ABSTRACT

EQUILIBRIUM CONCENTRATIONS OF INORGANIC PHOSPHORUS AND ADSORBED PHOSPHORUS IN SOILS

By

Daulat Singh

Investigations were undertaken on 29 Michigan soil profiles to determine (1) equilibrium conc of inorganic P, (2) potential buffering capacity, and (3) P adsorption maximum as predicted by Langmuir adsorption isotherm.

Above determinations were made with increasing conc of $Ca(H_2PO_4)_2H_2O$ in 0.01 M $CaCl_2$. Equilibration time of 2 hrs. with a soil:solution ratio of 1:10 was adopted.

The podzolic sandy profiles and B horizons in particular had exceedingly low conc of inorganic P at equilibrium--conc as low as 8.3×10^{-8}MP for Emmett loamy sand Bihr was obtained. Only few A horizons, McBride sandy loam, Miami loam, Miami sandy loam, Spinks loamy sand, Brookston clay loam and Muck had equilibrium P conc adequate enough to support an optimum plant growth, if those conc were maintained during the plant's life. These higher P conc were probably either a consequence of recent treatment with P fertilizers and/or low bonding energy of P on soil complexes.

The free energy of adsorption of P on soil adsorbing complexes estimated by slope/intercept from the Langmuir adsorption equation indicated higher values for B horizons with possibly Al and Fe adsorption complexes than those with A horizons suggesting lower energy of adsorption of P with organic matter.

The potential buffering capacity and P adsorption maximum were highly correlated ($r = 0.954$). The higher correlation between potential buffering capacity and adsorption maximum alone, without the energy of adsorption term, i.e. K, was because of inter-correlation between adsorption maximum and K.

Data strongly indicated that the Langmuir adsorption equation may be used to predict P conc in soil suspension or given a desired P conc in soil suspension for optimum plant growth, the P needed to be added to soil may be calculated. Fine textured soils (high adsorption maximum and/or K) with no recent P additions, showed high P requirement to bring the P conc to any level compared to coarse textured soils. Data also suggested that P adsorption maximum, a unique propery of soil, should serve as indicator of soil's ability to continue supply P to plants.

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To My Wife

Prabha

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LIST OF SYMBOLS AND ABBREVIATIONS

μ = mu

θ = theta

g = gram (s)

mg = mg (s)

Kg = killogram (s)

ha = hectare (s)

no. = number (s)

conc = concentration (s)

M = mole (s)

meq = milliequivalent

pX = -log of activity of X

$potential^{cp}$ = chemical potential

$potential^{sp}$ = Schofield phosphate potential

$potential^{sp}_{eq}$ = equilibrium phosphate potentil

TP_{eq} = total phosphorus at equilibrium

INTRODUCTION

As a limiting factor in world food production, P ranks next but to N (Black, 1968) and perhaps to none in some parts. Consequently, much effort has been devoted to the chemistry of P in soil as related to plant growth. But the chemistry of P in itself and as it relates to plant growth is still not completely understood. Inorganic P in soil solution is the immediate source of P for plants. This quantity, however, is so small -- from below 10^{-7} M to about 10^{-6} M for P deficient soils and above 10^{-5} M in soils known to be well supplied (Russell, 1961) -- that a continuous replenishment of the soil solution is necessary to insure optimum plant growth. As a measure of the inorganic P conc in soil suspension, or rather strictly the ease with which P may be removed, Schofield (1955) has introduced the concept of phosphate potential, $1/2pCa+pH_2PO_4$ of monocalcium phosphate $[Ca(H_2PO4)_2H_2O]$ or potential^{sp} (White and Beckett, 1964). He further suggested that the soil's ability to maintain the appropriate chemical potential, that is replenishment of the soil solution against P withdrawal, was critical in a soil's ability to supply P to plants. Beckett and White (1964) have proposed that potential buffering capacity (PBC) of a soil reflects the soil's ability to maintain the potential^{sp} and have devised methods to obtain PBC.

Recent investigations (Murrmann and Peech, 1969a, Ozanne and Shaw, 1967, 1968, and Rennie and Mckercher, 1959) indicate that adsorbed P may be equally important in controlling the level of

P in soil suspension and hence have an important influence on plant available P; notwithstanding the emphasis on the crystalline phosphates as the soil-fertilizer reaction product of incorporated P in soils (Lindsay, Frazier and Stephenson, 1962; Murrmann and Peech, 1968; and Wright and Peech, 1960).

When P is placed in soil, most of it is traceable to Al-P and Fe-P (Bromfield, 1967; Coleman, Thorup, and Jackson, 1960; Dunbar and Baker, 1965; Harter, 1968; Hsu, 1964; Huffman and Taylor, 1963; and Mackenzie and Amer, 1964). Al-P fraction according to Chang and Jackson procedure (1957) contains P much of which is exchangeable with ^{32}P (Dunbar and Baker, 1965) indicating that the Al-P fraction must also include adsorbed or labile P in the soil. Recently Harter (1969) had concluded that P is adsorbed on organic matter through some type of anion exchange and significant linear correlation coefficients between Al and free iron oxides and P adsorbed were primarily due to inter-correlation between the independent variables.

The present investigation, therefore, was undertaken to determine:

1. Equilibrium phosphate potential^{sp} and hence equilibrium conc of inorganic P in soil solution of some Michigan soils.
2. Potential buffering capacity (PBC), and
3. The P adsorption maximum of the above soils and the interrelationships between the above parameters.

REVIEW OF LITERATURE

Schofield Phosphate Potential

Schofield (1949) introduced the concept of chemical potential of soil constituents and later (1955) suggested that -

> "it seems reasonable to suppose that availability of soil phosphate is mainly determined by the appropriate chemical potential and by its rate of decrease with phosphate withdrawal."

He also suggested that the appropriate potential was the chemical potential of $Ca(H_2PO_4)_2H_2O$. Several workers have examined this proposition -- some treating theoretical aspects and techniques of measurement (Larsen and Court, 1960; Barrow, 1965; and 1966) and others testing Schofield's hypothesis by measuring its ability to predict uptake of P by plants (Barrow, 1967; Kudeyarova, 1968; Mattingly, Russell, and Jephcott, 1963; Moser, Sutherland, and Black, 1959; Ramamoorthy and Subramanian, 1960; White and Haydock, 1967).

The theory below is essentially as presented by Larsen and Court (1960). In any multiphase system at equilibrium the chemical potential or partial molar free energies of all diffusible chemical components are equal. The chemical potential of a component X of a chemical system is defined by the equation:

$$\mu X = \mu^{O}X + RT(\ln aX)$$

Where $\mu^{O}X$ is the standard chemical potential referred to an arbitrary reference state, R is the universal gas constant, T

is the absolute temperature, and aX is the activity of the compound X.

The above equation can be rearranged to give:

$$\frac{\mu^{o}X - \mu X}{2.303\ RT} = -\log aX$$

By the usual convention, -log X is written as pX:

$$\frac{\mu^{o}X - \mu X}{2.303\ RT} = pX$$

In general, $\mu^{o}X$ is unknown and since the standard state is arbitrary, it is customary to define a modified chemical potential (μX) by the equation:

$$\mu X = pX$$

Using this and the relationship pH + pOH = pKw for water, the potentials of a salt, an acid, and a base can be defined by:

$$\mu \text{ salt} = 1/Z^{+}\ pM + 1/Z^{-}\ pA$$

$$\mu \text{ acid} = pH + 1/Z^{-}\ pA$$

$$\mu \text{ base} = pH - 1/Z^{+}\ pM$$

Where Z^{+} is the charge on the cation M and Z^{-} is the charge on the anion A.

For a system consisting of a solution phase in contact with a solid phase (e.g. soil system), the chemical potential at equilibrium of any component in solid phase is equal to that of the component in the solution phase and since the latter potential

is easily determined from activity measurements, the potential of the solid phase can be found.

Schofield's Ratio law (1947) requires that for a given soil with a given component of Ca and P ions the activity product ($aCa\frac{1}{2} \times aH_2PO_4$) in the soil solution be independent of electrical potential differences and hence of other ions in the soil solution. Aslying (1950) and Nethsinghe (1958) have confirmed this postulate for a number of soils. The validity of ratio law depends on a number of assumptions which Schofield (1947) and Nethsinghe (1958) have shown do not always apply. Apart from this, RTln ($aCa\frac{1}{2} \times aH_2PO_4$) is a single valued property of the soil over the range of Ca and P conc normally found in soil solution, whereas RTln aH_2PO_4 is not.

RTln ($aCa\frac{1}{2} \times aH_2PO_4$) is a measure of the sum of the chemical potential of both Ca and P ions in whatever part of the soil controls their potential in the soil as a whole. The phosphate potential^{sp} was defined as the activity product $aCa\frac{1}{2} \times aH_2PO_4$ or rather strictly its logarithmic equivalent $\frac{1}{2}$ pCa + pH_2PO_4. Nevertheless, for soils of comparable Ca status RTln-($aCa\frac{1}{2} \times aH_2PO_4$) may also be used as a measure of the potential^{sp} of labile P in the solid phase of the soil.

The use of phosphate potential^{sp} as a measure of P availability depends on certain assumptions. The first is that the soils of which the potential^{sp} is measured confirm to the ratio law. The second assumption in the use of phosphate potential^{sp}

to compare the availability of soil P to plants is that the potential of Ca in the soil solids is much less variable than the phosphate potential. The third assumption is that the act of measurement does not substantially alter the potential^{cp} of P and Ca in the solid phase, nor the potential^{cp} of any complementary ions such as Fe^{3+}, Al^{3+} or OH^- which may also influence the value of the activity product. The method of interpolation used in this work measures the potential^{sp} without altering the amount of P held by the soil. If the potential^{sp} also depends on the potentials^{cp} of other ions, it may be necessary to employ additional interpolations to obtain the equilibrium activities in solution of these other ions.

The first experimental studies were made by Aslying (1950, 1954, and 1964). After shaking samples for 1-2 hours in both 0.01M and 0.001M $CaCl_2$ solution, he found that the activity product was constant for a given ratio of soil to solution and independent of actual magnitude of individual activities. Cole and Olsen (1959) obtained similar results in calcareous soils where the partial pressure of CO_2 was controlled experimentally. Wild (1959) confirmed the dependence on the soil:solution ratio and also reported a variation with the time of shaking of the soil suspensions. Nethsinghe (1958), and Larsen and Court (1960) had also noted the dependence on the soil:solution ratio. As the conc of soil suspension increases these authors found a increase in the potential^{sp}. It must, however, be noted that although the P conc decreases, the amount of P extracted per unit weight of soil increaseswith decreasing soil:solution ratio.

Several explanations, not all independent, are possible. Larsen and Court (1960) suggested the following explanations assuming the presence of a one component P system. Similar postulates could be made for a multicomponent system.

(1) Energy effects -- as P is removed, the mean bonding energy of P that remains in soil may be higher than the initial mean bonding energy.

(2) Adsorption effects -- the equilibrium P conc may be dependent on the mechanism of adsorption and desorption which may be influenced by soil:solution ratio.

(3) Incongruent dissolution of P mineral -- mutually disagreeing solubility forms may come in the dissolution process and cause change in P conc with soil:solution ratios.

(4) The presence of a mineral containing a definite solubility product but for which the conc of one or more ionic compounds other than P also varies with soil:solution ratio so as to compensate for P changes.

(5) P of indefinite forms (adsorption complex) for which a constant solubility product would not be expected.

(6) Differences due to the uncertain form associated with soil organic matter -- Organic P compounds

are not hydrolyzed in the analytical procedure for P and the solubilizing effect of organic matter will be negligible at the electrolyte conc of 0.01M $CaCl_2$ used.

(7) Variation of cation balance with soil:solution ratio -- large changes however are not expected and small change will not affect the chemical potential since the compensating action of ionic strength means that at 0.01M a 10% change of conc brings about only a 1% change of potential^{sp}.

Attention need be paid only to the first five explanations. Definite mechanisms are implied by (3), (4), and (5); whereas, explanation (2) is a quantitative description of relationships of postulate (5), and (1) is a quantitative thermodynamic description of all the others without regard to mechanism.

These authors measured the P conc in solution after shaking a soil with a solution containing no P initially. The phosphate potential^{sp} determined this way depends on the amount of P released from the soil and thus on the soil:solution ratio. Ramamoorthy and Subramanian (1960) have rightly drawn attention to the discrepancies between potential^{sp} measured by a "null" method (the equilibrium phosphate potential^{sp}) and the potential^{sp} obtained by equilibrating a soil with a solution containing no P initially. The "soil:solution ratio effect" is interpreted by White and Beckett (1964) in terms of P

desequilibrium -- a condition in soils in situ which can be due to either nonuniform removal of P or nonuniform distribution of soluble P recently added to soil. White and Beckett (1964) also found that upon allowing soil P to achieve equilibrium by prolonged storage under constant environmental conditions, the equilibrium potential^{sp} and slope dQ/dI (the potential buffering capacity) remained constant and independent of soil:solution ratio.

