DAP) were prepared and reacted with soils, CaCO_3 and MgCO_3 . Two hundred milliliters of solution was shaken with 300 g. of air dried

soil or carbonates for 15 minutes at room temperature. The samples were placed in a Buchner funnel and suction applied. An additional 100 ml. of phosphate solution was passed through the soil or carbonates. The filtrates obtained were stored at room temperature and after 10 days the pH of the filtrate measured. The solution was filtered and the precipitate which had formed in the solutions upon standing washed with small portions of ethanol and air dried. The products were subjected to X-ray diffraction analysis.

The soils used in the two experiments were the Balmoral I and Balmoral II soils. The Balmoral I soil contained large amounts of magnesium and the Balmoral II soil contained large amounts of calcium. The characteristics of these soils were outlined in Table VII.

Orthophosphates added to the soils as a pellet were precipitated as DCPD or DMPT (Table VIII). The Balmoral I soil precipitated the added phosphorus as DMPT in most instances. Both DCPD and DMPT was detected in the sample which had received MAP. The Balmoral II soil precipitated the MKP as DMPT and DCPD. The MAP and DAP were precipitated as DCPD and DMPT respectively. Usually orthophosphates acid in reaction form more soluble products than orthophosphates alkaline in reaction. However, similar products, regardless of the reaction of the orthophosphate used, were formed in the soils when the orthophosphates were added as a pellet. It is possible that the phosphorus concentration in the soil solution was relatively high, thus even with the carriers alkaline in reaction, fairly soluble reaction products were formed. The pH

Table VIII. Reaction products of orthophosphates in soils

Soil	Phosphate added	Reaction product	check	pH Distance from pellet			
				1/4"	1/3"	1/2"	3/4"
Balmoral I	MKP	DMPT	8.30	8.02	8.10	8.30	8.60
	DKP	DMPT		8.72	8.95	8.65	8.60
	MAP	DMPT+DCPD		8.00	8.05	8.30	8.55
	DAP	DMPT		8.50	8.65	8.65	8.60
Balmoral II	MKP	DMPT+DCPD	8.05	8.05	8.10	8.05	8.50
	DKP	none detected		8.42	8.30	8.40	8.40
	MAP	DCPD		8.05	8.10	8.30	8.50
	DAP	DMPT		8.30	8.35	8.35	8.40

near the phosphate pellet was also quite similar for acid and alkaline carriers. Thus one may expect similar products. The pH of the soil adjacent to the phosphate pellet was lowered or remained the same as the check soil as a result of adding orthophosphates acid in reaction. The pH of the soil increased as the distance from the phosphate pellet increased. The pH of the soil adjacent to the phosphate pellet was higher than that of the check soil when an orthophosphate alkaline in reaction was added. The pH of the soil increased, then decreased, as the distance from the pellet increased for the Balmoral I soil. The pH of the Balmoral II soil remained relatively constant as the distance from the pellet increased. The increase in soil pH, resulting from the additions of phosphate, was probably due to the formation of potassium or ammonium bicarbonate. These salts have a high pH in solution and certainly could form in a phosphate fertilizer reaction zone.

Phosphorus added in solution was precipitated as DCPD or DMPT or both when an acid solution was used (Table IX). Phosphate added in an alkaline solution was precipitated as OCP and $\text{TMP} \cdot 4 \text{H}_2\text{O}$. The MAP and MKP added to the Balmoral I soil was precipitated as DCPD and DMPT. The DKP was precipitated as OCP. The MAP and MKP added to the Balmoral II soil was precipitated as DCPD and DMPT. The DAP and DKP was precipitated as OCP and $\text{TMP} \cdot 4 \text{H}_2\text{O}$. Some DCPD was found in the sample that received DAP. The MKP and MAP added to CaCO_3 was precipitated as DCPD; the DAP and DKP was precipitated as OCP. MAP and MKP was precipitated as DMPT in the MgCO_3 . Some $\text{TMP} \cdot 4 \text{H}_2\text{O}$ was detected in

Table IX. Reaction products of orthophosphates in soils,
 CaCO_3 and MgCO_3

<u>Soil</u>	<u>Phosphate added</u>	<u>Solution pH</u>	<u>Reaction product</u>
Balmoral I	MKP	5.65	DMPT + DCPD
	DKP	9.25	TMP.4 H_2O + OCP
	MAP	5.70	DMPT + DCPD
	DAP	7.70	OCP
Balmoral II	MKP	5.95	DCPD
	DKP	9.20	TMP.4 H_2O + OCP
	MAP	6.45	DMPT + DCPD
	DAP	7.85	DMPT + DCPD + OCP
CaCO_3	MKP	5.20	DCPD
	DKP	9.50	OCP
	MAP	5.20	DCPD
	DAP	8.10	OCP
MgCO_3	MKP	6.50	DMPT
	DKP	9.55	DMPT + TMP.4 H_2O
	MAP	5.70	DMPT + TMP.4 H_2O
	DAP	8.25	DMPT + TMP.4 H_2O

the sample that received MAP. The DKP and DAP was precipitated as DMPT and TMP . 4 H₂O in the MgCO₃. Since the pH of the orthophosphate solutions were markedly different, more insoluble phosphates formed with the orthophosphates alkaline in reaction than with the orthophosphates acid in reaction. In the previous study (Table VIII), when the orthophosphates were added as a pellet, only one phosphate reaction product was usually identified. Reacting the soils with saturated orthophosphate solutions resulted in the formation of both calcium and magnesium phosphates in most instances. It is therefore possible that both calcium and magnesium phosphates were formed, when orthophosphates were added as a pellet, but only the one present in major amounts was detected.

Chemical analyses conducted on the products, obtained as a result of reacting the soils with the saturated orthophosphate solutions, showed that potassium and ammonium were present in the samples. This was especially true of the DKP and DAP treatments where as much as 10 percent potassium and 5 percent ammonium were found in the products.

Hydrolysis Products of Dicalcium Phosphate
Dihydrate and Dimagnesium Phosphate Trihydrate

DCPD and DMPT are metastable and in solution will release phosphoric acid and form a more alkaline phosphate (21, 33). DCPD has been found to form OCP in long contact with soil solutions or water (19). The OCP is then converted to an apatite (33). The hydrolysis products of DMPT in contact with soil solutions have not been reported. Due to the lack of this information, an experiment was designed in which the hydrolysis products of DCPD and DMPT were determined in various soils, CaCO_3 and MgCO_3 .

One-tenth gram of laboratory synthesized DCPD or DMPT was placed between layers of soil in plastic cylinders. The layers of soil were separated by four filter papers. The DCPD or DMPT was placed between the filter papers so that the soil constituents would not contaminate the DCPD or DMPT. The soils were kept in a moist state. Periodically, a portion of the DCPD or DMPT was removed, air dried, and subjected to X-ray diffraction analysis. The products were sampled at 1, 3 and 6 months after incubation was initiated.

Four soils; Balmoral I, Balmoral II, Darlingford and Red River, and two carbonates CaCO_3 and MgCO_3 were used in the study. The soil characteristics were outlined in Tables VI and VII.

OCP was detected in the DCPD placed in the CaCO_3 after one months hydrolysis time (Table X). $\text{Mg}_3(\text{PO}_4)_2 \cdot 22 \text{H}_2\text{O}$ (TMP $\cdot 22 \text{H}_2\text{O}$) was detected in the DMPT placed in the Balmoral I soil and MgCO_3 after three months of incubation (Table XI). No further change occurred in either

the DCPD or DMPT as the period of hydrolysis was increased to six months time (Table XII). The transformation of DMPT to $\text{TMP} \cdot 22 \text{H}_2\text{O}$ occurred in the samples that had large quantities of magnesium.

The $\text{TMP} \cdot 22\text{H}_2\text{O}$ detected in the samples gave the same X-ray diffraction pattern as that obtained for the laboratory synthesized $\text{TMP} \cdot 22\text{H}_2\text{O}$. It is most likely, had the hydrolysis of these products been continued, that a change in the products would have occurred in other samples as well.

Table X. Hydrolysis products of DCPD and DMPT after one month of incubation

<u>Sample</u>	<u>DCPD added</u>	<u>DMPT added</u>
Balmoral I	-	-
Balmoral II	-	-
Red River	-	-
Darlingford	-	-
CaCO ₃	OCP	-
MgCO ₃	-	-

Table XI. Hydrolysis products of DCPD and DMPT after three months of incubation

<u>Sample</u>	<u>DCPD added</u>	<u>DMPT added</u>
Balmoral I	-	TMP . 22H ₂ O
Balmoral II	-	-
Red River	-	-
Darlingford	-	-
CaCO ₃	OCP	-
MgCO ₃	-	TMP . 22H ₂ O

Table XII. Hydrolysis products of DCPD and DMPT after six months of incubation

<u>Sample</u>	<u>DCPD added</u>	<u>DMPT added</u>
Balmoral I	-	TMP . 22H ₂ O
Balmoral II	-	-
Red River	-	-
Darlingford	-	-
CaCO ₃	OCP	-
MgCO ₃	-	TMP . 22H ₂ O

Solubility of Dicalcium Phosphate Dihydrate, Dimagnesium Phosphate Trihydrate and Trimagnesium Phosphate.

The phosphate minerals present in a soil govern the concentration of phosphate in the soil solution (6). The formation of a crystalline solid phase phosphate in soils results in a fixed relation between its component ions in solution at equilibrium. It is, therefore, possible to establish the presence of crystalline phosphates in soils by the application of solubility data (6).

The solubilities of the different phosphates have been represented on a single diagram by including all the constituent ions as coordinates. The solid phases $\text{Ca}(\text{H}_2\text{PO}_4)_2$, $\text{Mg}(\text{H}_2\text{PO}_4)_2$, CaHPO_4 , MgHPO_4 , $\text{Ca}_4\text{H}(\text{PO}_4)_3$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and $\text{Mg}_3(\text{PO}_4)_2$ contain Ca or Mg, OH or H and the three orthophosphate species H_2PO_4 , HPO_4 , and PO_4 . It is necessary to calculate the activity of only one phosphate species as they are all related to one another by dissociation constants and the H ion activity. A three dimensional plot with the activity of Ca or Mg, OH and H_2PO_4 as coordinates would be necessary for the phosphates. However, it is possible to construct a two coordinate diagram in terms of the compounds $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ for the calcium phosphates and $\text{Mg}(\text{OH})_2$ and $\text{Mg}(\text{H}_2\text{PO}_4)_2$ for the magnesium phosphates (6). These compounds are assumed to be in solution and completely dissociated. In this diagram the solubility isotherms are represented as straight lines of varying slopes. An example for the case of CaHPO_4 will illustrate the development of the diagram.

If one assumes that the concentration of phosphorus in a soil

solution is due to DCPD, one determines the calcium, hydrogen and phosphate activities in the soil solution and test if these are consistent with a solution being saturated by DCPD. The formula for DCPD is written as $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and at equilibrium:

$$a_{\text{Ca}} \times a_{\text{HPO}_4} = \text{constant} \quad (1)$$

where a represents activities. By taking the negative logarithm of the ionic activities the following equation is obtained:

$$p_{\text{Ca}} + p_{\text{HPO}_4} = \text{constant} \quad (2)$$

$$\text{Since } \frac{[\text{HPO}_4]}{[\text{H}]} = \frac{\text{constant} \times [\text{H}_2\text{PO}_4]}{[\text{H}]} \quad (3)$$

$$\text{and } p_{\text{HPO}_4} = \text{constant} + p_{\text{H}_2\text{PO}_4} - p_{\text{H}} \quad (4)$$

Equation 2 becomes:

$$p_{\text{Ca}} + p_{\text{H}_2\text{PO}_4} - p_{\text{H}} = \text{constant} \quad (5)$$

Rearranging equation (5) leads to the expression:

$$(p_{\text{H}} - \frac{1}{2}p_{\text{Ca}}) - (p_{\text{H}_2\text{PO}_4} + \frac{1}{2}p_{\text{Ca}}) = \text{constant} \quad (6)$$

The term, $p_{\text{H}} - \frac{1}{2}p_{\text{Ca}}$, is known as the "lime potential." The higher the lime potential, the greater is the activity of $\text{Ca}(\text{OH})_2$ in solution.

The term, $p_{\text{H}_2\text{PO}_4} + \frac{1}{2}p_{\text{Ca}}$, is known as the "phosphate potential." It represents the negative logarithm of monocalcium phosphate in solution.

The larger this term, the lower is the activity of monocalcium phosphate in solution.

Similar equations relating the lime potential to the phosphate potential can be developed for DMPT, OCP, H.A. and TMP. For DMPT the equation is:

$$(p_{\text{H}} - \frac{1}{2}p_{\text{Mg}}) - (p_{\text{H}_2\text{PO}_4} + \frac{1}{2}p_{\text{Mg}}) = K \quad (7)$$

For OCP the equation is:

$$5(\text{pH} - \frac{1}{2}\text{pCa}) - 3(\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pCa}) = K \quad (8)$$

For H.A. the equation is:

$$7(\text{pH} - \frac{1}{2}\text{pCa}) - 3(\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pCa}) = K \quad (9)$$

and for TMP the equation is:

$$2(\text{pH} - \frac{1}{2}\text{pMg}) - (\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pMg}) = K \quad (10)$$

The values for K for DCPD, OCP and H.A. have been found to be 0.66 (30), 9.93 (1, 23), and 14.7 (7) respectively. The values for K for the equations derived for DMPT and TMP have not been reported. The values for K can be established by measuring the lime and phosphate potentials of the pure phosphate compounds in water. A graphical representation of the phosphate potential versus the lime potential can then be obtained by substituting values for the lime potential and calculating the phosphate potential or vice versa. In order to determine the form of soil phosphate, the lime and phosphate potentials of the soil solution are measured and related graphically to the equations developed above.

The lime potential, $\text{pH} - \frac{1}{2}\text{pCa}$, was calculated as follows:

$$\frac{1}{2}\text{pCa} = -\frac{1}{2}(\log_{10} \text{Conc}_{\text{Ca}} + \log_{10} F) \quad (11)$$

where $\log_{10} F = \frac{-A z^2 \sqrt{U}}{1 + B a |z| \sqrt{U}}$ (12)

and gives the activity coefficients of an ion as a function of the ionic strength of the solution. Equation 12 is known as the Debye - Hückel approximation for activity coefficients. In the equation A and B are constants depending upon the solvent used. The constants A and B

for the equation using water as a solvent at 25 deg. C. are 0.51 and 0.33×10^8 respectively. \bar{z} represents the valency of the ion and a_i the mean ionic diameter. U represents the ionic strength of the solution and was calculated from the expression: $U = \frac{1}{2} \sum C_i z_i^2$ (13)

where U is the ionic strength of the solution, C_i the concentration of the various ions in gram ionic weights per liter and z_i are the valencies of the respective ions. The concentration of calcium or magnesium and phosphate ions in solution was used as a measure of ionic strength for the aqueous solutions containing DCPD or DMPT or TMP. In studies where various salts were added to the solution, the concentration of the added salt was also taken into consideration when calculating the ionic strength of the solution. The ionic strength of the aqueous extracts obtained from soils was calculated using the concentration of calcium and magnesium in solution with the assumption that a monovalent anion was always present. This was done as the concentration of calcium and magnesium in solution usually exceeded the concentration of phosphorus in solution.

$\frac{1}{2}pMg$ was calculated in the same manner as $\frac{1}{2}pCa$.

The H_2PO_4 ion activity was calculated from the total phosphorus concentration, the ion activity coefficient, the pH, and the dissociation constants of phosphoric acid. As in calculating $\frac{1}{2}pCa$ or $\frac{1}{2}pMg$:

$$pH_2PO_4 = -(\log_{10} \text{Conc}_{H_2PO_4} + \log_{10} F) \quad (14)$$

The pH of the systems studied remained between pH 5 to 9 and thus only the H_2PO_4 and HPO_4 ions need be considered. Therefore:

$$\text{Total phosphoric concentration} - [P] = [H_2PO_4] + [HPO_4] \quad (15)$$

$$\text{and } \frac{[P]}{[H_2PO_4]} = 1 + \frac{[HPO_4]}{[H_2PO_4]} \quad (16)$$

$$\text{Since } \frac{[HPO_4]}{[H_2PO_4]} = \frac{K_2}{[H]} \quad (17)$$

$$\text{and } \frac{[P]}{[H_2PO_4]} = 1 + \frac{K_2}{[H]} \quad (18)$$

$$\text{and } \frac{[P]}{[H_2PO_4]} = \frac{[H] + K_2}{[H]} \quad (19)$$

Rearranging equation 19, the following equation is obtained:

$$[H_2PO_4] = P \times \frac{[H]}{K_2 + [H]} \quad (20)$$

By taking the negative logarithm of equation (20), the following equation is obtained:

$$-\log_{10} \text{Conc}_{H_2PO_4} = p[P] + p\left(\frac{[H]}{K_2 + [H]}\right) \quad (21)$$

$[P]$ is the total concentration of phosphorus in solution, $\left(\frac{[H]}{K_2 + [H]}\right)$

is a correction factor which relates the ratio of

H_2PO_4 / P to pH and K_2 is the second dissociation constant of phosphoric acid. By substituting the expression derived for $-\log_{10} \text{Conc}_{H_2PO_4}$ in equation (21) into equation (14), pH_2PO_4 can be calculated.

The lime potential ($pH - \frac{1}{2}pCa$) or ($pH - \frac{1}{2}pMg$) and the phosphate potential ($pH_2PO_4 + \frac{1}{2}pCa$) or ($pH_2PO_4 + \frac{1}{2}pMg$) can now be easily calculated.

Since the solubility constants for the magnesium phosphates have not been reported by previous workers, a study was conducted to establish the values for the constants relating the lime potential with the phosphate potential. Four compounds, DCPD, DMPT, TMP . 22H₂O and TMP were studied. The anhydrous TMP was obtained by dehydrating TMP . 22H₂O at 300 deg. C.

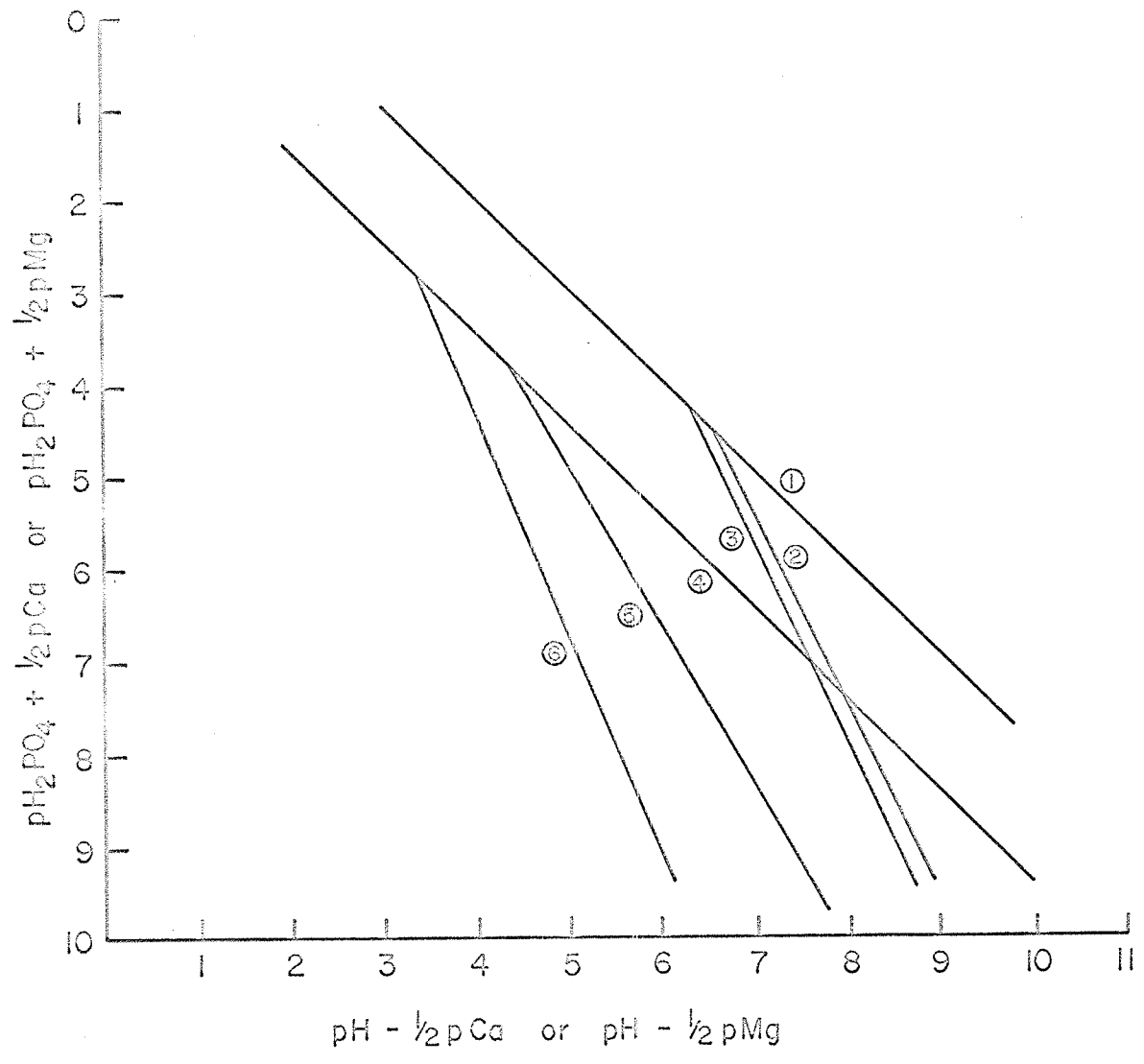
One-tenth gram of DCPD, DMPT, $\text{TMP} \cdot 22\text{H}_2\text{O}$ or TMP was placed into 50 ml. distilled water and equilibrated with shaking for 24 hours at $25 \pm 1^\circ \text{C}$. The pH of the suspension was measured and the suspension filtered. The calcium and magnesium contents of the filtrates were determined by the use of EDTA. The phosphorus content of the filtrates was determined colorimetrically. The coordinates for the solubility diagram were then calculated.

The pH of DCPD in solution was much lower than that for DMPT in solution (Table XIII). The concentrations of magnesium and phosphorus in solution from the added DMPT were higher than the calcium and phosphorus concentrations in solution from the added DCPD. The constant derived for the equation $(\text{pH} - \frac{1}{2}\text{pCa}) - (\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pCa})$ was found to be 0.52 for DCPD at 25 deg. C. The value of 0.52 for K is lower than 0.66 reported for equilibration at 18 deg. C. (30). The constant derived for the equation $(\text{pH} - \frac{1}{2}\text{pMg}) - (\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pMg})$ was found to be 1.82 for DMPT. The larger value of K for DMPT as compared to DCPD indicates that DMPT is more soluble than DCPD. The $\text{TMP} \cdot 22\text{H}_2\text{O}$ and TMP were found to be considerably less soluble than DCPD or DMPT. The constant derived for the equation $2(\text{pH} - \frac{1}{2}\text{pMg}) - (\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pMg})$ was found to be 8.31 for the hydrated TMP and 8.55 for the anhydrous form. The larger value of K obtained for the anhydrous form indicates that dehydration of the $\text{TMP} \cdot 22\text{H}_2\text{O}$ increased its solubility slightly.

Figure 4 shows the plot of the lime potential versus the phosphate potential for the calcium and magnesium phosphates. The lines were obtained as previously described. The solubility lines shown for OCP

Table XIII. Solubility of DCPD, DMPT, TMP.22H₂O and TMP

Sample	pH	$\frac{[Ca]^2}{X10^2M}$	$\frac{[Mg]^2}{X10^2M}$	$\frac{[P]^2}{X10^2M}$	$\frac{1}{2}pCa$	$\frac{1}{2}pMg$	pH ₂ PO ₄	$\frac{pH-}{2}pCa$	$\frac{pH-}{2}pMg$	$\frac{pH_2PO_4}{2}pCa$	$\frac{pH_2PO_4}{2}pMg$	K
DCPD (1)	6.13	.140		.277	1.49		2.62	4.64		4.11		.53
(2)	6.18	.134		.256	1.50		2.66	4.68		4.16		.52
(3)	6.28	.118		.229	1.52		2.72	4.76		4.24		.52
DMPT (1)	7.85		.301	.302		1.36	3.31		6.49		4.67	1.82
(2)	7.93		.307	.290		1.35	3.39		6.58		4.74	1.84
(3)	7.91		.293	.283		1.36	3.40		6.55		4.76	1.79
TMP.22H ₂ O (1)	9.12		.087	.051		1.58	5.24		7.54		6.82	8.26
(2)	9.30		.076	.052		1.61	5.41		7.69		7.02	8.36
TMP (1)	9.20		.122	.056		1.52	5.28		7.68		6.80	8.56
(2)	9.33		.100	.052		1.56	5.45		7.77		7.01	8.53



- ① DMPT $(pH - \frac{1}{2} pMg) - (pH_2PO_4 + \frac{1}{2} pMg) = 1.82$
- ② TMP $2(pH - \frac{1}{2} pMg) - (pH_2PO_4 + \frac{1}{2} pMg) = 8.55$
- ③ TMP·22 H₂O $2(pH - \frac{1}{2} pMg) - (pH_2PO_4 + \frac{1}{2} pMg) = 8.31$
- ④ DCPD $(pH - \frac{1}{2} pCa) - (pH_2PO_4 + \frac{1}{2} pCa) = 0.52$
- ⑤ OCP $5(pH - \frac{1}{2} pCa) - 3(pH_2PO_4 + \frac{1}{2} pCa) = 9.93$
- ⑥ H.A. $7(pH - \frac{1}{2} pCa) - 3(pH_2PO_4 + \frac{1}{2} pCa) = 14.7$

Figure 4. Solubility diagram for the calcium and magnesium phosphates.

and H.A. were not determined experimentally, but were obtained from the literature. The solubility diagram can be used to establish the existence of certain solid phase phosphates. One needs only to measure the lime and phosphate potentials of the soil solution and plot them on the diagram. The position of the point on the diagram would indicate the phosphate mineral governing the concentration of phosphorus in the soil solution. For example, if the point occurred on or near the solubility line for DCPD, it could be assumed that DCPD was probably the most soluble phosphate in the soil.

