BEHAVIOUR OF PHOSPHATES IN SOME CALCAREOUS MANITOBA SOILS

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ABSTRACT

The form of soil phosphate present in some calcareous Manitoba soils has been studied by application of the concept of chemical potential. The lime and phosphate potentials of 10^{-2} M $CaCl_2$ extracts of these soils were determined. Evidence was obtained that meta-stable octocalcium phosphate is present in most of these soils.

The adsorption of phosphate ions by four Manitoba soils of varying calcium carbonate content showed close agreement with the Langmuir isotherm up to a final phosphorus solution concentration of 20-25 ug. P./ml. Organic matter appeared to be equally important in determining the phosphorus adsorption maximum as the percentage calcium carbonate. Dicalcium phosphate dihydrate appeared to be the initial reaction product in some of these soil-water systems, on the addition on monocalcium phosphate.

The exchange of carrier-free radioactive phosphorus with the various fractions of native soil phosphorus was investigated. It was found that the amount of exchangeable phosphorus in the respective fractions varied with the percentage of calcium carbonate. On a soil with approximately one per cent calcium carbonate only 5.6 per cent of the total exchangeable phosphorus was in the 0.5 N H_2SO_4 fraction, while in another soil containing 42 per cent calcium carbonate 56.4 per cent of the total exchangeable phosphorus was present in the above fraction.

Indirect evidence has also been presented that the iron phosphates in soils may react with active groups present in the soil humus. This interaction probably results in the formation of a complex between iron, phosphate and the organic groups.

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I. INTRODUCTION

Interpretation of phosphate behaviour in soils involves some of the most interesting and baffling problems in the domain of soil science. This is largely due to the diversity of types of compounds in which the phosphate ion occurs, and the variety of associated complexes that affect the solubility of the phosphate carrier.

According to the U.S.D.A. definition (52), a calcareous soil "is a soil containing calcium carbonate, or one alkaline in reaction because of the presence of calcium carbonate." Phosphate fertility in calcareous soils, and the reactions of phosphatic fertilizers with these soils are the object of considerable research in order to ascertain the economic levels of phosphorus fertility, and to develop a reliable chemical method for evaluating phosphorus fertility.

The phosphate chemistry of calcareous soils is mainly that of the mutually interdependent variables; pH, calcium concentration, and the concentration of $H_2PO_4^-$ and $HPO_4^=$ ions. Calcium carbonate exerts a dominant effect on the nature and reactions of phosphate in calcareous soils mainly because of: (1) its reactive surface, (2) its effect on soil pH and (3) as a source of the common ion.

As regards the forms of native soil phosphate present, and the reactions occurring where soluble phosphate fertilizers are added to calcareous soils, comparatively little is known.

The objectives of the work reported here were to determine:-

(a) the form of native soil phosphate governing the phosphate solution concentration in calcareous soils.

(b) the reactions of added phosphorus in calcareous soil systems.

(c) exchange reactions of added radio-phosphorus with the native soil phosphates.

II. LITERATURE REVIEW

Only two mechanisms by which soils hold phosphate have been shown to be of great importance, namely, those involving iron and aluminium and those involving calcium. In acid soils iron and aluminium are the dominant cations which determine phosphorus solubility and reactivity (43). The principal aluminium and iron phosphates occurring in soils are probably:- variscite--$AlPO_4.2H_2O$, strengite--$FePO_4.2H_2O$, and barrandite--a mixture of the above two in almost any proportions. In addition a ferrous phosphate, vivianite--$Fe_3(PO_4)_2.8H_2O$ has been identified in poorly drained soils (43).

In calcareous soils it is the calcium ion which is of importance in determining phosphorus solubility. The calcium ions which hold phosphate in soils may be:- (1) calcium ions on the exchange complex of clays, (2) calcium ions in the soil solution and (3) calcium ions anchored on the surface of calcium carbonate crystals. Chang and Jackson (7) have estimated that 95% of the phosphorus contained in calcareous sub-soils is in calcium forms. The figure for surface soils would naturally be somewhat lower.

Calcium phosphates exist in several forms--the most important of which (as far as soils are concerned) are:-

1. Monocalcium phosphate (MCP) -- $Ca(H_2PO_4)_2.H_2O$. This form is water soluble and is the dominant phosphate of superphosphate fertilizers.
2. Dicalcium phosphate dihydrate (DCPD) -- $CaHPO_4.2H_2O$. This form is

only slightly water soluble, unstable, and is believed to be the initial reaction product formed when phosphatic fertilizers of high water solubility are applied to soils (28). It is believed to be formed both at the site of application due to hydrolysis of MCP and in the soil immediately surrounding it (35). It has also been shown that this form persists in soils for long periods of time (35).

Lehr et al. (27) have presented petrographic evidence for the existence of this form of phosphate in soils. The authors claimed that on formation DCPD changed slowly to the more basic octocalcium phosphate, which in turn is transformed slowly to hydroxyapatite. The solubility product of DCPD has recently been carefully determined by Moreno et al. (36). They found it to be 2.77×10^{-7} at 25°C.

3. Octocalcium phosphate (OCP) -- $Ca_4H(PO_4)_3.3H_2O$. This form of calcium phosphate may be prepared by precipitation under suitable conditions. Moreno et al. (37) have prepared OCP by hydrolysis of DCPD in dilute phosphorus acid solutions and in water. They found that OCP was precipitated when the pH of the solution was higher than 6.38. The extent of hydrolysis was larger the higher the initial pH of the solution. The authors defined the solubility product constant for OCP by the expression:-

$$4pCa^{++} + 3pHPO_4^{=} - 2pH^{+} = pK_{sp}$$

in which the terms on the left are negative logarithms of ionic activities and pK_{sp} is a constant. A value of 9.93 was obtained for pK_{sp} at 25°C. Bjerrum (4) reported pK_{sp} values of 11.8 and 9.3, depending on whether equilibration was approached by dissolution or by precipitation. Moreno et al. obtained only one value for both dissolution and precipitation.

OCP is believed to exist in some soils. Lehr et al. (27) have presented petrographic evidence for its existence in soils. Aslyng (2) conducted extensive solubility studies on several calcareous Rothamsted soils and concluded that OCP was the phase governing the phosphorus solution concentration in those soils. The formation of OCP has also been reported in an acid soil fertilized with superphosphate (29).

4. Tricalcium phosphate -- $Ca_3(PO_4)_2$. There is still some doubt if this compound can be formed by precipitation from aqueous solutions.

5. Hydroxyapatite (HAP) -- $Ca_{10}(PO_4)_6(OH)_2$. J. S. Clark (9) has measured the solubility product of HAP working in CO_2 free solutions. He defined the pK_{sp} according to the following equation:-

$$pK_{sp} = 10pCa + 6pPO_4 + 2pOH$$

and reported a value of 115.5 for pK_{sp} at 25°C. He found that when HAP was formed in the presence of CO_2 no equilibrium value could be obtained. Russel (43) later interpreted this to mean that equilibrium between solid apatites in the soil and calcium and phosphate ions in solution is reached only extremely slowly, in fact, true equilibrium may never be attained. The crystals of HAP are extremely small. A consequence of this small crystal size is that precipitates of HAP are not pure, since the surface layer can vary greatly from that of pure HAP. Thus precipitates giving the HAP structure have been found to have calcium:phosphorus ratios which vary from 1.4:1 to 1.8:1; the theoretical ratio being 1.67:1 (43). Evidence has been obtained (38) that the final reaction product formed by the application of superphosphate to calcareous soils is hydroxyapatite.

There is, however, no universal agreement among soil scientists that the reaction products of soluble phosphatic fertilizers in calcareous soils are compounds of well defined crystalline structure. Thus Clark and Peech (8) concluded from their solubility studies that neither DCP nor HAP was present in the clay or soil systems studied. Hagin and Hadas (22) have concluded from solubility studies in calcareous soil systems that either (1) no calcium phosphate compounds having well defined structure are formed on contact of MCP with soils, or (2) an equilibrium between the solid phase and solution was not attained.

Lindsay and Moreno (30) studied phosphate phase equilibria in calcareous soils and concluded that equilibrium was not likely to be reached and that phosphate solubility would not correspond to any known solubility product. Eisenberger <u>et al</u> (16) suggested that the composition of the reaction product of calcium carbonate and phosphate will be largely determined by the conditions under which precipitation occurred.

The concept of a range of solid solutions containing varying proportions of calcium phosphate and carbonate is held by some workers. McGeorge and Breazeale (33) postulated that in calcareous soils, calcium phosphate existed as the very insoluble molecular carbonato-apatite--$[Ca_3(PO_4)_2]3.CaCO_3$. The authors stated that the solubility of this compound is kept at a minimum by the calcium ion activity in the soil solution and the carbonate ion concentration in equilibrium with the calcium carbonate solid phase.

Numerous investigators have reported on detailed studies of the adsorption of phosphate ions on the solid phases in soil systems. Olsen *et al.* (40) have shown that a high level of phosphorus adsorption appears to occur on carbonate particles and precipitation reactions are relatively slow. These authors also believed that calcareous materials in soils do not behave like pure calcium carbonate in their reactions with phosphate. They attributed much of this difference to the colloidal nature of the soil carbonates and to their high surface area.

Cole *et al.* (10) studied the nature of phosphate sorption by calcium carbonate and found that the reaction of soluble phosphate with calcium carbonate consisted of a rapid monolayer sorption, followed by precipitation of DCPD or a compound having similar properties. These authors also showed that phosphate adsorption data followed closely the Langmuir adsorption isotherm. Earlier investigators (13, 24) had used the Freundlich adsorption isotherm for describing phosphate adsorption. The major advantage of the Langmuir equation over the Freundlich equation is that an adsorption maximum can be calculated. This value can be related to various soil properties which will give information about the nature of the reaction between soil and phosphorus. Later Olsen and Watanabe (39) showed that the adsorption maximum calculated by the Langmuir isotherm was very closely correlated with the surface area of soils as measured by ethylene glycol retention. They also found that for a given surface area acid soils held 2.17 times as much phosphorus as alkaline soils.

Cole and Olsen (11, 12) have developed a theoretical approach for studying the behaviour of the adsorbed phosphorus in calcareous soils. They used the mean activity of DCPD to express the solubility of adsorbed phosphorus. The authors found that the calculation of this function corrects for differences in the pH values, calcium concentrations and ionic strengths which are encountered when a number of soils are studied. The authors also investigated the effect of exchangeable phosphorus and soil texture on phosphorus solubility. A direct relationship was found to exist between the per cent saturation of the phosphate adsorbing surfaces and the DCP activities of the soil extracts. Recently Thompson et al. (49) have calculated the per cent saturation of the phosphate adsorbing surfaces of several soils. They found the per cent phosphate saturation was an excellent index for predicting the yield of phosphorus in plants.

Phosphorus behaviour in soils has also been studied extensively by the use of radioactive phosphorus--P32. Thus the reactivity of native soil phosphorus and also added phosphorus can be determined by their capacity to exchange with P32. The isotopically exchangeable soil phosphate is often termed the "labile" phosphate in the soil. It is a reasonably well defined quantity, although it increases slowly with time, particularly with some soils (43). McAuliffe et al. (32) found that the readily exchangeable phosphate correlates well with the phosphate fertility of the soil and was equal to the fraction for which the distribution of P32 between soil and solution changed logarithmically with time.

Later Wiklander (55) determined the rate at which labelled phosphate adsorbed on soils exchanged with phosphate ions in solution. He stated that the exchange was governed by the law of mass action.

Gunnarsson and Fredricksson (21) showed that there was a close relationship between the labile phosphorus (as measured by P32 exchange) and the phosphate taken up by wheat crops from soils in pot and field experiments.

Experiments by Amer et al. (1) showed that for a clay soil and a silt loam, the "labile-phosphate pool", determined after McAuliffe et al. (32), is always larger than the phosphate extracted by a chloride exchange resin. The rate curves for isotopic exchange with the soil, and the extraction of phosphate from the soil had the same pattern. Talibudeen (47) has conducted extensive research on the factors influencing the estimation of exchangeable phosphorus in soils. He investigated the influence of soil:solution ratio, orthophosphate ions added with the radio-phosphate, and the equilibrium pH on the determination of isotopically exchangeable phosphorus. He found that:- (a) at larger soil:solution ratios isotopic equilibrium was attained after much longer times; (b) in water suspensions soils of low phosphate status have very low equilibrium-phosphate concentration in solution, which resulted in difficulties in chemical and radio-chemical analyses; (c) at low soil:solution ratios in aqueous suspensions, such systems are unbuffered, which caused undesirable pH changes; (d) when solutions containing large amounts of tagged phosphate are added to soils, isotopic equilibrium is reached very slowly.

In another experiment Talibudeen (48) subdivided phosphate residues in soils into three fractions based on the extent of isotopic exchange of orthophosphate ions between the soil and the soil solution. Talibudeen also observed that the total labile phosphate was a smaller fraction of the total phosphorus in the heavier soils (about 20% clay) than in the lighter soils (1-10% clay). In comparable soils, the author concluded that recent manuring with superphosphate increased the ratio of the rapidly labile phosphate to the total labile phosphate.

R. Scot-Russel et al. (45) investigated the effect of sorption on the estimation of the isotopically exchangeable phosphorus content of soils. The authors stated that if the concentration of P32 added is large enough for color determination then sorption would occur simultaneously with isotopic exchange. In order to overcome the effect of sorption on the calculation of isotopically exchangeable phosphorus, the workers shook aliquots of soil with solutions containing known quantities of P31 and P32, and observed the changes in these quantities. Isotopically exchangeable phosphorus E_t was calculated by use of the following equation:-

$$E_t = \frac{a_t}{b_t} \cdot b - a$$

where a = P31 added

a_t = P31 in solution after time t

b = P32 added

b_t = P32 in solution after time t

The authors also stated that if it could be proved that the phosphorus which was sorbed by the soil remained in isotopic equilibrium with the bathing medium, then an unequivocal measure of the exchangeable soil phosphorus could be obtained.

III. ANALYTICAL PROCEDURES

Chemical Determinations

Soil Organic Matter

The soil organic matter content was determined by oxidation of the organic carbon with excess potassium dichromate solution, followed by titration of the excess with ferrous sulfate, according to the method of Walkey and Black (53).

Soil pH

The pH of soil samples was determined electrometrically by the use of a Universal pH meter 22. A soil:water ratio of 1:1 was usually employed unless otherwise stated.

$CaCO_3$ Content

The method outlined by Ridley (42) was used. A two g. soil sample digested in a 10% HCl for 10 minutes. The carbon dioxide evolved was sucked through a drying and absorption train consisting of concentrated H_2SO_4, dehydrite and $CaCl_2$, then absorbed by ascarite. The air stream flowing through the apparatus was freed of CO_2 by bubbling it through concentrated NaOH. The weight of CO_2 absorbed was determined and expressed as per cent $CaCO_3$ equivalent.

