TARC Report

Characteristics in Phosphate Adsorption of Major Soil Groups of Thailand

By HIDEO IMAI*, PRAPIT SANGTONG and WISIT CHOLITKUL****

***Department of Soils Fertilizer, National Institute of Agricultural Sciences**
(Yatabe, Ibaraki, 305 Japan)
****Agricultural Chemistry Division, Department of Agriculture**
(Bangken, Bangkok, Thailand)

Introduction

Phosphate, an essential nutrient for plants, is also considered to play a key role in nitrogen metabolism in soils and even in nitrogen fixation. In general, however, soils distributed widely in the tropics are deficient in phosphate. This is a main limitation to crop yields in paddy as well as in upland soils of the tropics. Therefore, it is very urgent and important to clarify the dynamic behavior of phosphate in the soils for better understanding of soil fertility and foundation of the rational system of phosphate application to crops in the tropical region.

In the present paper, the characteristics of the main Thai soils in P adsorption in terms of Langmuir adsorption model and equilibrium diagrams for phosphate compounds will be presented.

Materials and method

1) Materials

Soils used in this experiment are Acid Sulfate soils (ASS), Fresh Water Alluvial soils (FWA), Reddish Brown Lateritic soils (RBL), Grumusol, and Noncalcic Brown soils (NCB). Soil samples which passed through a 2 mm sieve were used. Some relevant properties of the soils are presented in Table 1.

2) Method

Two g each of air-dried soil samples was weighed and placed into a 50-m*l* polyethylene centrifuge tube, and then, 40 m*l* of P solution containing the required amount of 0.1 N HCl or 0.1 N NaOH to bring the equilibrium pH to desired values was added onto it. Concentration of the P solution added ranged from 1 to 20 ppm for FWA, RBL, and NCB and from 1 to 150 ppm for ASS and Grumusol. This P solution also contained $NaNO_3$ corresponding to 0.01 M. The mixture of the soil and P solution was shaked gently for 24 hr at room temperature. After the shaking, the suspension pH was measured and centrifuged. Supernatant was kept for P analysis.

Results and discussion

1) Acidmetric and alkalimetric titration of Thai soils

The acidmetric and alkalimetric titration curves of the five Thai soils used in P adsorption were very similar to those reported by Inoue et al.[3] ASS has a great buffer intensity around pH 5 because of its high content of free and exchangeable aluminium. With the increase of the pH, a hydrolysis of the aluminium associated with the release of proton proceeds, and OH added is consumed with the H released, consequently the pH remains unchanged.

Grumusol showed a great buffer intensity both in the low and high pH regions. This is due to $CaCO_3$ contained in a large amount in the soil.

FWA showed a steep increase in buffer intensity at a low pH region. This soil has a mixed clay mineralogy, i.e., Illite, Kaolinite, Mont-

Table 1. Some relevant properties of the soils used

Soil samples	pH H_2O	pH KCl	Clay mineralogy	CEC (meq/100 g)	Base saturation (%)	Organic matter (%)
ASS	4.3	3.7	Mixed (Ill. Mt. Kt.)	28	18	1.4
NCB	7.7	6.5	Kt. Mica	8	62	—
RBL	6.7	5.5	Kt.	16	82	—
Grumusol	8.1	7.4	Mt.	50	170	1.8
FWA	7.0	5.8	Mixed (Ill. Kt. Vt.)	20	90	1.1

Ill. : Illite, Kt.: Kaolinite, Mt.: Montmorillonite,Vt.: Vermiculite

morillonite, etc., and is considered to be fragile in its structure to some extent, especially in a strong acidity. Other two soils, RBL and NCB were very similar to each other and did not show any specific characteristics in their buffer intensity.