The Effect of Various Salts on the Solubility of Dicalcium Phosphate Dihydrate and Dimagnesium Phosphate Trihydrate

The soil solution contains ions other than those resulting from the dissolution of the solid phase phosphates. Ions such as Cl^- , $\text{SO}_4^{=}$, Ca^{++} , Mg^{++} , K^+ and Na^+ are found in the soil solution. Since the presence of these ions may affect the solubility of the solid phase phosphates, a study was conducted to determine the effect of various salts on the solubility of DCPD and DMPT.

The solubility of DCPD and DMPT was determined in .001, .002, .004, .006, .008, .010, .015 and .020 M solutions of CaCl_2 and MgCl_2 , and in .005 and .010 M CaSO_4 , MgSO_4 , KCl and K_2SO_4 solutions. One-tenth gram of DCPD or DMPT was placed into 50 ml. of solution and equilibrated with shaking for 24 hours at $25 \pm 1^\circ \text{C}$. The pH of the suspension was measured and the suspension filtered. The phosphorus and calcium or magnesium content of the filtrates were determined. The appropriate calculations were conducted.

Equilibration of DCPD in the CaCl_2 solutions resulted in a decrease in pH as the concentration of CaCl_2 was increased (Table XIV). The concentration of phosphorus in solution decreased with increased CaCl_2 concentration. The solubility constant, K, increased with increased CaCl_2 concentration. Equilibration of DCPD in the MgCl_2 solutions resulted in slight variations in pH with increased MgCl_2 concentration. The concentration of calcium and phosphorus in solution was increased with increasing MgCl_2 concentration. The K values increased as the concentration of MgCl_2 was increased. The solubility

Table XIV. The effect of salts on the solubility of DCPD

Solution	pH	$\frac{[Ca]_2}{X10^{-2}M}$	$\frac{[Mg]_2}{X10^{-2}M}$	$\frac{[P]_2}{X10^{-2}M}$	$\frac{pCa}{\frac{1}{2}pCa}$	$\frac{pH_2PO_4}{\frac{1}{2}pH_2PO_4}$	$\frac{pH}{\frac{1}{2}pCa}$	$\frac{pH_2PO_4}{\frac{1}{2}pCa}$	K	U
.001 M CaCl ₂	7.35	.142		.050	1.47	3.71	5.88	5.18	.70	.004
.002	7.32	.205		.042	1.40	3.79	5.92	5.19	.73	.006
.004	7.20	.398		.040	1.30	3.75	5.90	5.05	.85	.012
.006	7.10	.590		.030	1.23	3.82	5.87	5.05	.82	.018
.008	7.10	.772		.026	1.18	3.89	5.92	5.07	.85	.023
.010	7.08	1.164		.023	1.12	3.95	5.96	5.07	.89	.035
.015	7.02	1.526		.023	1.07	3.94	5.95	5.01	.94	.046
.020	6.98	1.930		.026	1.03	3.88	5.95	4.91	1.04	.058
.001 M MgCl ₂	7.42	.094	.099	.090	1.58	3.52	5.84	5.10	.74	.006
.002	7.53	.110	.163	.090	1.56	3.58	5.97	5.14	.83	.008
.004	7.50	.126	.373	.115	1.55	3.47	5.95	5.02	.93	.015
.006	7.50	.133	.550	.129	1.58	3.43	5.92	5.01	.91	.020
.008	7.48	.145	.739	.143	1.57	3.37	5.91	4.94	.97	.027
.010	7.45	.166	1.109	.165	1.57	3.30	5.88	4.87	1.01	.038
.015	7.35	.187	1.498	.184	1.56	3.22	5.79	4.78	1.01	.051
.020	7.40	.183	1.560	.192	1.55	3.22	5.85	4.77	1.08	.062
.005 M KCl	7.40	.094		.089	1.60	3.50	5.80	5.10	.70	.008
.010	7.50	.099		.091	1.60	3.53	5.90	5.13	.77	.014
.005 M CaSO ₄	7.05	.561		.037	1.25	3.73	5.80	4.98	.82	.022
.010	7.00	1.047		.031	1.15	3.80	5.85	4.95	.90	.040
.005 M MgSO ₄	7.45	.185	.423	.136	1.49	3.37	5.96	4.86	1.10	.024
.010	7.12	.239	.892	.198	1.47	3.05	5.65	4.52	1.13	.045
.005 M K ₂ SO ₄	7.62	.113		.111	1.59	3.57	6.03	5.16	.87	.019
.010	7.52	.126		.142	1.60	3.16	5.92	4.76	1.16	.035
Distilled H ₂ O	6.18	.134		.256	1.50	2.66	4.68	4.16	.52	.004

of DCPD increased in the CaSO_4 , MgSO_4 , KCl and K_2SO_4 solutions. The solubility of DCPD was greater in the MgCl_2 and MgSO_4 solutions than in the CaCl_2 and CaSO_4 solutions. In general, the solubility of DCPD increased with increased salt concentration.

Figure 5 shows the plot of the lime potential versus the phosphate potential for the solubility of DCPD in the various solutions. The solubility lines representing the solubility of DCPD, $\text{TMP} \cdot 22\text{H}_2\text{O}$ and DMPT in distilled water are shown on the diagram. The points obtained for the solubility of DCPD in the salt solutions lie between the lines representing the solubility of DCPD and DMPT in water. The points moved away from the DCPD solubility line towards the DMPT solubility line with increased salt concentration. A better comparison of the effects of the various salts on the solubility constant, K , of DCPD is afforded in Figure 6. The K values are plotted versus the ionic strength of the solution. All salt solutions increased the solubility of DCPD. The solubility of DCPD increased with increasing ionic strength. DCPD was more soluble in the MgCl_2 and MgSO_4 solutions than in the CaCl_2 and CaSO_4 solutions at equal ionic strengths. The MgSO_4 and 0.01 M K_2SO_4 solutions increased the solubility of DCPD to a greater extent than did the other salts at equal ionic strengths. A rapid increase in the solubility of DCPD with increasing ionic strength occurred at low ionic strengths. The solubility of DCPD increased only slightly with increased ionic strength at high ionic strengths.

The solubility of DMPT was depressed by the CaCl_2 solutions (Table XV). The depression in solubility was most marked at high

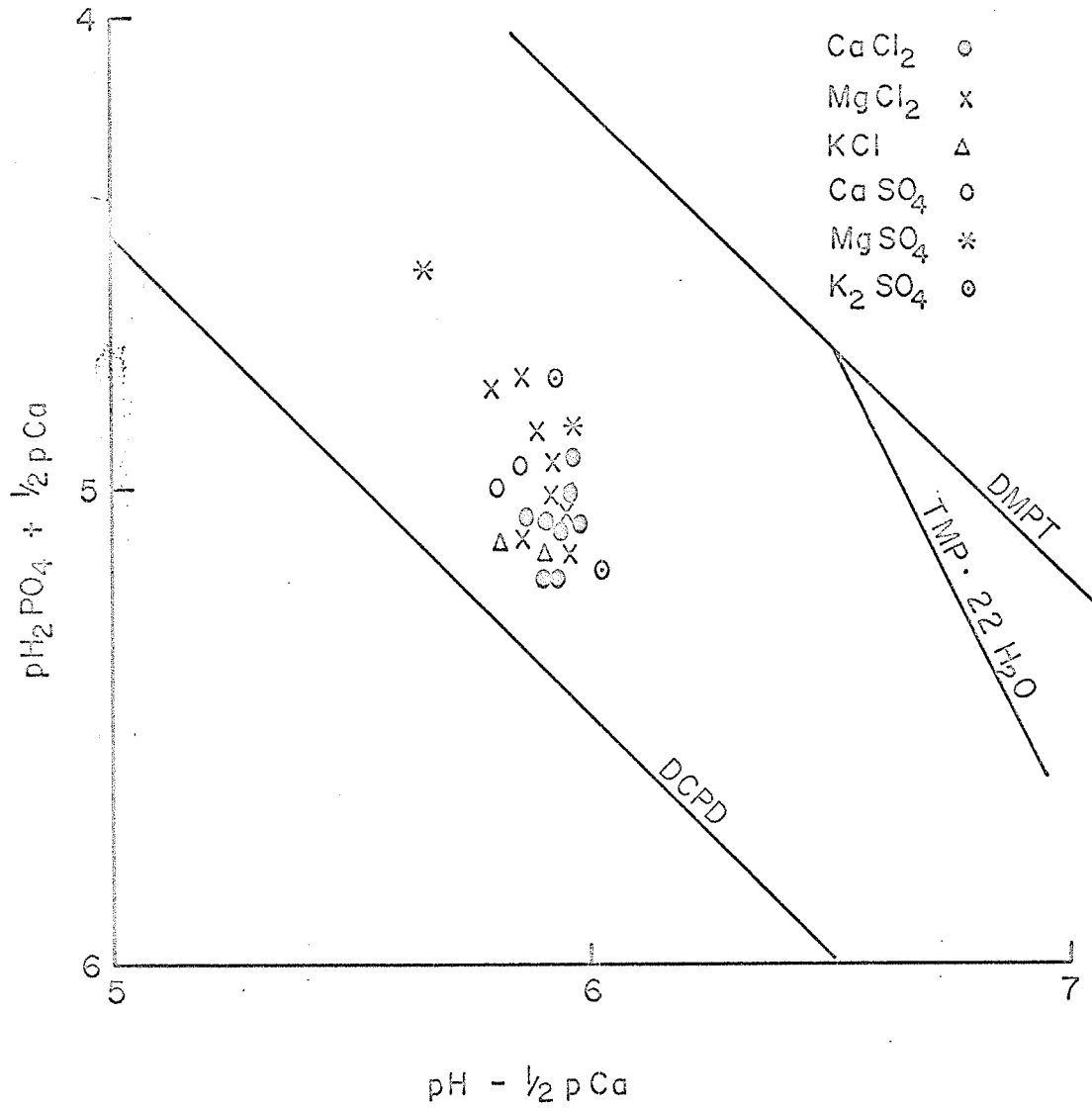


Figure 5. The effect of salts on the solubility of DCPD.

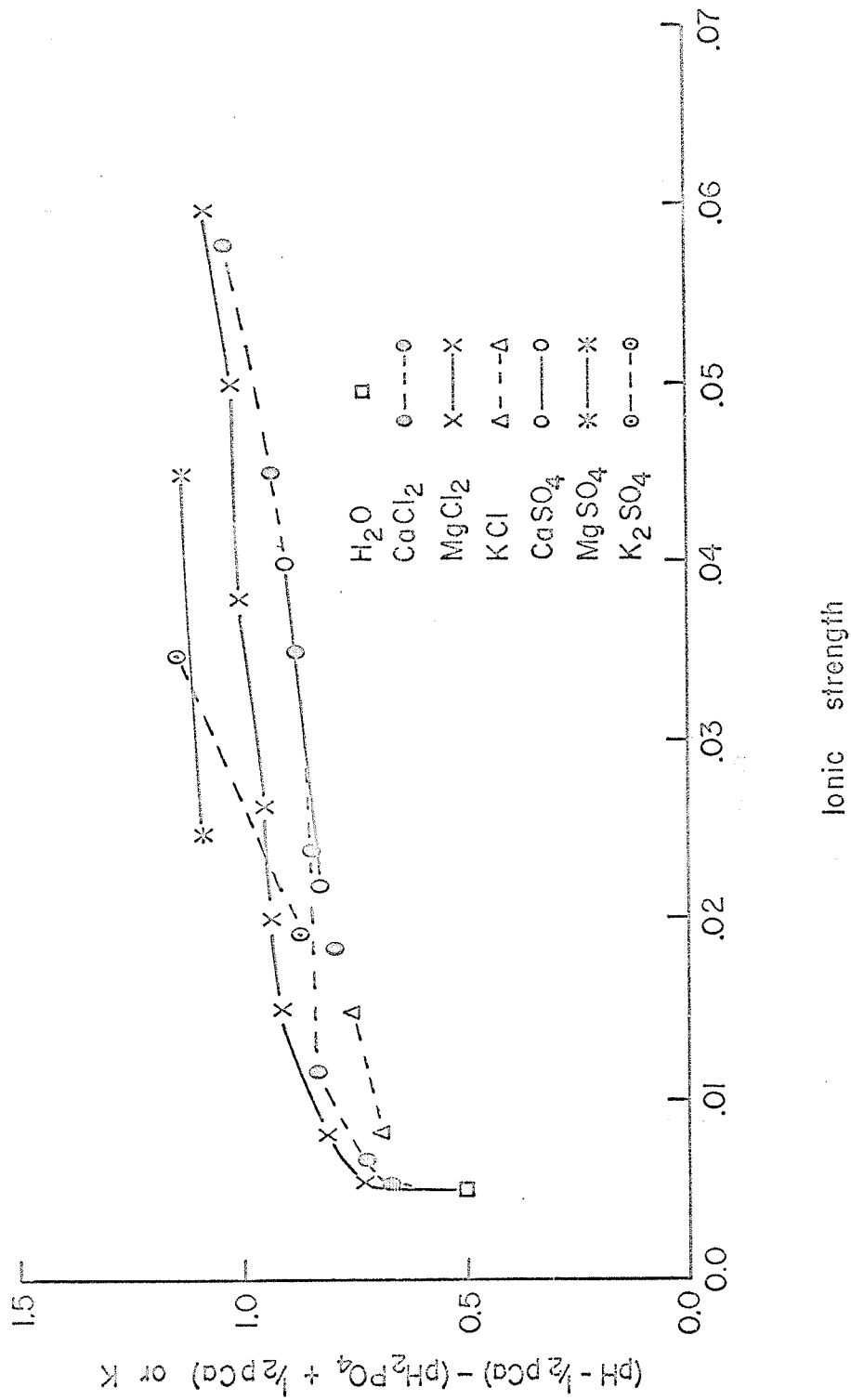


Figure 6. The effect of solution ionic strength on the solubility of DCPD.

Table XV. The effects of salts on the solubility of DMPT

Solution	pH	[Ca] $\times 10^2 M$	[Mg] $\times 10^2 M$	[P] $\times 10^2 M$	$\frac{1}{2} pMg$	pH ₂ PO ₄	pH	$\frac{1}{2} pMg$	pH ₂ PO ₄	K	U
.001 M CaCl ₂	7.48	.067	.335	.307	1.33	3.03	6.15	4.36	4.36	1.79	.012
.002	7.32	.102	.364	.335	1.32	2.89	6.00	4.21	4.21	1.79	.014
.004	7.00	.136	.534	.351	1.25	2.71	5.75	3.96	3.96	1.79	.020
.006	7.15	.109	.697	.263	1.21	2.92	5.94	4.13	4.13	1.81	.024
.008	7.13	.120	1.050	.239	1.13	2.97	6.00	4.10	4.10	1.90	.029
.010	6.73	.450	.738	.106	1.21	3.18	5.52	4.39	4.39	1.13	.036
.015	6.70	.608	1.080	.127	1.16	3.16	5.54	4.32	4.32	1.22	.051
.020	6.70	.970	.926	.066	1.20	3.44	5.50	4.64	4.64	.86	.058
.001 M MgCl ₂	7.68		.371	.263	1.29	3.22	6.39	4.51	4.51	1.88	.011
.002	7.73		.424	.249	1.28	3.29	6.45	4.57	4.57	1.88	.013
.004	7.68		.582	.211	1.23	3.33	6.45	4.56	4.56	1.89	.017
.006	7.60		.744	.197	1.19	3.32	6.41	4.51	4.51	1.90	.022
.008	7.60		.930	.184	1.15	3.36	6.45	4.51	4.51	1.94	.028
.010	7.53		1.304	.177	1.10	3.32	6.43	4.42	4.42	2.01	.039
.015	7.45		1.610	.172	1.06	3.28	6.39	4.34	4.34	2.05	.048
.020	7.40		2.002	.165	1.03	3.29	6.37	4.32	4.32	2.09	.060
.005 M KCl	7.84		.322	.335	1.36	3.25	6.48	4.61	4.61	1.87	.018
.010	7.82		.339	.340	1.36	3.25	6.46			1.85	.023
.005 M CaSO ₄	7.12	.146	.638	.316	1.24	2.82	5.88	4.06	4.06	1.82	.032
.010	7.10	.209	1.046	.257	1.16	2.91	5.94	4.07	4.07	1.87	.050
.005 M MgSO ₄	7.72		.708	.224	1.21	3.37	6.51	4.58	4.58	1.93	.028
.010	7.70		1.164	.202	1.13	3.40	6.57	4.53	4.53	2.04	.046
.005 M K ₂ SO ₄	7.93		.383	.376	1.34	3.27	6.59	4.61	4.61	1.98	.030
.010	8.00		.430	.421	1.35	3.31	6.65	4.66	4.66	1.99	.047
Distilled H ₂ O	7.85		.301	.302	1.36	3.31	6.49	4.67	4.67	1.82	.012

CaCl_2 concentrations. X-ray analysis of the phosphates remaining in the equilibration solution showed that both DCPD and DMPT were present in the samples receiving large amounts of CaCl_2 . Therefore, the decrease in the solubility of DMPT was probably due to secondary precipitation of the phosphorus in solution as DCPD.

The pH of the solutions decreased with increased MgCl_2 solution. The concentration of phosphorus in solution decreased with increased MgCl_2 concentration. The solubility constant for DMPT increased with increased MgCl_2 concentration. The solubility of DMPT increased in the KCl , MgSO_4 and K_2SO_4 solutions. CaSO_4 was found to have little or no effect on the solubility of DMPT.

Figure 7 shows the plot of the lime potential versus the phosphate potential for the solubility of DMPT in the various solutions. The solubility of DMPT was between that of DCPD and DMPT when measured in CaCl_2 solutions of 0.01 M concentration or higher. The solubility of DMPT in CaCl_2 solutions of less than 0.01 M concentration approximated that of DMPT in water. The solubility of DMPT in solutions of KCl , MgSO_4 , MgCl_2 and CaSO_4 was found to be greater than in water. The solubility of DMPT was not increased as greatly as that of DCPD by the salt solutions.

The increase in the solubility of DMPT with increasing ionic strength was not as marked as the increase in solubility obtained for DCPD (Figure 8). The solubility of DMPT increased only slightly as the ionic strength of the solution was increased.

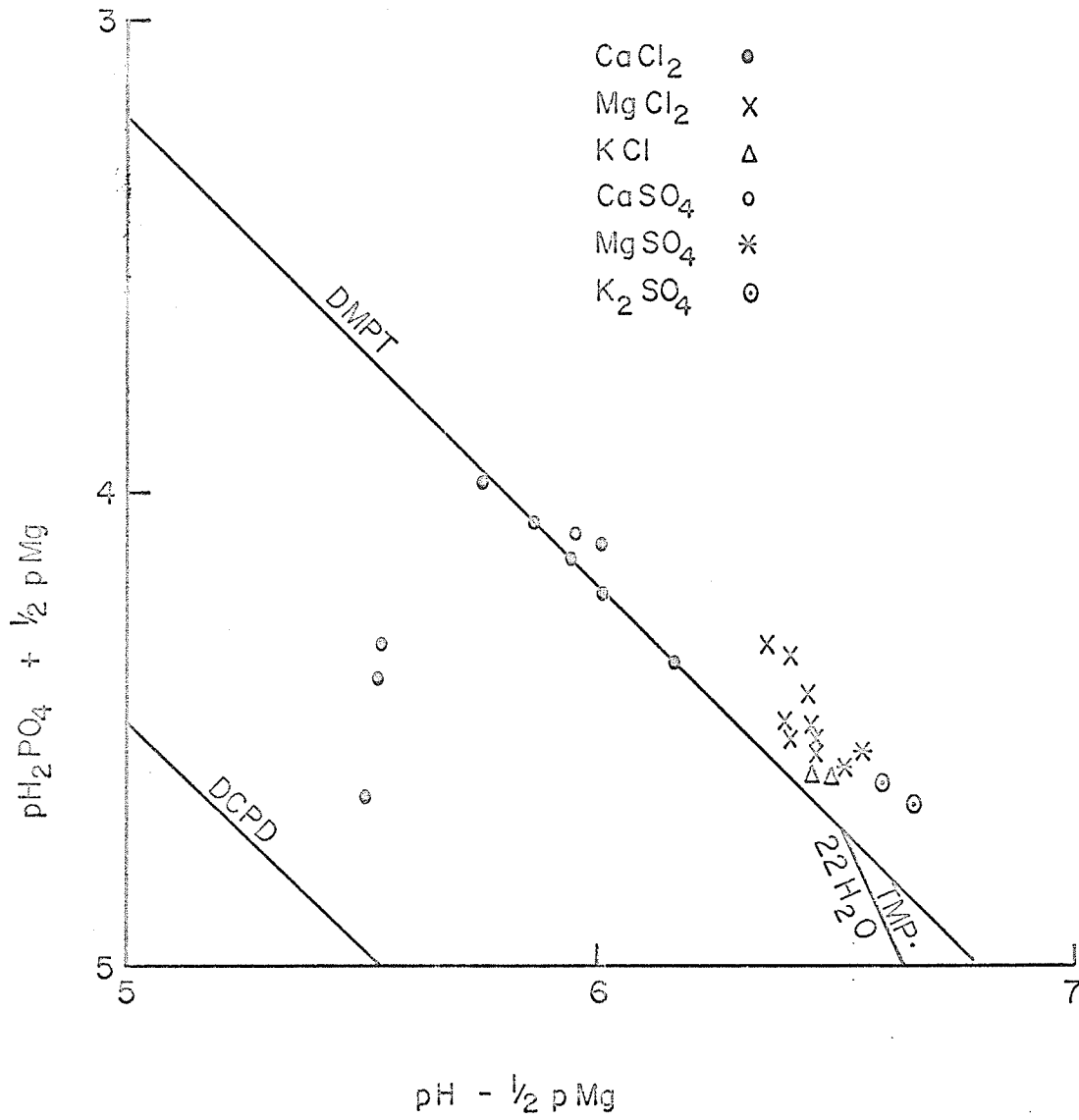


Figure 7. The effect of salts on the solubility of DMPT.

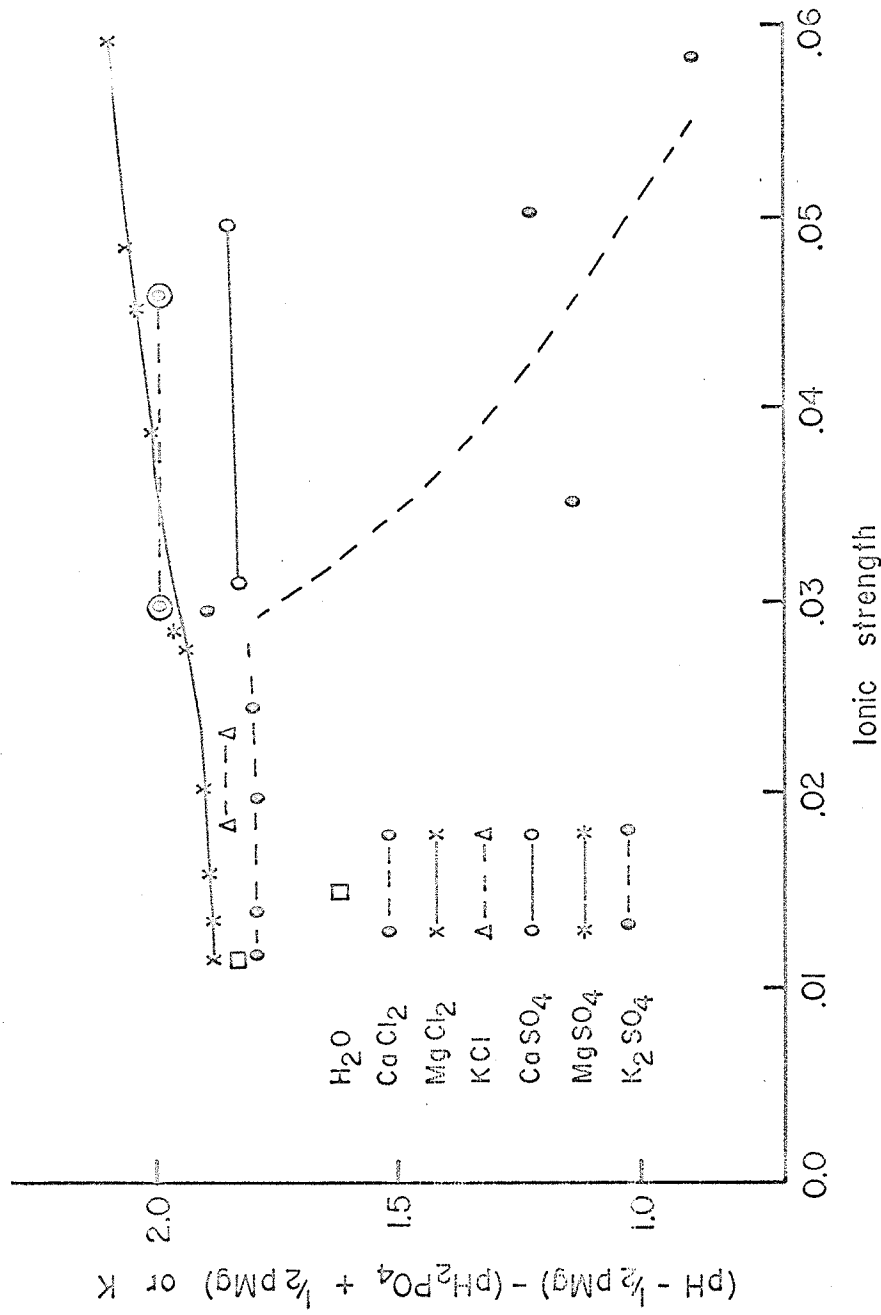


Figure 8. The effect of solution ionic strength on the solubility of DMPT.