Iron Determination

The iron content of solution was obtained colorimetrically by the formation of the ferric-thiocyanate complex. The color was developed in a solution containing a large excess of thiocyanate and which was 0.5 N with respect to hydrochloric acid. The color was measured at a wave length of 490 mμ (23).

Calcium and Magnesium Determinations

An indirect titration procedure was found to be the most reliable and simple for the determination of the calcium and magnesium contents of soil extracts (51). First the total Ca plus Mg content was obtained by titration with ethylene diamine tetraacetate (Versene), using Eriochrome Black T as indicator. On a separate aliquot Ca was precipitated with sodium tungstate. After filtration the Mg content was obtained by titration with Versene as above. Calcium was obtained by substraction.

Phosphorus Determinations

(a) Total Phosphorus Content of Soils. This was obtained by the Na_2CO_3 fusion method. Phosphorus was determined colorimetrically by the molybdophosphoric blue method of Dickman and Bray (14).

(b) Total Phosphorus in Plant Material. This was obtained by wet oxidation of the organic matter with a HNO_3-H_2SO_4-$HClO_4$ ternary acid mixture (23). The phosphorus released was determined colorimetrically by the vanado-molybdophosphoric yellow method as outlined by Jackson (23).

The inorganic soil phosphates were fractionated into the following forms according to the modified method of Chang and Jackson*.

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* Glenn, R. C., Hsu, P. H., Jackson, M. L., and R. B. Corey. Flow Sheet for soil phosphate fraction. Unpublished data, University of Wisconsin Madison, Wis. 1960.

(c) Aluminium Phosphate. This was obtained by extraction with 0.5 N NH_4F (pH 8.2) for one hour. An alkaline solution was employed because iron phosphate is not extracted in this basic medium. Phosphorus in the extract was determined by the method of Dickman and Bray (14), after removal of the fluoride ion interference through boric acid addition.

(d) Iron Phosphate. The iron phosphate content of soils was estimated by extraction with 0.1 N NaOH for 9-17 hours. The organic matter which was extracted was removed by precipitation with H_2SO_4. The colorimetric method of Truog and Meyer (50) was used for determining phosphorus.

(e) Calcium Phosphate. This was extracted with 0.5 N H_2SO_4. Phosphorus was determined according to the procedure of Truog and Meyer (50).

Radioactive Material and Techniques

The radioactive isotope used in these studies was carrier-free P32, obtained from Charles E. Frosst and Co., Montreal. The P32 was obtained as NaH_2PO_4. The isotope has a half-life of 14.3 days, and decays by β emission.

P32 was determined in all samples by placing a 1 ml. aliquot in a metal planchet. After evaporation the activity was measured by placing the planchet under the end window of a D-34 G.M. tube, connected to a Nuclear Chicago Model 161A Basic Binary Scalar. By comparison with a standard, the activity (C.P.M.) of the test samples was converted to microcuries P32.

IV. SOLUBILITY OF NATIVE SOIL PHOSPHATES

The inorganic phosphate content of agricultural soils is very low (about 0.02% phosphorus), and attempts to determine the nature of the phosphate compounds are beset with many difficulties. X-ray and optical methods cannot be used without first concentrating the phosphate fractions, and this concentration process may result in changes of phosphate form. Methods based on chemical extractions are not recommended since they do not act specifically on single phosphate compounds. In this investigation, the problem was approached through the use of solubility criteria, by relating the soil phosphate solubility to the solubilities of known pure phosphate compounds.

The solid phase calcium phosphates govern the concentration of phosphate in calcareous soils. The existence of a crystalline solid phase phosphate in soils will therefore result, at equilibrium, in a fixed relation between its component ions in solution. Thus it should be possible to prove the presence of phosphates in soils by application of solubility data.

One way of representing the solubilities of the different calcium phosphates on a single diagram is to include all the constituent ions as co-ordinates. In this diagram the solubility isotherms are represented as straight lines of varying slopes. An example for the case of hydroxyapatite (HAP) will illustrate the development of the diagram.

If one assumes that the concentration of phosphate in a soil solution is due to the solubility of HAP, one can determine the hydrogen, phosphate and calcium activities in the soil solution and test if these are consistent with the solution being saturated for apatite. The formula for HAP may be written as $Ca_5(PO_4)_3.OH$ and thus at equilibrium:-

$$a_{Ca}^{5} \times a_{PO_4}^{3} \times a_{OH} = \text{constant} \qquad (1)$$

where a represents the activities of the various ions in solution. By defining the negative logarithm of the ionic activities analogous to pH, and rearranging terms the following equation was obtained (43):-

$$7(pH - \tfrac{1}{2}pCa)-3(pH_2PO_4 + \tfrac{1}{2}pCa) = K \qquad (2)$$

The conversion from (PO_4) to (H_2PO_4) being made by use of the relationship (43):-

$$p(H_2PO_4) = \text{constant} + 2pH + p(PO_4) \qquad (3)$$

The value for the constant K in equation (2) above has been found to be 14.7 (9) at 25°C.

The first term in equation (2) viz. $(pH - \frac{1}{2}pCa)$ is known as the "lime potential", and the second term $(pH_2PO_4 + \frac{1}{2}pCa)$ is called the "phosphate potential" (43, 44). R. Schofield _et al._ (44) have shown that the term $(pH - \frac{1}{2}pCa)$ is a simple function of the chemical potential of calcium hydroxide in the soil sample, and hence have called it the "lime potential". Similarly, the term $(pH_2PO_4 + \frac{1}{2}pCa)$ is the negative logarithm of the activity of monocalcium phosphate in the solution, and is proportional to its negative thermodynamic potential (43).

Similar equations relating the lime potential to the phosphate potential have been developed for dicalcium phosphate dihydrate (DCPD) and octocalcium phosphate (OCP). For OCP the following equation has been developed (2, 37):-

$$5(pH - \tfrac{1}{2}pCa)-3(pH_2PO_4 + \tfrac{1}{2}pCa) = 9.93 \qquad (4)$$

For DCPD (43):-

$$(pH - \tfrac{1}{2}pCa)-(pH_2PO_4 + \tfrac{1}{2}pCa) = 0.66 \qquad (5)$$

For a pure calcium phosphate there is therefore a linear relation between the phosphate potential and the lime potential, the slope of which is governed by the chemical composition of the compound. Thus in order to determine the form of native soil phosphate in calcareous soils, one merely measures the lime and phosphate potentials of the soil solution and relate these graphically to the equations developed above.

Materials and Methods

Soils used in Study

Surface samples of 16 soils were selected from various areas in Manitoba. Some of the characteristics of these soils are shown in Table I. All samples were taken from a 0-6" depth, were air dried and ground to pass through a 0.5 mm. sieve. Soils Dicks, No. 10, Teulon 1, 2, and 3 have received recent applications of phosphatic fertilizers, while No. 6, McDonald, Campbell, and Winnipeg 1, 2, and 3 have never received any phosphorus fertilizer applications. The fertilizer history of Altona 1, 2, 3, 4, and Teulon 4 is unknown.

Inorganic carbon, organic matter, total phosphorus and pH

Table 1

Some characteristics of the soils used in solubility studies

Lab. No.	Soil Sample	Soil Association or Soil Series	Profile Type	Texture	pH	% $CaCO_3$	% O.M.	Total P. µg. P./g. soil
A	Dicks	Balmoral	Calcareous Rego Black	Very Fine Sandy Loam	7.5	11.5	5.3	740
B	No. 6	Red River	Orthic Meadow	Clay	6.9	0.7	5.2	762
C	No. 10	Red River	Orthic Meadow	Clay	7.0	0.8	7.3	1015
D	McDonald	Balmoral	Calcareous Meadow	Silty Clay	7.8	42.0	5.3	670
E	Campbell	Balmoral	Calcareous Meadow	Clay Loam	7.7	26.8	16.8	925
F	Altona I	Gnadenthal	Rego Black	Silty Clay Loam	7.3	0.6	7.9	774
G	Altona II	Gnadenthal	Rego Black	Silty Loam	7.7	0.5	4.7	677
H	Altona III	Gnadenthal	Rego Black	Silty Loam	7.9	9.2	2.9	708
I	Altona IV	Gnadenthal	Rego Black	Silty Loam	7.9	10.2	3.8	777
J	Winnipeg I	Lakeland	Calcareous Gleyed Black	Clay Loam	7.5	2.0	9.8	763
K	Winnipeg II	Lakeland	Calcareous Gleyed Black	Loam	7.8	14.6	9.6	915
L	Winnipeg III	Lakeland	Calcareous Gleyed Black	Loam	7.8	33.1	7.7	686
M	Teulon I	Lakeland	Calcareous Gleyed Black	Loam	7.9	24.3	4.4	494
N	Teulon II	Lakeland	Calcareous Gleyed Black	Loam	7.8	27.9	6.2	641
O	Teulon III	Lakeland	Calcareous Gleyed Black	Loam	8.0	29.3	4.9	528
P	Teulon IV	Isafold	Calcareous Rego Black	Clay Loam	6.6	2.0	12.7	935

determinations were carried out according to the procedures outlined on page 12.

Experimental Procedures

A preliminary experiment was conducted in order to investigate the following: (1) the effect of the liquid:soil ratio on the phosphate concentration of the extract and (2) the feasability of using 0.01 M $CaCl_2$ as the extractant in these solubility studies.

Various amounts of six soils were shaken in 50 ml. of 0.01 M $CaCl_2$ solution for twelve hours. The weights of soils used were 5, 10, 15, 20, and 40 g. respectively. The pH of the suspensions were determined, followed by centrifugation at 1000 rpm for 5 minutes. The calcium concentration of the supernatant was determined according to the procedure given on page 13. Phosphorus analyses were made according to the method of Dickman and Bray (14). The preliminary investigations led to a standardized procedure for all soil samples. Ten and 20 g. of each soil sample were shaken with 50 ml. 0.01 M $CaCl_2$ in centrifuge tubes for a period of 12 hours. The pH, phosphate and calcium concentrations were determined as above. The lime and phosphate potentials were calculated as described under Results and Discussion. The temperature of the equilibrating solutions varied from 24.5 to 25.3°C.

Results and Discussion

In calcareous soils the dominant cations present on the exchange complex are calcium and to a lesser extent magnesium. Calcium analysis of the $CaCl_2$ extracts of the six soils used in the preliminary investigations gave concentrations ranging from 0.92 to 1.08 x 10^{-2} M. In other words the concentration of the original $CaCl_2$ solution changed by ± 8%. Calculations in Table 2, however, show that the changes in the value of $\frac{1}{2}$pCa are much less.

Table 2

Calculation of $\frac{1}{2}$pCa for 0.01 M $CaCl_2$ extracts

Ca Concentration (x 10^2)	Ionic Strength (μ)	Activity Coefficient of Ca^{++} (γ)	a Ca^{++} x 10^3	$\frac{1}{2}$pCa
1.08	0.0324	0.535	5.78	1.119
1.00	0.030	0.545	5.45	1.132
0.92	0.0276	0.552	5.07	1.147

In the above calculations the ionic strength (μ) was calculated from the concentration of $CaCl_2$ used. The ionic strengths were calculated according to the procedure given by Glasstone (18). The contribution from other ions which occurs in the solutions e.g. $H_2PO_4^-$, K^+, Mg^{++}, was disregarded, as the concentrations are so small that they do not make any significant difference. Values for the activity coefficients of the calcium ion at different ionic strengths were obtained from data given by Cole and Olsen (11). These authors obtained values for the single ion activity coefficients of calcium ion at varying ionic strengths from values of the mean activity coefficients of KCl and $CaCl_2$. They assumed that $\gamma Cl^- = \gamma K^+ = \gamma_{\pm}$ KCl and substituted values of γCl^- into the corresponding values of $\gamma^{\pm}$ $CaCl_2$ in order to obtain γCa^{++}. Concentrations were thus converted to activities (a) by use of the proper single ion activity coefficient, through the relationship $m = \frac{a}{\gamma}$. These calculations are only approximate since the mean activity coefficients were determined in single electrolyte solutions and thus some loss of precision is introducted by their application to solutions of mixed electrolytes.

It is seen from Table 2 that the differences in the value of $\frac{1}{2}$pCa are small (± 1.4%), and considering the accuracy at which soil analyses can be carried out, it is quite justifiable (and practical) to assume a value of 1.13 for $\frac{1}{2}$pCa. This is the value which will be used in subsequent calculations of the lime and phosphate potentials of soil extracts. This value is slightly lower than that originally used by Aslyng (2), who found $\frac{1}{2}$pCa to be 1.17 in 0.01 M $CaCl_2$. The difference arises from the values used for the activity coefficient of the calcium ion. Some advantages to the use of 0.01 M $CaCl_2$ as extractant are:-

(1) The $CaCl_2$ solution is weak enough to justify the use of activity coefficients,

(2) The soil is well flocculated in this concentration of $CaCl_2$, thereby facilitating measurements of pH, phosphate and calcium concentrations,

(3) the calcium concentration of soil solutions displaced from calcareous soils has been found to vary from about 5×10^{-3} to

slightly more than 10^{-2} M (6).

(4) the phosphorus concentrations obtained are close to the concentration in the soil liquid in the field.

(5) this electrolyte concentration is such that measurements made with the usual glass electrode/saturated calomel cell give reproducible values.

The effect of varying the solution:soil ratio on the phosphate concentration of the extracts is shown in Table 3 and Figure 1. In Table 3 it is seen that the higher the liquid:soil ratio the lower was the phosphate concentration of the extract. In Figure 1 the reciprocal of the amount of soil used has been plotted against the molar concentration of phosphate. It is seen that the points fall approximately on a straight line for the six soils used, except for the 2 soils having a high phosphate concentration. By extrapolating the lines to the ordinate axis ("zero dilution") the dilution effect was avoided.

The standard procedure adopted for determining the phosphate and lime potential employed only two quantities of soils viz. 10 and 20 g. per 50 ml. $CaCl_2$ solution. By using these soil quantities in a 1:2 ratio the above extrapolation is simply achieved by adding the difference in phosphate concentrations to the concentration obtained for the larger quantity (20 g.) of soil. The "corrected" phosphate concentrations thus obtained were used for the calculation of $p(H_2PO_4)$.