White and Beckett (1964) also noted change in phosphate potential^{sp} with drying, changes in temperature and aeration conditions. But with the exception of anaerobic effects, changes induced in the equilibrium potential^{sp} were considerably smaller than the range of potential^{sp} of the field soils examined. Nethsinghe (1958) had earlier reported that air drying of soils caused a change in chemical potentials of soil P which was not reversable upon rewetting.

Following Schoefield (1949), Aslying (1954) used the chemical potential of $Ca(OH)_2$, the "lime potential", defined as (pH - 1/2 pCa) and the phosphate potential^{sp} in an attempt to assess the presence and nature of Ca-P compounds in calcareous soils. Similar basic solubility relationships were used in Lindsay and Moreno's phase diagrams (1960). For the general case, Clark and Peech (1955) represented the formation of a hypothetical Ca P as:

$$mCa(OH)_2 + nCa(H_2PO_4)_2 \rightleftharpoons Solid + zH_2O$$

Where m and n represent reacting moles of $Ca(OH)_2$ and $Ca(H_2PO_4)_2$ forming one mole of solid + zH_2O. If the reactants are completely dissociated, the linear plot of 1/2pCa + pH_2PO_4 (potential^{SP}) versus pH - 1/2pCa (lime potential) should have a slope of m/n characteristic of the solid species, i.e. octacalcium phosphate $Ca_4H(PO_4)_3$ would have a slope of 5/3 = 1.67.

Similar solubility diagrams may be constructed for $Al(OH)_3$ - $AlPO_4$, and $Fe(OH)_3$-$FePO_4$ systems. Taylor and Gurney (1962) equilibrated an acid soil in dilute $CaCl_2$ and plotted pH + pH_2PO_4 as a function of pH - 1/3 pAl. Points for the untreated soil fell on the variscite line. Since there are several reactions that may reduce the P conc in soil to a level whereby the points could fall on the variscite line, Taylor and Gurney (1962) concluded the finding of Al-P ion products similar to the solubility product of variscite is not a very satisfactory criterion for the existence of variscite in soil. To demonstrate that P status of a soil is governed by the precipitation or dissolution of a particular mineral the appropriate ion product must be proved independent of the base status and salt content of the soil.

Chakravarti and Talibudeen (1962) examined P equilbria in 54 British and Indian soils by plotting Fe potentials (pH - 1/3 Fe^{+3}) and Al potentials (pH - 1/3 Al^{3+}) as a function of potential $[1/3\ p(Al^{+3}$ or $Fe^{+3}) + pH_2PO_4]$. Equilibrium

conc were interpreted as related to soils grouped according to pH. A variscite type compound controlled P conc in temperate climate up to pH 4.7; above pH 4.7, nonstoichiometric P -- OH adsorption complexes may be controlling. In the tropical soils (pH 4.3 - 5.8) an Al-P similar to variscite but more basic in character than in temperate climate soils coexists with hydroxides. Temperate soils seemed free from strengite whereas in tropical soils it coexists with hydrated oxide over the entire pH range examined.

Wada (1964) reported that P equilibria in some Ando soils, red-yellow podzolic soils and alluvial soils in Japan were governed by Fe and Al compounds from pH 4 to 7. Below pH 5.2 P activity was apparently controlled by variscite and gibbsite or possibly by strengite and $Fe(OH)_3$. Stelly and Pierre (1943) compared the solubility versus pH curves of soils with those of known P minerals and found that a solubility pH curve similar to that of apatite was common with alkaline soils; whereas, acid soils usually displayed a solubility curve similar to that of Fe-P and/or Al-P. Similar results are also reported by Clark and Peech (1955); Lindsay, Peech, and Clark (1959); Lindsay and Moreno (1960); Rinkenberger (1966); Weir and Soper (1962); Withee and Ellis (1965); and Ulrich and Khanna (1968).

Wild (1964), on the basis of solubility product principle, calculated the P conc expected in the presence of variscite and various Ca-P compounds at different pH values and compared his

results with the P conc in several soil extracts determined by other workers. In the pH range 4.5 to 6.0 none of the phosphates considered could explain the level of P found in solution.

Larsen and Court (1960) obtained scattered distribution of the points on the solubility diagram from solubility data of a great number of British soils. Although some of the points fell near the lines for pure compounds, the overall distribution suggested that either no definite forms of Ca-P compounds can be inferred to exist in soils or that the apparent solubility relationships are influenced by other factors.

Solubility product concept and the chemical potential of P in soil suspensions, as evident from the above discussion, has been investigated by many workers for determining the nature of P compounds in soils. However, due to the complex nature of soil and the limitations of the solubility product principle itself in describing precipitation and dissolution phenomena, the results obtained may show the possibility of the existence of certain P compounds in soils, but do not show explicitely which form of the P will control the conc of P in the soil solution-solid system.

Phosphorus Sorption

Soils usually contain very low amounts of P, 0.04 to 0.11%, among which the phosphates of Ca, Fe and Al are believed to be the predominate forms (Hemwall, 1957). Ca phosphates are

abundant in alkaline or calcareous soils and Al and Fe phosphates are preponderant in acid soils (Hemwell, 1957; Dahnke and Malcolm, 1964; Kurtz, 1953; Olsen, 1953; and Smith, 1965). The overall P problem is threefold: (1) a small total amount present in soils, (2) the unavailability of such native forms, and (3) a marked fixation of added soluble P. Since crop removal of P is relatively low and world P supplies are huge, problem (1) of supplying total P is not serious. Increasing the availability of native soil P and retardation of fixation or reversion of added P are therefore of greatest importance.

The literature on factors governing P fixation and availability, (2) and (3), is enormous. Studies prior to 1953 on compounds formed during soil genesis and as a result of P fertilization in both acid and calcareous soils were reviewed by Kurtz (1953) and Olsen (1953). Smith (1965) has presented a recent review of Al and Fe phosphates in soils.

The nature of soil P after its sorption, even though the literature is flooded from contributions from all over the world, has been the subject of much controversy. Most of the controversy revolves around the question of whether soil phosphates are present as precipitates or as adsorbed anions. Kurtz, Deturk, and Bray (1946), Fried and Dean (1955), Baker (1960) and Murrnann and Peech (1969a) have shown that soil P acts like an adsorbed ion. Cole and Jackson (1950, 1951), Bradly

and Sieling (1953), and Metzger (1940) have concluded that P sorption is primarily a precipitation reaction. Kittrick and Jackson (1955) have even observed the crystalline precipitate under an electron microscope. Beaton, Charlton, and Speer (1963) have found dicalcium·phosphate dihydrate ($CaHPO_4$ $2H_2O$) and hydroxy apatite ($Ca_{10}(OH)_2(PO_4)_6$) to be the soil fertilizer reaction product in a calcareous soil. Lindsay, et al. (1962) have identified about 30 crystalline P compounds as soil fertilizer reaction products. Several others have related soil phosphate potential^{sp} to the potential of specific Ca-P compounds and solubility product principle to the presence of discrete P compounds in soils. Fried and Shapiro (1960) suggest that two approaches to P sorption, mineralogical precipitation and adsorption, are not necessarily incompatible. Since soil is a dynamic system, the possibility of both processes occuring is plausible (Smith, 1965). Bache (1964) using pure clay and oxide mineral systems had suggested that P sorption takes place in three stages of reaction:

(1) A high energy chemisorption of small amounts of P;

(2) Precipitation of a separate P phase, and

(3) A low energy sorption of P onto precipitates.

Boischot, Coppenet and Hebert (1950) and Olsen (1953) had reported that the mechanism of P sorption in calcareous soils was dependent on the amount of P in solution. The P was

adsorbed onto the $CaCO_3$ until a critical higher P conc was reached in solution, then precipitation occurred and equilibrium conc of P dropped below that found before precipitation began.

The primary objective of defining the nature of soil-P system is basically two fold: (1) creation of knowledge through basic research, and (2) prediction of the pattern of P supply to growing plants. Considerable effort has been devoted to the second objective. Total soil P failed to correlate with plant uptake of P. Extraction of soils with various chemical mixtures designed to remove all or a portion of P postulated to be absorbed by plants have been tried. Although the theoretical basis for this approach is very doubtful, as a purely empirical procedure, it has proved useful among soils of the similar characteristics.

Methods have been proposed to measure the P adsorbing capacity of acid soils (Bass and Sieling, 1950; and Dean and Rubins, 1947) and evidence presented to show how such measurements aid in the problem of estimating soil P availability. Recent studies have suggested that the adsorbed soil P (Fried and Shapiro, 1956; Ozanne and Shaw, 1967; and Rennie and Mckercher, 1959) and percentage P saturation of the adsorption maximum is closely related with the equilibrium P conc in soil and hence have an important influence on plant available P.

The Langmuir adsorption isotherm has a sound theoretical derivation to obtain an adsorption maximum and is discussed in the following section.

The Langmuir Adsorption Isotherm

A model for the adsorption process and particularly for the chemisorption process was presented by Langmuir in 1918 and led him to a simple but important theoretical derivation of an adsorption isotherm. The adsorption isotherm for an ideal case which is pertinent to the present study is discussed here. For such a case Langmuir made the following assumptions:

(1) A unimolecular layer of adsorption -- only one layer of adsorbate adsorbed on the surface of the adsorbent.

(2) Uniformity in adsorption sites -- each adsorbate has an equal probability of access, i.e. adsorption to each site and also the heat of adsorption is the same for all sites and does not depend on the fraction covered θ.

(3) The solid surface contains a fixed number of adsorption sites.

(4) Non-interacting adsorption -- occupancy of one site exerts no influence upon those adjacent (no adsorbate interaction).

The Langmuir theory suggests that the rate of evaporation is proportional to the fraction of the surface covered and can be written, therefore, as $K_1\theta$, where K_1 is some proportionality constant. This simple proportionality is an assumption that ignores the complications that often make the heat of adsorption dependent on the extent of coverage. The rate of condensation furthermore is taken to be proportional both to the gas pressure, which according to the kinetic molecular theory determines the number of molecular collisions per unit area per unit time, and to the fraction of the surface not already covered by adsorbed molecules, i.e. to $1-\theta$. It is assumed that only collisions with this exposed surface can lead to the adsorption of a molecule to the surface. At equilibrium then, the rate of evaportation must equal the rate of condensation, i.e.:

$$K_1\theta = K_2P(1-\theta) \qquad (1)$$

where K_2 is another proportionality constant. Rearrangement gives

$$\theta = \frac{K_2P}{K_1+K_2P} \qquad (2)$$

$$= \frac{KP}{1+KP} \qquad (3)$$

where K is the new constant $\frac{K_2}{K_1}$, sometimes called adsorption coefficient.

Inspection of equation (3) shows that a chemisorption type isotherm is obtained from this theory. At small values of P, where KP in the denominator can be neglected compared with 1, equation (3) reduces to a simple proportionality between θ and P and this behavior is that corresponding to the initial steep rise of the chemisorption curve. For sufficiently large values of P, θ approaches the constant maximum value of unity. For adsorption up to a monolayer, the amount of gas X/m, adsorbed at some pressure P and the amount of gas b needed to form a monolayer are related to θ according to:

$$\frac{X/m}{b} = \theta \tag{4}$$

and equation (3) becomes

$$X/m = \frac{KbP}{1+KP} \tag{5}$$

A more convenient form of the above equation is obtained by the arrangement

$$\frac{P}{X/m} = \frac{1}{Kb} + \frac{P}{b} \tag{6}$$

A plot of $\frac{P}{X/m}$ versus P will, if the experimental data are in accord with the Langmuir theory, yield a straight line with the intercept $\frac{1}{Kb}$ and the slope with the constant $\frac{1}{b}$. The

adsorption maximum b, the amount of gas needed to form a monolayer is simply the reciprocal of the slope of the regression line. The success of equation (6) in fitting experimental chemisorption type curves must not, of course, be taken as necessarily confirming the model and assumptions that have been used in the derivation.

The same equation often applies to the adsorption of a solute from a solution onto a solid adsorbent (Graham 1953), although the process is even more difficult to treat theoretically and hence the same rigorous theoretical basis is not as fully developed.

When Langmuir adsorption isotherm is applied to liquids or ions, P (pressure of the gas) in equation (6) is simply replaced by C; conc of adsorbate in solution.

Considering a function which represents adsorption equilibrium, Langmuir adsorption equation may also be derived for an ideal case as below:

For the adsorption process:

Free adsorbate molecules + vacant adsorptive sites = occupied sites; adsorption complex.