Since the solubility of DCPD and DMPT was increased by most of the salt solutions, it would be expected that DCPD or DMPT in a soil system would have a solubility greater than that measured for the compounds in water.

The Effect of CaCl_2 and MgCl_2 on the Solubility of Phosphorus Added to Soils

The solubility of DCPD and DMPT increased with increased ionic strength. Since the solubility of the products were increased by the presence of salts, an experiment was conducted to determine the effects of CaCl_2 and MgCl_2 on the solubility of phosphorus added to soils. Twenty-five milliliters of 0.4 M H_3PO_4 solution was added to 50 g. air dried soil, incubated at room temperature for one day and air dried. The solubility of the added phosphate was determined in, water, 0.01 M CaCl_2 , and 0.01 M MgCl_2 . Ten grams of soil was placed into 100 ml. of solution and equilibrated with shaking for 24 hours at $25 \pm 1^\circ \text{C}$. The pH of the suspension was measured and the suspension centrifuged and filtered. The calcium, magnesium and phosphorus contents of the filtrates were determined and the lime and phosphate potentials calculated.

Two soils containing large amounts of carbonates (Aneda and Balmoral I) and two soils containing small amounts of carbonates (Red River and Darlingford) were studied. The Aneda and Darlingford soils contained large amounts of calcium. The Red River and Balmoral I soils contained large amounts of magnesium.

The pH of the soil suspension in CaCl_2 and MgCl_2 was markedly lower than that of the soil suspension in water (Table XVI). Addition of the 0.01 M CaCl_2 to the soils increased the concentration of magnesium in solution, (as compared to the soils equilibrated in water) and the addition of the 0.01 M MgCl_2 increased the concentration of calcium in solution. This is due to the displacement of magnesium held on the

Table XVI. The solubility of phosphorus added to Aneda, Balmoral I, Red River, and Darlingford soils in .01 M CaCl₂, .01 M MgCl₂ and water

Soil	Solution	pH	$\frac{[Ca]_2}{X10^2 M}$	$\frac{[Mg]_2}{X10^2 M}$	$\frac{[P]_2}{X10^2 M}$	$\frac{1}{2}pCa$	$\frac{1}{2}pMg$	$\frac{pH_2PO_4}{pCa}$	$\frac{pH}{pMg}$	$\frac{pH_2PO_4}{pCa}$	$\frac{pH_2PO_4}{pMg}$
Aneda	H ₂ O	6.00	.392	.012	.810	1.30	2.10	2.17	4.70	3.90	4.27
	CaCl ₂	5.68	1.208	.069	.638	1.11	1.72	2.27	4.57	3.96	3.99
	MgCl ₂	5.68	.788	.613	.703	1.21	1.26	2.24	4.47	4.42	3.45
Red River	H ₂ O	4.90	.237	.368	1.188	1.42	1.31	1.97	3.48	3.59	3.32
	CaCl ₂	4.60	.790	.719	1.146	1.21	1.23	2.02	3.39	3.37	3.23
	MgCl ₂	4.70	.364	1.216	1.204	1.39	1.12	2.00	3.31	3.58	3.12
Balmoral I	H ₂ O	7.12	.082	.317	.372	1.64	1.35	2.75	5.48	5.77	4.10
	CaCl ₂	6.80	.406	.712	.160	1.34	1.22	3.02	5.46	5.58	4.24
	MgCl ₂	6.90	.177	1.159	.343	1.53	1.13	2.72	5.37	5.77	3.85
Darlingford	H ₂ O	5.41	.467	.125	1.105	1.28	1.56	2.00	4.13	3.85	3.56
	CaCl ₂	5.13	1.198	.238	.993	1.12	1.47	2.08	4.01	3.66	3.55
	MgCl ₂	5.20	.689	.919	1.123	1.25	1.19	2.03	3.95	4.01	3.22

exchange complex by the added calcium or vice versa. The concentration of phosphorus in the solutions used, remained relatively constant for the Red River and Darlingford soils. The concentration of phosphorus in solution was lower in the CaCl_2 and MgCl_2 solutions than in water for the Aneda and Balmoral I soils.

Figures 9, 10, 11 and 12 illustrate the solubility of the added phosphorus for the four soils in CaCl_2 , MgCl_2 and water. The solubility of the added phosphate is shown in two manners. First, considering the pH, calcium ion and H_2PO_4^- ion activities in solution for the calculation of the phosphate and lime potentials, and second, considering the magnesium ion activity rather than the calcium ion activity in calculation of the lime and phosphate potentials. The two methods of calculation are designated as Ca-P and Mg-P respectively.

The phosphate solubility values obtained for the Aneda soil varied with the equilibrating solution used and the method of calculation (Figure 9). The solubility of the added phosphate remained between that of DCPD and DMPT in most instances. The solubility of phosphorus was between that of DCPD and DMPT or near that of DMPT for the Balmoral I soil regardless of the solution used (Figure 10). The use of various equilibrating solutions had small but noticeable effects on the solubility of phosphate. The phosphorus appeared to be more soluble in the soil containing large amounts of magnesium (Balmoral I) than in the soil containing large amounts of calcium (Aneda). The solubility of phosphorus remained near that of DCPD or H.A. in the Red River soil (Figure 11). The use of 0.01 M CaCl_2 or 0.01 M MgCl_2

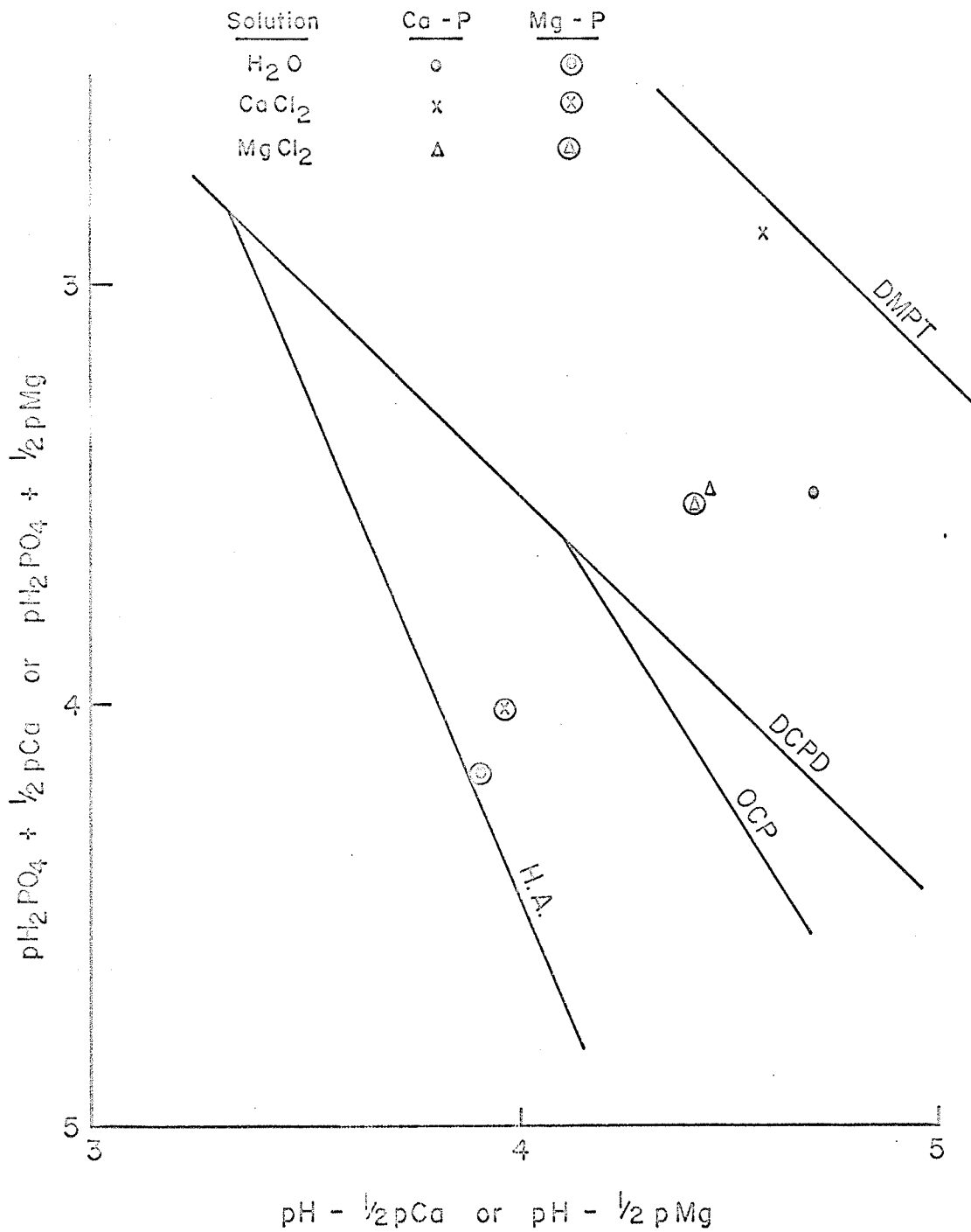


Figure 9. The solubility of phosphorus added to Aneda soil in .01M CaCl₂, .01M MgCl₂, and water.

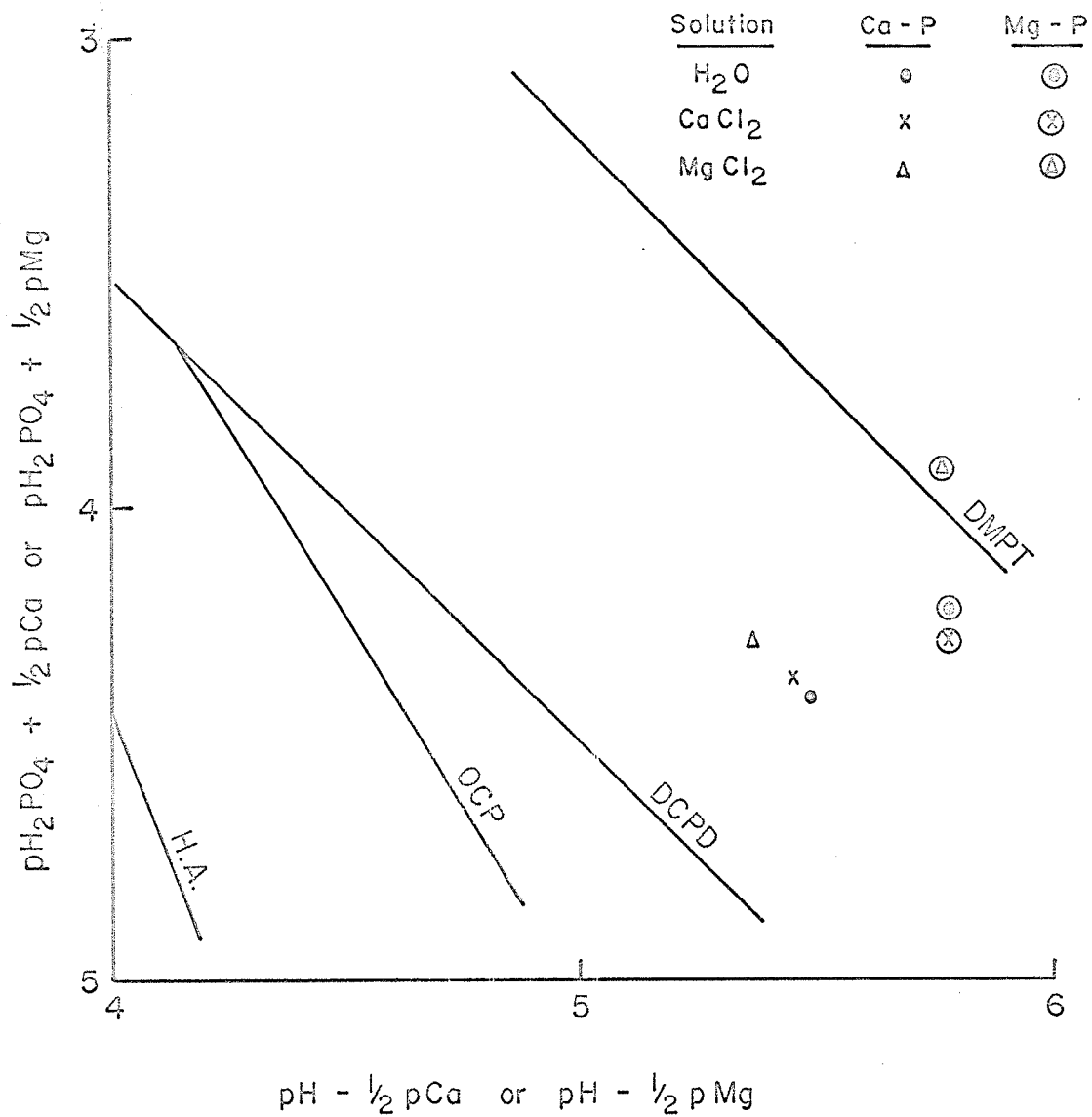


Figure 10. The solubility of phosphorus added to Balmoral I soil in .01M CaCl₂, .01M MgCl₂ and water.

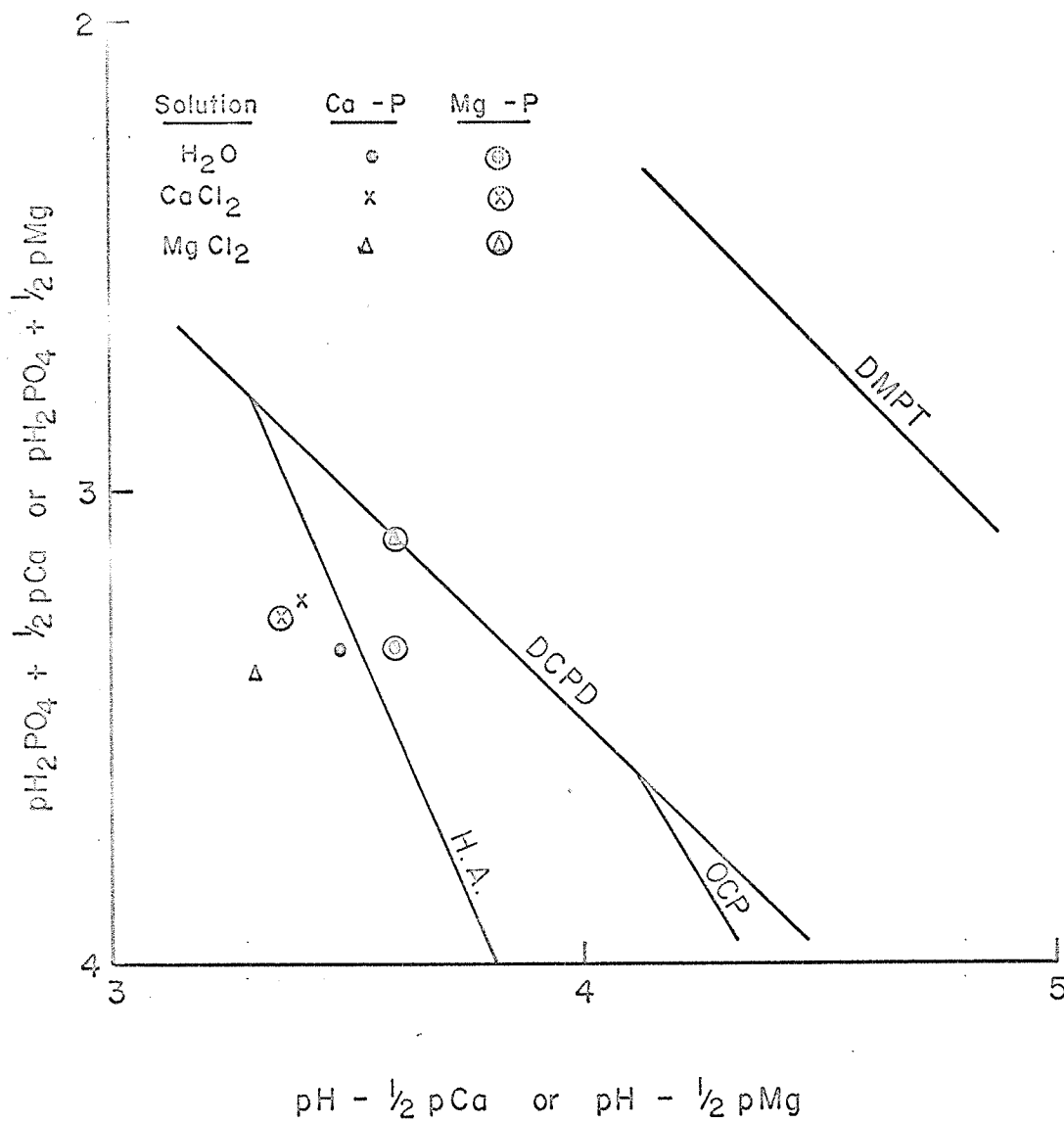


Figure II. The solubility of phosphorus added to Red River soil in .01 M CaCl₂, .01 M MgCl₂ and water.

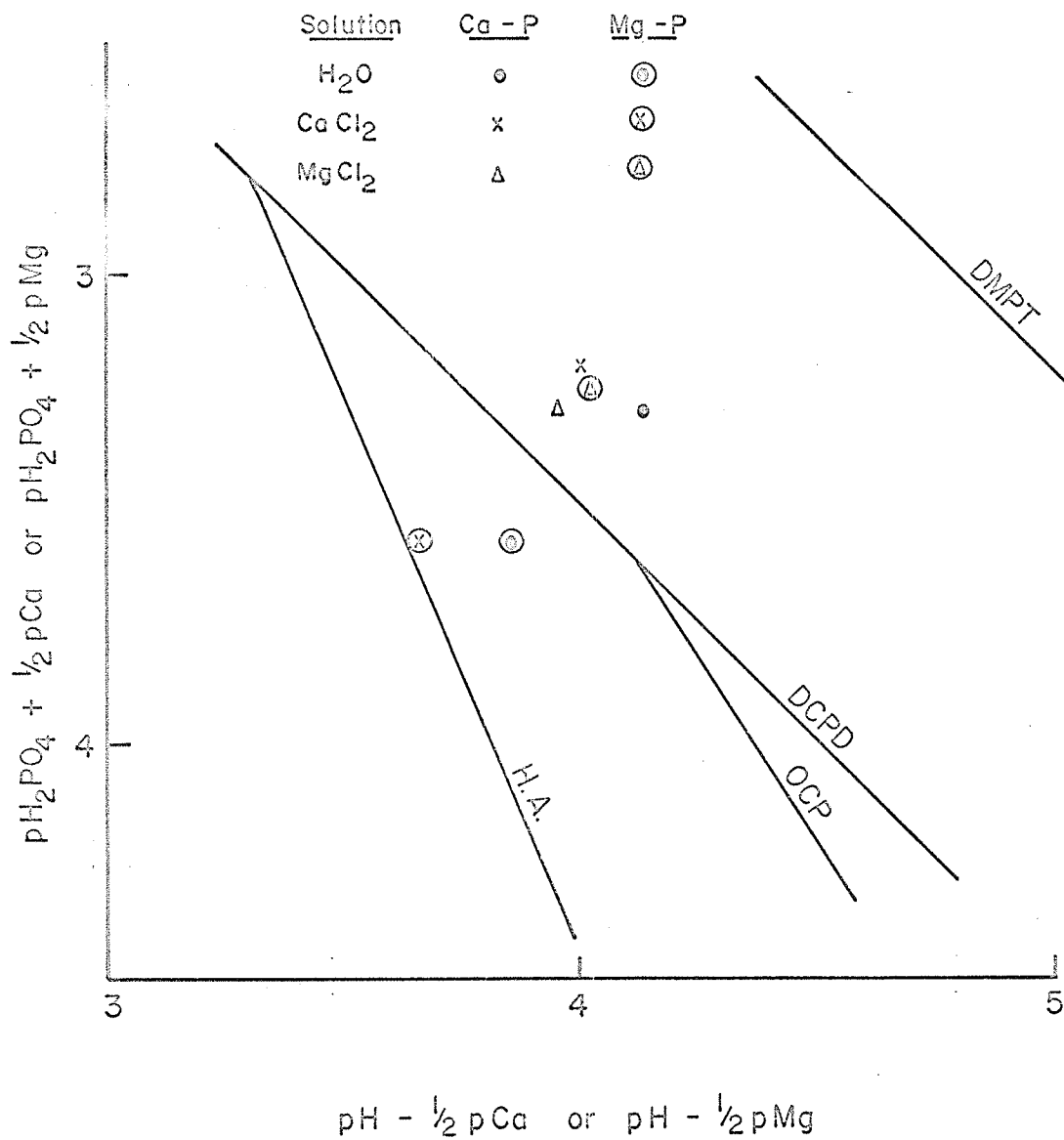


Figure 12. The solubility of phosphorus added to Darlingford soil in .01 M Ca Cl₂, .01 M Mg Cl₂ and water.

as equilibrating solutions had small but noticeable effects on the solubility of phosphorus. The solubility of phosphorus remained near that of DCPD or between that of DCPD and H.A. in the Darlingford soil (Figure 12). As with the Red River soil, which also contained small amounts of carbonates, small but noticeable effects on phosphate solubility occurred as a result of using 0.01 M CaCl_2 or 0.01 M MgCl_2 as the equilibrating solution.

The solubility of the phosphorus added to the soils was altered by the addition of CaCl_2 or MgCl_2 . This was particularly noticeable on the soils containing large amounts of carbonates (Aneda and Balmoral I). It has been a practice, by some workers, to use 0.01 M CaCl_2 as the equilibrating solution in solubility studies. This procedure resulted from the false assumption that the magnesium content of soil solutions was negligible and could be neglected. It also assumed that only calcium phosphates were formed in soils. The use of 0.01 M CaCl_2 offered the advantage of having a relatively constant calcium concentration in solution, and therefore $\frac{1}{2}\text{pCa}$ need not be calculated for all samples. The presence of large amounts of calcium in solution caused flocculation of soil clays, thereby eliminating the problems associated with the filtration of water soil suspensions. Although the use of 0.01 M CaCl_2 as an equilibrating solution offers several advantages, the use of 0.01 M CaCl_2 or 0.01 M MgCl_2 as equilibrating solutions should be avoided as the results obtained may in some instances lead one to make erroneous conclusions.

The Solubility of Phosphorus Added as KH_2PO_4 , H_3PO_4 and K_2HPO_4 in Aneda, Balmoral I, Red River and Darlingford Soils

A determination of the solubility of phosphorus added to soils yields information as to the reaction products formed between the added phosphorus and soil cations. Information as to the availability of the added phosphate is also obtained.

The solubility of phosphorus added as KH_2PO_4 , K_2HPO_4 and H_3PO_4 to four Manitoba soils was determined. Soils, Aneda, Balmoral I, Red River and Darlingford were used in the study. In order to determine the solubility of the phosphorus added as KH_2PO_4 , 0.2, 0.4, 0.6, 0.8 and 1.0 g. KH_2PO_4 was added to 10 g. soil in 100 ml. water and equilibrated with shaking for 24 hours at $25 \pm 1^\circ\text{C}$. The solubility of the phosphorus added as K_2HPO_4 was determined in the same manner. Only two rates of K_2HPO_4 , 0.2 and 0.6 g. per 10 g. soil in 100 ml. water, was used. The H_3PO_4 was added to the soils in a dilute solution. One hundred ml. of 0.01 M H_3PO_4 solution was added to 10 g. soil and equilibrated with shaking for 24 hours. The pH of the suspensions were measured after the shaking period. The calcium, magnesium and phosphorus concentrations of the filtrates were determined and the lime and phosphate potentials calculated. The solubilities were calculated in two manners, i.e., as Ca-P and Mg-P.