Calculation of $p(H_2PO_4^-)$

Since most soil solutions have pH values between about 4.0 and 8.3 it is quite justifiable to assume that only $(H_2PO_4^-)$ and $(HPO_4^=)$ ions

Table 3

pH and phosphate concentrations when different amounts of soils were shaken with 50 ml. of 10^{-2} M $CaCl_2$

G. Soil	pH	P. m./l. x 10^6	G. Soil	pH	P. m./l. x 10^6
A. Dicks Soil			D. McDonald Soil		
5	7.52	3.85	5	7.86	0.50
10	7.53	4.08	10	7.84	0.80
15	7.49	4.30	15	7.83	0.85
20	7.49	4.30	20	7.82	0.85
40	7.47	4.43	40	7.83	1.00
B. No. 6 Soil			E. Campbell Soil		
5	7.05	4.05	5	7.79	0.93
10	7.11	4.67	10	7.75	1.20
15	7.03	4.81	15	7.82	1.35
20	7.05	5.00	20	7.71	1.35
40	7.07	5.19	40	7.78	1.48
C. No. 10 Soil			F. Altona I Soil		
5	7.09	8.02	5	7.21	9.60
10	7.07	10.40	10	7.24	12.40
15	7.11	10.95	15	7.17	13.10
20	7.08	11.22	20	7.14	13.45
40	7.04	11.40	40	7.11	14.00

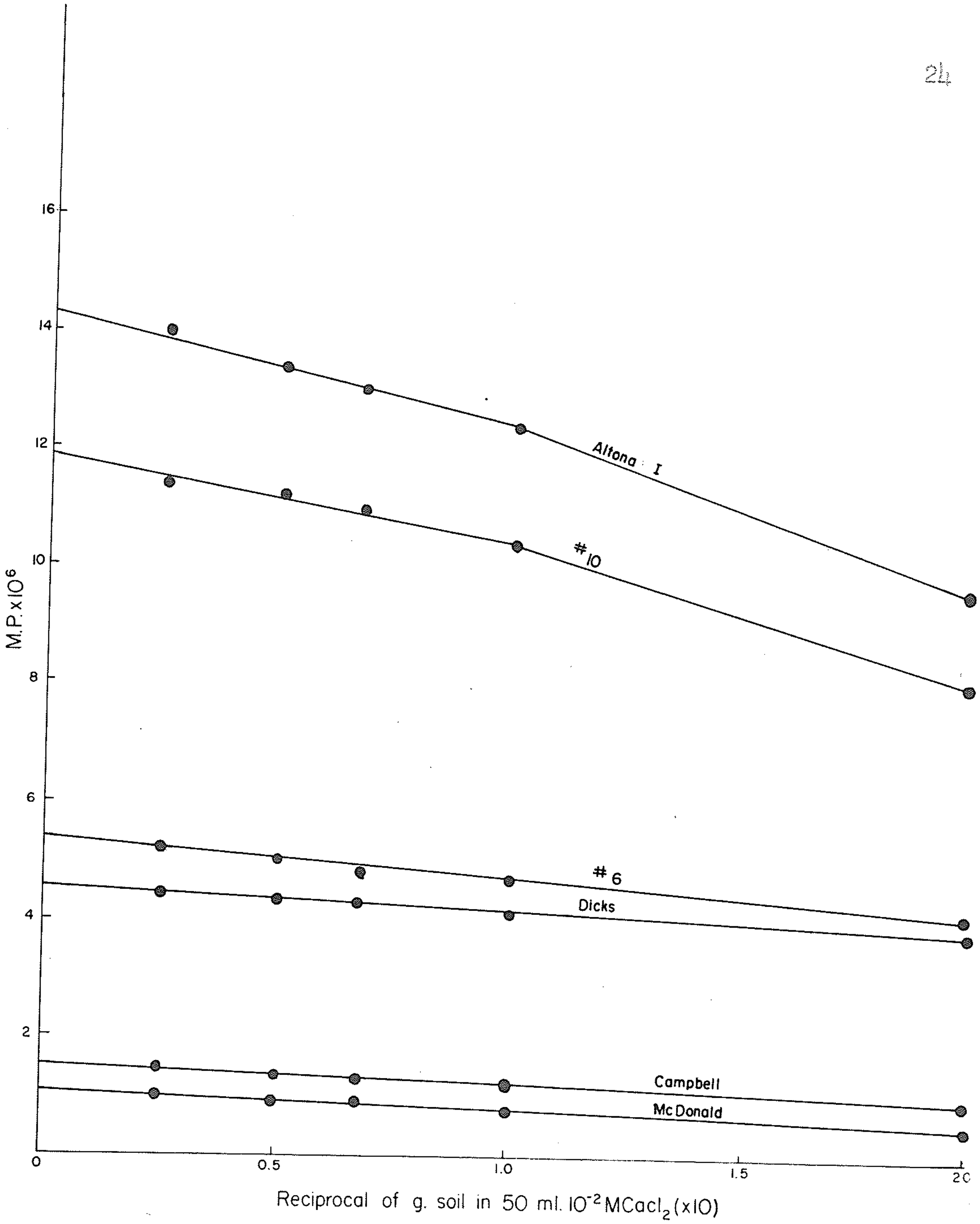

Figure I. The effect of varying the solution:soil ratio on the phosphate concentration of the extracts.

are present. Thus we may write:-

$$P = (H_2PO_4^-) + (HPO_4^=) \qquad (6)$$

By using Debye and Huckel's (18) approximation for the activity coefficients of ions Aslyng (2) was able to show that the apparent second dissociation constant of phosphoric acid is:-

$$pK_2 = 7.22 - 1.5\sqrt{\mu} + 1.05\,\mu \text{ at } 20°C \qquad (7)$$

where μ = ionic strength.

Thus for a 10^{-2} M $CaCl_2$ solution:-

$$pK_2 = 7.22 - (1.5 \times 0.173) + (1.05 \times 0.03) \qquad (8)$$

whence $pK_2 = 6.99$.

As there is some uncertainty in the calculation of activities in soil extracts it is quite sufficient to use a value of 7.00 for pK_2 for 10^{-2} $CaCl_2$ extracts.

By using values for the activity coefficient of the $H_2PO_4^-$ and $HPO_4^=$ ions (11), at an ionic strength of 0.03, and the value for pK_2 calculated above, the activity of the $H_2PO_4^-$ ion was obtained through combination of equation (6) above with the following expression:-

$$\frac{a(H_2PO_4)}{a(HPO_4)} = \frac{a(H)}{K_2} \qquad (9)$$

The term pH_2PO_4 was then calculated from aH_2PO_4 as described on page 16.

Table 4 shows the lime and phosphate potentials of the 16 soils used. The value of $\frac{1}{2}pCa$ was taken as 1.13 for all soil extracts. It is seen that the highest lime potentials found for the soils are about 6.6-6.7. This is about the maximum possible for calcareous soils. If a $CaCO_3$ suspension has a CO_2 pressure equal to that of atmospheric air

Table 4

Calculation of lime and phosphate potentials of soil extracts

Soil		pH	P. m./l. x 10^6	$p(H_2PO_4)$	$\frac{1}{2}pCa + p(H_2PO_4)$	$pH - \frac{1}{2}pCa$
Lab. No.	Sample					
A	Dicks	7.47	4.51	6.19	7.32	6.34
B	No. 6	7.08	5.30	5.83	6.96	5.95
C	No. 10	7.04	11.80	5.46	6.59	5.91
D	McDonald	7.83	1.02	7.15	8.28	6.70
E	Campbell	7.78	1.54	6.92	8.05	6.65
F	Altona I	7.11	14.30	5.42	6.55	5.98
G	Altona II	7.39	3.55	6.24	7.37	6.26
H	Altona III	7.45	1.93	6.55	7.68	6.32
I	Altona IV	7.50	2.25	6.52	7.65	6.37
J	Winnipeg I	7.38	3.54	6.23	7.36	6.25
K	Winnipeg II	7.18	6.12	5.84	6.97	6.05
L	Winnipeg III	7.73	1.29	6.97	8.10	6.60
M	Teulon I	7.55	6.40	6.11	7.24	6.42
N	Teulon II	7.63	4.11	6.37	7.50	6.50
O	Teulon III	7.47	4.18	6.22	7.35	6.34
P	Teulon IV	6.60	6.09	5.51	6.64	5.47

the calcium concentration is about 0.8×10^{-3} M (2). The value of $\frac{1}{2}$pCa will therefore be nearly 1.6 and using the value for $\frac{1}{2}pCO_2$ of 1.7, it has been shown that the pH of the suspension is given by the expression (2):-

$$pH = 5.0 + 1.6 + 1.7 = 8.3 \qquad (10)$$

Thus the lime potential: $(pH - \frac{1}{2}pCa) = 6.7$. Since the CO_2 pressure is usually higher in soils than in atmospheric air, the calcium concentration will be higher and therefore the lime potential for soils will be lower than 6.7.

The plot of lime potential against phosphate potential is graphically shown in Figure 2. The lines for HAP, OCP and DCPD were obtained as described on pages 16 and 17. It appears that the phosphate present in these calcareous soils is more soluble than HAP but less soluble than DCPD, and could well approach OCP. More careful study of Figure 2 reveals that some points are nearer to the solubility line for OCP than others. Thus the points for soils B, D, E, G, H, I, J, K and L are well below the solubility line for OCP. As was stated on page 17 soils B, D, E, J, K and L (which correspond to No. 6, McDonald, Campbell, Winnipeg I, II, and III) have never received any additions of phosphate fertilizer. Although the fertilizer history of soils G, H, and I is unknown, it would appear that these soils are also unfertilized with respect to phosphorus. Figure 2 further reveals that those soils which have received recent additions of phosphate fertilizer viz. A, C, M, N, and O (Dicks, No. 10, and Teulon I, II and III) have phosphate solubilities either close to or somewhat above that for OCP.

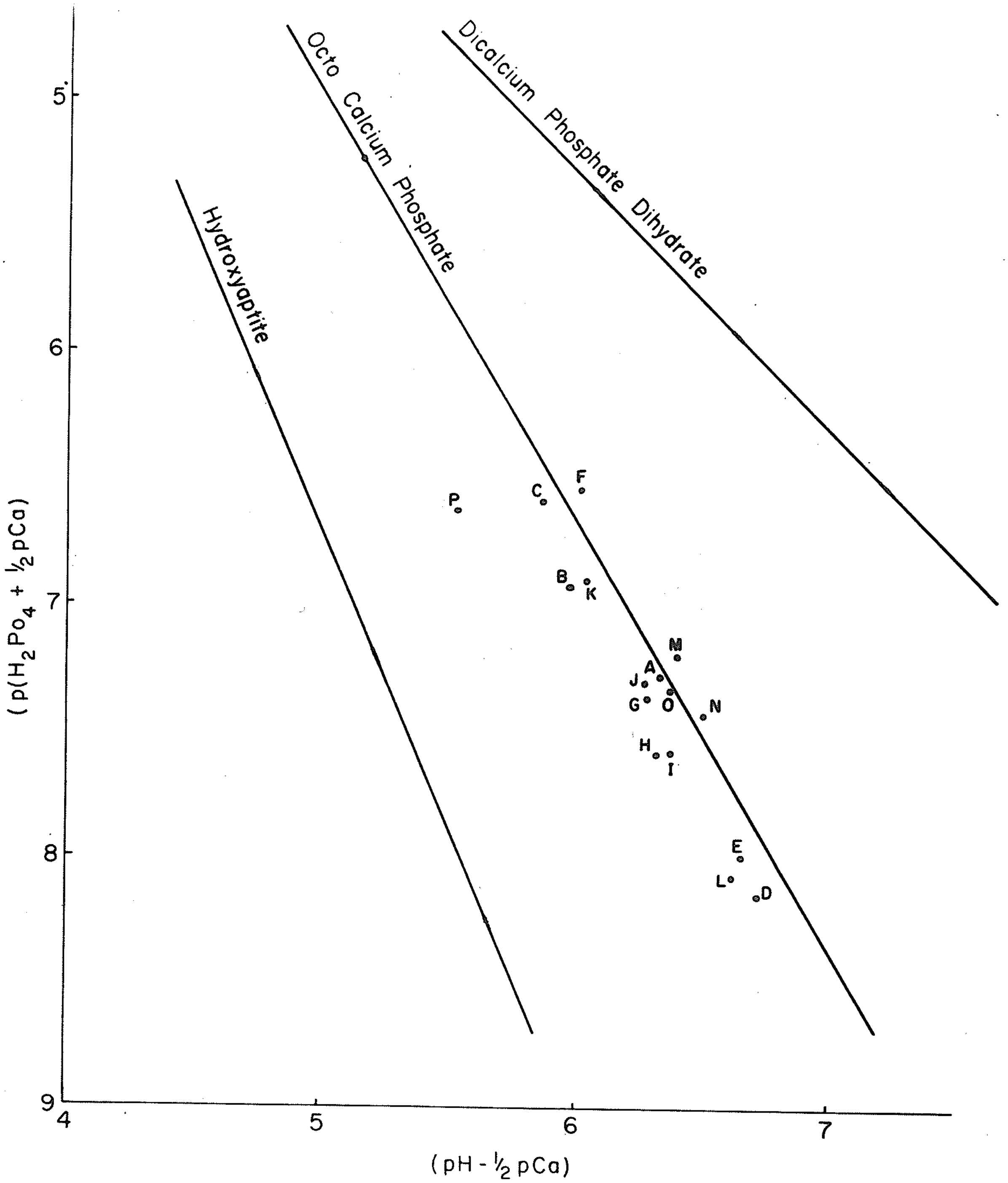

Figure 2. Solubility diagram for the calcium phosphates

Soils No. 6 (B), and No. 10 (C) provide a good illustration of the effect of fertilizer additions on phosphate and lime potentials. Soil No. 6 represents a check soil (no fertilizer) while No. 10 has received fertilizer additions for over forty years. It is seen in Figure 2 that the lime potentials of both soils are quite close (5.95 and 5.91), but the phosphate potential of No. 6 is 6.96 while No. 10 is 6.59.

The results of these solubility studies also correlate quite closely with greenhouse studies on these soils (17). Thus it was found that soils A, F, M, N, and O gave poor response to phosphate fertilizers when oats were grown, whereas soils E, G, H, I, J, K, and L gave good response to phosphate fertilizers.

Summary and Conclusions

The concept of chemical potential has been applied in studying the form of soil phosphates present in calcareous surface soils. A 10^{-2} $CaCl_2$ solution was used for soil analyses. By so doing $\frac{1}{2}$pCa can be assumed to be constant for all soil extracts. The phosphorus concentration of the extract is quite close to the actual concentrations in the soil solution in the field. The procedure adopted was independent of the solution:soil ratio. The lime and phosphate potentials of the soils were determined and compared with the solubility of the various calcium phosphates which may occur in soils.

Generally for all the soils studies the soil phosphates were more soluble than hydroxyapatite, but less soluble than dicalcium phosphate. Evidence has been obtained for the existence of octocalcium phosphate in unfertilized and fertilized calcareous soils. The conclusion reached is that octocalcium phosphate is most likely an important intermediate phosphate reaction product in calcareous soils. It is believed that the precipitation and dissolution of this compound can occur much more readily than that of the more insoluble hydroxyapatite.

An important and a very practical conclusion can be drawn from these solubility studies. It appears that these calcareous soils can be divided quite broadly into fertility classes by the OCP solubility isotherm. In addition it seems that one can predict whether soils will respond to phosphate fertilizers or not by use of these solubility studies.

The present study was centered on the dissolution and precipitation of inorganic phosphate compounds in soils. By so doing, it was not intended to minimize the role of adsorbed or organic forms of phosphorus, which undoubtedly are of great importance in determining the behaviour of phosphorus in soils. A study of phosphate adsorption by some calcareous soils is presented in the following section.