The equation for the equilibrium constant is written -

$$k = \frac{\text{(activity of occupied sites)}}{\text{(activity of vacant sites) (activity of free adsorbate molecules)}}$$

It is assumed that the activity coefficients of the occupied and unoccupied sites are the same and the equation becomes:

$$k = \frac{(\theta)}{(1-\theta)C} \qquad (7)$$

It is interesting to note that the equation for the equilibrium constant can be rewritten:

$$\theta = \frac{KC}{1+KC} \qquad (8)$$

which is the familiar Langmuir adsorption isotherm with kinetic terms replaced by constants readily determined from equilibrium data.

The standard free energy of adsorption may be calculated for an ideal system from the equilibrium constant -

$$-\triangle F^{o} = R\ T\ \ln K$$

This quantity represents the decrease in free energy of the system and constitutes a measure of the strength of the adsorption bond.

If K is known from equation (6), equation (7) may be used to predict the conc of adsorbate molecules in solution to any percentage saturation of adsorption maximum.

P adsorption data have commonly been described by Freundlich Isotherm (Boischat, et al, 1950; Russell and Low, 1954; and Kurtz, Deturk and Bray, 1946) an empirical equation of the form -

$$X/m = KC^{1/n}$$

where n is a constant greater than unity. This equation is not specific and generally applies to wide range of equilibrium P conc (not likely to be encountered in normal fertilizer applications of P) and cannot be used to calculate the adsorption maximum.

Olsen and Watanabe (1957) and Friend and Shapiro (1956) have shown that constants calculated from Langmuir isotherm permit a sound theoretical approach to some of the problems of P sorption in soils. In the present investigation therefore, Langmuir adsorption equation was used to calculate the P adsorption maximum.

MATERIALS AND METHODS

Materials

Soil profiles no. 1-9 from the podzol region in the northern one-half of the lower peninsula of Michigan were collected by Drs. A. E. Erickson and B. G. Ellis in the summer of 1967. Sixteen additional profile samples were obtained in the Fall of 1967. Four additional soil profiles no. 10-13, collected in 1961, were added to the above list. These samples were air dried, ground, mixed thoroughly, passed through a 2mm sieve, and stored for soil P to achieve equilibrium (White and Beckett, 1964). The profiles and their locations are given in Table 1.

Analytical Methods And Procedures

Time Adsorption Curves

A preliminary study undertaken to determine the time of equilibration or adsorption indicated a soil type and time interaction altering the rate of initial adsorption reaction and second or precipitation phenomenon. Data indicated however, that a 2-hour shaking period would permit completion of the adsorption reaction and eliminate complicating secondary reactions. White and Beckett (1964) also had reported that

Table 1. Profile no. horizons, soil types and locations of soils

Soil Profile no.	Horizon	Soil Type	Location
1	C	Dune Sand	Silver Lake (Oceana Co.)
2	A_1	Rubicon Sand	Silver Lake (Oceana Co.)
	A_2	" "	" "
	B	" "	" "
	C	" "	" "
3	A_0 & A_1	Rubicon Sand	Lake of Woods (Antrim Co.)
	A_2	" "	" "
	B	" "	" "
	C	" "	" "
4	A	Rubicon Sand	Otsego Lake (Otsego Co.)
	B	" "	" "
	C	" "	" "
5	A_2	Emmett Loamy Sand	West Branch of Sturgeon (Otsego Co.)
	AB	" "	" "
	Bir	" "	" "
	B_2	" "	" "
	C	" "	" "
6	A_1	Emmett Loamy Sand	West Branch of Sturgeon (Otsego Co.)
	A_2	" "	" "
	AB	" "	" "
	Bihr	" "	" "
	B_2	" "	" "

Table 1, cont'd

Soil Profile no.	Horizon	Soil Type	Location
7	A_1 & A_2	Grayling Sand	East Branch of Au Sable (Crawford Co.)
	B	" "	" "
	Bihr	" "	" "
	C	" "	" "
8	A_1 & A_2	Roseland Sand	Au Sable River (Crawford Co.)
	B	" "	" "
	C	" "	" "
9	A_1 & A_2	Rubicon Sand	Au Sable River (Crawford Co.) below Grayling
	Bihr	" "	" "
	C	" "	" "
	C_2	" "	" "
10	A_1	Kalamazoo Loam	Richland (Kalamazoo Co.)
	B_1	" "	" "
	B_{21}	" "	" "
	B_{22}	" "	" "
	B_3-C_1	" "	" "
	D	" "	" "
11	A_1	Warsaw Loam	Schoolcraft (Kalamazoo Co.)
	B_1	" "	" "
	B_{21}	" "	" "
	B_{22}	" "	" "

Table 1 cont'd

Soil Profile no.	Horizon	Soil Type	Location
11	B_{23}	Warsaw Loam	Schoolcraft (Kalamazoo Co.)
	D	" "	" "
12	A_1	Ontonagon Clay	Ewen (Ontonagon Co.)
	A_2	" "	" "
	AB	" "	" "
	B_{21}	" "	" "
	B_{22}	" "	" "
	C	" "	" "
13	Ap	Munising Sandy Loam	Larson Farm (Houghton Co.)
	Bir	" "	" "
	A_2	" "	" "
	B	" "	" "
	C	" "	" "
14	A	Sims Clay Loam	Schean Farm (Saginaw Co.)
	B	" "	" "
	C	" "	" "
15	A	McBride Sandy Loam	Comden Farm (Montcalm Co.)
	B	" "	" "
	C	" "	" "

Table 1, cont'd

Soil Profile no.	Horizon	Soil Type	Location
16	A	Conover Loam	Sloan Creek (Ingham Co.)
	B	" "	" "
	C	" "	" "
17	A	Parkhill Clay Loam	Davis Farm (Sanilac Co.)
	B	" "	" "
	C	" "	" "
18	A	Montcalm Loamy Sand	Hey Farm (Montcalm Co.)
	B	" "	" "
	C	" "	" "
19	A	Hillsdale Sandy Loam	Deercreek (Ingham Co.)
	B	" "	" "
	C	" "	" "
20	A	Miami Loam	Deercreek (Ingham Co.)
	B	" "	" "
	C	" "	" "
21	A	Spinks Loamy Sand	Sloan Creek (Ingham Co.)
	B	" "	" "
	C	" "	" "

Table 1, cont'd

Soil Profile no.	Horizon	Soil Type	Location
22	A	Spinks Loamy Sand	Water-shed (Ingham Co.)
	B	" "	" "
	C	" "	" "
23	A	Brookston Clay Loam	College Farm (Ingham Co.)
	B	" "	" "
24	A	Brookston Loam	Sloan Creek (Ingham Co.)
	B	" "	" "
	C	" "	" "
25	A	Sims Sandy Clay Loam	Ferden Farm (Saginaw Co.)
	B	" "	" "
	C	" "	" "
26	A	Miami Sandy Loam	College Farm (Ingham Co.)
	B	" "	" "
	C	" "	" "
27	A	Conover Loam	College Farm (Ingham Co.)
	B	" "	" "
	C	" "	" "
28	A	Spinks Loamy Sand	Water-shed (Corn) (Ingham Co.)
	B	" "	" "

Table 1, cont'd

Soil Profile no.	Horizon	Soil Type	Location
28	C	Spinks Loamy Sand	Water-shed (Corn) (Ingham Co.)
29	A	Muck	Muck Experimental Farm (Clinton Co.)
	B	"	" "
	C	"	" "

an equilibration period of 1 or 2 hours is sufficient for (a) most of the labile inorganic P to come in equilibrium with ambient solution and (b) for period greater than 2 hours, onset of microbial activity is pronounced causing a decrease in equilibrium P conc or increase in potential^{sp} measured.

Typical time adsorption curves indicate an initial fast reaction followed by a secondary reaction which proceeds at a slow and almost constant rate. Studies on the effect of soil: solution ratio on the Freundlich isothorm had shown this variation to be small (Davis, 1935; and Kurtz et al., 1946). Since recent investigations by White and Beckett (1964) have confirmed that the potential$^{sp}_{eq}$ is independent of soil:solution ratio for soils under prolonged storage, this variable was not investigated further and a soil:solution ratio of 1:10 with a 2 hours equilibriation time was adopted.

Potential^{sp}

Five gram soil samples were equilibrated for 2 hours with 50.0 ml of 0.01 M $CaCl_2$ of varying P conc ($Ca(H_2PO_4)_2\ H_2O$). Conc of P used varied in general between 0 and 50.0×10^{-5} M. For certain soils a level of P as high as 150.0×10^{-5} M was used, for at lower levels equilibrium P conc in solution was too low to detect accurately. The suspensions were cleared by filtering and/or centrifuging at 3000 rpm for 5 minutes.

Total inorganic P was determined by the Mo blue method in sulfuric acid system (Jackson, 1958).

The pH of the supernatant solution was measured with a Beckman Model G pH meter using glass electrode. Ca was determined on 303 Perkin Elmer Absorption Spectrophotometer. The latter did not change significantly from 0.01 M nor did the pH values vary over the range of P conc studied. The potentials[sp] were calculated according to White and Beckett (1964) as outlined below:

$$1/2\ pCa = 1/2\ (-\log(Ca))$$

$$(Ca) = f\ [Ca] \leftarrow \text{conc in moles}$$

Where:

(Ca) = activity of Ca

$$\log f = \frac{-0.AZ^2\sqrt{u}}{1+aB\sqrt{u}}$$

$A = 0.5$

a = "effective diameter" of the ion

Z = valency of the ion

u = the ionic strength $1/2 \sum_i M_i Z_i^2$ (M_i is molality of i ion)

B = constant for a given solvent

$$(H_2PO_4) = \frac{(H^+)}{\frac{(H^+)}{f_1} + \frac{K_2}{f_2}} \times \text{total P}$$

where (H^+) = H^+ activity (from pH measurements)

f_1 = activity coefficient of $H_2PO_4^-$

f_2 = activity coefficient of $HPO_4^=$

The ionic strength was taken to approximate that for $CaCl_2$ because of the preponderance of Ca ions in the system.

The potential^{sp} equals 1/2 p Ca + pH_2PO_4. Therefore, as the logarithm of a reciprocal, the potential^{sp} increases as the activity product $aCa^{\frac{1}{2}} \times aH_2PO_4$ decreases.

The difference between the initial P conc and equilibrium P conc of each solution gave the amount of P gained or lost by 5.0g of soil. Regression analysis by Controlled Data 3600 computer, was run between $\pm \Delta$ P/g P soil and the corresponding potential^{sp}. The potential$^{sp}_{eq}$ was calculated from the regression equation when $\Delta P = 0$. This is the potential^{sp} of the solution with which the original soil undergoes no net exchange of P during the equilibration time.

Potential Buffering Capacity (PBC)

Beckett and White (1964) following Schofield's suggestion (1955) proposed PBC as the quantitative measure of ability of a soil to maintain the potential^{sp} against P withdrawl. The PBC for P was defined as $(dQ/dI)_I$ or $(\Delta Q/\Delta I)_{I-I^1}$ at a given potential^{sp} (I) or over a given range of potential^{sp} (I-I^1), respectively. The Q and I represent the quantity of P (extensive parameter) and potential^{sp} or P activity (intensive parameter), respectively.

In the present study PBC of the soil was calculated by the regression equation between $\pm \Delta$ P/g soil and potential^{sp}.

P Adsorption Maximum

As discussed in the preceding chapter, Langmuir adsorption isotherms were run for the data used to calculate potential $\frac{sp}{eq}$. The zero levels of P however, were excluded from the run. The reciprocal of the slope $\frac{1}{b}$ of the Langmuir adsorption equation was obtained as the P adsorption maximum.

Extractable Al and Free Iron Oxide

Extractable Al was determined by "aluminon" method as described by Mclean (1965) and free iron oxides by "orthophenanthroline" method described by Olson (1965).

Bulk Density

Bulk density determinations were done in Soil Physics laboratory by "Core Method" Blakes (1965).

RESULTS AND DISCUSSION

Equilibrium Potential^{sp} and Equilibrium Conc of Inorganic P

A typical plot of potential^{sp} vs $\pm$ P/g soil is presented in Fig. 1. The soils for the plot were selected to give a range in the slope and the X intercept. The $\pm$ P/g soil showed a fairly good linear regression on potential^{sp}, and a "r" value on an average of 0.982 was obtained. The potential$^{sp}_{eq}$ and total P at equilibrium (i.e. at Δ P=0 herein after called TPeq) calculated from regression equation are given in Table 2. The TPeq was calculated by subtracting 1/2 pCa from potential$^{sp}_{eq}$ and then applying the following equation:

$$TPeq = \frac{(10^{-pH_2PO_4})}{f\ 1} + \frac{(10^{-pH_2PO_4}) \times 10^{-7.2}}{(10^{-pH}) f\ 2}$$

where f 1 and f 2 are the activity coefficients of $H_2PO_4^-$ and $HPO_4^=$ respectively, and were discussed earlier.