The phosphorus, calcium and magnesium concentrations in solution increased for all soils with increased rates of added KH_2PO_4 (Table XVII). The concentration of calcium was lower than the concentration of magnesium in the Balmoral I and Red River soils. The quantity of calcium

Table XVII. The solubility of phosphorus added as KH_2PO_4 in Aneda, Red River, Balmoral I and Darlingford soils

Soil	KH_2PO_4 added (g)	pH	$\frac{[\text{Ca}]}{\text{X}10^2\text{M}}$	$\frac{[\text{Mg}]}{\text{X}10^2\text{M}}$	$\frac{[\text{P}]}{\text{X}10^2\text{M}}$	$\frac{1}{2}\text{pCa}$	$\frac{1}{2}\text{pMg}$	pH_2PO_4	$\frac{\text{pH}}{1/2\text{pCa}}$	$\frac{\text{pH}}{1/2\text{pMg}}$	$\frac{\text{pH}_2\text{PO}_4}{1/2\text{pCa}}$	$\frac{\text{pH}_2\text{PO}_4}{1/2\text{pMg}}$
Aneda	.2	6.22	.250	.078	.103	1.40	1.65	2.08	4.82	4.57	3.48	3.73
	.4	5.95	.359	.083	.231	1.36	1.69	1.73	4.59	4.26	3.09	3.42
	.6	5.80	.453	.088	.380	1.35	1.70	1.53	4.45	4.10	2.88	3.23
	.8	5.70	.510	.101	.519	1.32	1.68	1.38	4.38	4.02	2.70	3.06
1.0	5.61	.566	.101	.644	1.32	1.70	1.30	4.29	3.91	2.62	3.00	
Red River	.2	6.32	.184	.280	.123	1.49	1.40	2.03	4.83	4.92	3.52	3.43
	.4	6.00	.318	.386	.251	1.40	1.36	1.70	4.60	4.64	3.10	3.06
	.6	5.75	.372	.547	.390	1.39	1.31	1.51	4.36	4.44	2.90	2.82
	.8	5.68	.389	.630	.519	1.40	1.29	1.39	4.28	4.39	2.79	2.68
1.0	5.60	.479	.653	.654	1.36	1.29	1.29	4.24	4.31	2.45	2.58	
Balmoral I	.2	6.95	.171	.286	.103	1.49	1.37	2.21	5.46	5.58	3.70	3.58
	.4	6.62	.198	.462	.222	1.49	1.31	1.82	5.13	5.31	3.31	3.13
	.6	6.50	.198	.526	.340	1.50	1.30	1.56	5.00	5.20	3.06	2.86
	.8	6.49	.199	.667	.444	1.51	1.26	1.44	4.98	5.23	2.95	2.70
1.0	6.43	.199	.778	.546	1.52	1.24	1.29	4.91	5.19	2.81	2.53	
Darlingford	.2	6.32	.215	.090	.123	1.44	1.64	2.01	4.88	4.68	3.45	3.65
	.4	6.02	.288	.095	.228	1.41	1.64	1.73	4.61	4.38	3.14	3.37
	.6	5.80	.330	.114	.359	1.40	1.64	1.54	4.40	4.16	2.94	3.18
	.8	5.70	.371	.131	.496	1.39	1.61	1.40	4.31	4.09	2.79	3.01
1.0	5.60	.414	.136	.636	1.37	1.60	1.30	4.23	4.00	2.67	2.90	

in solution was greater than the quantity of magnesium in solution for the other two soils. It is interesting to note that the concentration of calcium in solution for the Balmoral I soil and the concentration of magnesium in solution for the Aneda soil did not increase greatly with increased rates of added phosphorus.

The solubility of the phosphorus added as KH_2PO_4 remained between that of DCPD and DMPT in the Aneda soil (Figure 13). The solubility values plotted on the solubility diagram moved from right to left on the diagram with increased rates of KH_2PO_4 . This is due to the resulting lower lime and phosphate potentials as a result of increasing the rate of KH_2PO_4 added. The solubility of the phosphorus added as KH_2PO_4 was near that of DMPT in the Red River soil (Figure 14). The solubility of the phosphorus added as KH_2PO_4 remained near that of DMPT when small amounts of KH_2PO_4 were added to the Balmoral I soil (Figure 15). The solubility of phosphorus increased above that of DMPT when large amounts of KH_2PO_4 were added. The solubility of the phosphorus added as KH_2PO_4 was between that of DCPD and DMPT in the Darlingford soil (Figure 16). The results obtained are similar to those obtained on the Aneda soil.

The solubility of the phosphorus added as KH_2PO_4 was greater in the soils containing large amounts of magnesium (Balmoral I and Red River) than in the soils containing large amounts of calcium (Aneda and Darlingford). The solubility of phosphorus was high in all samples indicating that a relatively soluble compound was formed in the soils. The studies indicate that DCPD and/or DMPT were formed when

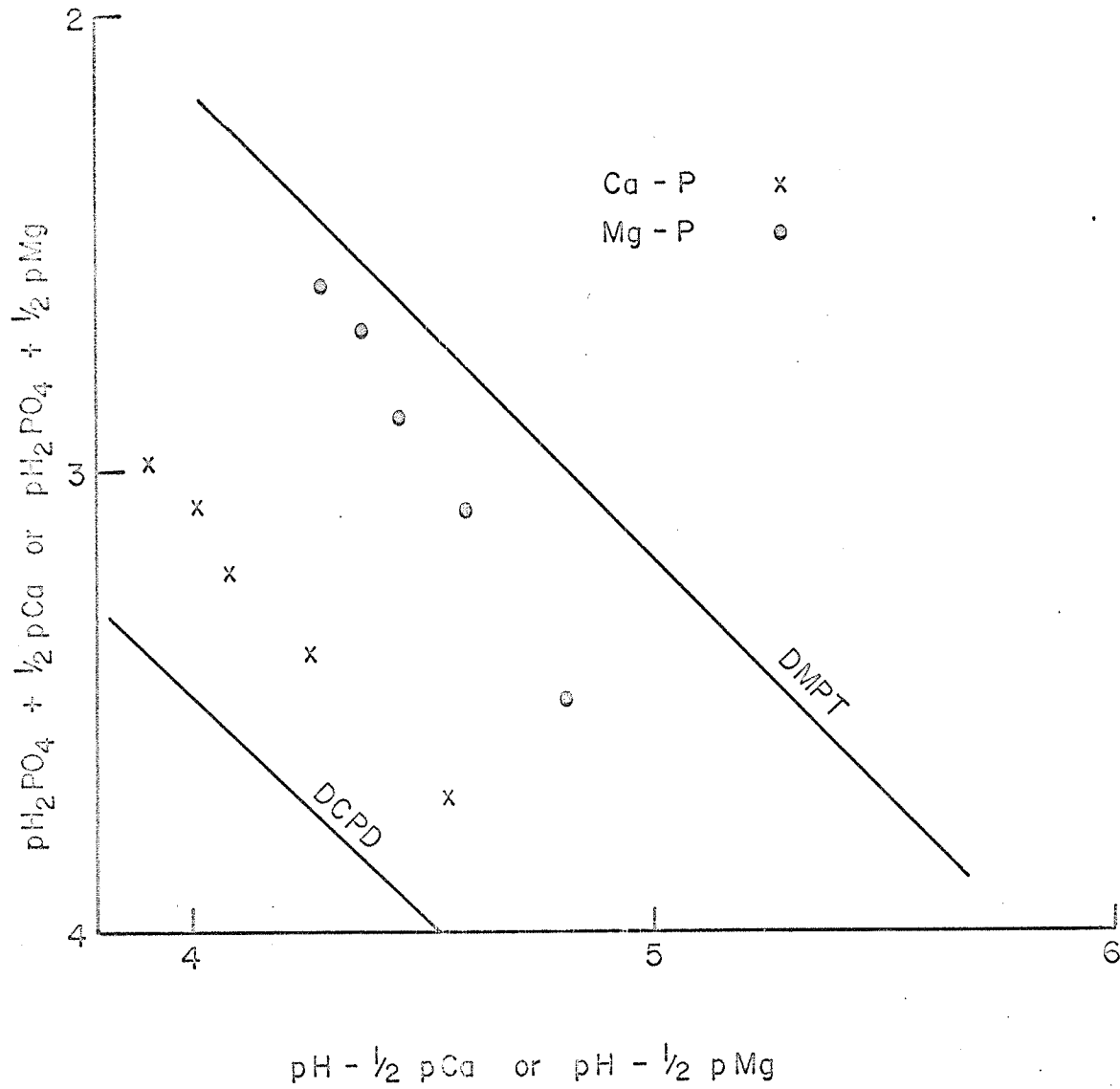


Figure 13. Equilibration of 10 g. of Aneda Soil and 100 ml. Water with 0.2 to 1.0 g. KH_2PO_4 .

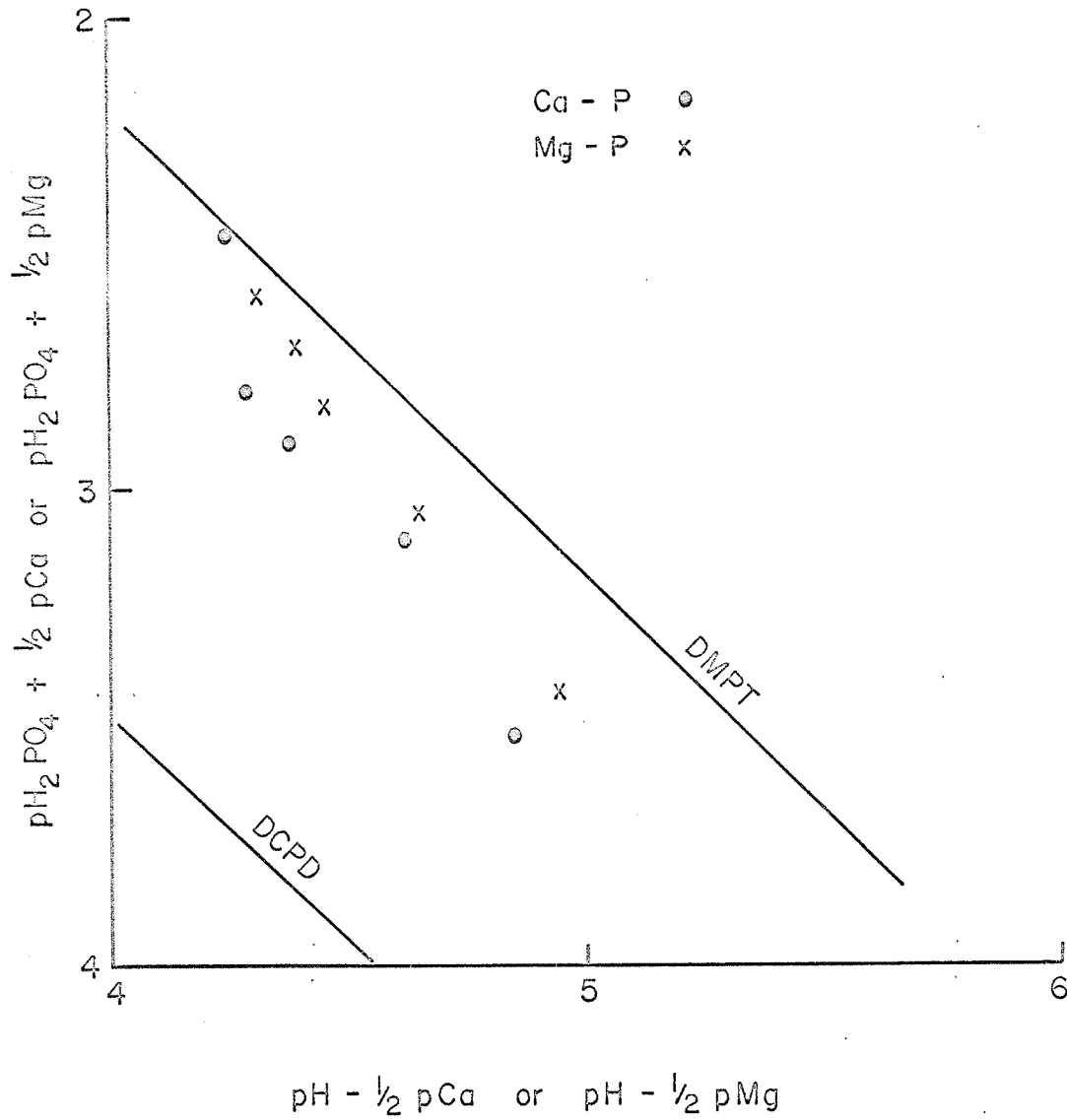


Figure 14. Equilibration of 10 g. Red River soil and 100 ml. water with 0.2 to 1.0 g. KH_2PO_4 .

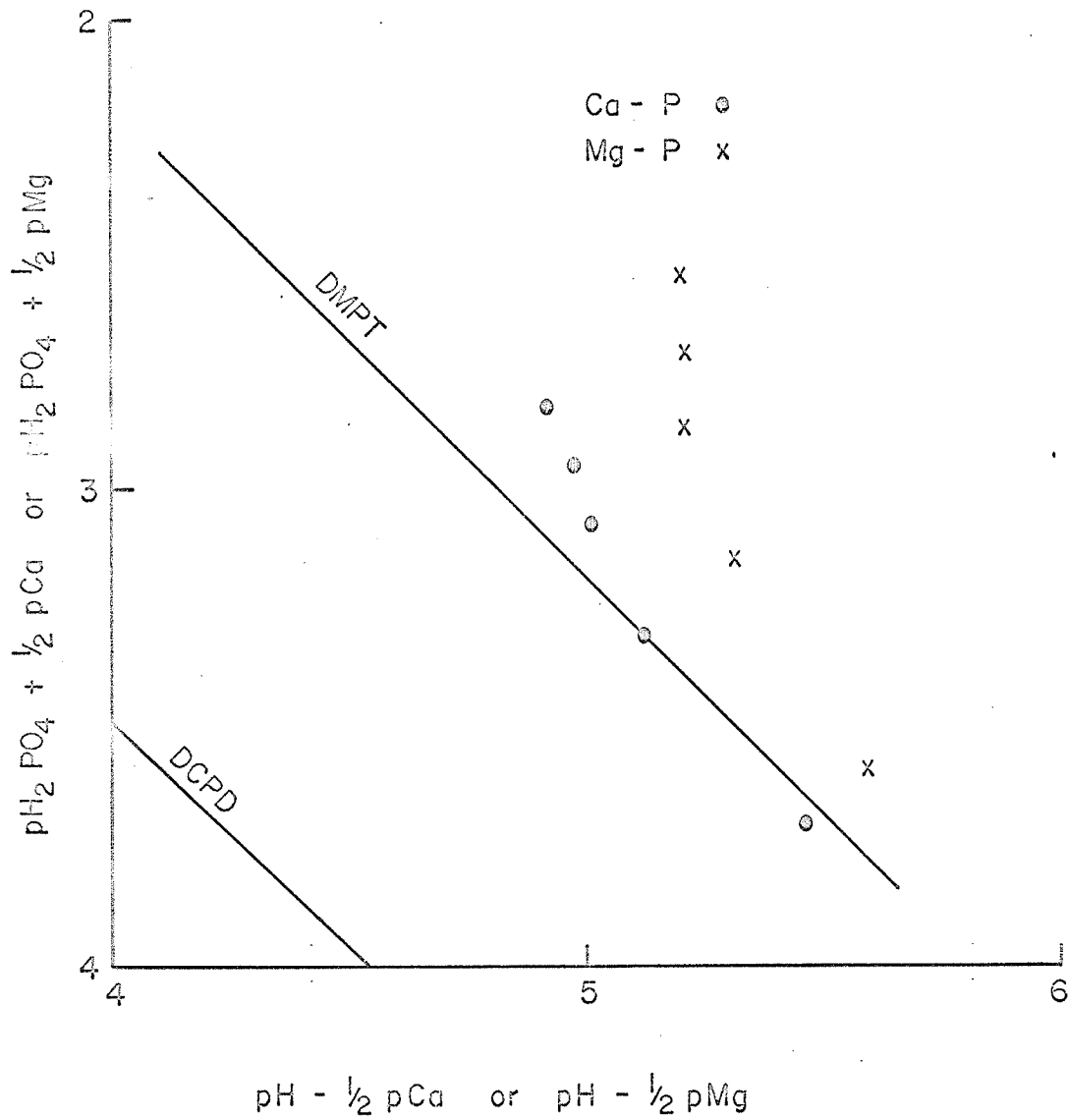


Figure 15. Equilibration of 10 g. Balmoral soil and 100 ml. water with 0.2 to 1.0 g. KH_2PO_4 .

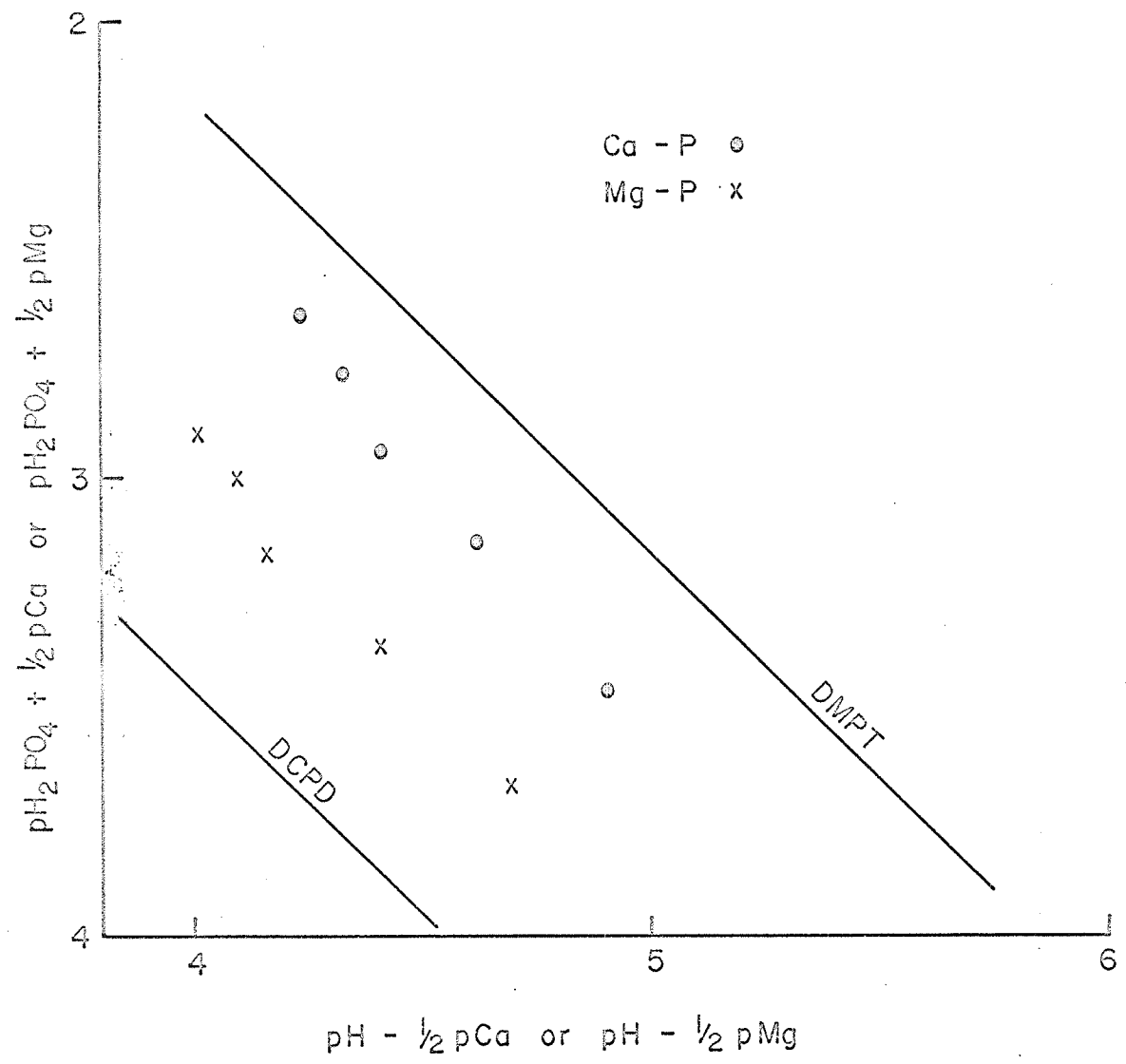


Figure 16. Equilibration of 10g. Darlingford soil and 100 ml. water with 0.2 to 1.0 g. KH₂PO₄.

KH_2PO_4 was added to the soils.

The pH of the soil solutions were higher in the samples receiving K_2HPO_4 than in the samples receiving H_3PO_4 or KH_2PO_4 (Tables XVII and XVIII). The pH of the soil suspensions increased with increased additions of K_2HPO_4 . Addition of K_2HPO_4 to the soils resulted in much larger amounts of phosphorus in solution than calcium and magnesium.

The solubility of phosphorus was between that of DCPD and DMPT in all soils when equilibrated with 100 ml. 0.01 M H_3PO_4 (Figure 17). The solubility of phosphorus added as H_3PO_4 was similar regardless of the amounts of calcium and magnesium contained in the soils. The solubility of phosphorus added as K_2HPO_4 remained between that of DCPD and DMPT in the Aneda soil (Figure 18). The solubility of phosphorus approximated that of DMPT when 0.6 g. K_2HPO_4 was added. The phosphorus added as K_2HPO_4 to the Red River and Balmoral I soils remained very soluble (Figures 19 and 20). The solubility of phosphate increased with increased rates of added phosphorus on both soils. The solubility of phosphorus was near that of DMPT in both soils. The solubility of the phosphorus added as K_2HPO_4 was between that of DCPD and DMPT in the Darlingford soil (Figure 21). The results obtained are comparable to those obtained on the Aneda soil.

The solubility of the phosphorus added as K_2HPO_4 approximated that of DMPT in the soils containing large amounts of magnesium. The solubility of phosphorus was between that of DCPD and DMPT in the soils

Table XVIII. The solubility of phosphorus added as H_3PO_4 and K_2HPO_4 in Aneda, Red River, Balmoral I and Darlingford soils

Soil	Phosphorus added	pH	[Ca] $\times 10^{-2} M$	[Mg] $\times 10^{-2} M$	[P] $\times 10^{-2} M$	$\frac{1}{2} pCa$	$\frac{1}{2} pMg$	pH- $\frac{1}{2} pCa$	pH- $\frac{1}{2} pMg$	$\frac{pH_2PO_4}{pCa}$	$\frac{pH_2PO_4}{pMg}$	$\frac{pH_2PO_4}{pCa}$	$\frac{pH_2PO_4}{pMg}$
Aneda	H_3PO_4	6.23	.476	.130	.918	1.27	1.56	4.96	4.67	3.41	3.41	3.70	3.70
Red River	H_3PO_4	5.95	.216	.334	.885	1.44	1.35	4.51	4.60	3.56	3.56	3.47	3.47
Balmoral I	H_3PO_4	6.65	.308	.396	.776	1.38	1.33	5.27	5.32	3.77	3.77	3.72	3.72
Darlingford	H_3PO_4	6.12	.470	.154	1.002	1.28	1.53	4.84	4.59	3.34	3.34	3.59	3.59
Aneda	.2g.DKP	7.05	.087	.054	.696	1.63	1.74	5.42	5.31	4.07	4.07	4.18	4.18
	.6g.DKP	7.40	.061	.052	2.492	1.81	1.84	5.59	5.56	3.93	3.93	3.96	3.96
Red River	.2g.DKP	7.40	.079	.186	.837	1.67	1.49	5.73	5.91	4.22	4.22	4.04	4.04
	.6g.DKP	7.52	.048	.345	2.527	1.86	1.43	5.66	6.09	4.05	4.05	3.62	3.62
Balmoral I	.2g.DKP	7.75	.031	.154	.907	1.87	1.53	5.88	6.22	4.63	4.63	4.29	4.29
	.6g.DKP	7.82	.029	.197	2.562	1.94	1.53	5.88	6.29	4.34	4.34	3.93	3.93
Darlingford	.2g.DKP	7.30	.063	.041	.889	1.74	1.83	5.56	5.47	4.27	4.27	4.36	4.36
	.6g.DKP	7.45	.050	.052	2.633	1.85	1.84	5.60	5.61	3.98	3.98	3.97	3.97

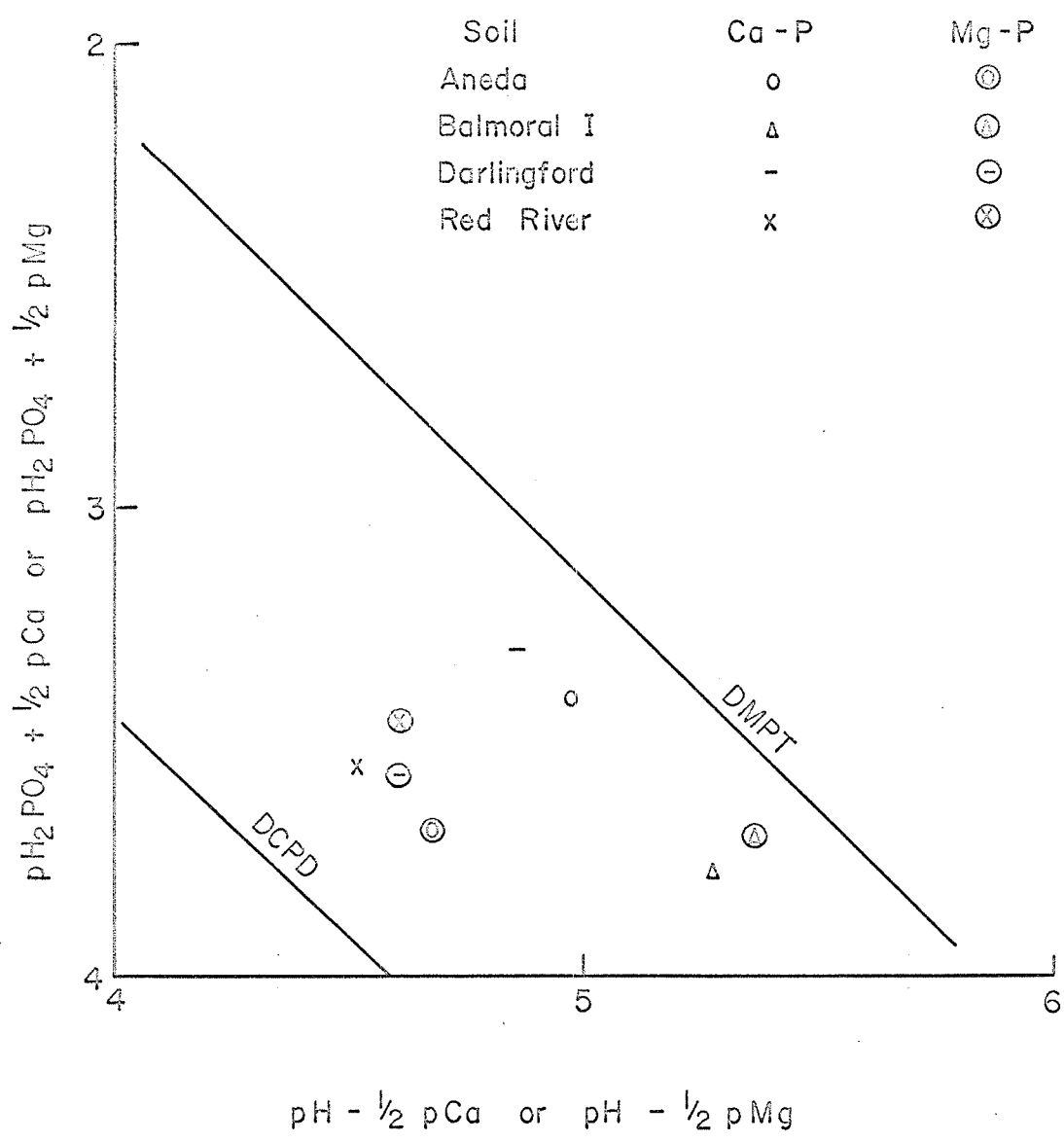


Figure 17. Equilibration of 10 g. soil with 100 ml. .01 M H_3PO_4 .