V. NATURE OF PHOSPHATE FIXATION IN SOME CALCAREOUS SOILS

Phosphate ions added to soils can become adsorbed on the surface of soil colloids. In addition, soluble phosphates added to soils may be converted into less soluble forms. In calcareous soils, phosphates may be converted into any one of the less soluble calcium phosphates.

Phosphorus adsorption data in soils can be described by the Langmuir adsorption isotherm (25). An adsorption isotherm may be defined as the relation between the amount of a substance adsorbed by an adsorbant, and the equilibrium concentration of the substance at constant temperature. The Langmuir adsorption equation is specific for small quantities of adsorbed phosphorus and dilute equilibrium phosphorus concentrations (more likely to be met in normal phosphate fertilizer applications). In addition, an adsorption maximum can be readily calculated when using this equation (39).

The langmuir adsorption equation was originally developed to describe gas adsorption on solids. Although the same rigorous, theoretical basis is not as fully developed, the same equation has been used successfully for the adsorption of liquids and ions from solutions by solids. As applied to liquids or ions, the following equation is used in this study (39):-

$$\frac{x}{m} = \frac{k\ b\ c}{1 + kc} \qquad (1)$$

where $\frac{x}{m}$ = ug. P. adsorbed/g. soil b = adsorption maximum

k = constant related to the bonding energy of the adsorbent for phosphorus

c = equilibrium P. concentration in ug. P./ml.

In linear form equation (1) becomes:-

$$\frac{c}{x/m} = \frac{1}{k\,b} + \frac{c}{b} \qquad (2)$$

A straight line plot of $\frac{c}{x/m}$ versus c will therefore indicate an adsorption reaction. When such a reaction occurs, it can be assumed that a unimolecular adsorbed layer is present on the soil adsorbing surfaces.

The following experiments reported in this section were designed to provide some information on the following:-

(i) the nature and reactions of phosphorus adsorbed on soil surfaces,

(ii) the effect of calcium carbonate on the adsorption of phosphorus by soils,

(iii) the crystal species initially formed on addition of water soluble phosphates to calcareous soils, and the stability of this crystal species.

Materials and Methods

Soils Used in Study

The four soils used in this investigation were Dicks, McDonald, No. 6 and No. 10. Some characteristics of these soils were given in Table 1 on page 18.

Experimental Procedure

(i) Adsorption of Phosphorus

The amount of surface phosphorus initially present in the soils was determined by shaking 0.5 g. aliquots of the soils in 50 ml. distilled water containing 5 microcuries P32 for 120 hours. A soil solution ratio of 1:100 was chosen as it was found (page 56) that working at this soil:solution ratio, isotopic equilibrium was virtually attained in 120 hours.

The suspensions were centrifuged and aliquots of the centrifugate removed for P31 and P32 analyses. The activity measurements were conducted as described on page 14. The amount of surface phosphorus, (i.e. isotopically exchangeable phosphorus) was calculated from the isotope-dilution law at isotopic equilibrium:-

$$P31_{(surface)} = \frac{P32(surface)}{P32_{(solution)}} \times P31_{(solution)}$$

P31 analyses were made according to the method of Dickman and Bray (14).

Data for plotting the Langmuir isotherms were obtained by using a precedure similar to that of Rennie and McKercher (41). Five grams of each soil were shaken in 50 milliliters of KH_2PO_4 solution of concentrations ranging from 10 to 200 micrograms P./milliliter. The suspensions were shaken for 6 hours, centrifuged at 2000 rpm for 10 minutes, and the amount of phosphorus remaining in solution determined in order to obtain the amounts adsorbed by the soils. Analysis for phosphorus was made by the colorimetric method of Dickman and Bray (14).

The temperature of the soil suspensions varied from 23.5 to 24.0°C.

A 6-hour shaking time was used, although earlier preliminary investigations indicated that a 1-hour shaking was sufficient for completion of the initial adsorption reaction. This was due to the difficulty in obtaining reproducible results at shorter periods of contact between soil and the phosphorus solutions.

(ii) Exchangeability of Adsorbed Phosphorus

In order to determine how much of the adsorbed phosphorus was exchangeable in 96 hours, 5 microcuries of P32 were added to each of the equilibrium solutions obtained on shaking 5 g. soil in the various phosphate solutions. After equilibrating for 96 hours, the suspensions were centrifuged and P31 and P32 analyses carried out as above.

(iii) Equilibration of Soils with MCP

Three 10 g. samples of Dicks, McDonald, and No. 6 soils were each thoroughly mixed with one gram of analytical reagent grade monocalcium phosphate (MCP) and equilibrated with 100 ml. distilled water in 250 ml. centrifuge tubes. The suspensions were centrifuged at the end of 6 hours, 3 days and 1 week respectively. The calcium, magnesium and phosphorus concentrations were determined as described on page 13 The pH values of the centrifugates were also determined. The temperature of the equilibrating solutions varied from 24.5 to 25.7°C.

Results and Discussion

(i) Adsorbed Phosphorus

Ideally, the adsorption should be determined in a system in which the surface is free of the absorbate ion. Since it is not feasible to obtain soils free of adsorbed phosphorus, the amount of surface phosphorus initially present on the four soils was determined. These values are given in Table 5. These amounts were added to the quantities adsorbed from the solutions in order to obtain the true values of adsorbed phosphorus.

The procedure used for estimating surface phosphorus is somewhat different from that used by Rennie and McKercher (41). These authors determined surface exchangeable phosphorus by shaking 50 g. soil in 50 ml. water containing 2 μc. P32, for 24 hours. It is doubtful if isotopic equilibrium is attained in 24 hours when a soil:solution ratio of 1:1 is used. This might account for the very low values for surface exchangeable phosphorus reported by these workers.

Table 5

Initial surface exchangeable phosphorus of soils used in adsorption studies

Soil	Surface P. μg. P./g. soil
No. 6	91.3
No. 10	159.0
Dicks	32.5
McDonald	39.7

The adsorption isotherms obtained for the four soils are shown in Figure 3. The soils can be arranged in the following order of increasing adsorption of phosphorus--Dicks, McDonald, No. 6 and No. 10. The adsorption data (Table 6), plotted according to the Langmuir equation are illustrated in Figure 4. As pointed out above correction for the initial surface phosphorus has been made. Justification for this correction is derived from the fact that the surface phosphorus is related to the equilibrium phosphorus concentration according to equation (1). Figure 4 shows that phosphorus adsorption by all four soils follows the Langmuir equation up to a concentration of about 20-25 µg. P./ml. remaining in solution. Figure 4 further reveals that a second adsorption isotherm can be drawn through the points obtained at higher final solution concentration. Thus a second reaction, which obeys the Langmuir equation, is operative at higher final solution concentrations. This secondary reaction could be a true adsorption or a precipitation reaction.

The calculated values of the adsorption maxima are also shown in Figure 4. These values were determined by use of equation (2) given on page 32. It is seen that No. 6 and No. 10 soils (containing 0.7 and 0.8 per cent $CaCO_3$ respectively) have higher adsorption maxima than Dicks and McDonald soils (11.5 and 42.0 per cent $CaCO_3$ respectively). This perhaps can be attributed to the fact that No. 6 and No. 10 soils have a higher percentage of clay than the other two soils. It is also apparent that an increase in the organic matter content of No. 6 soil

Table 6

Adsorption of phosphorus by soils

P. added µg. P./g. soil	No. 6		No. 10		Dicks		McDonald	
	P. in soln. µg. P./ml.	P. ads. µg. P./g. soil	P. in soln. µg. P./ml.	P. ads. µg. P./g. soil	P. in soln. µg. P./ml.	P. ads. µg. P./g. soil	P. in soln. µg. P./ml.	P. ads. µg. P./g. soil
100	3.75	62.5	4.17	58.3	4.30	57.0	3.14	68.6
150	5.90	91.0	6.80	82.0	7.59	74.1	5.20	98.0
200	8.35	116.5	9.23	107.7	10.64	93.6	7.10	129.0
250	10.50	145.0	11.87	131.3	14.07	109.3	9.83	151.7
300	13.20	168.0	14.90	151.0	17.50	125.0	12.70	173.0
400	19.00	210.0	21.70	183.0	24.00	160.0	20.00	200.0
500	28.00	220.0	28.00	220.0	---	---	---	---
600	---	---	33.98	260.2	37.43	225.7	32.45	275.5
800	49.99	301.0	50.90	291.0	54.00	260.0	43.00	370.0
1000	63.94	360.6	65.56	344.4	71.96	280.4	60.92	391.8

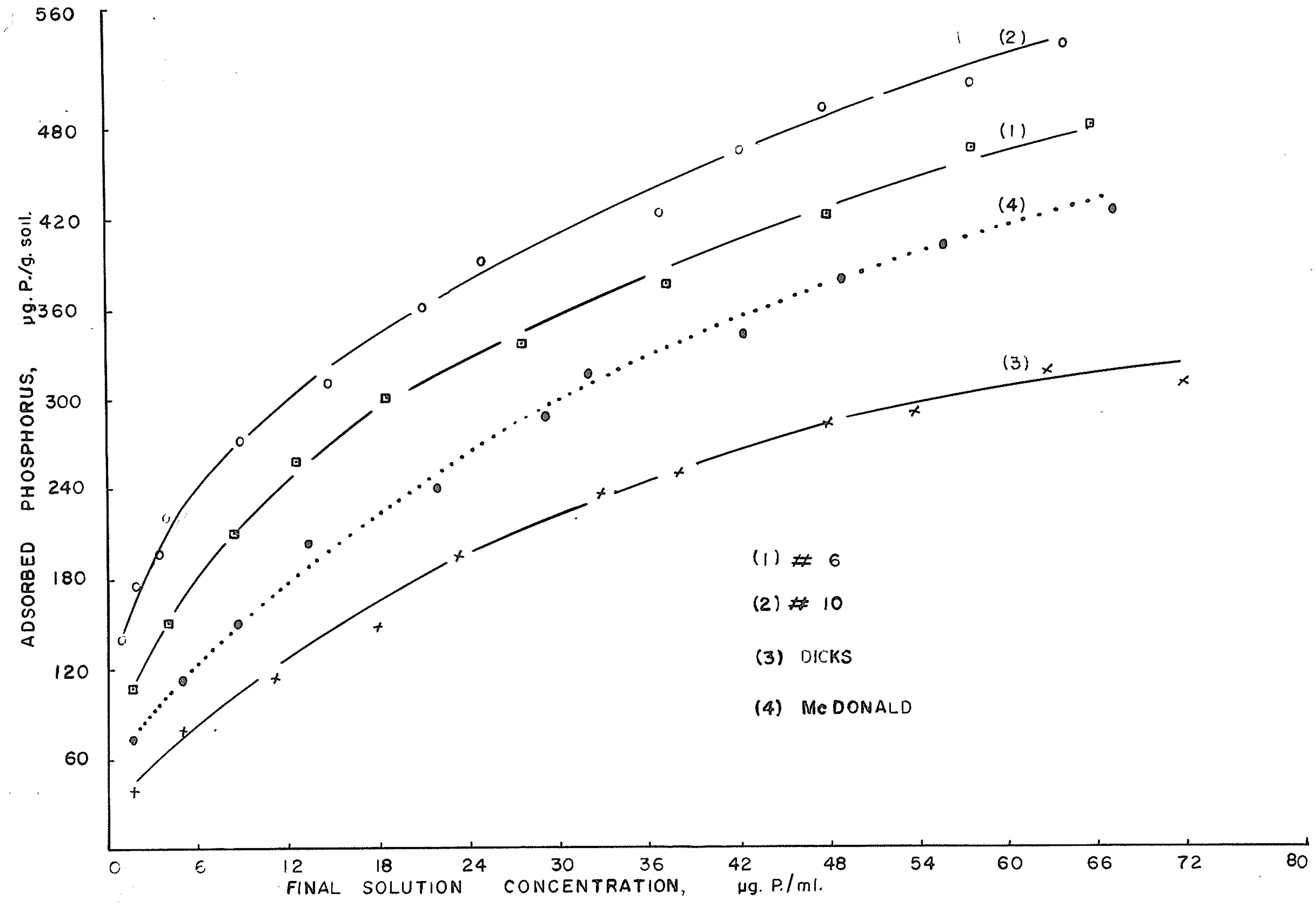

Figure 3. Phosphorus adsorption isotherms for the soils used in adsorption studies

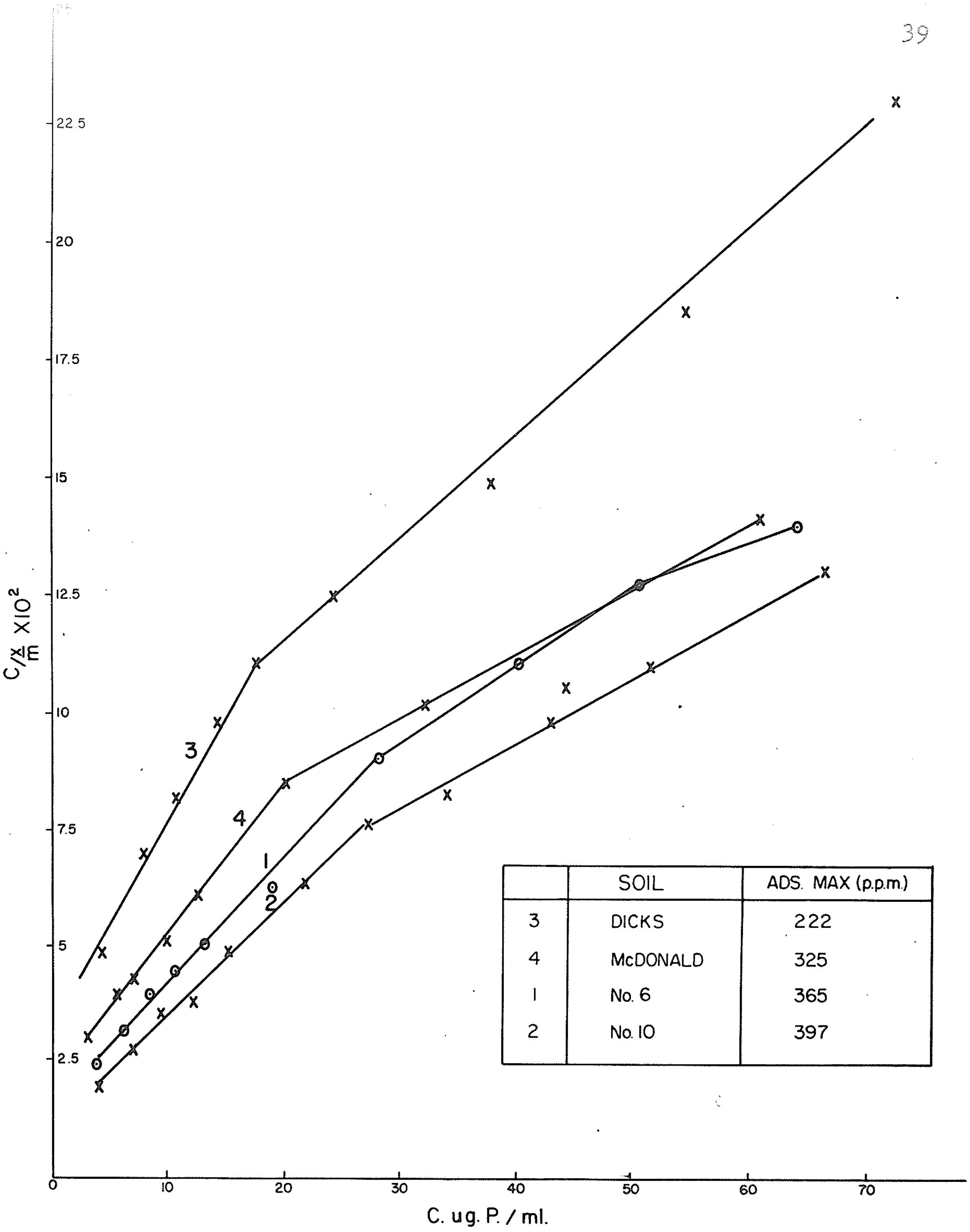

Figure 4. Langmuir plot of adsorption data for the soils used in adsorption studies.

from 5.2 to 7.3 per cent has resulted in an increase in the adsorption maximum from 365 to 397 ppm P. This difference is also illustrated in the values of the surface exchangeable phosphorus of these two soils, as shown in Table 5.