Data in Table 2, in general, reveal low amounts of TPeq. The TPeq however, ranged from 0.08 x 10^{-6}M for Emmett loamy sand Bihr (6) to 17.37 x 10^{-6}M for Spinks loamy sand A (22). The podzolic profiles no. 1-9, and Munising sandy loam (13) had in general lower TPeq or higher potential$^{sp}_{eq}$ than found in other profiles. In particular, the B horizons have exceedingly low amounts of P at equilibrium. The A horizon in general had higher TPeq within the group. This trend appears to be negatively correlated with the P adsorption maximum for the soil horizons discussed later.

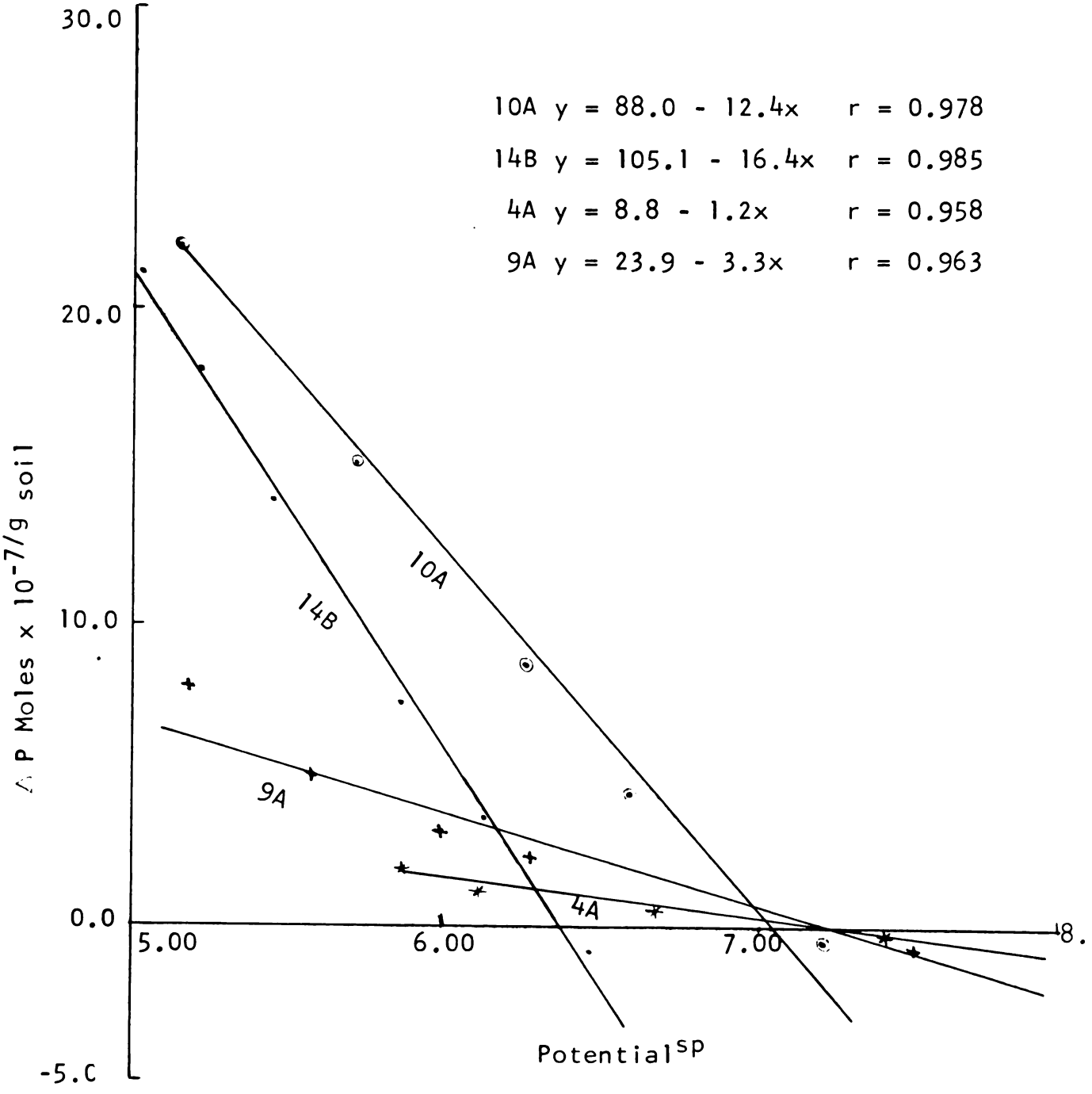


Fig. 1. Relationship between potential^{sp} and P/g soil.

Table 2. The potential$^{sp}_{eq}$ and TPeq in 29 Michigan soil profiles

Soil type		pH	Potential$^{sp}_{eq}$	TPeq
				Mx10-6
1 Dune Sand		6.5	7.392	0.98
2 Rubicon Sand	A_1	7.2	7.912	0.62
	A_2	6.8	7.967	0.33
	B	6.7	7.658	0.62
	C	6.4	7.523	0.68
3 Rubicon Sand	A_o-A_1	6.7	7.696	0.56
	A_2	5.5	7.283	0.94
	B	4.9	7.422	0.66
	C	5.7	7.069	1.58
4 Rubicon Sand	A	6.4	7.400	0.90
	B	6.5	7.455	0.84
	C	6.6	7.677	0.54
5 Emmett Loamy Sand	A_2	7.0	7.481	1.28
	AB	6.6	7.583	0.67
	Bir	6.9	7.657	0.75
	B2	6.8	7.758	0.54
	C	7.1	7.833	0.65
6 Emmett Loamy Sand	A1	7.1	7.562	1.21
	A_2	6.9	7.711	0.67
	AB	6.8	8.061	0.27
	Bihr	6.5	8.460	0.08
	B_2	6.8	7.858	0.43
7 Grayling Sand	A1 & A2	5.6	7.301	0.91
	B	6.5	7.499	0.76
	Bihr	7.4	8.460	0.25
	C	7.0	8.049	0.34
8 Roseland Sand	A_1,A_2	5.8	7.148	1.33
	B	6.8	8.139	0.22
	C	6.5	7.701	0.48
	D	6.3	8.037	0.20

Table 2, cont'd

Soil type		pH	Potential $^{sp}_{eq}$	TPeq
				Mx10^{-6}
9 Rubicon Sand	A1 & A_2	4.1	7.529	0.51
	Bihr	4.8	7.834	0.26
	C	6.1	7.549	0.57
	C2	6.2	7.721	0.39
10 Kalamazoo Loam	A1	6.6	7.20	1.63
	B_1	6.7	7.380	1.17
	B_{21}	6.0	7.590	0.50
	B_{22}	6.7	7.392	1.34
	B_3-C_1	6.9	7.617	0.83
	C	7.5	7.947	0.96
11 Warsaw Loam	A	6.6	7.166	1.77
	B_1	5.0	7.346	0.79
	B_{21}	4.9	7.346	0.79
	B_{22}	4.7	7.323	0.83
	B_{23}	5.3	7.504	0.56
	C	5.9	7.791	0.31
12 Ontonagon Clay	A_1	5.4	7.321	0.85
	A_2	5.4	7.253	1.00
	AB	5.2	7.394	0.71
	B_{21}	6.5	7.375	1.02
	B_{22}	6.9	7.519	1.04
	C	7.2	7.717	0.98
13 Munising Sandy Loam	AP	5.6	7.199	1.15
	Bir	5.4	7.573	0.48
	A_2	4.8	7.552	0.49
	B	4.4	7.433	0.64
	C	5.0	7.586	0.46
14 Sims Clay Loam	A	7.2	7.578	1.35
	B	5.7	6.509	7.25
	C	7.1	7.459	1.54
15 McBride Sandy Loam	A	6.1	6.591	5.18
	B	6.3	7.108	1.69
	C	5.2	7.401	0.70

Table 2, cont'd

Soil type		pH	Potential $\frac{sp}{eq}$	TPeq
				$Mx10^{-6}$
16 Conover Loam	A	6.1	7.000	2.01
	B	6.6	7.199	1.64
	C	6.8	7.295	1.56
17 Parkhill Clay Loam	A	6.9	7.141	2.49
	B	6.1	7.009	1.97
	C	6.9	7.660	0.75
18 Montcalm Loamy Sand	A	6.8	7.430	1.45
	B	5.6	7.151	1.29
	C	5.7	7.246	1.05
19 Hillsdale Sandy Loam	A	6.2	7.121	1.57
	B	6.3	7.263	1.18
	C	6.5	7.179	1.60
20 Miami Loam	A	6.9	6.906	4.28
	B	6.9	7.518	1.04
	C	6.7	7.454	0.99
21 Spinks Loamy Sand	A	6.3	7.192	1.39
	B	6.1	7.319	0.96
	C	6.2	7.460	0.72
22 Spinks Loamy Sand	A	6.3	6.100	17.37
	B	6.4	7.506	0.71
	C	6.8	7.155	2.16
23 Brookston Clay	A	6.5	6.476	8.12
	B	6.2	7.357	0.91
24 Brookston Loam	A	6.9	7.762	0.59
	B	6.6	7.818	0.39
	C	7.3	7.716	1.15

Table 2, cont'd

Soil type		pH	Potential ϕ_{eq}^{sp}	TPeq
				$M \times 10^{-6}$
25 Sims Sandy Clay Loam	A	6.7	6.949	3.17
	B	6.5	7.726	0.45
	C	6.8	7.960	0.34
26 Miami Sandy Loam	A	6.1	6.766	3.45
	B	7.2	7.449	1.82
	C	6.8	7.824	0.46
27 Conover Loam	A	6.1	7.413	0.77
	B	5.8	7.558	0.52
	C	6.7	7.477	0.94
28 Spinks Loamy Sand	A	5.7	6.86	3.82
	B	5.8	7.047	1.68
	C	6.7	7.233	1.64
29 Muck	A	6.0	6.147	14.05
	B	6.8	7.036	2.85
	C	6.2	6.894	2.66

The Sims clay loam B (14), McBride sandy loam A (15), Miami loam A (20), Miami Sandy loam (26), Spinks loamy sand A (22,28), Brookston clay loam A (23), and Muck A (29) had higher TPeq conc than other soils. These P levels fall in the range needed for optimum plant growth (Aslying, 1954). Aslying (1954) found crops growing on soils with potential^{sp} greater than 8, corresponding to a P conc in the soil solution of 10^{-7}M or less, usually responded very well to P fertilizer; whilst crops on soils with potential^{sp} of 6 or less, P conc of 10^{-5}M or more, rarely responded. Recently Ozanne and Shaw (1968) found that pasture plants growing on soils not adsorbing P from equilibrium solution containing 10^{-5}M P or more did not respond to applied P. Russell (1961) also writes -

> "Experiments to measure the minimum concentration of phosphate needed for good plant growth are technically difficult to carry out, but there seems no doubt that most crops can make adequate and possibly optimum growth if phosophate concentration around their roots is kept at 10^{-5}M, many crops may be able to make good growth if it is as low at 10^{-6}M, provided the conditions of growth allow good root development, but that for at least some crops 10^{-7}M is much too dilute; and these results are concordant with the observed field behaviour."

The higher TPeq in soil suspension in all the foresaid soil horizons are either because of high percentage saturation of the adsorption maximum, which probably is a consequence of recent treatment with P fertilizers, and/or bonding energy of P on adsorbent. Recently Murrmann and Peech (1969a) observed simultaneous increase in labile and soluble P in 31 soil samples

collected from old fertilizer experiments in Illinois, Kentucky, Ohio, and Pennsylvania. Spinks loamy sand A (22) which showed highest TPeq, 17.37×10^{-6}M has a low adsorption maximum (4.98 mg/100g, Table 3) and is also highly fertilized, (A.E. Erickson, 1969, Personal communication, Michigan State University). The same is true for Spinks loamy sand A (28) except it has twice the adsorption maximum of Spinks loamy sand A (22) and it is probably for this reason the TPeq conc in the former is approximately 1/5th of the latter.

All horizons of Muck profile have higher TPeq with the A horizon as high as 14.05×10^{-6}M P. Apart from the degree of P saturation of the adsorption maximum, the low energy of adsorption of P on organic matter (Table 3) is probably another reason for the observed higher TPeq. Harter (1969) had attributed most of the P adsorption on organic matter to anion exchange and this will have a lower energy of adsorption than Fe and Al-P adsorption complex. Further the lack of Fe and Al in all the horizons of muck will decrease the chances of precipitation of adsorbed P. But the reason for an unusually high P content in Sims clay loam B (14) is not apparent.

The uptake of 10 to 20 kg. of P/ha by an average crop requires hundreds of times as much P as is normally present in solution in a fertile soil at one time within the depth of rooting. Therefore replenishment of the soil solution, i.e. rate of release of P from soil to the solution, is of paramount

importance. The P adsorption maximum and potential buffering capacity is discussed in this context in the following sections.