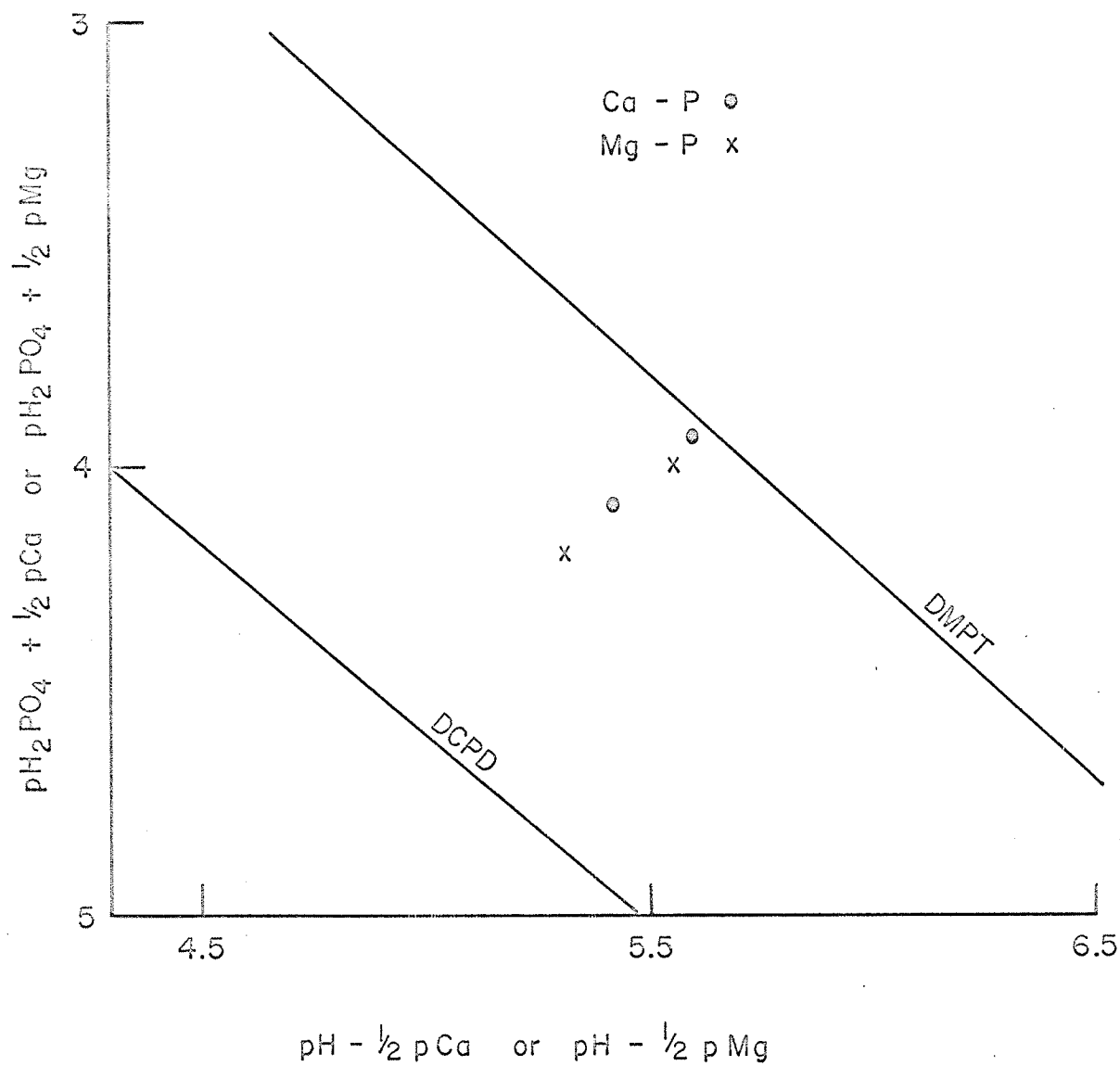


Figure 18. Equilibration of 10 g. Aneda soil and 100 ml. water with 0.2 and 0.6 g. K_2HPO_4 .

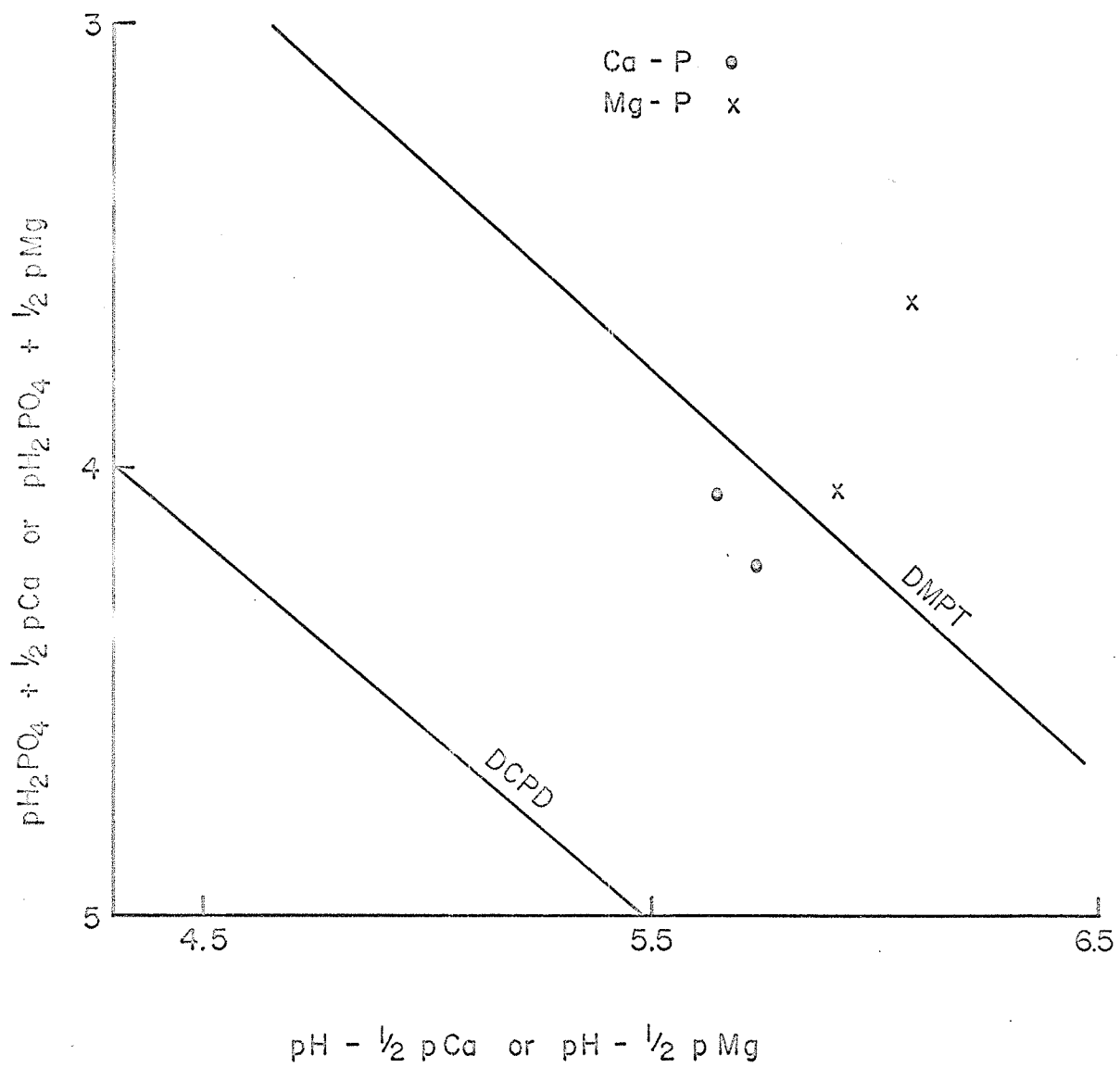


Figure 19. Equilibration of 10g. Red River soil and 100 ml. water with 0.2 and 0.6 g. K_2HPO_4 .

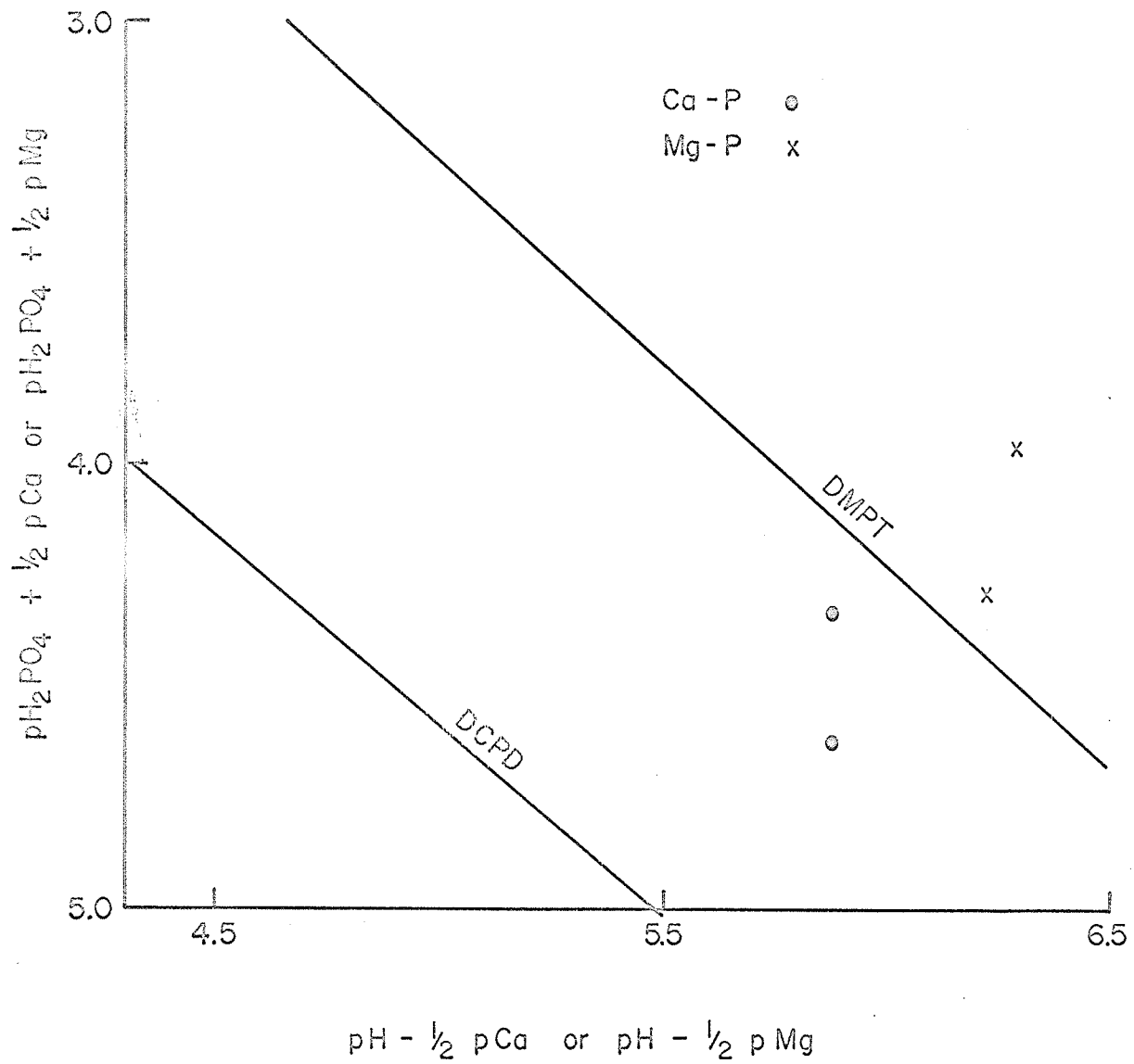


Figure 20. Equilibration of 10 g. Balmoral I soil and 100 ml. water with 0.2 and 0.6 g. K_2HPO_4

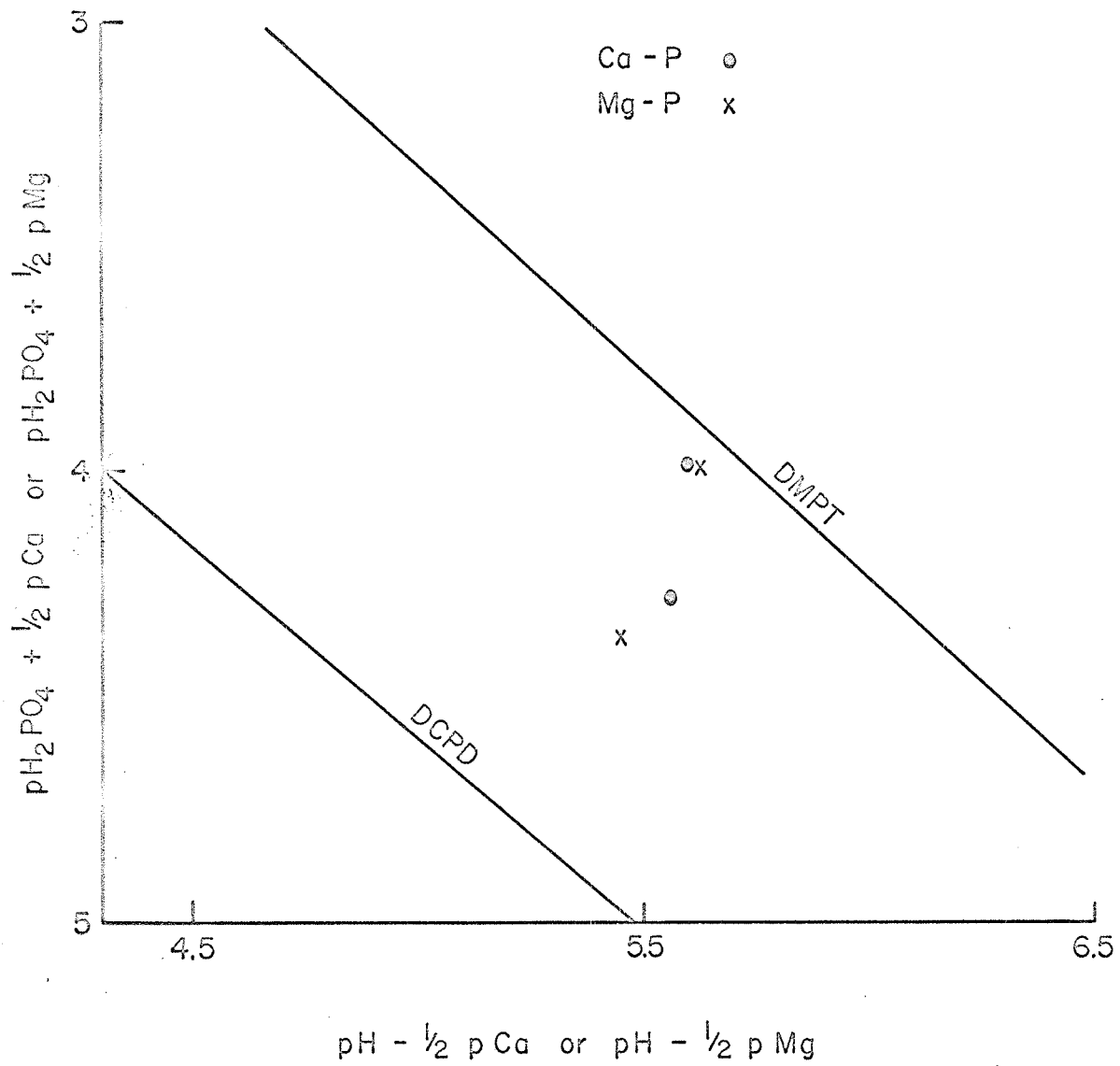


Figure 21. Equilibration of 10 g. Darlingford soil and 100 ml. water with 0.2 and 0.6 g. K_2HPO_4

containing large amounts of calcium.

It is most likely that the reaction products of the added H_3PO_4 , KH_2PO_4 and K_2HPO_4 were DCPD and/or DMPT in the soils studied. The solubility of the added phosphorus was high in all soils indicating that phosphorus added to these soils would remain relatively available for plant use.

Nature of Phosphate Fixation in a Calcium Saturated Clay,
Magnesium Saturated Clay, and Balmoral I and Aneda Soils

Phosphate ions added to soils can become adsorbed on the surface of soil colloids or they can be precipitated as phosphate minerals. It is believed that a monomolecular layer of phosphate is initially formed, followed by the precipitation of phosphate with increased additions of phosphate. The purpose of the following study was three fold. The first objective was to determine the effect of calcium and magnesium held on montmorillonite clay on the amount of phosphorus adsorbed, the adsorption maximum and the energy with which the adsorbed phosphate is held. A study of the amounts of phosphate adsorbed, the adsorption maximum and the bonding energy for phosphate by two soils varying in calcium and magnesium contents was also planned. The second objective was to determine the solubility of the adsorbed and precipitated phosphate. The third objective was to determine the solubility of the adsorbed and precipitated phosphate after removal of the initial phosphate saturating solution.

The adsorption of phosphate in soils can be described by the Langmuir adsorption isotherm (18). An adsorption isotherm gives the relation between the amount of a substance adsorbed by an adsorbent and the equilibrium concentrations of the substance. The Langmuir adsorption equation is specific for small quantities of adsorbed phosphate and dilute phosphate concentrations. An adsorption maximum can be calculated when using the Langmuir equation (25).

The Langmuir equation was developed to describe gas adsorption

on solids, but, the equation has been successfully used for the adsorption of liquids and ions from solution by solids. The following equation is used in the study (25):

$$\frac{x}{m} = \frac{Kbc}{1+Kc} \quad (1)$$

where $\frac{x}{m}$ = ug. P. adsorbed per g. soil,

b = adsorption maximum,

K = constant related to the bonding energy of the adsorbent for phosphate,

and c = equilibrium P. concentration in ug. P. per ml.

The linear form of the equation becomes:

$$c/\frac{x}{m} = \frac{1}{Kb} + \frac{c}{b} \quad (2)$$

where $\frac{1}{b}$ = slope and therefore the adsorption maximum, b , = reciprocal

of the slope and $\frac{1}{Kb}$ = the intercept and therefore the bonding energy,

K , = $\frac{\text{slope}}{\text{intercept}}$. A straight line plot of $c/\frac{x}{m}$ versus C will indicate

an adsorption reaction. When an adsorption reaction occurs, it can be assumed that a monomolecular layer is present on the soil adsorbing surfaces.

Data for plotting the Langmuir isotherms was obtained by following a procedure outlined by Rennie and McKercher (28). Five g. soil was shaken in 50 ml. KH_2PO_4 solutions of concentrations ranging from 10 to 200 ug. P./ml. The suspensions were shaken for 24 hours and the pH of the suspensions measured. The suspensions were centrifuged and the amount of phosphorus remaining in solution determined in order

to obtain the amounts adsorbed by the soils or clays. The calcium and magnesium contents of the filtrates were determined in order to obtain data for calculation of solubility of the added phosphate. The soil or clay remaining in the centrifuge bottle was washed twice with distilled water as follows: Fifty ml. of distilled water was added to the soils or clays. The suspensions were shaken for a brief period, centrifuged, and the filtrate decanted. The washing procedure was conducted in order to remove the phosphate solutions added. An additional 50 ml. of distilled water was added and the samples equilibrated with shaking for 24 hours. The pH of the suspensions were measured and the suspension centrifuged. The phosphorus, calcium and magnesium contents of the filtrates were determined. The data obtained was used to calculate the solubility of the phosphate retained by the soils or clays.

In addition to the montmorillonite clay samples, two soils, Aneda and Balmoral I were used in the study. The calcium saturated clay contained 106 meq./100 g. NH_4Ac displaceable calcium and 4 meq./ 100 g. NH_4Ac displaceable magnesium. The magnesium saturated clay contained 108 meq./ 100 g. NH_4Ac displaceable magnesium and 3 meq. / 100 g. NH_4Ac displaceable calcium. The clays were prepared by leaching them with .01 M CaCl_2 or .01 M MgCl_2 . The samples were washed free of chlorides.

The adsorption isotherms obtained for the clays and soils are shown in Figure 22. The adsorption of phosphorus by the two soils was very similar. The adsorption of phosphate by the calcium and magnesium

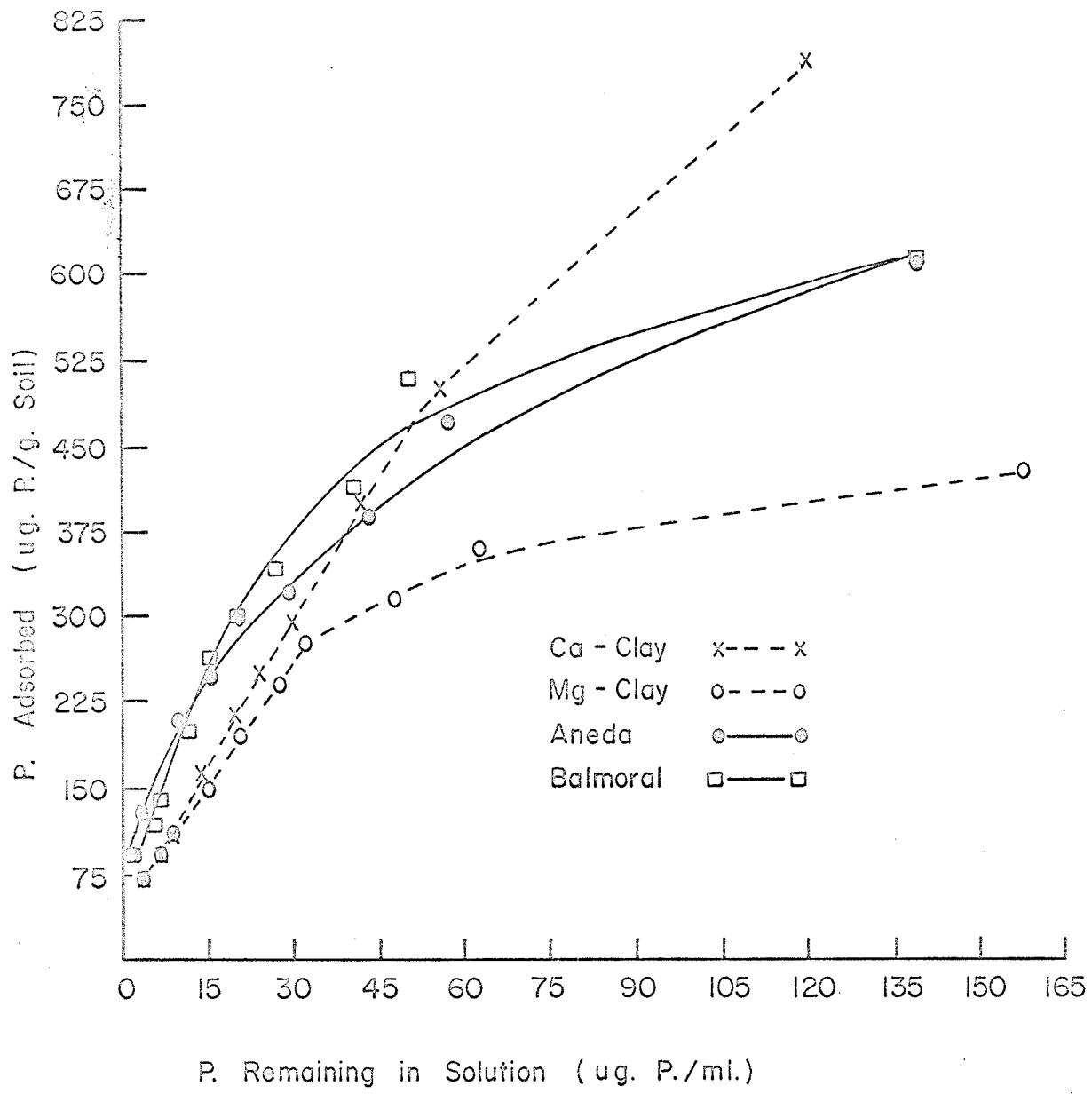


Figure 22. Phosphorus adsorption isotherms for the clays and soils used in adsorption studies.

saturated clays was similar at low phosphate concentrations. The calcium saturated clay fixed more phosphate than did the magnesium saturated clay at high phosphate concentrations. The adsorption data (Tables XIX and XX), plotted according to the Langmuir equation are illustrated in Figure 23. The adsorption of phosphate by the soils and clays follows the Langmuir equation up to a concentration of about 20 - 30 ug. P./ml. remaining in solution. A second reaction is operative at higher final solution concentrations. This secondary reaction could be a further adsorption reaction or a precipitation reaction.