(ii) Exchangeability of Adsorbed Phosphorus

Table 7 shows that the phosphate adsorbed initially from dilute solution by these calcareous soils is essentially all exchangeable with P32. As the phosphorus concentration in solution increases, less of the adsorbed phosphorus is exchangeable with P32. Further examination of Table 7 reveals that the soils have most of the adsorbed phosphorus exchanged below the adsorption maximum. These data would imply a monolayer of phosphorus over the range of concentrations which follows the Langmuir equation. It has also been shown (54) that after drying, some of the adsorbed phosphorus became non-exchangeable with P32, and therefore not in equilibrium with the solution phosphate.

Uses and limitations of the Langmuir equation

In the derivation of the Langmuir adsorption equation, it was implicitly assumed that the only force interfering with the kinetic movement of the gas particles is the attraction by solids. However, in the present study, the kinetic movement of phosphate ions in an aqueous soil solution is affected by other ions in the solution. Since the adsorption by all soils followed the Langmuir equation (up to a concentration of about 20 to 25 µg. P./ml. remaining in solution), it seems that the interference force due to the interacting ions was constant.

Table 7

Amount of adsorbed phosphorus that exchanges with P32 in 96 hours

No. 6		No. 10		Dicks		McDonald	
P. ads. ug. P./g. soil	% of ads. P. that is exchge.	P. ads. ug. P./g. soil	% of ads. P. that is exchge.	P. ads. ug. P./g. soil	% of ads. P. that is exchge.	P. ads. ug. P./g. soil	% of ads. P. that is exchge.
62.5	102.0	58.3	99.1	57.0	98.7	68.6	103.1
91.0	98.4	82.0	102.2	74.1	94.7	98.0	101.2
116.5	100.3	107.7	97.3	93.6	103.2	129.0	97.7
145.0	98.0	131.3	93.1	109.3	92.7	151.7	98.2
168.0	92.2	151.0	91.3	125.0	89.0	173.0	90.9
210.0	94.5	183.0	98.7	160.0	87.1	200.0	90.0
301.0	83.7	291.0	80.4	260.0	77.0	370.0	76.5
360.6	71.2	344.4	77.7	280.4	73.1	391.8	69.7

As applied to gases, agreement of the adsorption isotherm with the Langmuir equation is considered evidence for a monolayer of adsorbed gases on a surface (25). As far as phosphorus adsorption by soils is concerned, agreement with the Langmuir equation suggests strong evidence for a monolayer but not final proof. Exchange studies suggested a monolayer of phosphate over the range of concentrations which follow the Langmuir isotherm.

Furthermore, agreement of the phosphate adsorption data with the Langmuir equation, does not consitute indisputable evidence that an unknown reaction is an adsorption. Many precipitation reactions can be characterized by this isotherm. The results presented here do not exclude the possibility that phosphate compounds, once formed, can be adsorbed by the colloidal inorganic fractions of the soils by Van der Waals forces. Also, it is possible that these phosphate compounds, once they are precipitated or adsorbed, can adsorb phosphate ions in a manner analogous to the adsorption of chloride ions by silver chloride precipitates, especially if the particles of the precipitate are of colloidal size. Thus it would be fallacious to characterize phosphorus fixation as purely adsorption on the basis of compliance with an adsorption alone.

As far as phosphate adsorption by soils is concerned, the main advantage of using the Langmuir isotherm is that is provides a method for characterising the behaviour of the adsorbed phosphorus. In addition an adsorption maximum can be obtained which has been shown (39) to be closely related to a characteristic property of soils--the surface area.

Also a constant (k) relating to the bonding force of the soil for phosphorus can be calculated. In the present study the values of this constant were found to be 0.14, 0.15, 0.18, and 0.20 for Dicks, McDonald, No. 6, and No. 10 soils respectively. As the value of the constant increases, the bonding energy of the soil for phosphorus increases. However, it was found that the value of the constant k is greatly affected by experimental errors, and therefore it is not believed that the differences obtained are significant. The average value for these soils was 0.167, which is quite similar to the 0.141 value of Rennie and McKercher (41) but much lower than the 0.92 value reported by Olsen (39) for soils with an alkaline pH.

(iii) Equilibration of Soils with MCP.

The results of this experiment are shown in Table 8. It is seen that the concentrations of calcium and phosphorus decreased with time, whereas the pH of the solutions increased with time. The activities of the Ca^{++} and $H_2PO_4^-$ ions were calculated by determining the single ion activity coefficients of these ions as the various ionic strengths. The ionic strengths (μ) of the solutions were estimated from the concentrations of (Ca + Mg), and assuming a 2:1 electrolyte.

The approximate activity coefficients of the ions were calculated from the measured concentrations on the basis of the second approximation to the Debye-Hückel equation (18):-

$$-\log \gamma_i = \frac{A Z_i^2 \sqrt{u}}{1 + 1.5\sqrt{u}} \qquad (1)$$

where γ_i represents the activity coefficient of an ionic species of

Table 8

Solution compositions obtained from equilibrating 1 g. MCP with 10 g. soil in 100 ml. water

Sample		pH	P M x 10^3	Ca M x 10^3	γ Ca	$\frac{1}{2}$pCa	γH_2PO_4	pH_2PO_4	pH - $\frac{1}{2}$pCa	pH + pH_2PO_4
Soil	Time of equil.									
Dicks	6 hours	4.31	107	54	0.292	0.92	0.734	1.11	3.39	5.42
Dicks	3 days	4.39	103	41	0.317	0.95	0.750	1.11	3.44	5.50
Dicks	1 week	4.44	71	31	0.341	0.99	0.762	1.27	3.45	5.71
McDonald	6 hours	4.48	84.5	32	0.341	0.98	0.762	1.20	3.50	5.68
McDonald	3 days	5.05	40	16	0.394	1.10	0.792	1.50	3.95	6.55
McDonald	1 week	5.17	25	11	0.415	1.17	0.802	1.70	4.00	6.87
No. 6	6 hours	4.13	113	46	0.311	0.93	0.746	1.07	3.20	5.20
No. 6	3 days	4.16	108	47	0.312	0.92	0.747	1.10	3.24	5.26
No. 6	1 week	4.49	73	30	0.351	0.99	0.769	1.25	3.50	5.74

valence Z_i; and A is a constant, the value of which depends on the solvent and on the termperature. For aqueous solutions A is 0.509 at 25°C. (18). In these calculations a value of 0.50 was used for A. Thus the two equations used for determining the activity coefficients of the Ca^{++} and $H_2PO_4^-$ ions are:-

$$-\log \gamma = \frac{2.0\sqrt{u}}{1 + 1.5\sqrt{u}} \quad \text{for } Ca^{++} \tag{2}$$

and:

$$-\log \gamma = \frac{0.5\sqrt{u}}{1 + 1.5\sqrt{u}} \quad \text{for } H_2PO_4^- \tag{3}$$

By defining the negative logarithm of the ionic activities analagous to pH (page 16), the terms $\frac{1}{2}pCa$ and pH_2PO_4 were obtained. The plot of $(pH - \frac{1}{2}pCa)$ against $(pH_2PO_4 + pH)$ is shown in Figure 5.

This graphical representation is somewhat different from that used on page 28, where $(pH - \frac{1}{2}pCa)$ was plotted against $(pH_2PO_4 + \frac{1}{2}pCa)$. The equations used for construction of the solubility isotherms in Figure 5 were obtained from data given by Moreno et al.(35). The equation for obtaining the DCPD isotherm is:-

$$(pH + pH_2PO_4) = 2(pH - \tfrac{1}{2}pCa) - (\log K_{sp} - \log K_2) \tag{4}$$

In the above equation the solubility product of DCPD (25°C.) was taken as 2.77×10^{-7} (36), and the second dissociation constant of phosphoric acid (K_2), was taken as 6.34×10^{-8} (10).

It is apparent from Figure 5 that the solutions became saturated with DCPD in less than 6 hours and remained so for after one week. It is noted that the points do not all fall on the line for DCPD. This

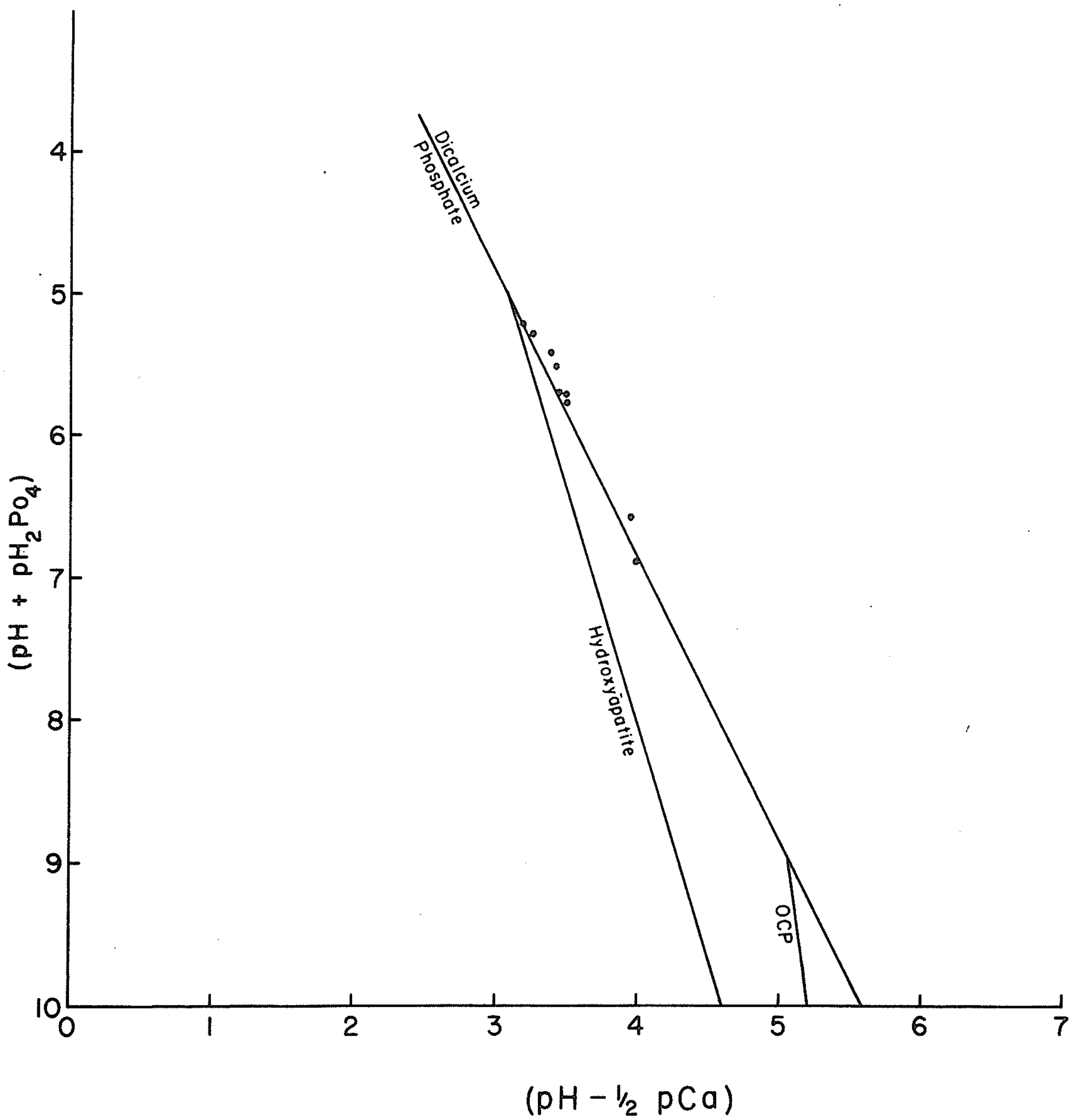

Figure 5. Equilibration of 10 g. of soil and 100 ml. water with 1 g. $Ca(H_2PO_4)_2 \cdot H_2O$ for periods up to 7 days.

may be attributed to experimental error, or to the approximate values assigned to the activity coefficients of the ions. Nevertheless, the results do strongly suggest the persistence of DCPD in soil solutions to which MCP has been added.

These results are in agreement with recent petrographic studies of Lehr et al. (27) who have shown that DCPD is one of the major products formed on addition of MCP to soils. Moreno et al. (35) have also shown that DCPD is formed when MCP is added to acid soils.

Summary and Conclusions

Adsorption of phosphorus by four Manitoba soils from dilute phosphorus solutions showed close agreement with the Langmuir isotherm when the final solution concentrations were less than about 20 ug. P./ml. This corresponds to a molar phosphorus concentration of approximately 6.4×10^{-4} M/litre. Calculated adsorption maxima for the four soils were 222, 325, 365, and 397 ug. P./g. soil for Dicks, McDonald, No. 6, and No. 10 soils respectively. The average value of the constant k was found to be 0.167.

In addition it was found that essentially all the phosphorus adsorbed in the range of equilibrium concentrations where the Langmuir equation applies was exchangeable with P32. However, when the isotherm deviates from a straight line, only a portion of the adsorbed phosphorus was exchangeable with P32 in 96 hours.

It would appear that the amount of $CaCO_3$ in a soil does not greatly affect the value of the adsorption maximum. The two soils which contained small quantities of $CaCO_3$ viz. No. 6 and No. 10, did have higher adsorption maxima than the other two soils, which had larger contents of $CaCO_3$. However, Dicks soils with 11.5% $CaCO_3$ had a much lower adsorption maximum than McDonald soil which contained 42% $CaCO_3$. Obviously other factors (for example, organic matter and clay content) also govern the phosphorus adsorption maxima of soils.