P Adsorption Maximum

The adsorption maximum for the soils studied and K, the constant proportional tofree energy of adsorption is given in Table 3. A typical Langmuir adsorption plot of the data is presented in Fig. 2.

Surface P already present in soil is related to the equilibrium P conc according to the equation $X/m = \frac{Kbc}{1+Kc}$. Ideally the adsorption would be determined on an adsorbate free surface, but because of nonfeasibility of this restriction with soils, a correction by adding the amount of surface P determined by a separate analysis to the X/m is made. Since this correction has negligible effect on $\frac{1}{b}$ (Olsen and Watanabe, 1957) particularly on nonfertile soils, no attempt was made to correct the data for the amount of surface P present initially on the soils.

The data (Fig. 2) show satisfactory agreement with the Langmuir isotherm as a straight line relationship and a r value, on an average of 0.985 was obtained.

The soils studied show a great deal of variation in their ability to adsorb P (Table 3). This is also true for the horizons of most profiles, particularly the sandy podzolic group. The

Table 3. P adsorption maximum and K, the free energy of adsorption for 29 Michigan soil profiles

Type		Bulk density[x]	$K \times 10^4$	Adsorption Maximum	
		g/cm^3	$\frac{1}{M} \times 10^4$	mg/100g	Kg/ha
1 Dune		1.49	4.51	1.88	85.4
2 Rubicon Sand	A1	1.24	0.77	4.24	160.1
	A2	1.49	1.97	3.88	176.0
	B	1.41	4.00	10.23	826.4
	C	1.50	5.81	10.75	491.6
3 Rubicon Sand	A0-A1	1.24	1.57	3.47	131.2
	A2	1.49‡	0.99	4.40	200.1
	B	1.41+	5.93	11.28	482.9
	C	1.50+	2.70	11.49	525.5
4 Rubicon Sand	A	1.24+	3.90	1.07	40.4
	B	1.41+	5.14	27.78	1193.8
	C	1.50+	4.44	12.50	571.5
5 Emmett Loamy Sand	A2	0.62	1.63	4.43	83.6
	AB	1.42+	3.06	10.20	441.6
	Bir	1.42	3.43	9.71	420.2
	B2	1.64	3.22	9.71	485.3
	C	1.64+	3.10	4.81	240.3
6 Emmett Loamy Sand	A1	1.17+	1.81	5.08	181.0
	A2	1.41+	1.98	4.63	199.0
	AB	1.42+	4.52	10.53	455.6
	Bihr	1.42+	3.83	9.01	389.9
	B2	1.64+	4.09	10.64	531.8
7 Grayling Sand	A1&A2	1.17+	2.32	8.77	312.8
	B	1.42+	6.27	14.49	627.3
	Bihr	1.46+	7.43	19.23	855.8
	C	1.60+	4.70	10.64	518.8

x - Data were provided by courtesy of Dr. A. E. Erickson, 1969 Michigan State University, East Lansing.

+ - An estimate

Table 3, cont'd

Type		Bulk density	$K \times 10^4$	Adsorption Maximum	
		g/cm^3	$\frac{1}{M} \times 10^4$	mg/100g	Kg/ha
8 Roseland Sand	A0&A1	1.17+	2.81	7.41	264.1
	B	1.42+	8.80	22.73	983.7
	C	1.44	9.17	18.18	831.3
	D	1.60+	6.44	9.71	473.5
9 Rubicon Sand	A0&A1	1.17	36.70	2.73	97.2
	B	1.46	8.00	41.67	1854.2
	C	1.50	7.55	12.05	550.8
	C2	1.55+	2.64	6.89	325.8
10 Kalamazoo Loam	A1	1.34+	2.24	9.71	396.5
	B1	1.50+	1.69	20.41	933.1
	B21	1.50+	11.17	14.93	682.4
	B22	1.50+	5.71	12.50	571.5
	B3	1.60+	6.00	7.94	387.1
	D	1.60+	3.59	9.62	468.9
11 Warsaw Loam	A1	1.34+	3.00	18.52	756.4
	B1	1.50+	4.17	40.00	1828.8
	B21	1.50+	5.00	50.00	2286.0
	B22	1.50+	5.00	22.22	1016.0
	B3-C	1.60+	6.01	10.99	535.9
	D	1.60+	5.45	4.60	223.7
12 Ontonagon Clay	A1	1.34+	2.22	50.00	2042.2
	A2	1.34+	3.75	33.33	1361.4
	AB	1.50+	5.67	29.41	1344.7
	B21	1.50+	4.50	18.52	846.7
	B22	1.50+	3.94	14.93	682.4
	C	1.60+	4.12	14.29	696.7
13 Munising Sandy Loam	Ap	1.34+	5.13	24.39	996.7
	Bir	1.50+	10.50	23.81	1088.6
	A2	1.50+	7.80	12.82	586.2
	B	1.50+	4.80	20.83	952.5
	C	1.60+	3.33	10.00	480.8
14 Sims Clay Loam	A	1.35	3.70	30.00	1234.4
	B	1.36	0.79	12.20	505.5
	C	1.56	5.56	20.00	951.0

Table 3, cont'd

Type		Bulk density	$K \times 10^4$	Adsorption Maximum	
		g/cm^3	$\frac{1}{M} \times 10^4$	mg/100g	Kg/ha
15 McBride Sandy Loam	A	1.47	2.46	10.42	466.7
	B	1.49	4.11	12.82	582.3
	C	1.46	7.30	13.70	609.6
16 Conover Loam	A	1.58	3.37	10.99	529.2
	B	1.62	5.57	25.64	1266.1
	C	1.83	4.41	13.33	743.7
17 Parkhill Clay Loam	A	1.04	6.28	5.00	158.5
	B	1.47	2.31	8.85	396.5
	C	1.60+	6.67	16.67	812.8
18 Montcalm Loamy Sand	A	1.80	4.41	6.14	336.6
	B	1.58	5.19	9.17	441.8
	C	1.50	3.38	5.32	245.8
19 Hillsdale Sandy Loam	A	1.49	3.16	12.66	574.9
	B	1.50	5.00	11.11	508.0
	C	1.75	3.79	10.99	586.2
20 Miami Loam	A	1.51	1.15	16.67	767.1
	B	1.66	5.93	12.05	609.6
	C	1.78	4.77	16.13	875.7
21 Spinks Loamy Sand	A	1.26	2.68	10.10	387.9
	B	1.40	6.33	13.16	561.4
	C	1.18	3.54	7.63	274.6
22 Spinks Loamy Sand	A	1.39	1.50	4.98	210.8
	B	1.50	2.98	8.00	365.8
	C	1.45	1.16	11.49	508.0
23 Brookston Clay Loam	A	1.32	0.56	27.03	1087.4
	B	1.44	6.44	17.24	756.7
24 Brookston Loam	A	1.39	6.00	18.52	784.6
	B	1.61	6.89	16.13	791.5
	C	1.77	2.96	14.08	759.83

Table 3, cont'd

Type		Bulk density	$K \times 10^4$	Adsorption Maximum	
		g/cm^3	$\frac{1}{M} \times 10^4$	mg/100g	Kg/ha
25 Sims Sandy Clay Loam	A	1.00	1.56	12.50	381.0
	B	1.51	2.95	17.86	821.9
	C	1.60	10.20	19.61	956.2
26 Miami Sandy Loam	A	1.34	0.53	10.87	443.9
	B	1.58	1.97	14.08	678.3
	C	1.54	10.80	18.52	869.3
27 Conover Loam	A	1.45	2.26	10.53	465.2
	B	1.61	11.17	14.92	732.4
	C	1.80	6.08	13.70	751.6
28 Spinks Loamy Sand	A	1.28	1.48	11.49	448.4
	B	1.44	1.02	17.54	770.0
	C	1.40	1.23	8.40	358.6
29 Muck	A	0.50+	0.56	19.50+	297.2+
	B	0.55+	0.60	28.57	478.0
	C	0.60+	0.60	21.28	389.11

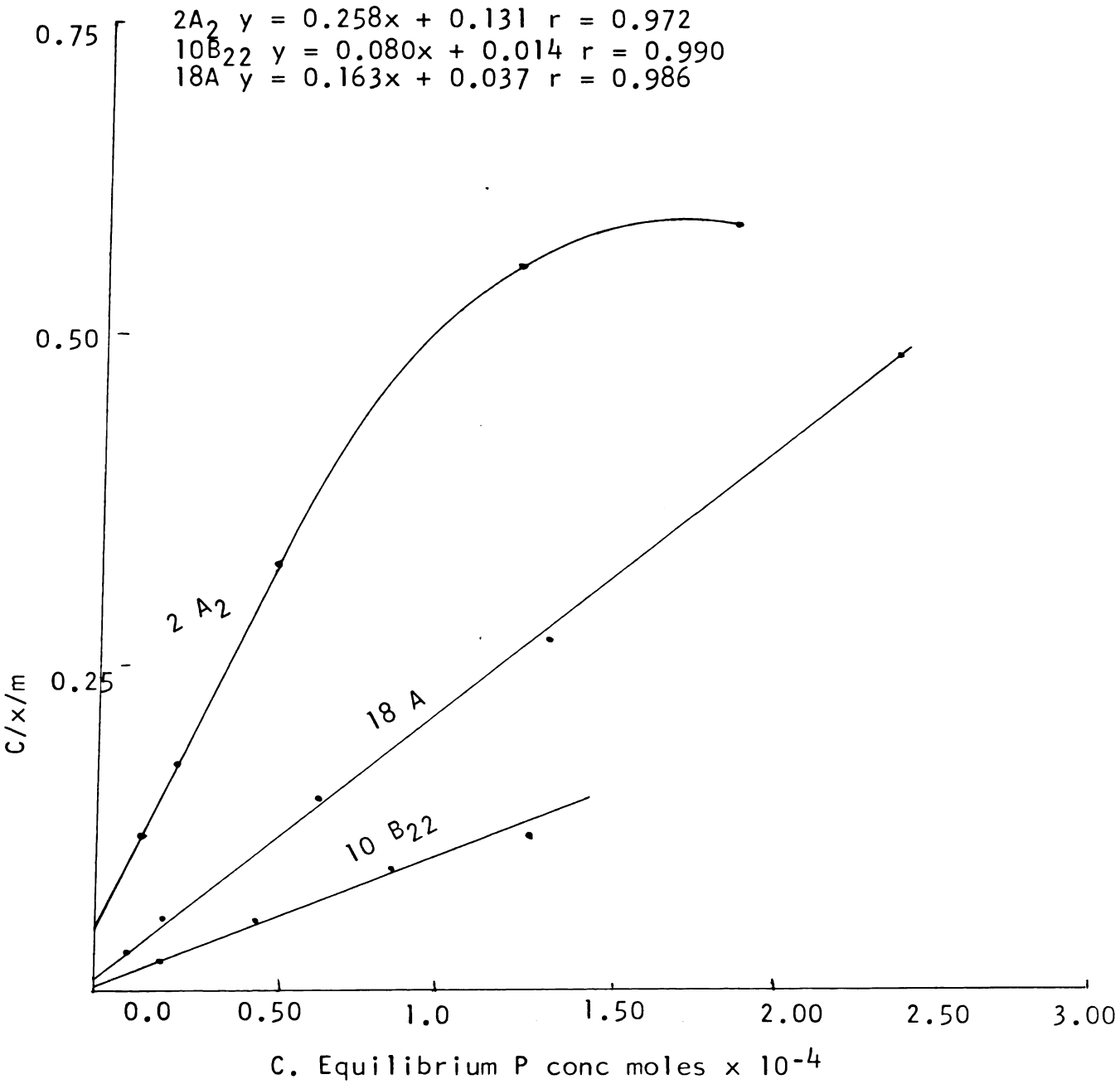


Fig. 2. Langmuir adsorption plot for P adsorption data

two extremes in P adsorption maximum were 40.4 and 2042.2 Kg/ha for Rubicon sand A (4) and Ontonagon clay A (12), respectively. The Ontonagon Clay (12) has a very high free iron oxide content (39.57 meq/100g) and has very high clay content; whereas, Rubicon sand A (4) represents minimal soil development and contains low amounts of free iron oxide (5.14) and extractable Al (0.067 meq/100g soil). A regression of P adsorption maximum on extractable Al and free iron oxide had 0.002 and 0.163 partial correlation coefficients respectively, when all the soils were pooled together. However, when regression was run for the individual soils (soil with more than 3 horizons, since multiple correlation cannot be computed with only 3 points), significant correlation coefficients between extractable Al and free iron oxides on one hand, and P adsorption maximum on the other were obtained. This suggests that factors other than Al and iron oxide, such as the clay content (its quantity and quality) and others are important in P sorption and hence were masking the regression of P adsorption on Al and Fe when all soils were considered together.