The bonding energy of the calcium saturated clay for phosphorus was $.042 \text{ (ug. P./ ml.)}^{-1}$. The bonding energy for phosphorus by the magnesium saturated clay was $.077 \text{ (ug. P./ ml.)}^{-1}$. The adsorption maximum was 475 ppm. and 300 ppm. for the calcium saturated clay and the magnesium saturated clay respectively. The bonding energy of the Aneda and Balmoral I soils for phosphorus was $.187$ and $.095 \text{ (ug.P./ml.)}^{-1}$ respectively. The adsorption maximum was 360 ppm. for the Aneda soil and 475 ppm. for the Balmoral I soil. Since the adsorption maximum is related to texture (28), it would be expected that the Balmoral soil which was a heavier textured soil than the Aneda possess a higher adsorption maximum.

From the studies conducted on the clays, it would appear that a soil containing large amounts of calcium would adsorb more phosphorus than a soil containing large amounts of magnesium. The results obtained for the clays also suggest that the phosphate adsorbed on a calcium

Table XIX. Adsorption of phosphorus by montmorillonite clay

P. added ug.P./g. soil	<u>Calcium saturated clay</u>			<u>Magnesium saturated clay</u>		
	P. remaining in solution ug.P./ml.(C)	P adsorbed ug.P./g. soil (x/m)	c/x m	P. remaining in solution ug.P./ml.(C)	P. adsorbed ug.P./g. soil (x/m)	c/x m
100	3.7	73	.051	3.6	74	.049
150	5.8	92	.063	5.8	92	.063
200	8.2	118	.069	8.3	117	.071
300	13.3	167	.080	15.0	150	.100
400	18.7	213	.088	19.7	203	.097
500	24.8	252	.098	26.2	238	.110
600	30.4	296	.103	33.0	270	.122
800	40.0	400	.100	48.2	318	.152
1000	49.7	503	.099	63.4	366	.173
2000	121.6	784	.155	157.0	430	.365

Table XX. Adsorption of phosphorus by Aneda and Balmoral I soils

P. added ug.P./g. soil	Aneda				Balmoral I			
	P. remaining in solution ug.P./ml.(C)	P. adsorbed ug.P./g. soil (x/m)	c/x m	P. remaining in solution ug.P./ml.(C)	P. adsorbed ug.P./g. soil (x/m)	c/x m		
100	1.6	84	.019	1.8	82	.022		
150	2.9	121	.024	3.5	115	.030		
200	-	-	-	5.8	142	.041		
300	9.2	208	.044	9.4	206	.046		
400	15.4	246	.063	13.8	262	.053		
500	20.2	298	.068	20.2	298	.068		
600	28.1	319	.088	25.2	348	.072		
800	41.8	382	.109	38.4	416	.092		
1000	52.8	472	.112	48.2	518	.093		
2000	138.9	611	.227	138.9	611	.227		

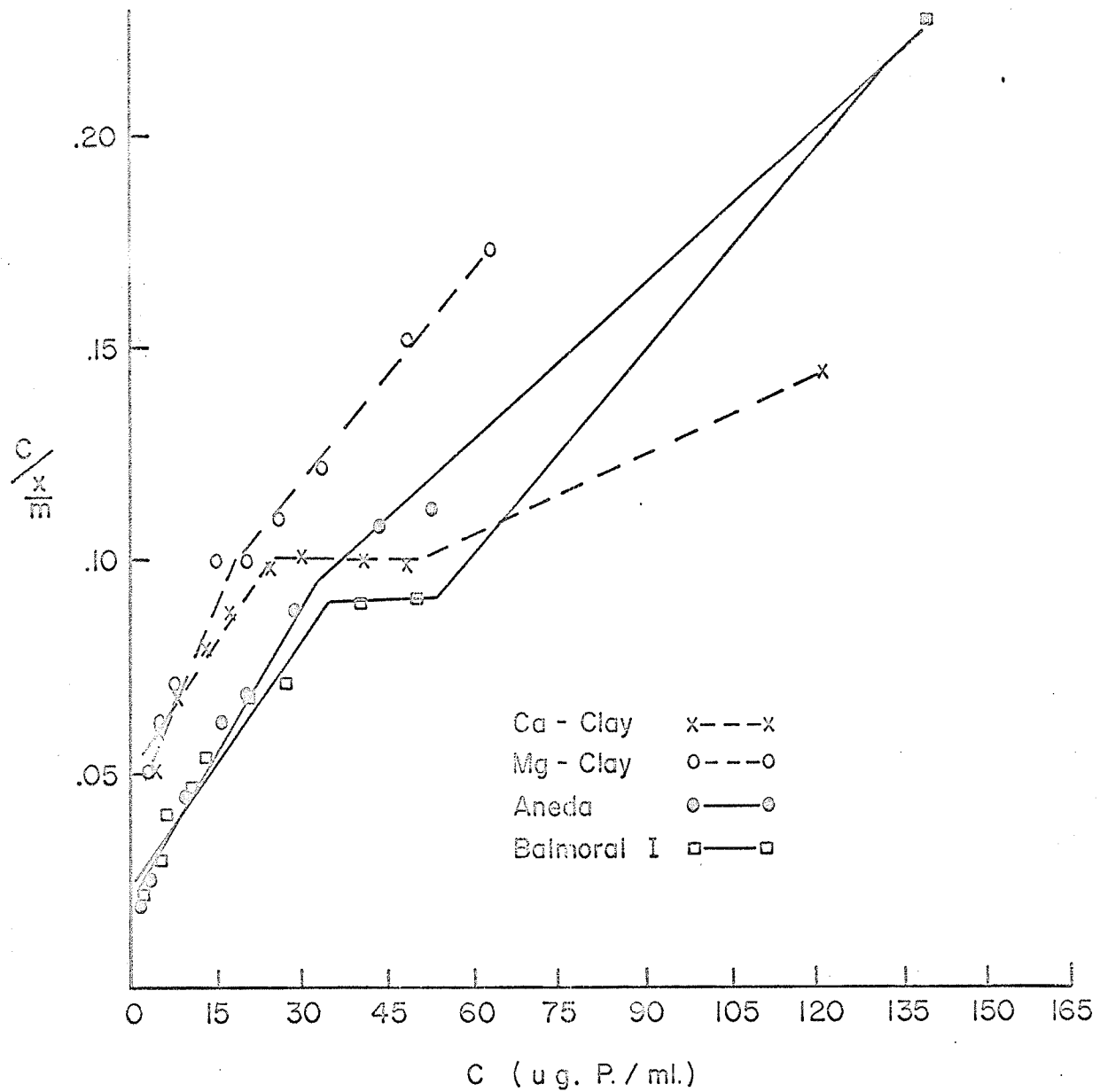


Figure 23. Langmuir plot of adsorption data for the clays and soils used in adsorption studies.

saturated soil would not be held as tightly as phosphate adsorbed on a magnesium saturated soil. These observations, however, were not verified on the two soils studied.

The pH of the magnesium saturated clay was higher than that of the calcium saturated clay (Table XXI). The pH of both systems decreased with progressive additions of KH_2PO_4 . The addition of KH_2PO_4 also resulted in displacing more magnesium into solution than calcium from their respective clay systems. The concentration of calcium or magnesium in solution increased with increased additions of KH_2PO_4 .

The solubility of phosphate added to the calcium saturated montmorillonite was between that of OCP and DCPD when small amounts of phosphorus were added (Figure 24). The solubility of the added phosphate increased with increasing amounts of added phosphate, particularly at low phosphate concentrations. The solubility of the added phosphate remained slightly above that of DCPD at high phosphate concentrations. The increase in solubility occurred at phosphorus concentrations below the adsorption maximum. Above the adsorption maximum no notable increase in solubility of phosphate occurred. This indicates that after the surfaces of the clay particles were covered with phosphate ions, the added phosphate was possibly precipitated as DCPD. The solubility of the phosphate added to the magnesium saturated clay approximated that of the phosphate added to the calcium saturated clay at low phosphate concentrations. The solubility of the phosphate was similar in the calcium and magnesium clay system at phosphorus concentrations below the adsorption maximum. The solubility

Table XXI. Solubility of phosphorus added to a calcium and a magnesium saturated montmorillonite

Sample	P. added ug.P./g. soil	pH	[Ca] x10 ² M	[Mg] ² x10 ² M	[P] ² x10 ² M	$\frac{1}{2}$ pCa	$\frac{1}{2}$ pMg	pH ₂ PO ₄	pH ⁻ $\frac{1}{2}$ pCa	pH ⁻ $\frac{1}{2}$ pMg	pH ₂ PO ₄ $\frac{1}{2}$ pCa	pH ₂ PO ₄ $\frac{1}{2}$ pMg
Ca - clay	100	8.02	.058		.012	1.65		4.83	6.37		6.48	
	150	7.90	.078		.019	1.60		4.53	6.30		6.13	
	200	7.88	.074		.026	1.61		4.36	6.27		5.97	
	300	7.78	.075		.043	1.62		4.08	6.16		5.70	
	400	7.64	.073		.060	1.61		3.83	6.03		5.43	
	500	7.52	.084		.080	1.58		3.61	5.94		5.19	
	600	7.40	.098		.098	1.56		3.46	5.84		5.02	
	800	7.10	.098		.129	1.56		3.17	5.54		4.73	
	1000	6.93	.104		.160	1.55		3.01	5.38		4.56	
	2000	6.55	.188		.392	1.44		2.53	5.11		3.97	
Mg - clay	100	8.08		.073	.012		1.61	4.89		6.47		6.50
	150	8.02		.072	.019		1.62	4.74		6.40		6.36
	200	7.90		.064	.027		1.64	4.37		6.26		6.01
	300	7.82		.086	.049		1.58	4.06		6.24		5.64
	400	7.75		.087	.064		1.58	3.87		6.17		5.45
	500	7.64		.100	.085		1.55	3.68		6.09		5.23
	600	7.55		.109	.107		1.54	3.51		6.01		5.05
	800	7.42		.141	.156		1.49	3.26		5.93		4.75
	1000	7.28		.170	.205		1.45	3.06		5.83		4.51
	2000	6.80		.310	.507		1.35	2.49		5.45		3.84

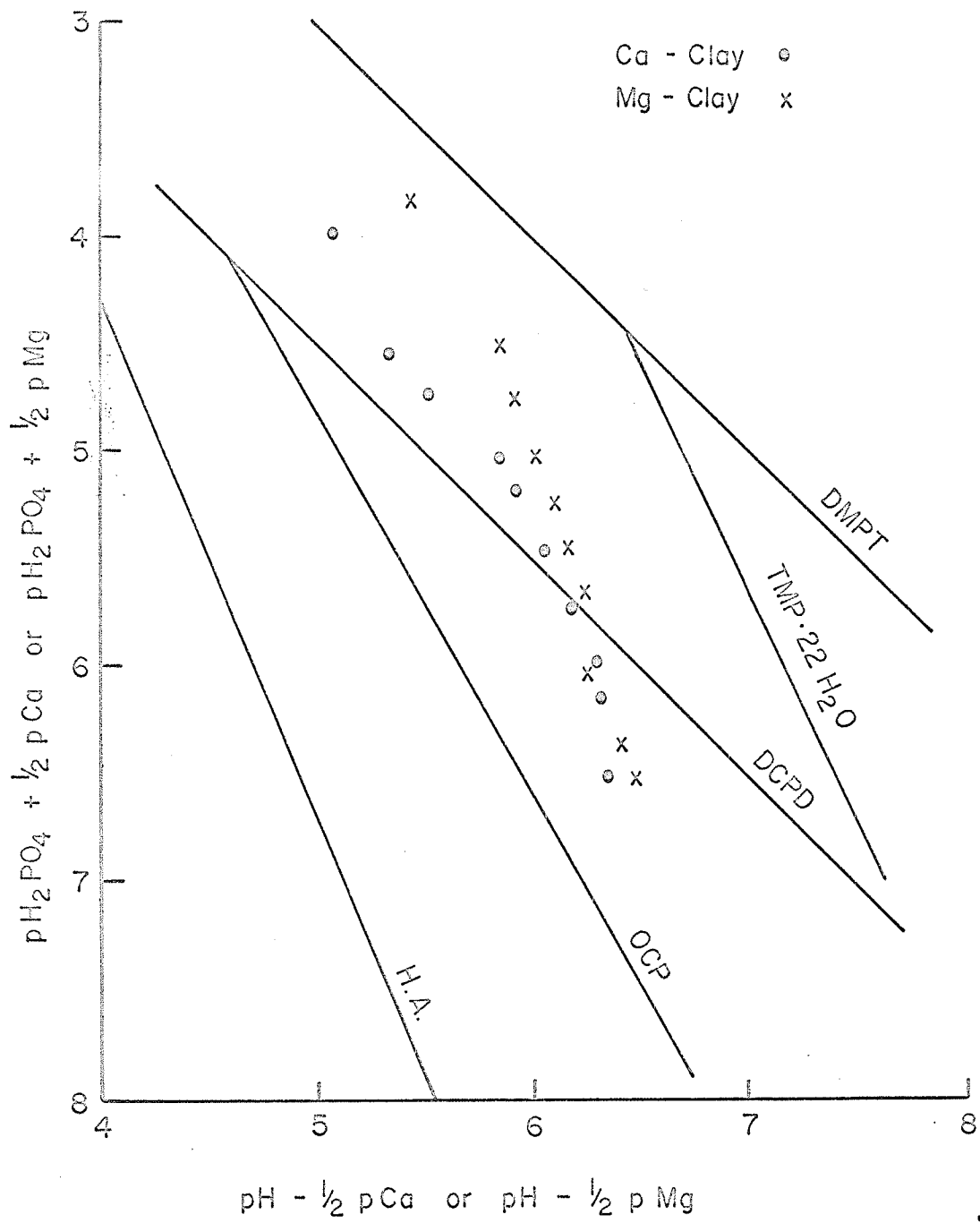


Figure 24. Solubility of added phosphorus in a calcium and a magnesium saturated montmorillonite.

of phosphate in the magnesium saturated clay was greater than in the calcium saturated clay at phosphorus concentrations above the adsorption maximum. Addition of 2000 ug. P./ g. magnesium saturated clay resulted in a phosphate solubility approaching that of DMPT. The solubility of the phosphate added to the magnesium clay increased with increased rates of added phosphorus. There was no evidence of a definite compound being formed above the adsorption maximum as in the calcium saturated clay where DCPD was most likely formed.

The data obtained for the solubility studies conducted on the Aneda and Balmoral I soils are recorded in Table XXII and illustrated graphically in Figures 25 and 26. The pH of the Aneda soil was lower than the pH of the Balmoral I soil (Table XXII). The aqueous extracts obtained from the Aneda soil contained large amounts of calcium and the extracts obtained from the Balmoral I soil contained large amounts of magnesium. The solubility of phosphorus when small amounts of KH_2PO_4 were added to the Aneda soil was near that of OCP (Figure 25). The solubility of phosphorus when large amounts of KH_2PO_4 were added was near that of DCPD. There was no apparent abrupt change in solubility of phosphorus at the adsorption maximum. The solubility of phosphorus when small amounts of KH_2PO_4 were added to the Balmoral I soil was between that of OCP and DCPD (Figure 26). The solubility of phosphate increased with additions of KH_2PO_4 up to the adsorption maximum. The solubility of phosphate increased only slightly at phosphate concentrations above the adsorption maximum. This may again be received as evidence for the occurrence of a precipitation reaction above the

Table XXII. Solubility of phosphorus added to Aneda and Balmoral I soils

Soil	P. added ug P./g. soil	pH	[Ca] X10 ⁻² M	[Mg] X10 ⁻² M	[P] X10 ⁻² M	1/3Ca	1/3Mg	pH ₂ PO ₄ 1/3Ca	pH ₂ PO ₄ 1/3Mg	pH ₂ PO ₄ 1/3Ca	pH ₂ PO ₄ 1/3Mg
Aneda	100	7.60	.088	.014	.005	1.58	1.99	4.87	6.02	5.61	6.86
	150	7.55	.082	.024	.009	1.59	1.86	4.57	5.96	5.69	6.43
	200	-	-	-	-	-	-	-	-	-	-
	300	7.40	.086	.028	.030	1.58	1.82	3.97	5.82	5.58	5.79
	400	7.25	.093	.030	.050	1.57	1.82	3.66	5.68	5.43	5.48
	500	7.00	.102	.030	.065	1.55	1.83	3.43	5.45	5.17	5.26
	600	6.91	.108	.033	.091	1.54	1.80	3.25	5.37	5.11	5.05
	800	6.85	.114	.039	.135	1.53	1.77	3.06	5.32	5.08	4.83
	1000	6.79	.121	.045	.170	1.52	1.74	2.95	5.27	5.05	4.69
	2000	6.53	.178	.056	.448	1.46	1.71	2.47	5.07	4.82	4.18
Balmoral I	100	7.95	.032	.083	.006	1.80	1.59	5.09	6.15	6.36	6.68
	150	8.05	.034	.064	.011	1.79	1.65	4.89	6.26	6.40	6.54
	200	8.13	.047	.057	.019	1.71	1.67	4.74	6.42	6.46	6.41
	300	8.00	.046	.079	.030	1.73	1.61	4.42	6.27	6.39	6.03
	400	8.02	.040	.093	.045	1.76	1.57	4.27	6.26	6.45	5.84
	500	8.02	.048	.100	.065	1.72	1.56	4.11	6.30	6.46	5.67
	600	7.90	.050	.106	.081	1.71	1.55	3.90	6.19	6.35	5.45
	800	7.78	.059	.110	.124	1.68	1.55	3.62	6.10	6.23	5.17
	1000	7.60	.065	.133	.156	1.66	1.51	3.39	5.94	6.09	4.90
	2000	7.32	.090	.208	.448	1.69	1.44	2.76	5.63	5.88	4.45

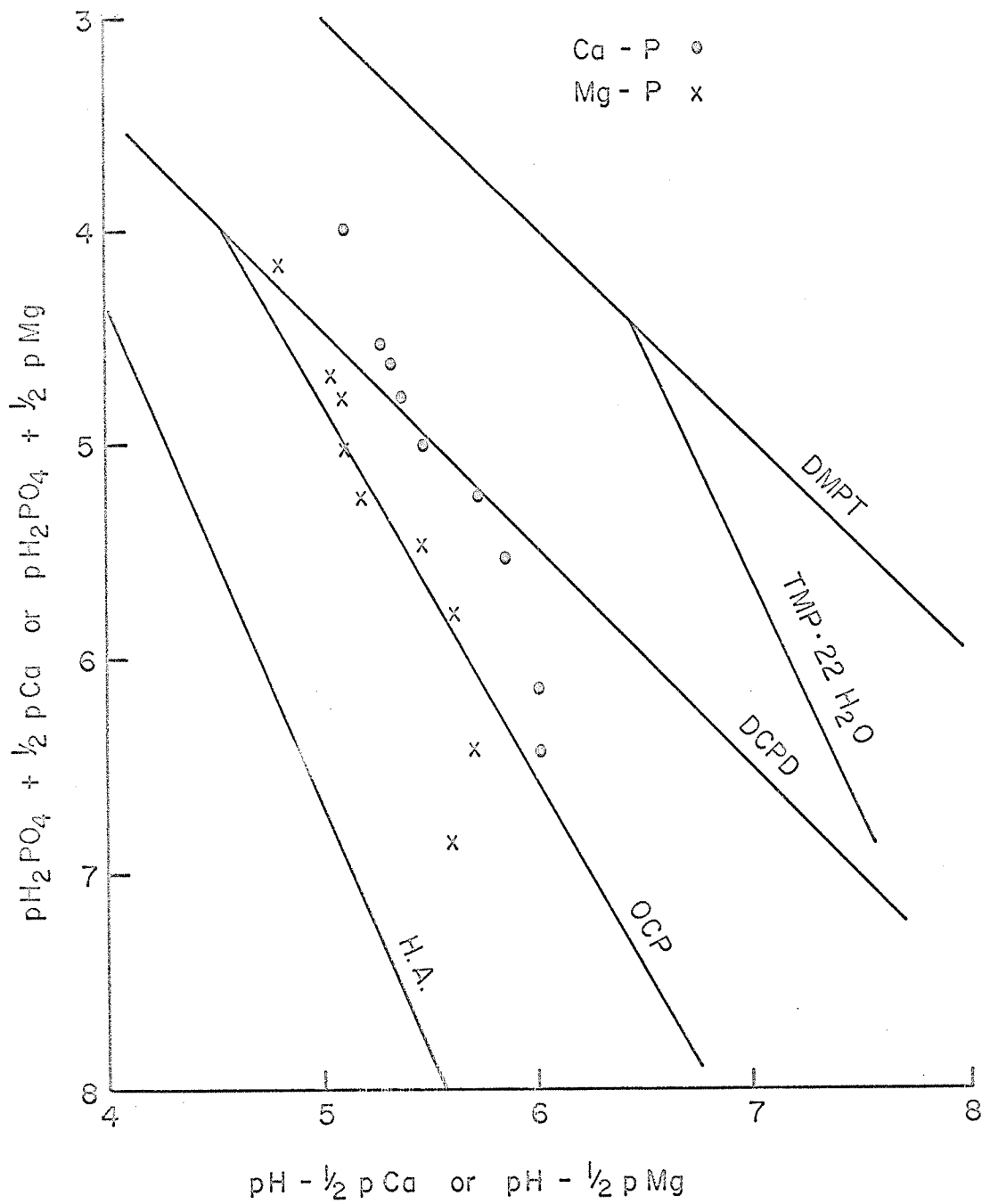


Figure 25. Solubility of added phosphorus in Aneda soil.