Evidence was also presented that dicalcium phosphate dihydrate (DCPD) is the initial phosphate reaction product formed when monocalcium phosphate is added to these soils. It was also shown that this crystal species of phosphorus was stable in the soil-water system employed, for periods up to seven days.

VI. ISOTOPICALLY EXCHANGEABLE PHOSPHORUS IN SOME MANITOBA SOILS

When a soil is shaken with a solution of P32, it is found that the radioactivity in solution diminishes, and that simultaneously the ratio of $\frac{P31}{P32}$ in solution increases. One of the objects of this investigation is to prove that the disappearance of P32 from solution is through the process of isotopic exchange. Since any isotopic exchange reaction follows the first order kinetics (34), a logarithmic relationship between the disappearance of the isotope from solution and time, should be obtained if the exchange is with only one soil form of the element. If such a relationship does not exist, it can be concluded that there are two or more exchange reactions taking place.

The total isotopically exchangeable phosphorus of any soil is believed (20) to be almost all inorganic phosphates. Direct exchange with phosphorus in combination with organic residues (inositol phosphates, nucleic acid and its nucleotides, etc.) is negligible, and the quantity of P32 incorporated into organic forms by microbial systhesis is also insignificant (20).

In this section the contribution of aluminium, iron and calcium phosphates to the total isotopically exchangeable phosphorus was studied by a combination of P32 equilibration with the Jackson's phosphorus fractionation procedure (7). In addition, the effect of organic matter on the isotopically exchangeable phosphorus content, (in particular, the exchangeable iron phosphates) was investigated.

Materials and Methods

Soils Used in Study

The four soils used in this section were the same as those employed in the preceeding one, and were described on page 17 and in Table 1. Additional information, pertinent to this present study are given in Table 9.

Table 9

Characteristics of soils used in exchange studies

Soil	Total Phosphorus ug. P./g. soil	Phosphorus Extracted ug. P./g. Soil			
		H_2O extract	NH_4F extract	NaOH extract	H_2SO_4 extract
No. 6	762	12.1	81.2	76.0	203
No. 10	1015	59.1	135.0	105.3	325
Dicks	740	8.5	42.1	7.2	300
McDonald	670	2.4	20.2	4.0	322

Experimental Procedure

(i) A preliminary experiment was first conducted to determine whether the P32 removed from solution was through the process of exchange. Two sets of three centrifuge tubes, numbered A_1, A_2, A_3 and B_1, B_2, and B_3, and each containing 0.5 g. soil in about 48 ml. water, were shaken for an initial period of 48 hours. Next 5 uc. carrier-free P32 was added to tubes A_1, A_2, and A_3, the volume of all adjusted to 50 ml., and shaking continued for a further 48 hours. After centrifugation, the activity of the labelled extracts from A_1, A_2, and A_3 was determined on described on page 14. The unlabelled extracts (i.e. from tubes B_1, B_2, and B_3) were then added to the soil residues in tubes A_1, A_2, and A_3 and equilibrated for a period of 48 hours. The activity of these extracts was also determined as above.

(ii) Rate of equilibration and fractionation of exchangeable phosphorus.

Ten 0.5 gram samples of each soil were shaken with about 48 ml. distilled water for an initial period of 2 days, 5 microcuries P32 added, and the volume adjusted to 50 ml. with water. After equilibrating for various periods of time, viz. 1/4, 1/2, 1, 2, 4, 12, 24, 48, 72, and 120 hours respectively, the suspensions were centrifuged and P31 and P32 analyses carried out on the centrifugates. The soils remaining in those tubes which had been equilibrated with P32 for 4, 48, and 120 hours respectively were washed with 1N NaCl, and fractionated into Al, Fe, and Ca phosphates according to the modified procedure of Chang and Jackson. Details of this procedure are given on page 14. Analyses for P31 and P32 were performed on the respective fractions.

Results and Discussion

(i) The results of the preliminary experiment which was designed to show that the added P32 disappeared from solution through the process of exchange are shown in Table 10. It should be pointed out that only the results for soil No. 6 are shown. Similar results were obtained for the three other soil samples which were used.

Table 10

Activities of labelled extracts from No. 6 soil after equilibrating for 48 hours with P32

Sample	% P32 in soil extracts after shaking for 48 hours	% P32 in soil ext. after removal of labelled ext. and addition of unlabelled soil ext.	
		Observed	Calculated
A_1	12.1	10.5	10.6
A_2	12.7	10.8	11.0
A_3	12.4	10.4	10.8

Shaking for an initial period of 48 hours (before addition of the P32) was done in order to allow the phosphorus in the solid phase to come to equilibrium with the solution phase. The results in Table 10 clearly show that the phosphorus in solution (P31 and P32) is in kinetic equilibrium with a part of the solid phase phosphorus. In other words, P32 disappeared from solution via the process of exchange. Under the conditions of the experiment, all the P32 would have remained in the solution phase if there had been no solid phase phosphorus with which the phosphorus ions in solution were exchanging.

The exchange that takes place between solution P32 and solid phase P31 may be represented as:-

$$P32_{solution} + P31_{solid} \rightleftarrows P32_{solid} + P31_{solution} \qquad (1)$$

The equilibrium constant is given by:-

$$\frac{P32_{solid} \times P31_{solution}}{P32_{solution} \times P31_{solid}} = K = 1 \qquad (2)$$

The equilibrium constant is unity because of the near identity of the isotopes. The foregoing expression may be rearranged to:-

$$P31_{solid} = \frac{P32_{solid}}{P32_{solution}} \times P31_{solution} \qquad (3)$$

The $P31_{solid}$ represents the quantity of solid phase phosphorus with which the added P32 has equilibrated.

(ii) Rate of equilibration and fractionation of exchangeable phosphorus.

The results of shaking 0.5 g. portions of each soil in 50 ml. water containing 5 uc P32 for various periods are shown in Table 11. Figure 6 represents a plot of log (1-F) vs. time, where F represents the fraction of P32 which has undergone exchange. In other words, (1-F) is the fraction of radioactivity remaining in solution. Since any isotopic exchange reaction obeys the first order kinetics (34), then if the exchange was with only one soil form of phosphorus, a straight line would have resulted from the plot of log (1-F) vs. time. The fact that a curve was obtained means that there is more than one exchange reaction taking place. The observed rate of dissappearance is the summation of the simultaneous reactions. No attempt will be made here to analyse by graphical or other methods the composite curves illustrated in Figure 6.

It can be seen from Figure 6 that the time required for attainment of isotopic equilibrium varied greatly among the soils. Thus No. 6

Table 11

The amounts of P32 remaining in solution after shaking 0.5 g. soil for various periods in 50 ml. water containing 5 uc. P32

Time of shaking	No. 6		No. 10		Dicks		McDonald	
	% P32 in soln.	log (1-F)	% P32 in soln.	log (1-F)	% P32 in soln.	log (1-F)	% P32 in soln.	log (1-F)
1/4 hour	69.5	-0.16	36.5	-0.44	--	--	--	--
1/2 hour	67.0	-0.17	35.5	-0.45	75.5	-0.12	33.2	-0.48
1 hour	55.3	-0.26	34.0	-0.47	69.5	-0.16	23.3	-0.63
2 hours	54.2	-0.27	29.1	-0.54	55.0	-0.26	18.2	-0.74
4 hours	34.0	-0.47	25.2	-0.60	43.7	-0.36	14.0	-0.85
12 hours	19.0	-0.72	25.1	-0.60	42.0	-0.38	13.2	-0.88
24 hours	12.4	-0.91	--	--	37.2	-0.43	11.0	-0.96
48 hours	12.5	-0.90	25.3	-0.61	33.5	-0.47	8.4	-1.08
72 hours	12.0	-0.91	--	--	21.7	-0.64	5.8	-1.24
120 hours	11.7	-0.93	26.0	-0.59	20.7	-0.68	5.7	-1.25

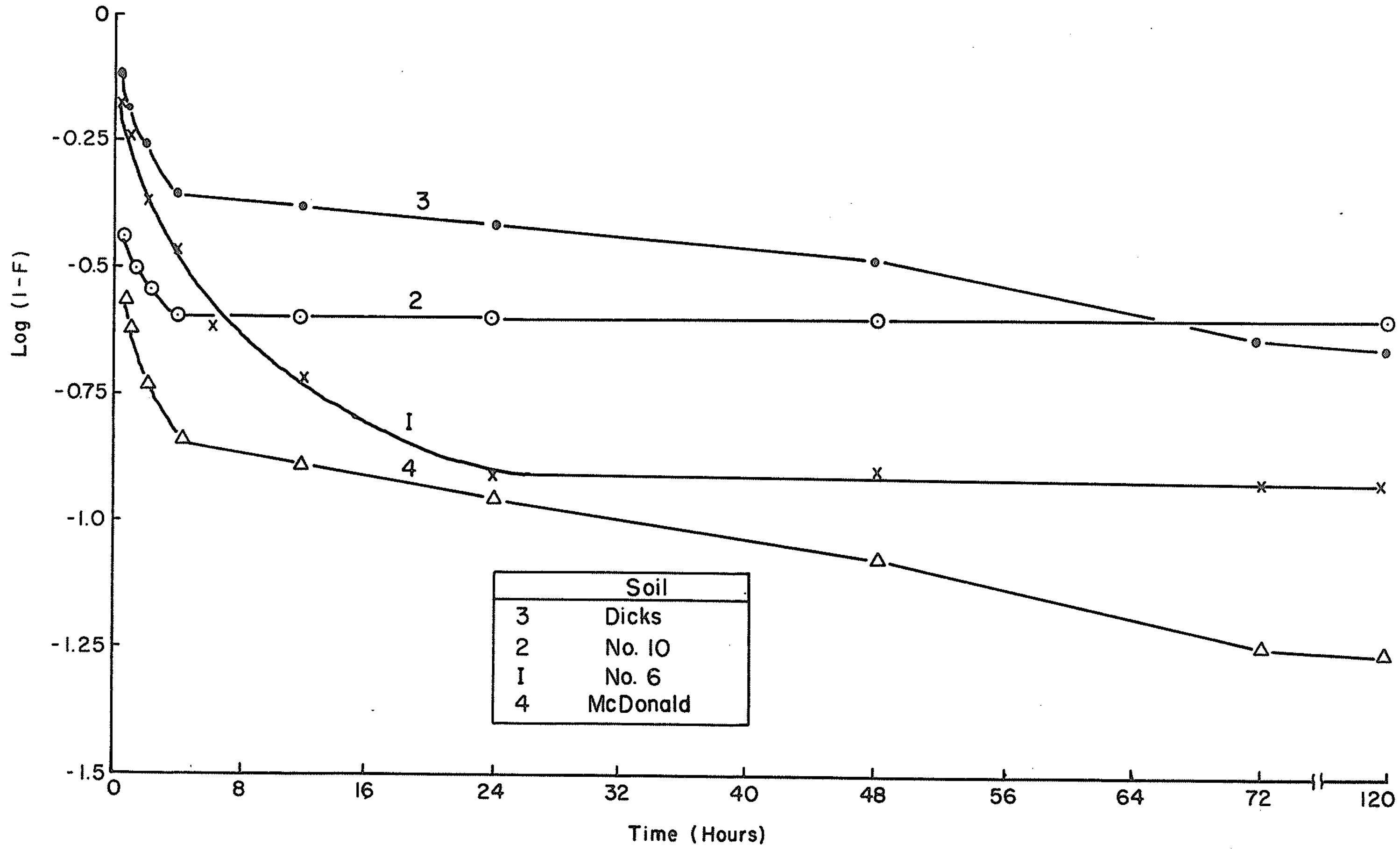

Figure 6. Rate of disappearance of P32 from the soil solution, when 0.5 g. soil was shaken in 50 ml. water containing 5 uc. P32

and No. 10 soils reached isotopic equilibrium in about 24 and 4 hours respectively, whereas for Dicks and McDonald the time necessary was approximately 120 hours. In other words, it would appear that those soils high in $CaCO_3$ are characterized by slower isotopic exchange of phosphorus than soils containing smaller quantities of $CaCO_3$. On the other hand, the effect of increasing the organic matter content is to decrease the time necessary for establishment of isotopic equilibrium. This is obvious when soils No. 6 (5.2% O.M.) and No. 10 (7.3% O.M.) are compared.

The results of the fractionation of these samples which had been equilibrated for 4, 48, and 120 hours are presented in Table 12. In Table 13 the isotopically exchangeable phosphorus, at the respective times for each phosphate fraction, are given. These values were calculated by use of the concept of specific activity i.e. uc P32/ug. P31.

It should be stated that the values of isotopically exchangeable phosphorus so calculated are not entirely exact because the assumed condition of equilibrium is not attained in all soils. However, they do provide a valuable means of obtaining a conception of soil phosphate behaviour. This reservoir of solid phase P31 was very large in comparison to the solution phase phosphorus with with the P32 equilibrated. The contrast in relative magnitudes would be even larger under natural field conditions, where the ratio of water to soil would be very much smaller than that employed experimentally.

The three extractants employed in this fractionation scheme are

Table 12

Equilibration of P32 with the various fractions of soil phosphorus

Hours shaking	% P32 in extract				Hours shaking	% P32 in extract			
	Water ext.	NH_4F ext.	NaOH ext.	H_2SO_4 ext.		Water ext.	NH_4F ext.	NaOH ext.	H_2SO_4 ext.
No. 6					No. 10				
4	34.4	39.1	26.4	2.4	4	25.2	25.0	39.6	4.5
48	12.5	38.6	46.2	4.4	48	25.3	25.3	40.5	5.4
120	11.7	39.0	44.2	5.0	120	26.0	24.2	40.2	6.5
Dicks					McDonald				
4	42.0	26.5	6.0	28.2	4	14.0	20.0	16.6	52.0
48	33.5	28.2	13.2	23.0	48	8.4	20.2	22.1	50.1
120	20.7	28.5	29.0	19.5	120	5.7	19.4	21.7	52.8

Table 13

Isotopically exchangeable phosphorus

Soil	NH_4F-extractable P. ug./g. soil			NaOH-extractable P. ug./g. soil			H_2SO_4-extractable P. ug./g. soil		
	4 hrs.	48 hrs.	120 hrs.	4 hrs.	48 hrs.	120 hrs.	4 hrs.	48 hrs.	120 hrs.
No. 6	11.7	40.2	41.0	7.6	48.2	45.8	0.7	5.0	5.2
No. 10	52.0	52.5	53.4	93.7	93.1	90.2	11.0	13.8	15.1
Dicks	4.4	8.5	11.4	1.1	4.1	11.7	4.7	6.9	8.0
McDonald	3.6	5.7	8.1	3.0	5.8	9.0	9.3	14.3	22.1

not believed to be absolutely specific in extracting the appropriate forms of soil phosphorus. Thus NH_4F may extract not only aluminium phosphates but also phosphorus adsorbed on soil surfaces. No experimental verification of the above statement will be given, as this was not the purpose of this investigation. Thus in this discussion, the following terms will be used:- (i) "NH_4F-extractable phosphorus", for aluminium phosphate, (ii) "NaOH-extractable phosphorus", for iron phosphate and (iii) "H_2SO_4-extractable phosphorus" for calcium phosphate. However, it should be pointed out that this fractionation scheme does provide an excellent tool for characterizing inorganic soil phosphates.