In general the A_1 and A_2 horizons in sandy podzolic group have the lowest adsorption maximum and B horizons have comparatively very high adsorption capacity within the group. This trend is correlated with extractable Al and free iron oxide content of the horizons (Table 4). For Rubicon sand (2)

Table 4. Extractable Al and free iron oxide content of the 29 Michigan soil profiles

Type		Extractable Al	Free iron oxides
		meq/100g soil	
1 Dune Sand		0.044	3.429
2 Rubicon Sand	A	0.027	5.929
	A2	0.156	2.679
	B	1.822	11.072
	C	1.106	3.857
3 Rubicon Sand	A0&A1	0.059	9.643
	A2	0.128	5.357
	B	1.283	10.00
	C	1.195	5.536
4 Rubicon Sand	A	0.067	5.143
	B	2.056	16.429
	C	1.278	6.429
5 Emmett Loamy Sand	A2	0.043	9.143
	AB	0.293	13.943
	Bir	0.847	9.357
	B2	0.267	11.572
	C	0.161	8.00
6 Emmett Loamy Sand	A1	0.034	11.286
	A2	0.108	9.626
	AB	0.301	12.50
	Bir	0.389	14.643
	B2	0.194	17.143
7 Grayling Sand	A1&A2	0.256	8.572
	B	1.245	11.286
	Bihr	1.828	11.57
	C	0.780	7.714
8 Roseland Sand	A1&A2	0.687	6.429
	B	2.278	12.50
	C	2.278	7.50
	D	0.989	3.35

Table 4, cont'd

Type		Extractable Al	Free iron oxides
		meq/100g soil	
9 Rubicon Sand	A1&A2	0.220	3.07
	Bihr	3.634	16.429
	C	0.894	4.286
	C2	0.354	1.714
10 Kalamazoo Loam	A1	0.110	22.85
	B1	0.289	25.00
	B21	0.398	32.00
	B22	0.293	25.715
	B3C1	0.089	28.286
	D	0.133	26.429
11 Warsaw Loam	A1	1.283	29.286
	B1	2.222	33.572
	B21	2.889	32.00
	B22	1.561	19.786
	B23	0.709	13.215
	C-D	0.221	5.714
12 Ontonagon Clay	A1	0.955	39.572
	A2	0.689	40.572
	AB	0.672	39.00
	B21	0.394	39.00
	B22	0.361	39.00
	C	0.220	34.286
13 Munising Sandy Loam	Ap	2.211	25.00
	Bir	3.545	18.286
	A2	1.383	16.00
	B	1.828	22.286
	C	0.513	13.715
14 Sims Clay Loam	A	0.269	37.715
	B	0.733	12.143
	C	0.153	18.143
15 McBride Sandy Loam	A	0.366	15.429
	B	0.831	14.286
	C	0.304	24.143

Table 4, cont'd

Type		Extractable Al	Free iron oxides
		meq/100g soil	
16 Conover Loam	A	0.116	20.715
	B	0.522	22.143
	C	0.311	35.715
17 Parkhill Clay Loam	A	0.133	8.572
	B	0.256	13.857
	C	0.228	10.00
18 Montcalm Loamy Sand	A	0.209	34.286
	B	0.917	19.429
	C	0.367	6.429
19 Hillsdale Sandy Loam	A	0.598	21.429
	B	0.528	27.858
	C	0.598	18.572
20 Miami Loam	A	0.167	20.572
	B	0.639	21.429
	C	0.411	26.572
21 Spinks Loamy Sand	A	0.222	15.00
	B	0.950	15.00
	C	0.311	11.857
22 Spinks Loamy Sand	A	0.133	20.286
	B	0.222	20.286
23 Brookston Clay Loam	A	0.089	22.143
	B	0.197	30.00
24 Brookston Loam	A	0.100	12.143
	B	0.278	28.572
	C	0.211	29.143
25 Sims Sandy Clay Loam	A	0.057	27.143
	B	0.132	32.858
	C	0.200	30.858

Table 4, cont'd

Type		Extractable Al	Free iron oxides
		meq/100g soil	
26 Miami Sandy Loam	A	0.079	21.429
	C	0.333	29.143
27 Conover Loam	A	0.098	21.429
	B	0.361	35.144
	C	0.311	19.429
28 Spinks Loamy Sand	A	0.247	26.429
	B	0.339	35.144
	C	0.211	16.857
29 Muck	A	0.072	10.00
	B	0.076	7.857
	C	0.106	5.357

partial correlation coefficients of 0.999 and 0.979 for the regression of P adsorption maximum on extractable Al and free iron oxides respectively were obtained (Table 5). From the correlation coefficient data for other soils too, it appears that extractable Al is rather more important in P sorption for short equilibriation periods than the free iron oxide content of the soils. With the latter, negative correlation coefficients were even obtained (Table 5). However, not much reliance should be put on these correlations, because only one degree of freedom for error term was involved.

Of the fine textured soils, the Warsaw loam B_1, B_{21} and B_{22} (11), Ontonagon clay A_1, A_2 and AB (12) Munising sandy loam, Ap, Bir and B (13), Sims clay loam A (14), Conover loam B (16), and Brookston clay loam A (23), possess exceptionally high adsorbing capacities. These horizons also have relatively higher extractable Al contents. The P adsorption maximum for the various horizons of the finer textured profiles were not as distinctly differentiated as for the sandy podzolic group. Correspondingly there was a lack of such a distinction in the Al and Fe content of the horizons. Parkhill clay loam (17) has the lowest adsorption maximum for the A and B horizons among the fine textured soils. This is probably because of its calcareous nature and relatively lower content of Al and Fe.

Table 5. Correlation coefficients between P adsorption maximum and Fe and Al in soils

Soil Type	Correlation Coefficients	
	Free iron oxides	Extractable Al
2 Rubicon Sand	0.979*	0.999*
5 Emmett Loamy Sand	0.765ns	0.730ns
6 Emmett Loamy Sand	0.811ns	0.532ns
7 Grayling Sand	-0.268ns	0.976*
8 Roseland Sand	0.319ns	0.947*
9 Rubicon Sand	-0.996*	0.999**
10 Kalamazoo Loam	-0.9.428ns	0.790ns
11 Warsaw Loam	-0.403ns	0.957*
12 Ontonagon Clay	-0.912*	0.995**
13 Munising Sandy Loam	0.906	0.956*

* significant at 5% level

** significant at 1% level

ns non significant

The bonding energy calculated from the Langmuir plot of the data (Table 3), (K = slope/intercept) has a large error term inherent in the method of calculation. However, there is a trend for higher energy of adsorption of P with B horizons or horizons with higher Al and Fe content. The surface horizons often have lower bonding energy. The value of the bonding term calculated from the Langmuir equation provides an estimate of the average bonding energy of P on the major adsorbing surfaces. However, the P reacting initially at low surface coverage may be bound more strongly than that reacting subsequently if the bulk of the sorption sites are occupied. A linear fit of the data, however, with the Langmuir isotherm suggests near uniformity in bonding energy of P for the conc of P used.

Investigators have shown two stages of P sorption -- a rapid initial reaction followed by a relatively slow reaction (Low and Black, 1950). They indicated that this latter reaction would reach a definite end point with time.

The rapid initial sorption involves P ions becoming attached to exchangeable Al^{+3}, Fe^{+2+3}, and Ca^{+2} ions of the clay and hydrous oxides or these same ions held in the outer edges of the lattice. This reaction is a type of chemical adsorption involving primary valence bonds rather than a physical adsorption. It seems plausible to suggest that the extent of this initial reaction is determined by the adsorption maximum from the Langmuir isotherm.

Cole, Olsen and Scott (1953) have presented evidence that in the range of equilibrium conc where the Langmuir equation applies, essentially all of the P adsorbed on $CaCO_3$ was exchangeable with ^{32}P. Similar data implying a monolayer adsorption were found for P adsorbed on ferrated IRC 50 cation exchange resin (Fried and Dean, 1955) over the range of conc which followed the Langmuir isotherm. With higher P levels, however, less of the adsorbed P was exchangeable with ^{32}P and the isotherms deviated from a straight line. The deviation from the straight line was also noted in the present investigation at higher P conc for some soils, especially sandy podzolic A and A_2 horizons and certain low adsorbing fine textured soils.

The equation $C = \frac{\theta}{(1-\theta)K}$ discussed earlier suggests that a close relationship exists between percentage saturation of the adsorption maximum and TPeq in soil suspension. The theoretical relationship between these two variables for few typical A horizons representing the textural groups is illustrated in Fig. 3. The observed C values for the corresponding percent saturation of the adsorption maximum are also indicated. The close correlation between the percentage saturation of adsorption maximum and the corresponding TPeq, indicates that the amount of P in soil suspension closely reflects the degree of P saturation on the adsorbing surfaces

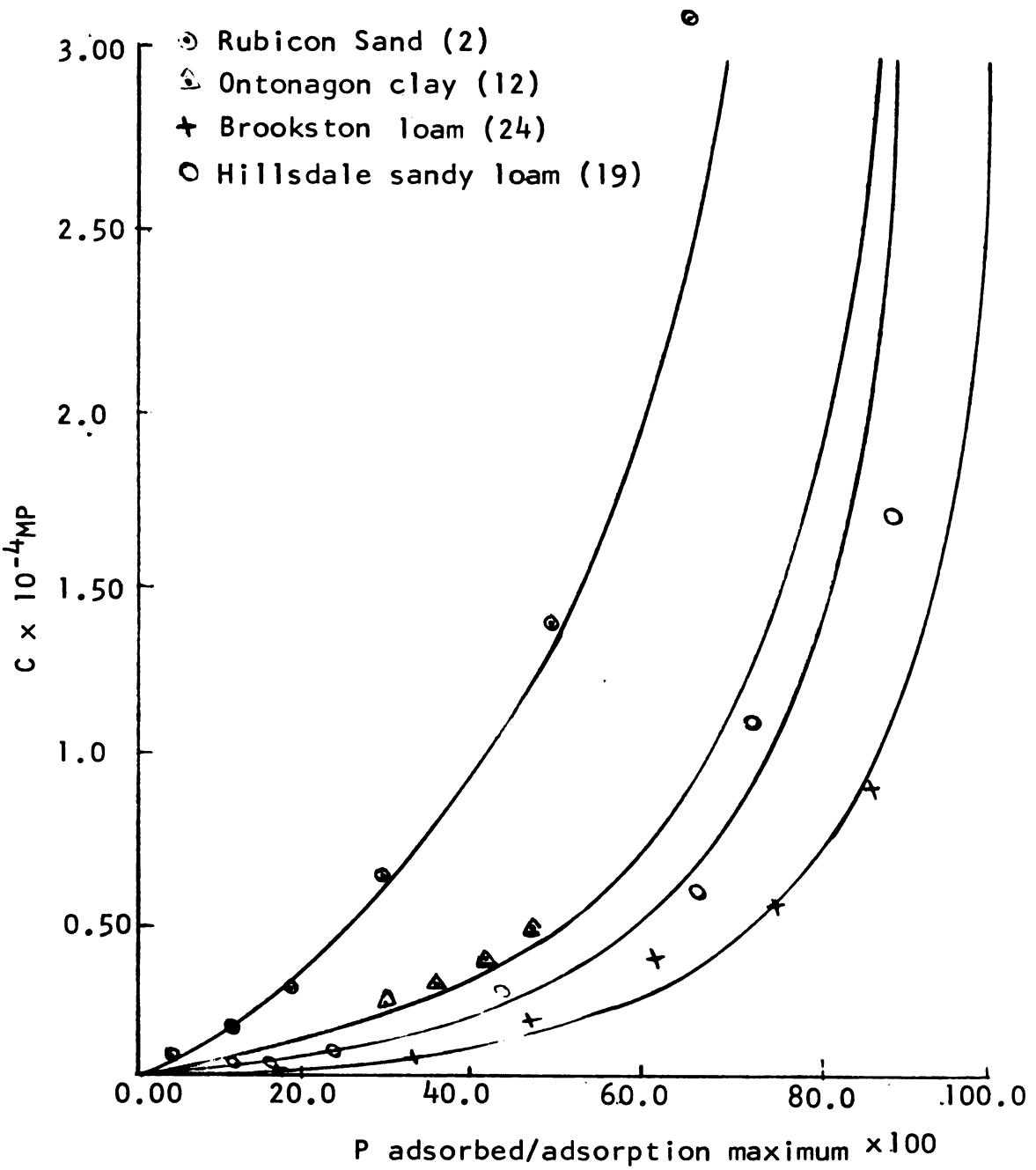


Fig. 3. Relationship between percent saturation of adsorption maximum and equilibrium P conc in soil solution

of soil complex. This relationship, however, appears to deviate at higher saturation in some cases. Beyond this point the predicted and the observed C's for the corresponding percent saturation of the adsorption maximum fell wide apart. This probably was because of precipitation at higher conc where data also deviate from the Langmuir isotherm. For normal soil fertilization practice however, the evidence presented herein strongly suggests that the adsorption maximum of a particular soil may be used to predict the TPeq; thus, given a required TPeq in soil suspension for optimum plant growth the degree of saturation of the adsorption maximum which is necessary to obtain the desired level may be calculated.