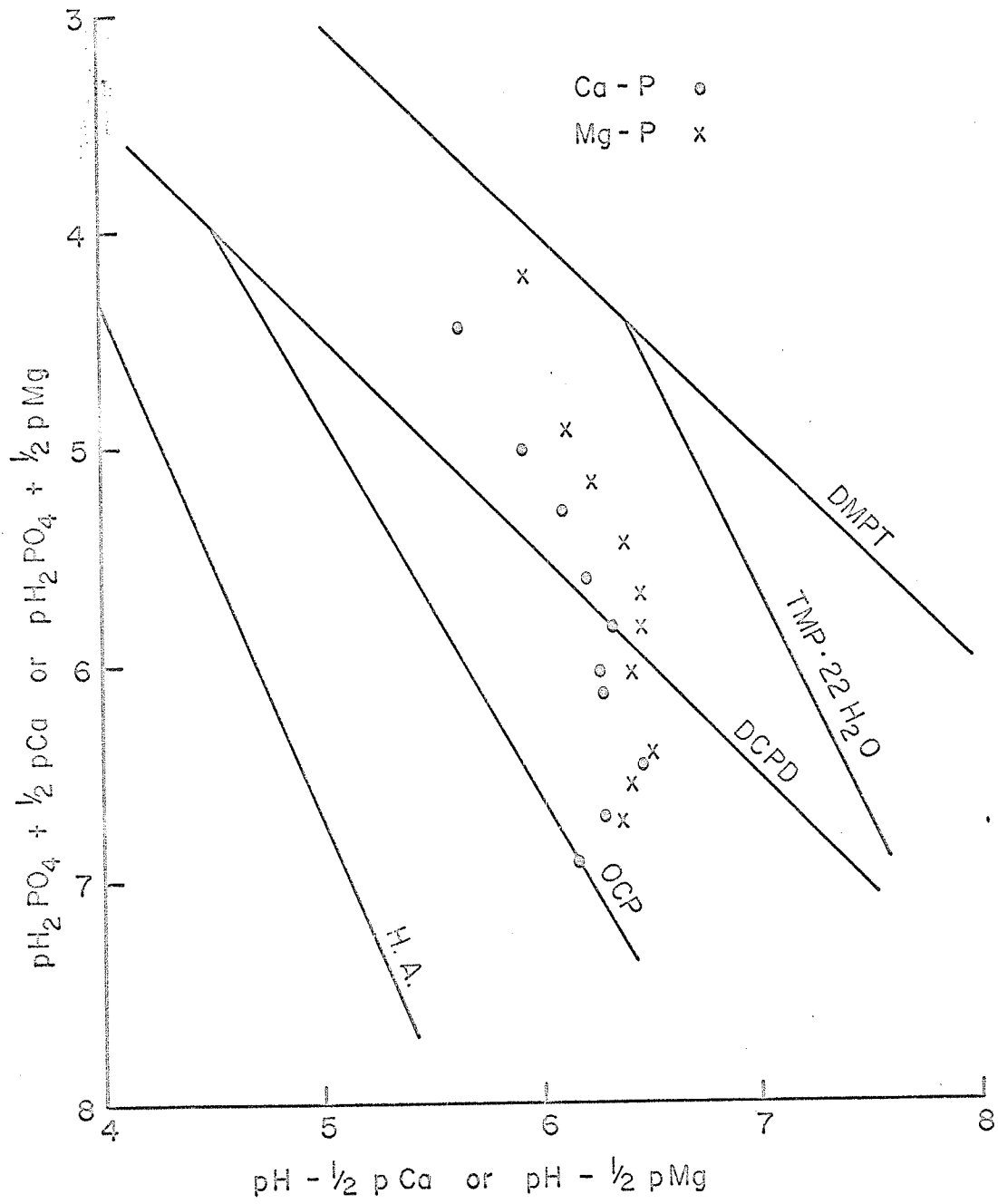


Figure 26. Solubility of added phosphorus in Balmoral I soil.

adsorption maximum. The solubility of phosphorus was between that of DCPD and DMPT above the adsorption maximum.

The data obtained for the solubility studies conducted on the samples after removal of the added phosphorus solutions are recorded in Tables XXIII and XXIV and shown graphically in Figures 27, 28 and 29. The pH of the soils and clays increased following the removal of the added phosphate solutions (Tables XXIII and XXIV). The concentrations of calcium and magnesium in the extracts were lower than prior to washing of the samples. The solubility of phosphorus in the calcium saturated montmorillonite remained slightly above that of OCP. (Figure 27). The solubility of phosphate in the magnesium saturated clay approximated the solubility of phosphate in the calcium saturated clay at low phosphate concentrations. The solubility of phosphate was higher in the magnesium clay than in the calcium clay at high phosphate concentrations. The solubility of the phosphate remaining in the Aneda soil was near that of OCP (Figure 28). The solubility of the phosphate remaining in the Balmoral I soil was between that of OCP and DCPD (Figure 29). The solubility of residual phosphate in the magnesium saturated clay was also less than that of $\text{TMP} \cdot 22\text{H}_2\text{O}$ (Figure 27). Since the majority of phosphate in the Balmoral I soil and magnesium saturated clay was probably held by magnesium, it would appear that a magnesium phosphate of a solubility lower than that of TMP may have been present in these systems. $\text{Mg}_2(\text{PO}_4)\text{F}$ has been found in nature. It is possible that a compound similar to this, with the OH^- ion replacing the F^- ion, may have been formed in the magnesium saturated montmorillonite and the Balmoral I soil.

Table XXIII. Solubility of residual phosphorus in a calcium and a magnesium saturated montmorillonite

Sample	P. added ug.P./g. soil	pH	[Ca] ²⁺ X10 ⁻² M	[Mg] ²⁺ X10 ⁻² M	[P] ²⁻ X10 ⁻² M	$\frac{1}{2}$ pCa	$\frac{1}{2}$ pMg	pH ₂ PO ₄	pH ₂ PO ₄ $\frac{1}{2}$ pCa	pH ₂ PO ₄ $\frac{1}{2}$ pMg	pH ₂ PO ₄ $\frac{1}{2}$ pCa $\frac{1}{2}$ pMg
Ca - clay	100	7.80	.052		.004	1.68		5.07	6.12		6.75
	150	7.90	.052		.007	1.68		4.97	6.22		6.65
	200	7.78	.047		.008	1.70		4.79	6.08		6.49
	300	7.68	.046		.012	1.71		4.54	5.97		6.25
	400	7.63	.049		.015	1.69		4.41	5.94		6.10
	500	7.62	.051		.019	1.68		4.30	5.94		5.98
	600	7.60	.054		.021	1.67		4.25	5.93		5.92
	800	7.45	.054		.019	1.67		4.20	5.78		5.87
	1000	7.42	.046		.020	1.70		4.15	5.72		5.85
	2000	7.20	.064		.031	1.64		3.86	5.56		5.50
Mg - clay	100	8.00		.047	.004		1.70	5.35		6.30	7.05
	150	7.95		.052	.006		1.68	5.10		6.27	6.78
	200	7.90		.044	.008		1.71	4.91		6.19	6.62
	300	7.80		.050	.011		1.69	4.70		6.11	6.39
	400	7.85		.049	.015		1.69	4.60		6.16	6.29
	500	7.80		.055	.019		1.67	4.45		6.13	6.12
	600	7.75		.059	.020		1.66	4.39		6.09	6.05
	800	7.75		.058	.022		1.66	4.34		6.09	6.00
	1000	7.75		.059	.026		1.66	4.27		6.09	5.93
	2000	7.62		.066	.041		1.63	3.97		5.99	5.60

Table XXIV. Solubility of residual phosphorus in Aneida and Balmoral I soils

Soil	P. added ug.P./g.soil	pH	[Ca] ²⁺ X10 ⁻³ M	[Mg] ²⁺ X10 ⁻³ M	[P] ²⁻ X10 ⁻³ M	1/2Ca	1/2Mg	pH ₂ PO ₄	pH _{1/2Ca}	pH _{1/2Mg}	pH ₂ PO ₄ 1/2Ca	pH ₂ PO ₄ 1/2Mg
Aneida	100	7.65	.083	.031	.003	1.59	1.81	5.18	6.06	5.84	6.77	6.99
	150	7.70	.067	.024	.003	1.63	1.86	5.18	6.07	5.84	6.81	7.04
	200	-	-	-	-	-	-	-	-	-	-	-
	300	7.70	.073	.019	.007	1.62	1.91	4.81	6.08	5.79	6.43	6.72
	400	7.60	.062	.028	.007	1.65	1.82	4.71	5.95	5.78	6.36	6.53
	500	7.51	.071	.028	.010	1.62	1.82	4.53	5.89	5.69	6.15	6.35
	600	7.48	.066	.034	.011	1.64	1.79	4.45	5.84	5.69	6.09	6.24
	800	7.50	.071	.030	.015	1.62	1.81	4.32	5.88	5.69	5.94	6.13
	1000	7.52	.061	.024	.018	1.66	1.86	4.27	5.86	5.66	5.93	6.13
	2000	7.45	.064	.023	.029	1.64	1.87	4.01	5.81	5.58	5.65	5.88
Balmoral I	100	8.63	.024	.059	.003	1.86	1.66	6.04	6.77	6.97	7.90	7.70
	150	8.70	.026	.051	.003	1.84	1.69	6.06	6.86	7.01	7.90	7.75
	200	8.72	.022	.056	.003	1.88	1.67	5.91	6.84	7.05	7.79	7.58
	300	8.51	.026	.063	.007	1.85	1.64	5.51	6.66	6.87	7.36	7.15
	400	8.52	.025	.061	.010	1.85	1.65	5.40	6.67	6.87	7.25	7.05
	500	8.49	.025	.064	.013	1.85	1.64	5.23	6.64	6.85	7.08	6.87
	600	8.50	.026	.061	.014	1.84	1.66	5.20	6.66	6.84	7.04	6.86
	800	8.50	.027	.059	.019	1.83	1.66	5.10	6.67	6.84	6.93	6.76
	1000	8.43	.027	.056	.024	1.83	1.67	4.90	6.60	6.76	6.73	6.57
	2000	8.25	.024	.077	.038	1.86	1.61	4.53	6.39	6.64	6.39	6.14

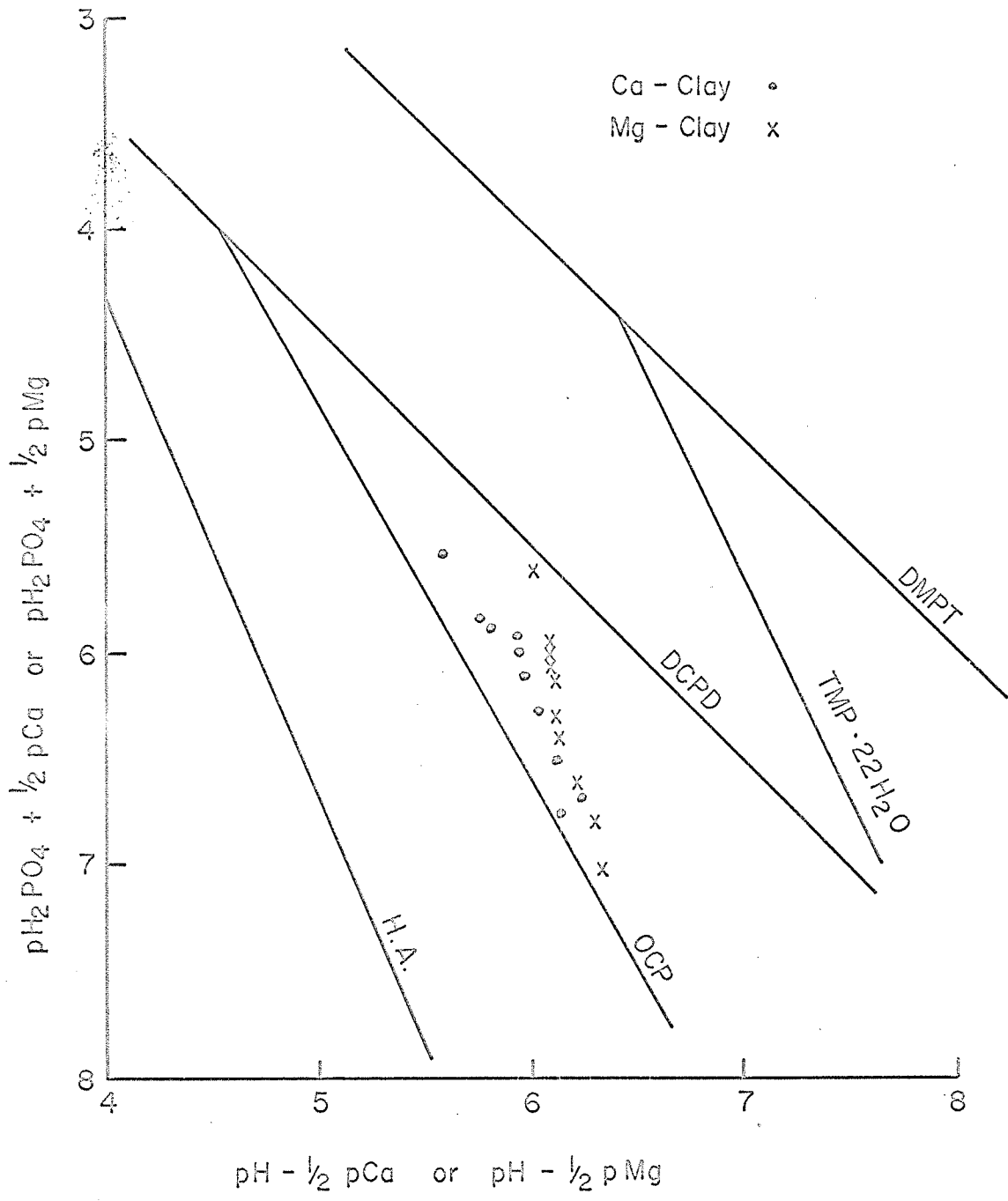


Figure 27. Solubility of residual phosphorus in a calcium and a magnesium saturated montmorillonite.

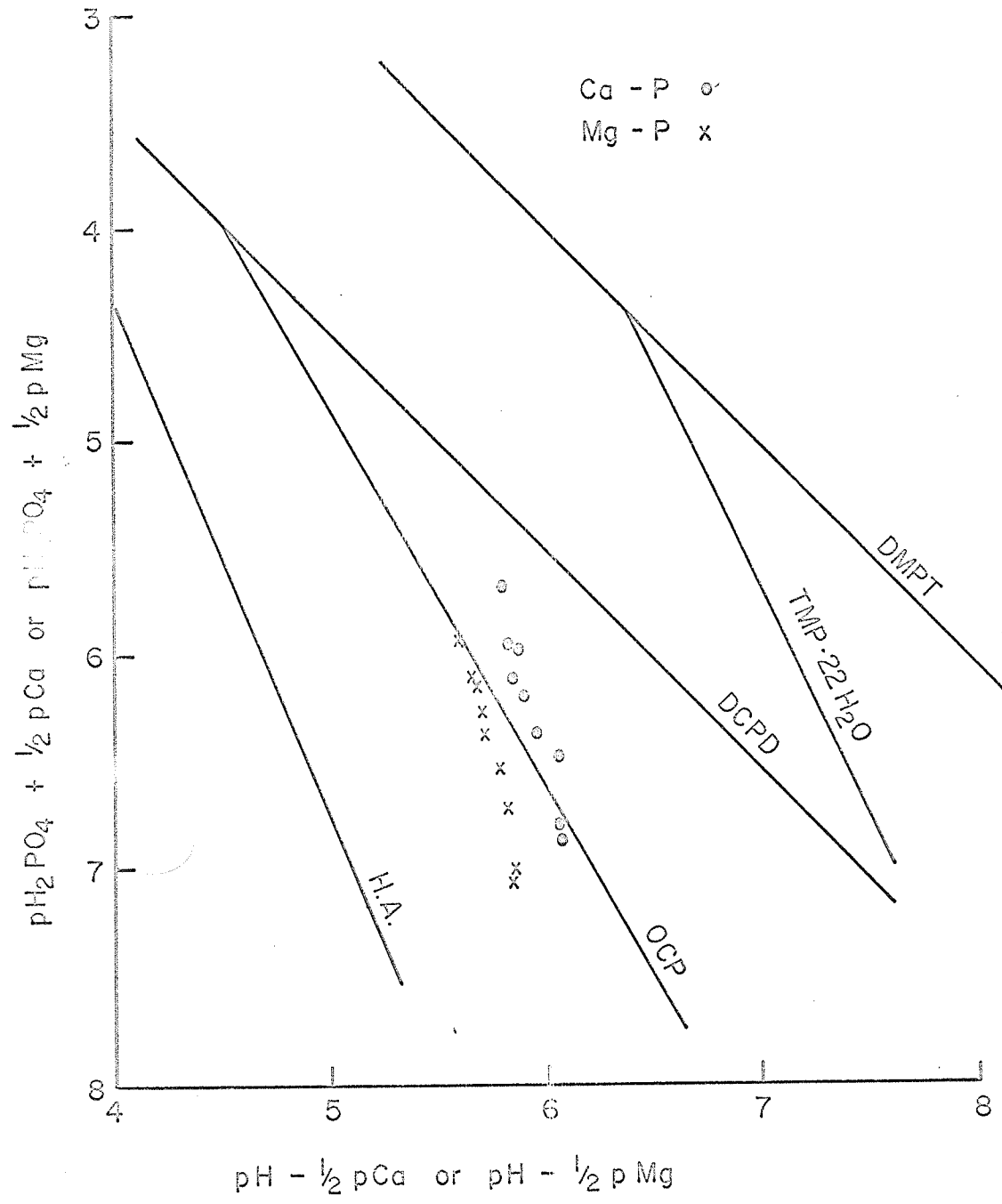


Figure 28. Solubility of residual phosphorus in Aneda soil.

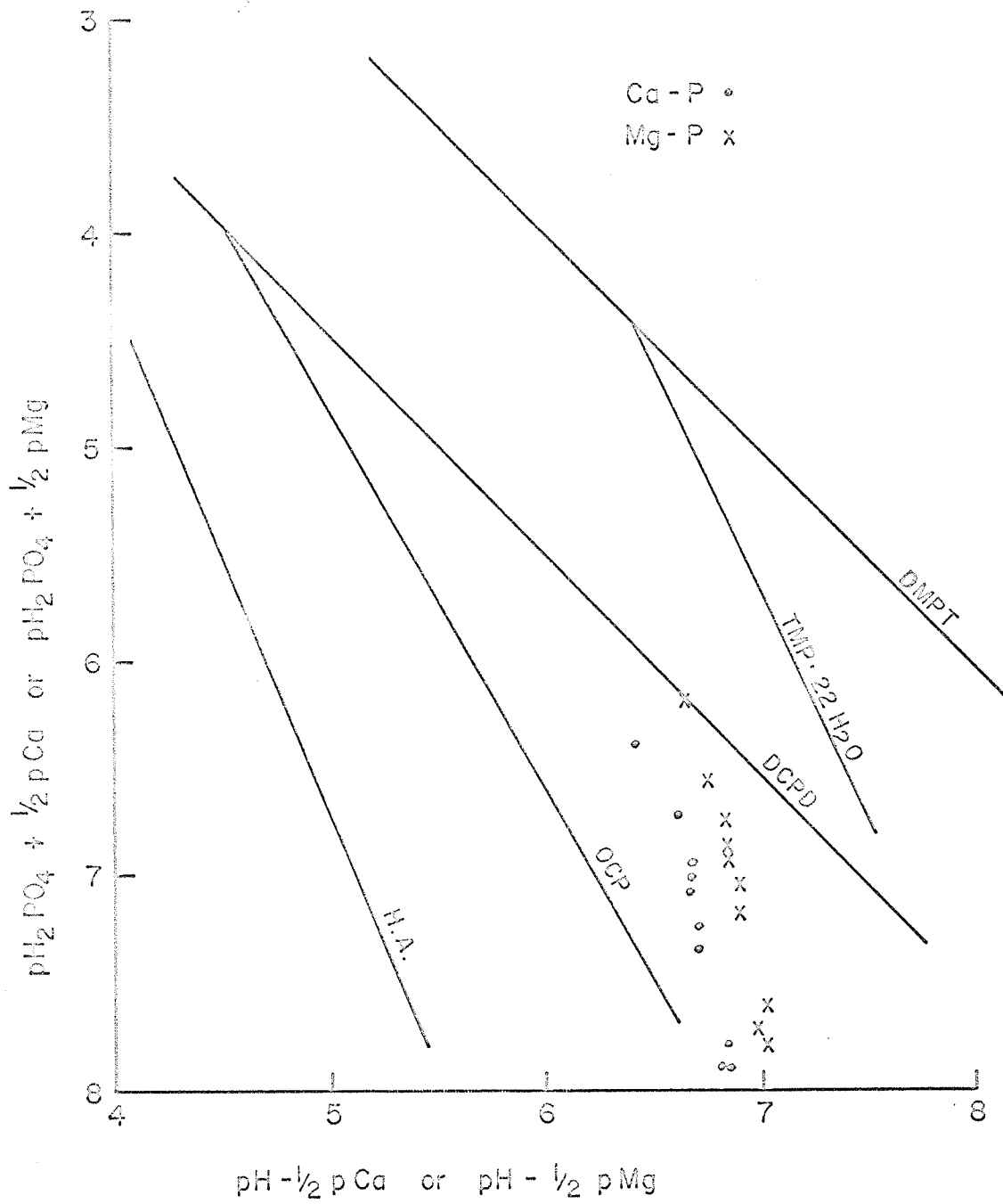


Figure 29. Solubility of residual phosphorus in Balmoral I soil.

Fractionation of Added Phosphates in Balmoral I
and Balmoral II Soils and CaCO_3 and MgCO_3

Phosphorus added to a soil is held predominantly by calcium, magnesium, iron and aluminum. The role of each cation in holding phosphate can be evaluated by using extractions specific for each form of phosphate. Jackson's (16) method of fractionating the inorganic phosphates offers a method of separating the inorganic phosphates into: (1) water soluble and loosely bound phosphorus, (2) aluminum phosphates, (3) iron phosphates and, (4) calcium phosphates. The procedure involves the extraction of the various phosphates in sequence on a one gram soil sample. First, the sample is treated with 50 ml. 1 N NH_4Cl for 1/2 hour with shaking to remove the water soluble and loosely bound phosphates. This extraction is followed by extraction of the aluminum phosphates using 50 ml. 0.5 N NH_4F at pH 8.2 for one hour. The sample is then treated with 50 ml. 0.1 N NaOH for 17 hours to obtain the phosphorus bound with iron. The calcium phosphate fraction is then obtained by treating the sample with 50 ml. 0.5 N H_2SO_4 for one hour. This extractant would also remove any phosphate bound by magnesium. The extractants used may not be completely specific for extracting their respective phosphate fractions, however, they do offer a good indication of the amount of phosphorus being held by the various cations.

An experiment was designed to determine if added phosphorus would be equally extractable from soils containing large amounts of calcium, soils containing large amounts of magnesium, CaCO_3 and MgCO_3 .

Various phosphate compounds were used so that the behaviour of several phosphates be known. One hundred ppm. of phosphorus, as KH_2PO_4 , K_2HPO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ was added to the Balmoral I and Balmoral II soils and to CaCO_3 and MgCO_3 . The soils were incubated at field capacity for one week, air dried, and ground to proper size. The pH of a 5 g. soil in 100 ml. water suspension was measured. The phosphorus present in the soils was then fractionated according to the procedure outlined by Jackson (16). The values obtained were recorded as ppm phosphorus contained in the soil.

An additional extraction, 5 g. soil in 100 ml. 0.5 M NaHCO_3 buffered at pH 8.5, was conducted (26). This extraction procedure has been developed to assess the availability of phosphorus for plant growth on alkaline or calcareous soils. It has been found to be a good method for evaluating the availability of phosphorus in Manitoba soils containing large amounts of carbonates (31).

NaHCO_3 extracted approximately 30 percent of the phosphate added to the Balmoral I soil and 37 percent of the phosphate added to the Balmoral II soil (Table XXV). The major portion of the added phosphate was extracted by NaHCO_3 from the CaCO_3 samples. Only 24 percent of the added phosphate was removed from the MgCO_3 by the NaHCO_3 extractant. The large difference in the amount of phosphorus extracted from the carbonates was probably due to the pH of the systems. The MgCO_3 had a much higher pH than did the CaCO_3 and, therefore, the solubility of the phosphate in the MgCO_3 samples would be lower than in the CaCO_3 .

Table XXV. Extraction of added phosphorus on Balmoral I and Balmoral II soils and CaCO_3 and MgCO_3 (PPM)

Soil	P. added	pH	NaHCO_3	NH_4Cl	NH_4F	NaOH	H_2SO_4	Total Fractionation
Balmoral I	None	8.30	4	6	22	11	163	202
	MKP	8.30	34	29	51	13	185	278
	DKP	8.30	34	28	48	15	186	277
	MAP	8.30	33	30	49	14	187	280
	DAP	8.30	34	30	50	15	184	280
Balmoral II	None	7.95	17	21	25	17	171	233
	MKP	7.90	53	56	31	20	192	299
	DKP	7.90	54	57	34	19	202	312
	MAP	7.85	55	56	32	19	203	310
	DAP	7.90	57	57	32	18	202	309
CaCO_3	None	8.10	0	0	0	0	0	0
	MKP	8.75	81	77	2	1	18	98
	DKP	8.55	70	76	4	0	18	99
	MAP	8.25	78	78	2	0	19	99
	DAP	8.15	80	76	2	1	18	96
MgCO_3	None	9.40	0	0	0	0	0	0
	MKP	9.50	24	49	20	0	22	92
	DKP	9.45	22	51	21	0	24	95
	MAP	9.50	24	51	20	0	23	94
	DAP	9.50	25	52	20	0	24	96

The amount of phosphate extracted by NaHCO_3 was independent of the carrier used.

NH_4Cl extracted about 25 percent of the phosphate added to the Balmoral I soil and about 36 percent of the phosphate added to the Balmoral II soil. This indicates that a large portion of the added phosphate was loosely bound or easily soluble. The NH_4Cl extractant recovered approximately 75 percent of the phosphorus added to the CaCO_3 and approximately 50 percent of the phosphorus added to the MgCO_3 .

NH_4F recovered more of the added phosphorus from the Balmoral I soil than it did from the Balmoral II soil. NH_4F , also extracted a large portion of the added phosphate from the MgCO_3 , but extracted very little from the CaCO_3 . It may be possible that NH_4F which is used to extract phosphorus bound with aluminum may also extract some of the phosphorus bound by magnesium.