If one examines the data given in Tables 9 and 13, it is observed that the total surface exchangeable phosphorus does not increase in a linear fashion with the quantity of phosphorus present in the soil solution. Thus the phosphorus concentration of the solution phase is probably not a very accurate indication of the exchangeable phosphorus in the solid phase, even though the two co-exist in direct contact, and continuous exchange occurs between them. This unexpected phenomenon can be attributed to:- (a) differences in the ionic composition of the solutions (b) differences in the sites to which phosphate ions are attached in the solid phase, resulting in differences in exchangeability of phosphate ions, and (c) precipitation and solubility of precipitated forms of phosphorus in these calcareous soils.

Table 9 shows that the total H_2SO_4-extractable phosphorus (calcium phosphate) in the four soils varies from approximately 200 to

325 micrograms P./gram soil, however, the exchangeable phosphorus (at 120 hours) in this fraction varies from only 5.2 to 20.2 (Table 13). In other words, only a very small fraction (less than 6 per cent) of the H_2SO_4-extractable phosphorus exchanges with P32. Thus the native calcium phosphates of these soils are characterized by slow exchange with radioactive phosphorus.

The isotopically exchangeable phosphorus in the respective fractions can also be expressed as percentages of the total exchangeable phosphorus in the particular soil. When this is done it is apparent that in No. 6 and No. 10 soils only 5.6 per cent and 9.5 per cent, respectively, of the exchangeable phosphorus is in the H_2SO_4 extract. The corresponding values for Dicks and McDonald soils are 25.7 and 56.4 per cent respectively.

The behaviour of the NaOH-extractable phosphorus (iron phosphate) merits particular attention, especially in the case of No. 6 and 10 soils. On a percentage basis, this NaOH-extractable phosphorus, viz. the iron phosphate fraction, is the most labile of the soil phosphates. Detailed comparison of Tables 9 and 13 reveals that in No. 6 soil 63 per cent of the total NaOH-extractable phosphorus exchanged with P32 in 120 hours, whereas approximately 90 per cent of this phosphorus fraction was exchangeable in No. 10 soil. In other words, an increase in the organic matter content of a soil (brought about through cumulative additions of manure) has resulted in a marked increase in the lability of the iron phosphates. The total NH_4F- and H_2SO_4-extractable phosphorus also increased significantly (66 and 60 per cent respectively) with an increase in the organic matter, however, no similar increase in the lability of these phosphorus fractions was observed.

It is believed that this increase in the lability of the NaOH fraction on addition of organic matter is due to the formation of complexes between phosphate, iron, and organic matter. A study of the interaction of iron and phosphorus with extracts of organic matter (humic acid) is presented in the next section of this Thesis.

Summary and Conclusions

Carrier-free P32 added to soil-water suspension disappeared from solution through the process of isotopic exchange. Essentially 100 per cent of the P32 was recovered in the four extracts studied, viz. water, NH_4F, NaOH, and H_2SO_4. In the four soils studied, it is seen that, regardless of the calcium carbonate content, only a very small fraction of the total H_2SO_4-extractable phosphorus (calcium phosphates) was exchangeable with P32. However, a much larger percentage of the NH_4F extract, and an even larger fraction of the NaOH-extractable phosphorus exchanged with P32. Thus it would appear that the NaOH-extractable phosphorus of soils constitutes a labile fraction of soil phosphorus, the lability of which increases with an increase in organic matter content.

The time necessary for attainment of isotopic equilibrium varied among the soils. Generally, the two soils with high calcium carbonate content reached isotopic equilibrium after much longer times than the other soils with low calcium carbonate content.

VII. INTERACTION OF PHOSPHORUS AND IRON WITH HUMIC ACID EXTRACTS OF SOIL ORGANIC MATTER

In Section VI the Jackson's fractionation procedure (7) was employed in studying the isotopic exchange of P32 with the various fractions of native soil phosphates. It was observed that the sodium hydroxide-extractable phosphorus, viz, the iron phosphate fraction was, on a percentage basis, the most labile of the soil phosphates. Furthermore, an increase in the organic matter content of the soil resulted in a marked increase in the lability of this phosphate fraction.

This is illustrated in the following table, obtained in the study of the exchange of P32 with the inorganic soil phosphates.

Table 14

Influence of organic matter content on the exchangeability of the NaOH-extractable phosphate fraction

Soil	% O.M.	NaOH extr. P. (Fe-P.) ug. P./g. soil	Isotopically exchge. P. extr. with NaOH ug. P./g. soil	% NaOH-extr. P. that is exchge.
#6	5.2	76.0	45.8	60.3
#10	7.3	105.3	93.7	89.1

From these observations, the hypothesis was put forward that the iron phosphates in soils can react with groups present in the organic matter of soils, resulting in the dissolution of the iron phosphates and formation of a complex between the organic group, iron and phosphate. The phosphorus thus held is believed to be more labile than when bound as ferric phosphate.

In the following experiments, an attempt will be made to demonstrate that active groups present in soil humus are capable of holding iron and phosphorus. Humic acid dispersions were used, since it is believed that this material represents fairly closely the whole of the soil humus (43). It must be pointed out that the term "Humic Acid" as used in this study, represents that fraction of the soil organic matter which is soluble in alkali but insoluble in acid. The term, of course, has no strict chemical definition, and therefore should not be given any exact chemical or physical connotation.

The idea that humic acid extracts can hold iron in solution is by no means novel. Several workers (3, 15, 19, 31, 46) have observed this phenomenon. Some workers are of the opinion that the bond between the metal ion and the anion involves complex formation. It is also thought (3) that the bonding of probably one of chelation, i.e. the metallic cation causing the closing of a cyclic ring structure in the organic groups.

The idea that the complex between iron and humic acid can hold phosphate ions is relatively new. To date only one reference (26) has been found in the literature concerning this phenomenon. In this report organic soils were found to fix phosphorus, the fixation increasing with the addition of iron and aluminium.

Materials and Methods

Experimental

(i) Interaction of humic acid extracts with ferric iron.

In these studies the "humic acid" (HA) fraction of soil organic matter was used as the reactive component of the organic matter.

(a) The HA fraction was obtained by extracting the soil with 0.1 N NaOH (using a 1:10 soil:solution ratio) for a period of about 6 hours. The HA was separated from the "fulvic acid" fraction by precipitating it with excess dilute hydrochloric acid. After washing the HA residue several times with water, it was finally redissolved in distilled water to which a few drops of dilute sodium hydroxide was added.

(b) The quantity of iron, added as a standard solution of ferric chloride, required to produce a visible amount of precipitation in the HA solutions at a given pH value was termed the iron holding capacity of that solution. This iron holding capacity was determined by making small additions of ferric salt, and adjusting the pH after each small increment of iron with dilute sodium hydroxide solution. Dilute hydrochloric acid was next added dropwise, and the appearance of a precipitate was ascertained by viewing the solution before a strong light source; with due care a quite definite and reproducible end point was obtained in these titrations. The organic matter content of the extracts was determined by dichromate oxidation (page 12), the solutions being first evaporated to dryness on a steam bath. The amount of iron held by the HA was determined by first destroying the organic carbon with hydrogen peroxide, and estimating the iron in solution according to the procedure described on page 13.

(c) In order to obtain some information on the nature of the bonding between the iron and the HA, solutions of iron and HA were shaken with one gram each of a potassium and barium saturated resin for 4 hours. The amount of iron removed by the resins was determined. The potassium and barium saturated resins were prepared by passing dilute solutions of potassium chloride and barium chloride through a sulfonated polystyrene, cation exchange resin (hydrogen form), until the pH of the effluent was the same as the pH of the eluent. Methylation of the HA was next performed. In this procedure the HA was repeatedly methylated (four times) with demethyl sulfate after the procedure of Gilman (19). After this treatment, the iron holding capacity of this methylated HA at different pH values was determined as above.

(ii) Interaction of Phosphate with (Fe-HA) complex.

Aliquots of the (HA-Fe) complex (containing 1.42 mg. Fe and 20 mg. organic carbon), at various pH values, were shaken with 0.5 g. of a phosphate resin for 3 hours. The phosphate resin was made by passing successive quantities of dilute potassium dihydrogen phosphate solution through a column containing a polyamine anion exchange resin-hydroxyl form, until the pH of the effluent was the same as the pH of the eluent.

The amount of phosphate held by the (HA-Fe) solutions against the resin was determined by first oxidizing the organic matter with hydrogen peroxide, and then determining the phosphate content by the Dickman and Bray (14) procedure.

(iii) Reactions of Phosphorus associated with the (Fe-HA) complex.

In order to characterize the phosphorus held by (HA-Fe) complex the following experiments were conducted.

(a) Aliquots of the HA solution containing known amounts of iron and phosphorus were shaken 0.5 g. each of hydroxide and chloride resin at a pH of approximately 7.5 for 3 hours. The amounts of phosphorus removed by the resins were determined by leaching the resins with dilute hydrochloric acid and determining the phosphorus obtained as above.

(b) The exchangeability of the phosphorus held by the (Fe-HA) complex was estimated in the following manner. Known amounts of a standard phosphate solution were added to aliquots of the (Fe-HA) complex at a pH of 7.5 The amount of phosphate added was larger than the quantity of phosphate which the complex can hold at pH 7.5. Five microcuries of P32 were than added to each solution, and after mixing for a period of 3 hours, one gram of a hydroxide resin was added. The amounts of P32 and P31 removed by the resin were determined by the appropriate methods.

(c) Finally, the availability of the phosphorus associated with the (HA-Fe) complex to sunflower plants, grown in nutrient solutions in the greenhouse was determined. Before incorporating in the nutrient solutions, the phosphorus held by the (HA-Fe) complex was passed through a column containing either:- (a) a chloride resin or (b) a hydroxide resin. This provided two sources of phosphorus. Two other sources of phosphorus were used:- (c) humic acid and phosphorus and (d) phosphorus alone. Thus sources (c) and (d) represents phosphorus not associated with (Fe-HA) complex, i.e. "free phosphorus". Each of the sources contained 1.480 mg. phosphorus. The relative availabilities of these phosphate sources were obtained by growing the sunflower plants for three weeks in the nutrient solutions, and then determining the total phosphorus uptake according to the procedure described on page 13.

Results and Discussion

(i) Interaction of HA Extracts with Iron.

The amount of iron held by HA extracts as a function of pH is illustrated in Figure 7 (solid lines). It is seen that as the pH of the HA solutions increase, the amount of iron held increases. The relationship, however, is not linear.

The exact mechanism by which HA holds metallic ions has been the object of considerable investigation, and up to date, there is no universal agreement on this matter. Preliminary experiments showed that the iron held by the HA was not removed (at any pH) by shaking the HA with a barium or potassium saturated resin. Thus the bond between iron and HA is stronger than the bond between iron and resin. In contrast to this, when similar amounts of iron in the absence of HA were shaken with a cation resin the iron was completely removed from solution.

The results of the methylation studies are also shown in Figure 7

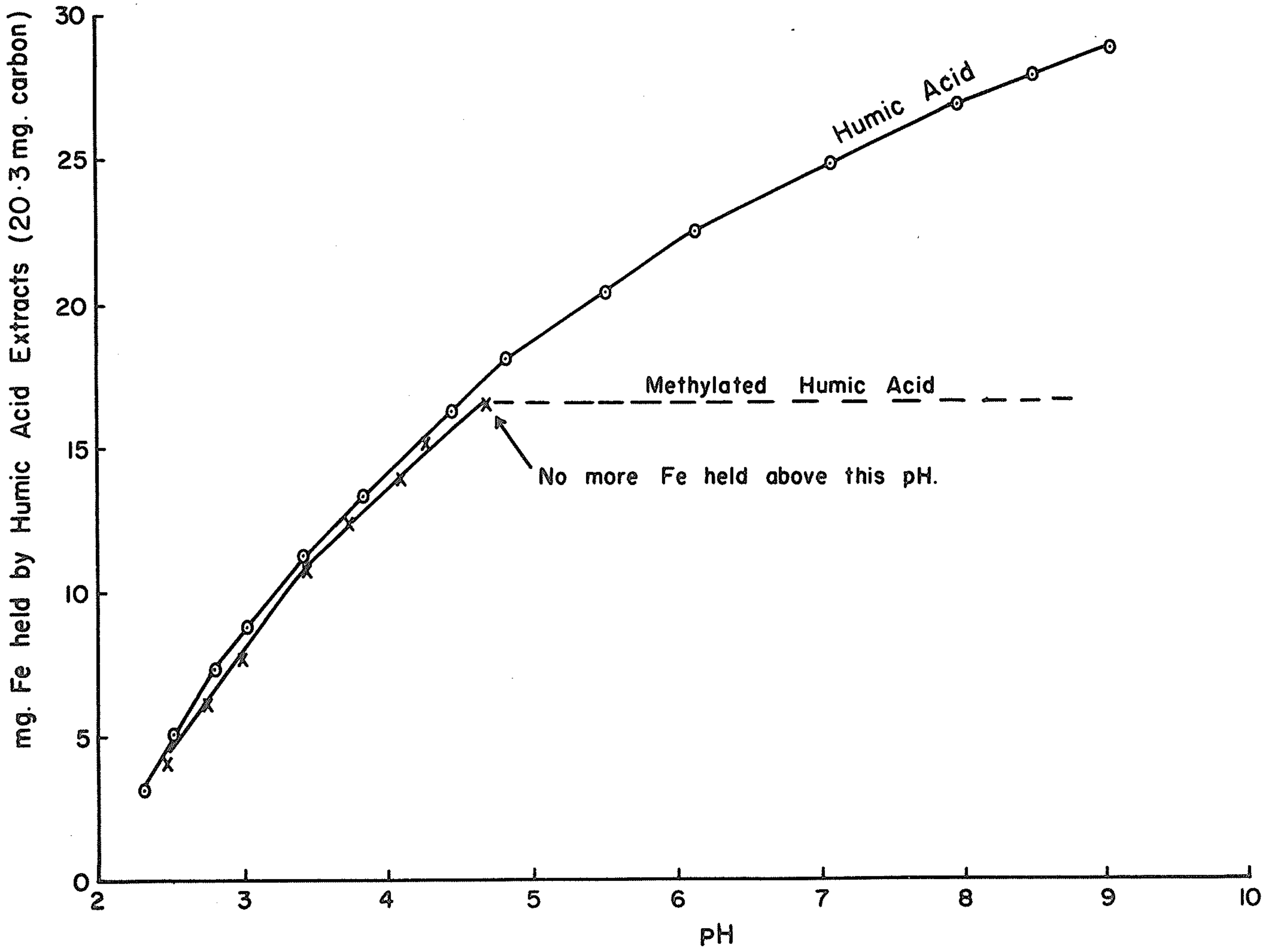

Figure 7. Amount of iron held by Humic Acid vs pH

(dotted lines). Methylation results in a conversion of the non-carboxylic hydroxyls into methoxyls. This treatment therefore removes all those hydroxyls which dissociate hydrogen ions in neutral or alkaline conditions, but leave the carboxylic groups functional. Figure 7 shows that up to a pH of approximately 4.7, the methylated HA behaves almost identically with HA, in respect to the amount of iron held. Above this pH, however, the methylated HA hold no more iron. This would suggest that the non-carboxylic hydroxyls are quite important as bonding sites for iron. The results also support the idea that bonding of HA and iron involves chelation (3). However, recent potentiometric titration data by Martin and Reeve (31) have indicated that the metal ion on adsorption did not displace sufficient hydrogen ions for simple chelate formation.