The degree of saturation of the adsorption maximum required to give a 1.0×10^{-5}MP in soil suspension and P (Kg/ha 22.86 cm) required to bring the soil to that level is given in Table 6. The conc of 1.0×10^{-5}MP was chosen since if this conc is maintained at soil-root interface, in the absence of other limiting factors, it should support optimum plant growth for most crops (Russell 1961, Ozanne and Shaw 1968). The fraction of the adsorption maximum already occupied was calculated using the equilibrium equation $C = \frac{\theta}{(1-\theta)K}$ and assuming that the TPeq obtained by White and Beckett procedure (1964) was governed by the above equation. Observed data do substantiate the assumption implied in calculation. Data in

Table 6. $Kg/ha_{0-22.86cm}$ of P needed to give 1.0×10^{-5}MP in soil solution

Soil type	Initial θ	θ Needed	P needed
			Kg/ha
1 Rubicon Sand	0.042	0.269	17.2
2 Rubicon Sand	0.007	0.120	14.3
3 Rubicon Sand	0.001	0.114	12.9
4 Rubicon Sand	0.034	0.281	7.5
5 Emmett Loamy Sand	0.020	0.140	7.5
6 Emmett Loamy Sand	0.018	0.159	20.2
7 Grayling Sand	0.021	0.189	39.4
8 Roseland Sand	0.036	0.220	43.5
9 Rubicon Sand	0.163	0.786	42.6
10 Kalamazoo Loam	0.035	0.183	44.0
11 Warsaw Loam	0.050	0.231	102.4
12 Ontonagon Clay	0.019	0.182	249.8
13 Munising Sandy Loam	0.051	0.339	211.2
14 Sims Clay Loam	0.048	0.270	271.5
15 McBride Sandy Loam	0.113	0.198	29.6
16 Conover Loam	0.063	0.253	74.9
17 Parkhill Clay Loam	0.135	0.386	29.8
18 Montcalm Loamy Sand	0.048	0.306	65.1
19 Hillsdale Sandy Loam	0.047	0.240	83.1
20 Miami Loam	0.047	0.104	32.4

Table 6, cont'd

Soil Type	Initial θ	θ Needed	P needed
			Kg/ha
21 Spinks Loamy Sand	0.036	0.211	51.0
22 Spinks Loamy Sand	0.207	0.130	--
23 Brookston Clay Loam	0.044	0.053	7.7
24 Brookston Loam	0.034	0.375	200.5
25 Sims Sandy Clay Loam	0.045	0.136	25.8
26 Miami Sandy Loam	0.018	0.050	10.8
27 Conover Loam	0.017	0.185	58.4
28 Spinks Loamy Sand	0.053	0.129	25.3
29 Muck	0.072	0.056	--

Table 5 demonstrate the differential capacity of soil to resist increase or decrease in P conc following addition or withdrawl of P bearing fertilizers to the soil. Ontonagon clay (12), Sims clay loam (14) and Brookston loam (24) have a very high requirement for P to yield desired P conc in solution; whereas, podzolic sands have a low requirement for P to bring the P conc to the same level. Moreover, at a given TPeq in soil solution, the adsorbed P in the soil solids is less in soils of coarse texture than of fine texture. The close agreement with the theoretical and observed values of TPeq in soil suspension had another very important implication, that adsorbed P being in equilibrium with the P in solution should serve as the primary source from which P is released upon depletion by plants. Machold (1962) had reported high correlations between P that equilibrated with ^{32}P and that absorbed by rye seedlings. In the light of the data obtained in the current investigation, Machold's (1962) findings may be interpreted to mean that P less accessible to exchange with ^{32}P, hence to equilibration, was also less available for uptake.

Since total adsorbed P does not reflect the TPeq in a soil suspension (at any one final solution conc a range of adsorbed P values were obtained depending on the characteristics of the soil) it would appear that surface P measurements alone will not be proportional to either available P or TPeq.

As the equation $C = \frac{\theta}{(1-\theta)K}$ suggests, K- the free energy of adsorption of P on the soil compex, besides θ; is important in producing a P buffering effect of soil against increase or decrease in P conc. The Ontonagon clay (12) had only a slightly greater requirement of P to bring the P level to 1.0×10^{-5}M compared to Brookston loam (24). The former, however, had an adsorption maximum of 2042 Kg/ha compared to 784 Kg/ha for the Brookston loam (Table 3). The greater P buffering effect of Brookston loam is because of its higher energy of adsorption of P compared to Ontonagon clay (Table 3). The same is true for Sims clay loam (14) which has an even higher P requirement than Ontonagon clay even though its adsorption maximum was only 2/3 of the latter. Since for surface horizons K is much less variable than the adsorption maximum, removal of a given quantity of P from soil should produce less decrease in P in solution for soils with higher adsorption maximum (fine textured, high Al, Fe and clay content) than those of low adsorption maximum because of greater capacity of the soil to supply P by dissolution. Olsen and Watanabe (1963) have suggested that the soils of fine texture would contain greater volume of water than would soils of coarse texture at the same matrix solution and hence fineness of texture should increase the rate of diffusion of P through the soil to the root.

Fried and Shapiro (1956) pointed out that a capacity factor or ability of the soil to continue to supply P should

be evaluated. The data presented here suggest that the percentage saturation of the adsorption maximum may serve as a measure of the capacity of the soil to supply P to the soil solution.

The relationship between degree of P saturation of the adsorption maximum and the TPeq also provides the evidence for the hypothesis that additions of P to the soil (in amounts not divorced too greatly from those experienced under normal conditions) is probably not immediately fixed but is adsorbed as a monolayer on the surface of soil colloids. The primary evidence presented for such adsorption is the close adherence of the data to the Langmuir adsorption equation. However, this is not fool proof evidence.

Potential Buffering Capacity (PBC)

The chemical potential of $(Ca(H_2PO_4)_2H_2O)$ as measured by potential^{sp} represents an intensity parameter (I) of the soil P. The corresponding extensive parameter is the quantity (Q) of the P present. The $(dQ/dI)_I$ or $(\triangle Q/\triangle I)_{I-I'}$ defined as PBC, is the soils ability to maintain the I parameter against P addition or withdrawal from the soil. The negative of PBC values for the soils included in this study are given in Table 7. PBC values were made positive since $(\triangle Q/\triangle I)_{I-I'}$ was negative because potential^{sp} is the negative logarithm of $H_2PO_4^-$ activity in suspension.

Table 7. PBC of 29 Michigan soil profiles

Soil type		PBC $PM \times 10^{-7}/g$ Potential^{sp}
1 Dune Sand		2.4
2 Rubicon Sand	A1	2.5
	A2	3.4
	B	22.9
	C	13.6
3 Rubicon Sand	AO-A1	3.7
	A2	3.3
	B	14.6
	C	15.4
4 Rubicon Sand	A	1.2
	B	38.7
	C	14.4
5 Emmett Loamy Sand	A2	5.1
	AB	10.3
	Bir	11.7
	B2	11.1
	C	5.6
6 Emmett Loamy Sand	A1	6.2
	A2	4.4
	AB	11.9
	Bir	19.8
	B2	16.6
7 Grayling Sand	A1A2	11.7
	B	36.1
	Bihr	19.8
	C	19.7
8 Roseland Sand	A1A2	8.8
	B	28.1
	C	20.3
	D	9.6

Table 7, cont'd

Soil type		PBC PMx10-7/g Potential^{sp}
9 Rubicon Sand	A1A2	3.3
	Bihr	47.3
	C	15.0
	C2	7.6
10 Kalamazoo Loam	A1	12.4
	B1	24.7
	B21	20.6
	B22	10.0
	B3-C1	10.0
	C	12.0
11 Warsaw Loam	A	25.9
	B1	49.0
	B21	66.2
	B22	29.5
	B23	12.9
	D	5.0
12 Ontonagon Clay	A1	44.0
	A2	42.0
	AB	38.9
	B21	24.8
	B22	19.9
	C	18.8
13 Munising Sandy Loam	Ap	35.3
	Bir	32.5
	A2	16.5
	B	26.0
	C	14.9
14 Sims Clay Loam	A	38.4
	B	16.4
	C	30.7
15 McBride Sandy Loam	A	17.6
	B	18.4
	C	18.2

Table 7, cont'd

Soil type		PBC PM$\times 10^{-7}$/g Potential^{sp}
16 Conover Loam	A	15.7
	B	40.7
	C	19.0
17 Parkhill Clay Loam	A	9.2
	B	11.5
	C	21.5
18 Montcalm Loamy Sand	A	7.9
	B	12.6
	C	6.5
19 Hillsdale Sandy Loam	A	16.5
	B	15.2
	C	15.1
20 Miami Loam	A	20.3
	B	16.6
	C	20.7
21 Spinks Loamy Sand	A	12.0
	B	17.0
	C	8.7
22 Spinks Loamy Sand	A	8.1
	B	8.9
	C	11.0
23 Brookston Clay Loam	A	28.8
	B	23.5
24 Brookston Loam	A	21.0
	B	17.6
	C	16.2
25 Sims Sandy Clay Loam	A	15.7
	B	17.5
	C	22.3

Table 7, cont'd

Soil type		$PM \times 10^{-7}/g \frac{PBC}{Potential^{sp}}$
26 Miami Sandy Loam	A	9.4
	B	17.8
	C	22.2
27 Conover Loam	A	10.4
	B	19.9
	C	17.6
28 Spinks Loamy Sand	A	15.6
	B	15.0
	C	8.6
29 Muck	A	30.7
	B	16.9
	C	14.2

For most of the soils and over the range of I values (expressed as potential^{sp}) there was a linear relation between I and Q so that for a given soil dQ/dI was nearly constant and independent of Ieq.

The PBC obtained after a given period of equilibration describes the Q/I relation of that fraction of the total inorganic P which was equilibrated with the solution in time. Equilibrium is achieved by transfer of P ions between solution and those adsorption sites which in time allowed can gain or loose P in response to changes in the amount of P in solution. Beckett and White (1964) have designated these sites as "nett exchange sites."

$$\text{Site - X} + H_2PO_4^- \rightleftharpoons \text{Site - } H_2PO_4^- + X_{solution}$$

where X is another anion capable of replacing P ions at nett exchange sites.

As proposed by Beckett and White (1964) the PBC is a measure of the ability of the soil to maintain the potential^{sp} of the soil solution against depletion. In the preceeding section, the adsorption maximum has already been shown to correlate with TReq in soil suspension. As expected a high linear correlation between P adsorption maximum and PBC was obtained and regression is plotted in Fig. 4.