A very small fraction of the added phosphate was recovered by the NaOH extractant. The amount of phosphorus extracted by NaOH from the soils was very low (10 to 20 ppm) and that extracted from the carbonates not detectable in many instances.

H_2SO_4 extracted 27 percent of the phosphorus added to the Balmoral I soil and 30 percent of the phosphorus added to the Balmoral II soil. Approximately 20 percent of the added phosphate was recovered from the carbonates by the H_2SO_4 extractant.

The calcium and magnesium phosphate fraction, extracted by H_2SO_4 , contained the largest portion of phosphorus for both soils.

Small amounts of phosphorus were found in the iron and aluminum phosphate fractions. These results show that in soils containing large amounts of calcium and/or magnesium, the phosphate is held predominantly by calcium and/or magnesium.

The amount of phosphorus recovered by the various extractants was independent of the phosphate carrier used. Approximately 75 to 78 percent of the phosphate added to the soils was recovered by the NH_4Cl , NH_4F , NaOH and H_2SO_4 extractants. Approximately 95 to 98 percent of the phosphate added to the carbonates was recovered by the various extractants.

Availability of Dicalcium Phosphate Dihydrate and
Dimagnesium Phosphate Trihydrate

Since a soluble orthophosphate acid in reaction is precipitated as DCPD or as DMPT in soils containing large amounts of dolomite, the solubility of the precipitate will markedly affect the amount of phosphorus a plant obtains from the added phosphate. In order to determine the relative availabilities of DCPD and DMPT several greenhouse experiments, using a variety of crops, were conducted.

DCPD and DMPT were prepared as described earlier in the Analytical Procedure section. The P^{32} "tagged" DCPD and DMPT, used in experiment 3, was prepared by adding P^{32} to the phosphate solutions used in the preparations. Chemical and X-ray diffraction analysis showed that both DCPD and DMPT were successfully prepared.

In the first experiment conducted, 100 mg. phosphorus as DCPD or DMPT was mixed throughout 1000 g. soil and placed into porcelain pots. An additional 24 mg. of P^{32} "tagged" phosphorus was added by pipetting 10 ml. of a KH_2PO_4 solution in a band one-half inch below the seed. The effect of the added DCPD and DMPT on the uptake of phosphorus from the band was determined by growing Acme soybeans for seven weeks and analyzing the above ground portion of the plants for total phosphorus (3, 15), radioactive phosphorus (34) and yield. Treatments included a check (no phosphorus added), 24 mg. P^{32} "tagged" phosphorus banded, 100 mg. phosphorus as DCPD mixed throughout the soil plus 24 mg. P^{32} "tagged" phosphorus banded, and 100 mg. phosphorus as DMPT mixed throughout the soil plus 24 mg. P^{32} "tagged" phosphorus banded.

The procedure followed for experiment 2 was the same as used in experiment 1. One additional treatment, 100 mg. phosphorus as monocalcium phosphate monohydrate mixed throughout the soil plus 24 mg. P^{32} "tagged" phosphorus banded, was added. Acme soybeans and Arlo rape were grown for seven weeks. There was no check treatment.

In the third experiment, 36 mg. of P^{32} "tagged" phosphorus as DCPD, DMPT or KH_2PO_4 was added to 1800 g. air dried soil placed in porcelain pots. The fertilizers were added in a band one-half inch below the seed and also mixed throughout the soil. The granular fertilizers were all ground to uniform size (<0.25 mm. but >0.10 mm.) prior to addition. Six barley plants were grown for one month, then yield, total phosphorus, and radioactive phosphorus measurements were made on the above ground portion of the plant. Three soils, two containing large amounts of carbonates and one containing small amounts of carbonates, were used in the study.

The treatments used in the experiments were replicated three times. Water was added to all pots to maintain the soils near field capacity. NH_4NO_3 was added in solution as a source of nitrogen to all pots.

All the soils used in the study were very low in $NaHCO_3$ extractable phosphorus except soil M used in experiment 3 (Table XXVI). The soils all contained large amounts of carbonates except soil D. Soils T and N contained large amounts of dilute HCl soluble and water soluble magnesium. Addition of KH_2PO_4 as a pellet to soils T and N resulted

Table XXVI. Some characteristics of surface soils used in the greenhouse

Soil	pH	Org. matter (%)	Inorg. CO ₂ (%)	NaHCO ₃ Extractable P (PPM)	Exch. K (PPM)	NH ₄ Ac displaceable (meq./100 g.)		Water soluble (meq./100 g.)		Dil. HCl soluble (%)	
						Ca	Mg	Ca	Mg	Ca	Mg
Exp. I T	8.0	3.60	16.7	3	68	13	8	0.88	1.16	6.54	3.31
Exp. II C	7.7	5.11	9.7	3	235	26	9	1.20	0.80	4.15	2.08
Exp. III	N	8.3	16.5	4	223	13	16	1.00	1.44	6.76	3.91
	M	8.1	18.49	9	295	43	14	1.70	0.80	13.52	3.16
	D	7.7	6.79	0.7	274	31	9	.93	0.36	1.24	0.39

in the formation of DCPD and DMPT. Soils C, M and D, which contained large amounts of water soluble calcium, precipitated added KH_2PO_4 as DCPD. Soils N and M were identified as Balmorals, T as Lakeland and D as Darlingford.

The yield and phosphorus content of soybeans was significantly increased by the addition of phosphate (Table XXVII). The differences in yield, percent phosphorus utilized from the band, and percent phosphorus in the tissue were not significantly different for the DCPD and DMPT treatments. Milligrams phosphorus per pot and "A" values, however, indicate that DMPT supplied more phosphorus to the plant than did DCPD. The greater availability of DMPT was also reflected in the yield and phosphorus content of the forage.

The results obtained from experiment 2 show that DCPD and DMPT were equally available to both rape and soybeans (Table XXVIII). It is interesting to note that both DCPD and DMPT supplied as much phosphorus to the plant as did MCPM.

The yield and phosphorus content of barley was significantly increased by additions of phosphate (Table XXIX).

The percent phosphorus utilized and the "A" values obtained when DCPD and DMPT were mixed throughout soil N indicate that DMPT was more available than DCPD. However, most of the measurements and calculations conducted show that DCPD and DMPT, banded or mixed into the soil, supplied about equal amounts of phosphorus to the plants grown on soil N. DCPD and DMPT, mixed throughout the soil produced greater yields and supplied larger quantities of phosphorus to the plant than

Table XXVII. Phosphorus utilization by soybeans as affected by additions of DCPD and DMPF - soil T

Treatment	Yield of forage (g.)	Uptake of P. from band (%)	Total P. in tissue (%)	Total P. per pot (mg.)	"A" value* (mg.)
Check	1.89	-	.17	3.1	-
DCPD mixed +P ³² band	3.82	7.9	.48	18.1	209
DMPF mixed +P ³² band	4.69	8.5	.53	24.8	273
P ³² band	3.01	25.7	.29	8.4	13
L.S.D. (.05P)	1.08	5.89	.09	2.01	33

* "A" value = $\frac{\text{P. in tissue from soil}}{\text{P. in tissue from fertilizer}}$ = x rate of P. added

Table XXVIII. Phosphorus utilization by rape and soybeans as affected by additions of DCPD and DMPT - soil C

<u>Treatment</u>	Yield of forage (g.)	Uptake of P. from band (%)		Total P. in tissue (%)		Total P. per pot (mg.)		"A" value (mg.)		
		<u>rape</u>	<u>soybeans</u>	<u>rape</u>	<u>soybeans</u>	<u>rape</u>	<u>soybeans</u>	<u>rape</u>	<u>soybeans</u>	
MCPM mixed +P ₃₂ band	5.97	7.62	14.3	16.1	.41	.46	24.39	34.57	147	190
DCPD mixed +P ₃₂ band	7.78	7.15	17.1	16.1	.38	.47	29.58	33.62	149	186
DMPT mixed +P ₃₂ band	6.56	6.73	14.1	16.7	.40	.52	26.23	35.07	164	186
P ₃₂ band	6.03	5.42	43.4	29.1	.21	.23	12.53	12.04	5	17
<hr/>										
L.S.D. (.05P)	1.17	1.81	5.3	3.4	.05	.08	3.43	3.91	25	26

Table XXIX. Phosphorus utilization by barley as affected by additions of DCPD and DMPT

Treatment	Yield of forage (g.)				Uptake of fertilizer P. (%)				Total P. in tissue (%)				Total P. per pot (mg.)				"A" Value (mg.)			
	soil		soil		soil		soil		soil		soil		soil		soil		soil			
	N	D	M	D	N	D	M	D	N	D	M	D	N	D	M	D	N	D		
No fertilizer	0.40	0.52	0.95	-	-	-	0.15	0.20	0.24	0.24	0.24	0.60	1.05	2.22	-	-	-	-		
DCPD band	0.82	0.97	1.74	3.63	3.15	9.18	0.23	0.23	0.28	0.28	1.88	2.23	4.92	16	35	19				
DCPD mixed	1.11	1.00	2.07	4.20	2.30	9.06	0.26	0.24	0.28	0.28	2.92	2.37	5.88	34	68	29				
DMPT band	0.97	0.83	1.97	3.85	2.75	11.47	0.26	0.22	0.29	0.29	2.03	1.85	5.71	17	30	14				
DMPT mixed	1.00	0.69	1.54	5.01	1.49	6.39	0.26	0.22	0.29	0.29	2.59	1.13	4.46	16	65	34				
MKP band	1.04	1.36	2.19	4.29	4.90	15.47	0.22	0.23	0.35	0.35	2.27	3.09	7.62	17	28	13				
MKP mixed	0.97	0.76	1.81	3.90	1.31	9.51	0.26	0.22	0.31	0.31	2.58	1.62	5.67	30	92	30				
L.S.D. P. Treat.	0.17				0.63				.02				0.46				5			
(.05P) Soils	0.11				0.45				.01				0.30				4			
P. Treat. x soils	0.28				1.06				.01				0.79				9			

did DCPD and DMPT added in a band. MKP was found to be no more available than DCPD or DMPT.

DCPD, banded or mixed into soil M, produced greater yields and supplied more phosphorus to the plant than did DMPT. MKP appeared to be the best source of phosphate when banded into the soil. DCPD was the best source of phosphate when the fertilizers were mixed into the soil. MKP and DMPT, added in a band, produced greater yields and supplied more phosphorus to the plant than did the MKP and DMPT mixed into soil M.

MKP, added in a band to soil D, supplied more phosphorus to the plant than did DCPD or DMPT added in a band. MKP and DCPD, mixed into soil D, supplied about equal amounts of phosphorus to the barley plants. DMPT, mixed into the soil was not as available as MKP or DCPD mixed into the soil. MKP and DMPT, added in a band produced greater yields and supplied more phosphorus to the plant than did the MKP or DMPT mixed into soil D.

The yields of forage obtained on soil D was significantly greater than the yields obtained on soils N or M. The yields on all soils, however, were very poor. Since the plants were grown for one month, the short growing period may explain some of the low yields. The plants grown on soils N and M showed phosphorus deficiency symptoms. It is possible that the plant roots may not have been able to utilize the very narrow band of granular phosphate added.

The soil had a marked influence on the relative availabilities of DCPD and DMPT. DMPT was found to be more available than DCPD on

soil T. DCPD and DMPT were found to be equally available on soils C and N. DCPD was found to be more available than DMPT on soil M. This may be due to the depressive effect of the high amounts of calcium contained in soil M on the solubility of DMPT. DMPT, added in a band, was more available than DCPD added in a band to soil D. DCPD, mixed into soil D, was more available than DMPT mixed into soil D. MKP was found to be the best source of phosphate when the phosphates were added in a band. MKP, mixed throughout the soil, was found to be no more available than DCPD or DMPT mixed throughout the soil.

V. CONCLUSIONS AND SUMMARY

The mechanisms by which soils hold phosphate are not clearly understood. Soil Scientists, who have studied the mechanisms by which alkaline soils hold phosphate, have considered only the role of the calcium ion in processes of phosphate fixation. The role of magnesium in phosphate retention has been completely ignored. Due to the occurrence of soils containing large amounts of magnesium in Manitoba, and the lack of knowledge on the role of magnesium in phosphate retention a study was conducted to determine the reactions of soil magnesium with phosphate added to soils.

Several studies were conducted to determine the reaction products of added orthophosphates in soils varying in calcium and magnesium content. KH_2PO_4 , added in a pellet, was precipitated as DMPT and DCPD in soils containing large amounts of magnesium and as DCPD in soils containing large amounts of calcium. In most instances both DCPD and DMPT were formed in the same soil sample. Several soils, containing large amounts of magnesium, precipitated the added KH_2PO_4 as DMPT only. Phosphorus from the added KH_2PO_4 diffused out into the surrounding soil to a distance about two cm. from the pellet. The precipitation of KH_2PO_4 as DCPD was associated with the formation of a ring one-half inch from the source of phosphate. The precipitation of KH_2PO_4 as DMPT was associated with the formation of small individual crystals around the pellet site.

Water soluble calcium and magnesium was found to be a good indicator as to the reaction products formed in the soils. It was found that if a soil had a water soluble calcium to magnesium ratio of 1.5 or less, that the formation of DMPT along with DCPD could be expected when KH_2PO_4 was added. Measuring the quantity of dilute HCl soluble and NH_4Ac displaceable calcium and magnesium in a soil did not afford a good indication as to the products that could be formed.

Addition of KH_2PO_4 , K_2HPO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ or $(\text{NH}_4)_2\text{HPO}_4$ in a pellet to a soil with a water soluble calcium to magnesium ratio of 0.70 resulted in the formation of DMPT in all instances except with the $\text{NH}_4\text{H}_2\text{PO}_4$ where DCPD was formed as well. The orthophosphates were precipitated as DCPD and DMPT in a soil with a water soluble calcium to magnesium ratio of approximately 2.0. The pH of the soil near the pellet was not altered greatly by the orthophosphate carriers used. This in part explains the formation of the same compounds regardless of the pH of the phosphate carrier used. Reaction of the soils with saturated solutions of KH_2PO_4 , K_2HPO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ resulted in the formation of relatively soluble products (DCPD and DMPT) in the acid filtrates and relatively insoluble products (OCP and T.M.P. $4\text{H}_2\text{O}$) in the alkaline filtrates.

The initial reaction products, DCPD and DMPT, were subjected to further reactions with the soil solution. DCPD and DMPT were found to dissolve incongruently leaving a residue of OCP and $\text{TMP} \cdot 22\text{H}_2\text{O}$ respectively. Although DCPD and DMPT are metastable, they would persist in soils for a long period of time, possibly years, once formed.

DCPD, DMPT, $\text{TMP} \cdot 22\text{H}_2\text{O}$ and TMP were prepared and their solubilities determined. The constant, K , derived for the equation, $(\text{pH} - \frac{1}{2}\text{pCa}) - (\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pCa})$, was found to be 0.52 for DCPD at 25.11 deg. C. The constant derived for the equation, $(\text{pH} - \frac{1}{2}\text{pMg}) - (\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pMg})$ was found to be 1.82 for DMPT. The larger value of K for DMPT as compared to the value of K for DCPD indicates that DMPT is more soluble than DCPD. The $\text{TMP} \cdot 22\text{H}_2\text{O}$ and anhydrous TMP were found to be considerably less soluble than DCPD or DMPT. The constant derived for the equation, $2(\text{pH} - \frac{1}{2}\text{pMg}) - (\text{pH}_2\text{PO}_4 + \frac{1}{2}\text{pMg})$, was found to be 8.31 for the hydrated TMP and 8.55 for the anhydrous form.

The solubility of DCPD and DMPT was determined in solutions of CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , KCl and K_2SO_4 of varying concentrations. The solubility of DCPD increased in all solutions. The solubility of DCPD increased as the ionic strength of the solution increased. DCPD was more soluble in the MgCl_2 and MgSO_4 solutions than in the CaCl_2 and CaSO_4 solutions. The increase in the solubility of DMPT with increasing ionic strength was not as marked as the increase in solubility obtained for DCPD. The solubility of DMPT increased only slightly as the ionic strength of the solution was increased. The addition of large amounts of calcium to DMPT resulted in the formation of DCPD and a reduction of phosphate in solution. The results of the study indicated that ions present in a soil solution would markedly affect the solubility of the phosphate compounds present in the soil. Therefore, it would be expected that DCPD and DMPT in a soil system would have a solubility greater than that measured for the compounds in water.

The feasibility of using .01 M CaCl_2 or .01 M MgCl_2 as an equilibration solution in solubility studies was investigated. The solubility of phosphate added to soils was changed by the addition of CaCl_2 or MgCl_2 to the equilibrating solution.

The solubility of phosphorus added as KH_2PO_4 , H_3PO_4 and K_2HPO_4 in soils varying in calcium and magnesium content was determined. All forms of added phosphate remained relatively soluble on all soils. The solubility of the added phosphate remained between that of DCPD and DMPT in most instances. The solubility of the added phosphate was greater in the soils containing large amounts of magnesium than in the soils containing large amounts of calcium. This is probably due to a larger portion of the added phosphate being precipitated as DMPT in the soils containing large amounts of magnesium.

The adsorption maximum and bonding energy for phosphate of calcium and magnesium saturated montmorillonite was determined. The magnesium saturated clay held phosphate more tightly than did the calcium saturated clay. The adsorption maximum of the calcium was higher than that of the magnesium saturated clay. These observations were not verified on the soils studied. The solubility of the added phosphate at low phosphate concentrations (below the adsorption maximum) was below that of DCPD or near that of OCP. The solubility of added phosphate was between that of DCPD and DMPT when phosphate concentrations above the adsorption maximum was used. An adsorption reaction was operative at low concentrations of added phosphorus. There was evidence

that a precipitation reaction was operative at high phosphate concentrations in the calcium saturated clay and Balmoral I soil. Removal of the added phosphate solution and washing the samples with water resulted in a lowering of phosphate solubility.

Phosphate added to Manitoba soils containing large amounts of carbonates was readily extracted by mild extractants such as NH_4Cl and NaHCO_3 . Calcium and magnesium hold the majority of the inorganic phosphate in these soils. Phosphate added as, KH_2PO_4 , K_2HPO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ was equally extractable when added to soils, CaCO_3 and MgCO_3 .

The availability of DCPD and DMPT was determined on several soils using a variety of crops. Both DCPD and DMPT supplied large quantities of phosphorus to the plants. The plants utilized phosphorus from DCPD and DMPT equally on most soils. The DCPD was a better source of phosphate than DMPT on a soil containing large amounts of calcium. In some instances, DMPT supplied more phosphorus to the plant than did DCPD. Both DCPD and DMPT were found to be slightly less effective in supplying phosphorus to the plant than did a readily soluble source such as KH_2PO_4 . It may be concluded that if a soil solution is saturated with DCPD or DMPT, enough phosphorus would be supplied to fulfill a plant's needs.

The studies reported in this manuscript certainly indicate that the role of magnesium in holding phosphate in soils of a high magnesium content is an important one. Magnesium was found to play

a significant role in holding phosphate in the soils studied. The behaviour of the magnesium phosphates, in many instances, are different than the behaviour of the calcium phosphates. Therefore, no parallelisms can be drawn between the two forms of phosphate.

Further studies, to investigate the behaviour of the magnesium phosphates in soils is advisable. It is also essential to determine the proportions of phosphorus held by calcium and magnesium. Only with continued studies will the role of magnesium in holding phosphate be clearly understood.

VI. BIBLIOGRAPHY

1. Aslyng, H.C. The lime and phosphate potentials of soils; the solubility and availability of phosphates. Royal Vet. and Agr. Col. Yearbook. Copenhagen, Den. 1 - 50, 1954.
2. Boilar, J.C. Jr. Calcium hydrogen orthophosphate -2- hydrate. Inorganic Synthesis IV: 20 - 21, 1953.
3. Barton, C.J. Photometric analysis of phosphate rock. Ind. and Eng. chem. 20: 1068 - 1073, 1948.
4. Beaton, J.D., Charlton, T.L., and Speer, R. Identification of soil - fertilizer products in a calcareous Saskatchewan soil by infra-red adsorption analysis. Nature 197: 1329 - 1330, 1963.
5. Bjerrum, N. Investigations on the solubility of calcium phosphates. Selected Papers 245 - 248. Copenhagen, Den. 1949.
6. Clark, J.S., and Peech, M. Solubility criteria for the existence of calcium and aluminum phosphates in soils. Soil Sci. Soc. Amer. Proc. 19: 171 - 174. 1955.
7. Clark, J.S. Solubility criteria for the existence of hydroxyapatite. Can. Jour. of Chem. 33: 1696 - 1700. 1955.
8. Dana, E.S. Dana's System of Mineralogy 2, 7th Ed. John Wiley and Sons. 709 - 714. 1951.
9. Dana, E.S. Dana's System of Mineralogy 2, 7th Ed. John Wiley and Sons. 753 - 754. 1951.
10. Dhar, N.R., and Sharma, D. Investigations in aluminum and other sparingly soluble phosphates, rock phosphates, and basic slags. Natl. Acad. Sci. India Proc. 25A: 519 - 521. 1956.
11. Halstead, R.L., MacLean, A.J., and Nielsen, K.F. Ca:Mg ratios in soil and the yield and composition of alfalfa. Can. J. Soil Sci. 38: 85-93. 1958.
12. Hibbard, P.L. Factors influencing phosphate fixation in soils. Soil Sci. 39: 337-358. 1935.
13. Hinman, W.C., Beaton, J.D., and Read, D.W.L. Some effects of moisture and temperature on transformation of monocalcium phosphate in soil. Can. J. Soil Sci. 42: 229-239. 1962.

14. Jackson, M.L. Soil Chemical Analysis. Prentice-Hall, Inc. Englewood Cliffs, N.J. 144-146. 1958.
15. Jackson, M.L. Soil Chemical Analysis. Prentice-Hall, Inc. Englewood Cliffs, N.J. 331-334. 1958.
16. Jackson, M.L. Soil Chemical Analysis. Prentice-Hall, Inc. Englewood Cliffs, N.J. 166-168. 1958.
17. Kolthoff, I.M., and Sandell, E.B. Textbook of Quantitative Inorganic Analysis. 3rd. Ed. The MacMillan Co. New York. 337-363. 1952.
18. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Amer. Chem. Soc. 40: 1361-1403. 1918.
19. Lehr, J.R., and Brown, W.E. Calcium phosphate fertilizers. II. A petrographic study of their alterations in soil. Soil Sci. Soc. Amer. Proc. 22: 29-32. 1958.
20. Lindsay, W.L., and Stephenson, H.F. Nature of the reactions of monocalcium phosphate in soils. Soil Sci. Soc. Amer. Proc. 23: 440-445. 1959.
21. Moreno, E.C., Lindsay, W.L., and Osborn, G. Reactions of DCPD in soils. Soil Sci. 90: 58-68. 1960.
22. Moreno, E.C., Brown, W.E., and Osborn, G. Stability of DCPD in aqueous solutions. Soil Sci. Soc. Amer. Proc. 24: 95-98. 1960.
23. Moreno, E.C., Brown, W.E., and Osborn, G. Stability of DCPD in aqueous solutions and solubility of OCP. Soil Sci. Soc. Amer. Proc. 24: 99-102. 1960.
24. Nagelschmidt, G., and Nixon, H.L. Formation of apatite from superphosphate in soils. Nature 154: 428-429. 1944.
25. Olsen, S.R., and Watanabe, F.S. A method to determine a phosphorus adsorption maximum of soils. Soil Sci. Soc. Amer. Proc. 21: 144-149. 1957.
26. Olsen, S.R., Cole, C.W., Watanabe, F.S. and Dean, L.A. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. U.S. Dept. Agr. Circ. 939. 1954.
27. Perkins, A.T. Phosphate solubility in relation to cations and pH: Magnesium. Soil Sci. Soc. Amer. Proc. 12: 185-187 1947.

28. Rennie, D.A., and McKercher, R.B. Adsorption of phosphorus by four Saskatchewan soils. *Can. J. Soil Sci.* 39: 64-75. 1959.
29. Ridley, A.O. Effect of mineral fertilizers and manures on the phosphorus content of a clay soil and on crop yields. Master's Degree Thesis submitted to the Faculty of Graduate Studies and Research, The University of Manitoba. Winnipeg. 1958.
30. Russel, E.W. *Soil Conditions and Plant Growth*. 9th Ed. Longmans. 483-487. 1961.
31. Soper, R.J., and El Bagouri, I.H.M. The effect of soil carbonate level on the availability of added and native phosphorus in some calcareous Manitoba soils. *Can. J. Soil Sci.* 44: 337-344. 1964.
32. Tucker, B.G., and Kurtz, L.T. Calcium and magnesium determinations by EDTA titration. *Soil Sci. Soc. Amer. Proc.* 25: 27-29. 1961.
33. Van Wazer, J.R. *Phosphorus and its Compounds, I*. Interscience Publishers. 517-540. 1958.
34. Veall, N. A Geiger-Muller counter for measuring beta-ray activity of liquids and its application to medical tracer experiments. *Brit. J. Radiol.* 21: 347-349. 1948.
35. Walkley, A., and Black, T.A. An examination of the Degljareff method for determining soil organic matter and a proposed modification of the chronic acid titration method. *Soil Sci.* 37: 29-38. 1934.