(ii) Interaction of (HA-Fe) complex with Phosphate.

Figure 8 shows the results of mixing aliquots of (HA-Fe) complex with 0.5 g. of a phosphate resin at various pH values. It is seen that the (HA-Fe) complex was able to hold considerable quantities of phosphate against the resin. It might be argued that ferric ions alone (in the absence of HA) could also complex phosphate ions. This is true. However, "free ferric ions" as such can only exist below a pH of 2.3. Above this pH, $Fe(OH)_3$ is completely precipitated (31). Since all these experiments were conducted in media above pH 2.3 it is clear that the complexing of phosphate was not due to the presence of free ferric ions. The term "free ferric ions" must be used with some

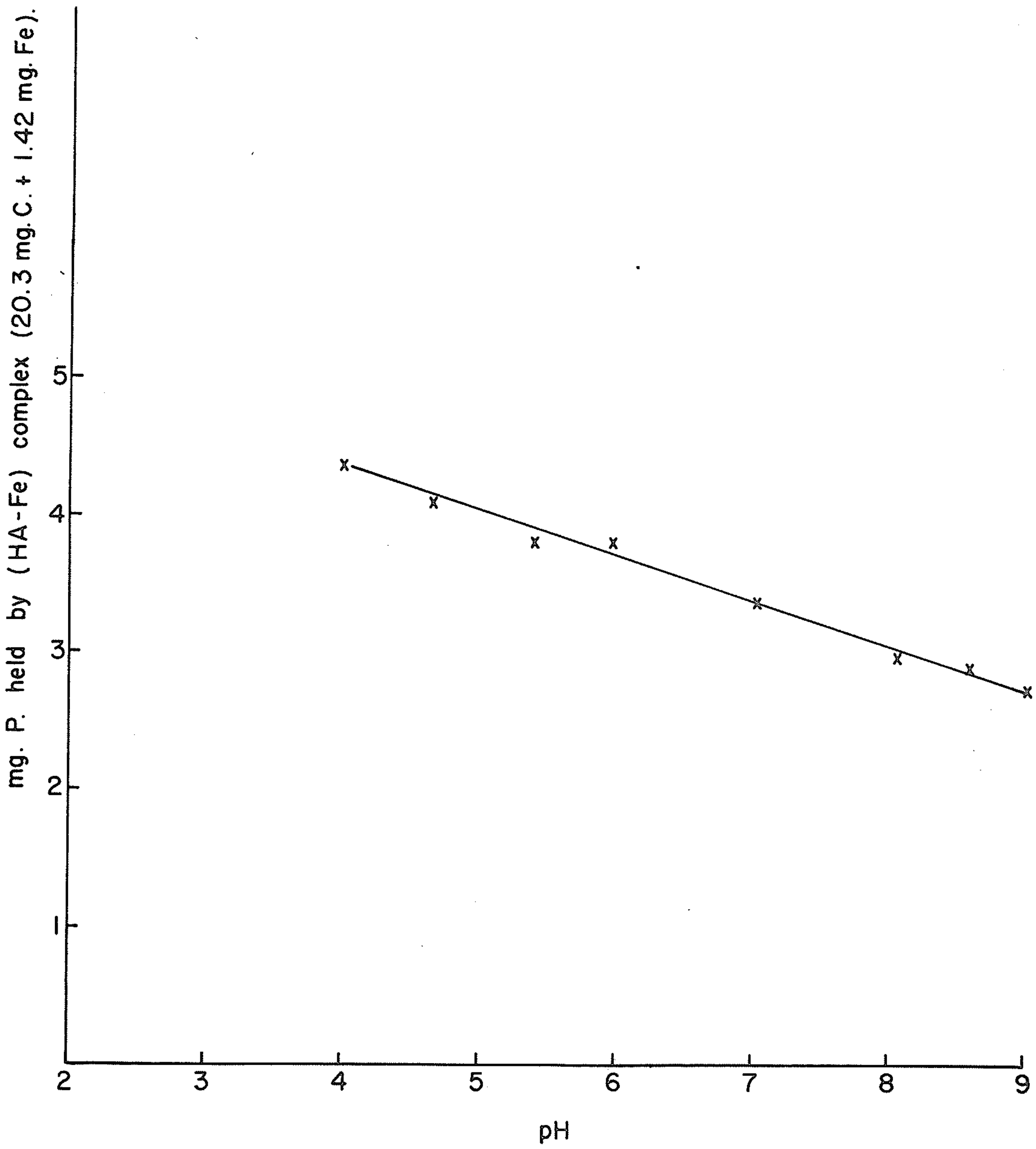

Figure 8. Amount of phosphate held by (HA-Fe) complex vs pH.

reservation, as the simple ferric ion is never found in aqueous solutions (though often written as such), because it has a great tendency to form coordinate bonds with any available molecules or ions which carry unshared pairs of electrons viz. water.

Figure 8 also reveals that less phosphate is held at higher pH values, also the relationship between pH and phosphate held is approximately linear. The fact that less phosphate is held at higher pH values can be partly explained by the fact that in acid medium phosphate is present predominantly in the $H_2PO_4^-$ form, while in slightly alkaline solutions the $HPO_4^=$ form predominates. Thus it is clear that less phosphate will be held by the complex as the pH increases.

(iii) Reactions of Phosphate associated with (Fe-HA) complex.

It was found that the phosphorus held by the (HA-Fe) complex was not removed by shaking with a hydroxide resin; however, when shaken with a chloride resin, approximately 68 per cent of the complex phosphorus was removed by the resin.

Exchange studies with carrier-free P32 showed that between 90 to 100 per cent of the phosphorus associated with the (HA-Fe) complex was exchangeable with P32 in 3 hours.

Table 15 shows the results of the experiment conducted to compare the availability to plants of phosphorus associated with (HA-Fe) complex, and "uncomplexed" phosphorus. As indicated on pages 66 and 67 four different sources of phosphorus were employed:-

(1) complexed phosphorus which was previously passed through a chloride resin

Table 15

Availability of the phosphorus associated with (HA-Fe) complex to sunflower plants grown in nutrient solutions

Treatment	% of P. taken up by plants
1.48 mg. P. + (HA-Fe)[1]	6.70
" "	7.11
" "	7.21
1.48 mg. P. + (HA-Fe)[2]	62.5
" "	64.7
" "	67.2
1.48 mg. P. + HA	67.0
" "	66.2
" "	68.3
1.48 mg. P.	69.5
" "	65.5
" "	72.0

1. Complexed P. previously passed through a Cl^- resin.

2. Complexed P. previously passed through a OH^- resin.

(2) complexed phosphorus which was previously passed through a hydroxide resin

(3) humic acid and phosphorus (i.e. "uncomplexed" phosphorus)

(4) phosphorus alone

Table 15 shows that approximately 60 to 70 per cent of the total phosphorus from sources (2), (3) and (4) was available to the sunflower plants while only 6 per cent of the total phosphorus from source (1) was available.

It is recalled that a hydroxide resin was unable to remove any of the phosphorus held by (HA-Fe) complex, while a chloride resin removed 68 per cent. When compared with the availability studies it appears that the plants and the chloride resin were quite similar in their capacity to extract phosphorus from the (HA-Fe) complex. It also is clear that although all the phosphate associated with the (HA-Fe) complex was exchangeable with radioactive phosphorus, only a portion of this phosphate is available for plant use.

Summary and Conclusions

Humic acid dispersions of soil organic matter had the capacity to hold ferric ions in solution against a cation resin. Thus although ferric ions normally precipitate as insoluble ferric hydroxide above pH 2.3, in the presence of HA considerable amounts of iron were held in solution. Methylation studies indicated that both carboxylic and non-carboxylic hydroxyl groups were involved in bonding iron.

The (HA-Fe) complex had the capacity to hold phosphate ions against an anion resin. The amount of phosphorus held was a function of (a) pH and (b) the type of anion resin. This phosphorus was not removed by shaking with an hydroxide resin, while approximately two-thirds was displaced by shaking with a chloride resin. In addition, nearly all of the phosphorus was exchangeable with P32. Since the properties of HA dispersions are believed to be quite similar to those of soil humus, the conclusion reached is that active groups present in soil organic matter can react with iron phosphates in soils resulting in the formation of a complex between the organic group, iron and phosphate. It is probable that such a compound may exist in some soils containing appreciable amounts of organic matter.

The availability of the complexed phosphorus to plants was found to depend on the previous treatment. Thus when the complexed phosphorus was first passed through a hydroxide resin, approximately 65 per cent of it was available to plants, whereas only 6 per cent was available when a chloride resin replaced the hydroxide resin. The amount of phosphorus removed from the complex by the plants was almost equal to the quantity displaced by a chloride resin.

VIII. GENERAL CONCLUSIONS

The investigations presented herein were initiated in order to characterize the behaviour of phosphorus in some calcareous Manitoba soil systems. These studies can be broadly divided into two sections viz. (1) solubility and (2) exchange studies.

In the solubility studies, the fundamental questions sought to be answered included, (a) the form of native soil phosphate which governs the solution concentration of phosphorus in these calcareous soils, (b) the phosphate species initially formed on addition of water soluble phosphates to calcareous soils, (c) the stability of the initially formed phosphate compound and (d) whether the calcium carbonate content of the soils had any effect on the form and behaviour of phosphorus in these soils. A series of soils with calcium carbonate levels varying from approximately one per cent to 42 per cent was used in these investigations.

The solubility product principle was employed to explain the chemical behaviour of added and native soil phosphates. It was found that calcium phosphates could account for the phosphorus content found in extracts from these soils. Thus octocalcium phosphate was found to be phosphate species governing the solution concentration of phosphate. However, when soluble monocalcium phosphate was added to these soil-water systems, dicalcium phosphate dihydrate was the phosphate species which was initially formed.

It is possible that dicalcium phosphate dihydrate which formed initially might eventually dissolve with concomitant precipitation of a less soluble calcium phosphate--perhaps octocalcium phosphate or hydroxyapatite. It must be pointed out, however, that such chemical transformations referred to here do not occur instantaneously. The rates of dissolution and precipitation in many of these reactions are perhaps very slow and this must be remembered when attempting to interpret solubility measurements of phosphate reactions in soils. In all probability, the less soluble calcium phosphate compounds (also slightly soluble iron and aluminium phosphates in acid soils), attain equilibrium with solution so slowly that solubility measurements in soils quite often do not correspond to any known solubility product.

Since phosphorus solubility in the soils studied conformed quite closely to the solubility isotherm for octocalcium phosphate, one may conclude that this species of phosphate is the only one present in these soils. However, this conclusion is not necessarily true, as the experimental results do not exclude the possibility that other phosphate compounds, much less soluble than octocalcium phosphate e.g. hydroxyapatite, may be also present in these soils.

In addition, it was found from these solubility studies that adsorption of phosphate from dilute solutions showed fairly close agreement with the Langmuir adsorption isotherm, when the final solution concentrations were less than about 20 ug. P./ml. Although the experimental results suggested a monolayer adsorption reaction over the range of equilibrium concentrations where the Langmuir equation applies, it is possible that both adsorption and precipitation reactions occur when dilute phosphorus solutions are added to the soil systems.

It was found that the level of calcium carbonate on the soil was not the only factor determining the adsorption reaction in these calcareous soils. The organic matter content and the clay content are believed to be also of great importance in determining phosphate adsorption. However, it was shown that the bonding energy of the soils for phosphorus was approximately the same for all soils. This would suggest that the same mechanism was involved in all the systems studied.

The results of these solubility studies are of great practical significance. The addition of water soluble phosphate fertilizer to calcareous soils was shown to result in the formation of dicalcium phosphate dihydrate. This species of phosphate, although unstable, persists for long periods in the soil, the hydrolysis and precipitation of this species to less soluble phosphate compounds is extremely slow. These results are in general agreement with the present belief that phosphate fertilizers added to calcareous soils remain in a plant available state for considerable periods of time. In a recent greenhouse investigation (17), fertilizer phosphates in calcareous soils remained available to plants even after five successive croppings.

In the exchange studies the reactivity of the soil inorganic phosphates (calcium, aluminium and iron phosphates), was studied through a combination of the Jackson's fractionation procedure with

P32 equilibration. It should be pointed out that this new approach to the study of the soil inorganic phosphates is unique in that the contribution of each of the inorganic phosphate to the total isotopically exchangeable phosphorus in any soil can be determined. Since the total isotopically exchangeable phosphorus ("labile phosphorus") is believed to be closely correlated with "available phosphorus", the study is of great practical importance.

A significant finding in these exchange studies was that the time necessary for establishment of isotopic equilibrium varied with the level of calcium carbonate in these soils. Thus in two soils containing approximately one per cent calcium carbonate, isotopic equilibrium was reached in less than 24 hours, while about 120 hours was the time necessary when the level of calcium carbonate in two other soils was 11.5 and 42 per cent respectively. It also appeared that increasing the organic matter content of a soil resulted in a decrease in the time necessary for attainment of isotopic equilibrium.

Of even greater significance was the observation that only about six per cent of the total H_2SO_4-extractable phosphorus (calcium phosphate fraction) exchanged with P32 in 120 hours. However, a much larger fraction of the NH_4F-extractable phosphorus (aluminium phosphate), and an even larger percentage of the NaOH-extractable phosphorus (iron phosphate) was exchangeable with P32 in 120 hours. Furthermore, it was apparent that an increase in the organic matter content resulted in an increase in the exchangeability of the iron phosphate fraction. This observation led to the hypothesis that the iron phosphates in soils can react with groups present in soil humus, which result in the dissolution of the iron phosphate and formation of a complex between the organic group, iron and phosphorus. The phosphorus thus held is believed to be more labile than when held as ferric phosphate.

Under the experimental conditions used in this investigation it was shown that a considerable amount of iron and phosphorus can be held by humic acid extracts of soil organic matter. It was shown that the phosphate thus held was virtually all exchangeable, but was only partly available for plant use.

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