The PBC or dQ/dI is a function of the number of adsorption sites (P adsorption maximum is a function of the latter) and K,

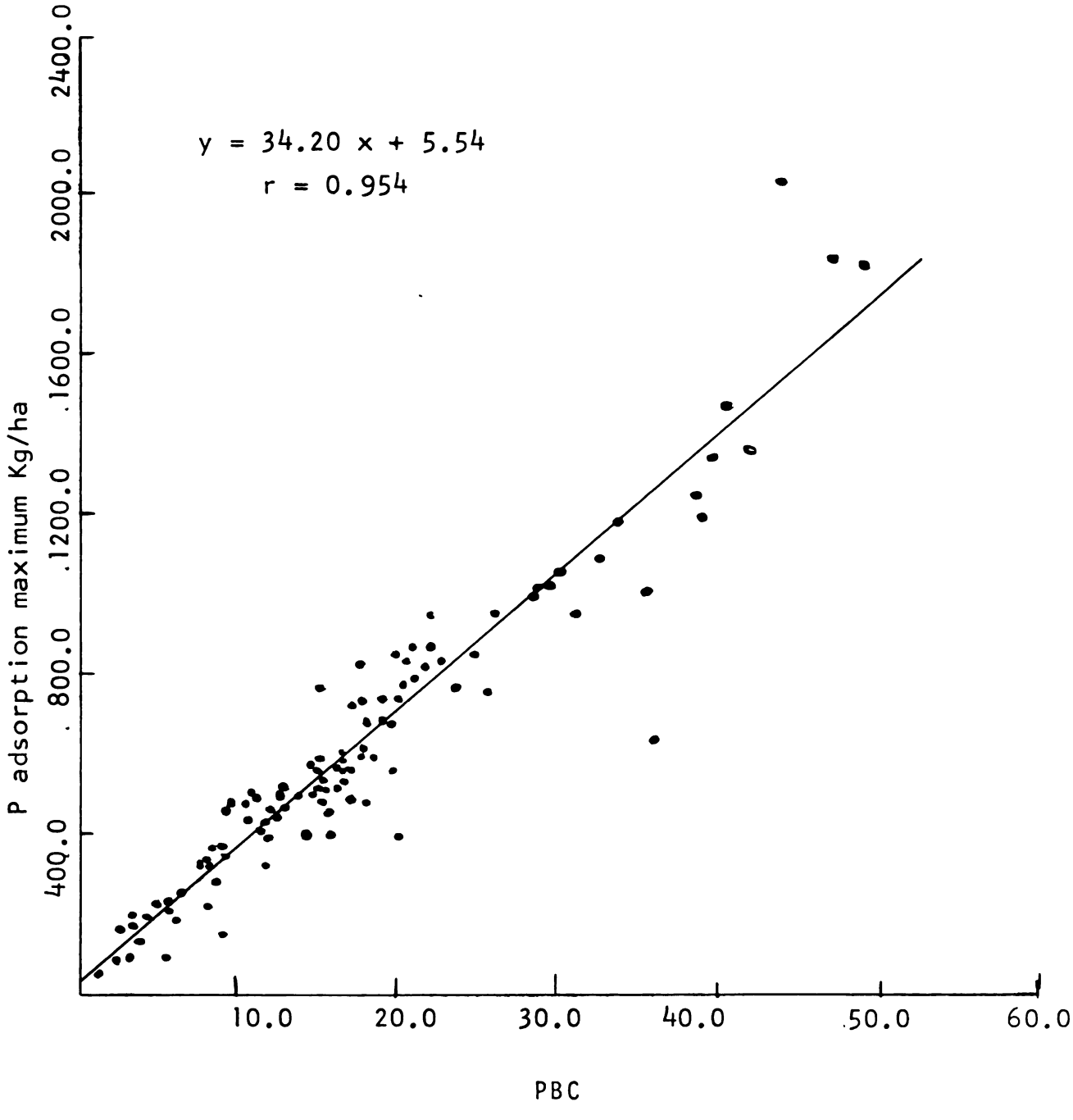


Fig. 4. Regression of adsorption maximum on PBC

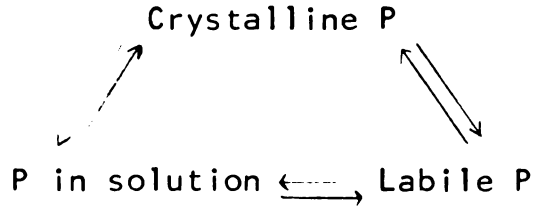
the bonding energy for P of these sites (Beckett and White 1964). A high regression of PBC on adsorption maximum alone in the present study suggests intercorrelation between adsorption maximum and K, the free energy of adsorption of P on adsorption sites. The data in Table 3 in fact suggest the intercorrelation between the adsorption maximum and K, with few exceptions. The relationship between potential^{sp} and $\pm\Delta$ P/g soil is linear over small range of potential^{sp} or for only lower TPeq in solution. Furthermore since potential^{sp} is logarithmic function of $H_2PO_4^-$ activity in solution, a slight variation in linearity could produce significant difference in PBC. Because of a better theoretical basis for calculation of the adsorption maximum and inherent analytical problems involved in the PBC determination, it is proposed again that the former or its degree of saturation should serve a better measure of the soil's ability to replenish the soil solution with P. It would appear that soil tests which displace adsorbed P and experience little resorption during extraction should theoretically be desirable.

The Q/I relations determined as here (i.e. constant 1/2 pCa, varied aH_2PO_4, no added Fe or Al) could not have the form observed if the processes they describe were controlled by the solubility products of insoluble salts. It is known (Murrmann and Peech 1969b) that the dissolution and precipitation of insoluble P commonly present in soils are often extremely

slow. The fact that a given soil with a given amount of labile P is usually able to maintain a constant value of $aCa^{\frac{1}{2}} \times aH_2PO_4$ at equilibrium does not require that an insoluble salt of appropriate solubility product be present to control the potential^{sp} of the labile pool (Clark and Peech, 1960; Taylor and Gurney, 1962).

Thus, from the Q/I relation it appears likely that the nett exchange sites lie on the surfaces of amorphous or imperfectly crystalline primary phosphates (Coleman, et al., 1960; Huffman, 1962; Moreno, Lindsay and Osborn, 1960) of Ca, Fe, or Al according to the pH of the soil. Such primary phosphates may lie on exchange surfaces of alumino silicate clays or on crystalline phosphates. They probably are of indeterminate composition and must possess a sufficiently disordered arrangement for reversible hydroxyl phosphate exchange to take place without crystalline rearrangement (Moreno, et al., 1960). Whether the primary phosphates are regarded as positively charged spots capable of adsorbing both P and OH^- ions or as mixtures of crystallites of oxides and phosphates seems immaterial. Nevertheless for a given soil, the adsorption surfaces must be sufficiently uniform in their spatial properties for the adsorption reaction to confirm to a simple Langmuir isotherm. The nature of the adsorbed P, hence, is unique compared to other P compounds since it includes the fraction of all P compounds present which will equilibrate readily with ^{32}P.

If not disturbed the disordered primary phosphates will gradually adopt crystalline form (Kittrick and Jackson, 1955) as slow rearrangement segregates distinct crystalline phases (Lindsey, et al., 1959; and Wright and Peech, 1960). Crystallization of amorphous compounds would be expected to reduce the number of adsorption sites so the dQ/dI should decrease. Crystallization may also reduce the range of affinities of their exchange reaction. Recent work by Juo and Ellis (1968) and Murrmann and Peech (1969b) however suggests that there exists an equilibrium;



whereby, crystalline P should dessegregate into disordered arrangement to compensate for the adsorbed P. Additional data, however, are needed to substantiate this postulate.

Beckett and White (1964) after comparing their total isotopically exchangeable P to the "A" values determined by three months of exhaustive cropping (Talibudeen and Mattingly, 1960) have divided the former functionally into four parts:

(1) P held at surface nett exchange sites, immediately labile -- requiring only to be displaced by OH^- or possibly other anions to be available for uptake;

(2) P held at occluded nett exchange sites, not immediately available but capable of mobilization as a result of slow counter diffusion and exchange of $H_2PO_4^-$ and OH^- in response to the depletion of (1) and the consequent lowering of P in the soil solution (Moreno, et al., 1960);

(3) P held at surface isotopic exchange sites on crystalline phosphates sufficiently regularly organized for P not to be exchangeable by OH^-, but nevertheless capable of moderately rapid mobilization provided the complimentary cations are also removed -- this fraction will be particularly sensitive to the chelating action (Moreno, et al., 1960) of root and microbial exudates; and

(4) P held within more perfect crystal lattices at sites from which P can only be mobilized both by the disposal of complementary cations and by subsequent crystal rearrangement.

Over short periods, depletion will fall entirely on (1) and the ruling activity product at any time will depend on the relative amounts of P and Ca removed and on changes in the number or affinity of the nett exchange sites. Over longer periods of depletion, transfer from (2) and (3) to (1) must become significant. During the phase of depletion the Ieq will presumably stand at a steady low value controlled by the percent saturation by P of sites (1) as above which in turn

will be regulated by the relative rates of uptake and transfer from (2) and (3).

The relevance of the above conjecture should form the research project for future study.

Results obtained in the current investigation have raised some inquiring questions and gaps in the knowledge gained. A tentative outline for future research is therefore presented.

(1) The nature of the adsorbed P and its subsequent reaction product with the soils under study should be investigated.

(2) The effect of time of equilibration, with effective control on microbial interference on prolonged equilibration period; on P adsorption maximum and its exchangeability with ^{32}P and adherence of the data so obtained with the Langmuir adsorption equation should be pursued. The exchangeability with ^{32}P will provide direct experimental evidence that adsorbed P is in equilibrium with P in solution.

(3) Initial surface P is calculated from the isotopic dilution law at isotopic equilibrium as -

$$^{31}P \text{ (surface)} = \frac{^{32}P \text{ (surface)}}{^{32}P \text{ (solution)}} \times {}^{31}P \text{ (solution)}$$

It is proposed that ^{31}P (surface) be obtained as Y intercept when X = 0 from a plot of ^{31}P (solution)

vs P gained or lost from soil by the actual data on the same soil sample, thus eliminating the need for a separate isotopic dilution technique for ^{31}P (surface) determination. In case of discrepency between the two values, further experiments to ascertain the reason should be initiated.

(4) The P sorption properties and buffering capacity of the soils should be compared with available or the best available soil P extractants to see if a theoretical approach to P requirement for soils is suitable.

(5) A careful evaluation of the factors responsible for variation in potential E_{eq}^{sp}, P adsorption maximum and PBC should be undertaken for clearer understanding of the importance of the above parameters in their ability to control the P conc and release in soil suspension.

(6) A regression equation involving adsorption maximum and independent variables, e.g. clay content (quantity and quality) organic matter, Al, Fe and surface area and interrelationship between the independent variables should be obtained. Thus the relative importance of soil characteristics on P

sorption would be obtained simultaneously enabling the researcher to obtain an estimate of P adsorption maximum when some or all independent soil characteristics are known.

SUMMARY AND CONCLUSIONS

Twenty nine Michigan soil profiles were analyzed for the equilibrium inorganic P conc and potential buffering capacity (PBC) following the procedures outlined by White and Beckett (1964) and Beckett and White (1964), respectively. The P adsorption maximum of these soils was obtained as the reciprocal of the slope of the Langmuir adsorption equation, $C/x/m = \frac{1}{Kb} + \frac{C}{b}$ (Olsen and Watanabe, 1957). Data showed fairly good agreement with the Langmuir plot, and a "r" value on an average of 0.985 was obtained.

The soils studied had large variation in all the parameters investigated.

The podzolic sandy profiles, in general, had lower equilibrium P conc than any other profile. In particular, the B horizons had very low equilibrium conc of inorganic P; conc as low as 0.083×10^{-6}M for Emmett loamy sand Bihr (6) was obtained. The A horizons contained lower equilibrium potential^{sp} or higher equilibrium conc of inorganic P within the group.

Very few A horizons had equilibrium P conc adequate to support an optimum plant growth if those conc were maintained during the plant's life. The A horizons of McBride sandy loam (15), Miami loam (20), Miami sandy loam (26), Spinks loamy sand (22,28), Brookston clay loam (23), and Muck (29), had

adequate P in solution at equilibrium. These higher equilibrium P conc were either (a) because of high percent saturation of the adsorption maximum which probably is a consequence of recent treatment with P fertilizers, and/or (b) low energy of bonding of P on adsorbent.

The P adsorption maximum varied considerably between and within the soil profiles. Ontonagon clay A (12) would adsorb 2046.2 Kg/ha (to a depth of 30.48 cm) of P compared to 40.4 for Rubicon sand (4). In general fine textured soils (higher extractable Al, free iron oxide, clay and organic matter content) had higher P adsorption maximum than the podzolic sandy profiles. With the podzolic sandy profiles B horizons had distinctly higher P adsorption maximum relative to their A and C horizons. The differentiation between different horizons of fine textured soils, however, was not clearly defined. This followed the trend of lack of differentiation of Al and Fe enriched horizons with the fine textured soils. Regression of adsorption maximum on extractable Al and free iron oxide showed no relationship when soils were pooled together; however, regression run on individual profiles indicated extractable Al rather more reactive and important in P sorption than Fe.

The free energy of adsorption of P on soil complexes estimated by K as slope/intercept from the Langmuir adsorption

equation indicated higher values for B horizons with possibly Al and Fe adsorption complexes than those with greater organic matter content.

The potential buffering capacity (PBC) and P adsorption maximums for the soils studied were highly correlated (r =.954) and the relationship is given by:

$$Y = 34.20\ X + 5.54$$

where Y = P adsorption maximum Kg/ha 30.48 cm

and X = -PBC.

The higher correlation between PBC and adsorption maximum alone without the energy of adsorption term, K, was because of inter-correlation between adsorption maximum and K.

Experimental evidence demonstrating predictable equilibrium conc of inorganic P in soil suspension with correctness, at a particular percent saturation of the adsorption maximum was presented. The equation used is -

$$C = \frac{\theta}{(1-\theta)K}$$

Although adsorption maximum (its degree of saturation) per se was not controlling the equilibrium P conc, nevertheless, since K, the energy of adsorption of P was much less variable it is proposed that P adsorption maximum should serve as indicator of the soil's ability to continue supply P to the growing plants.

Fine textured soils (high adsorption maximum, high Al, Fe, and clay content) with no recent P additions, showed high P requirement to bring the P conc at any level compared to coarse texture soils.

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