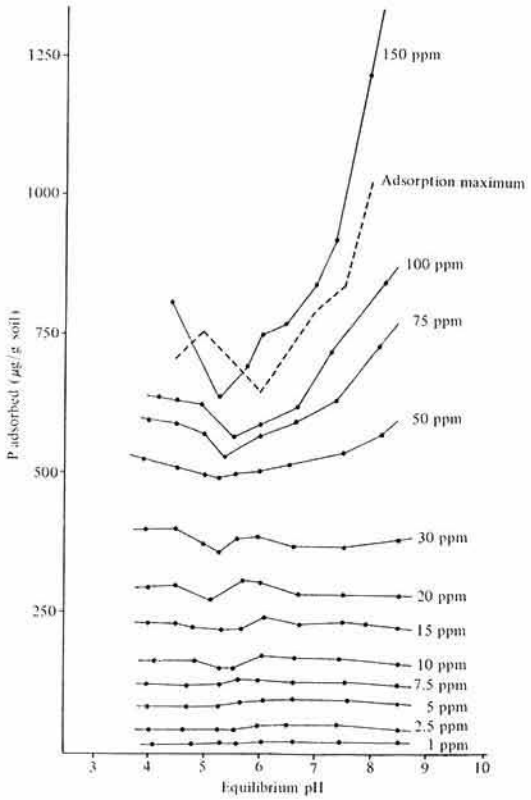

Fig. 1. Effect of equilibrium pH on P adsorption by Grumusol

2) P adsorption in Thai soils

Grumusol

The effect of equilibrium pH on P adsorption by Grumusol is presented in Fig. 1. In low to medium P concentrations (less than 30 ppm) the effect of pH is not so significant, and the optimum pH seems to lie at around 6. Since ZPC (zero point of charge) of this soil is at or above pH 7, the soil surface comes to wear negative charge above pH 7, so that P adsorption decreases due to electrostatic repulsion. With the increase of P concentration beyond 75 ppm, P adsorption increased steeply at pH above 6. Grumusol contains a large amount of $CaCO_3$, so that the steep increase occurs due to the precipitation of calcium phosphate compounds.

A plot of P adsorbed(x) vs. equilibrium concentration(C) also indicates that phosphate is precipitated as calcium compounds (figure is not presented here.). Therefore, we will discuss the effect of pH and P concentration on the dissolution and precipitation of some calcium phosphate compounds in terms of conditional solubility product. The solubility relationships necessary to compute solubilities of calcium phosphate compounds are given by reactions 1 through 5 shown in Table 2.[4] Equilibrium concentration constants and concentrations were converted to activity constants and activities, respectively using the extended Debye-Hückel equation(1) at I=0.01.

$$\log \gamma_i = -AZ_i^2 I^{1/2}/(1+Bd_i I^{1/2}) \quad \cdots\cdots(1)$$

where γ_i: activity coefficient, I: ionic strength, A,B: 0.509, 0.328×10^8 for water at 25°C, respectively. d_i corresponds roughly to the effective size of the hydrated ion.

The solubility of many compounds is not govern-

Table 2. Equilibrium constants for various phosphate reactions at I=0.01

Reaction No.	Equilibrium reaction	log ^{c*}Kso (I=0.01)
1	$CaHPO_4 \cdot 2H_2O$ (DCPD) $+ H^+ = Ca^{2+} + H_2PO_4^- + 2H_2O$	0.85
2	$CaHPO_4$(DCP) $+ H^+ = Ca^{2+} + H_2PO_4^-$	0.51
3	$Ca_4H(PO_4)_3 \cdot 2.5H_2O$(OCP) $+ 5H^+ = 4Ca^{2+} + 3H_2PO_4^- + 2.5H_2O$	12.57
4	$Ca_5(PO_4)_3OH$(hydroxyapatite) $+ 7H^+ = 5Ca^{2+} + 3H_2PO_4^- + H_2O$	15.44
5	$CaCO_3$(calcite) $+ 2H^+ = Ca^{2+} + CO_2(g) + H_2O$	9.91
6	$AlPO_4 \cdot 2H_2O$(variscite) $+ 2H^+ = Al^{3+} + H_2PO_4^- + 2H_2O$	−2.10
7	$H_6K_3Al_5(PO_4)_8 \cdot 18H_2O$ (K-taranakite) $+ 10H^+ = 3K^+ + 5Al^{3+} + 8H_2PO_4^- + 18H_2O$	−25.15
8	$-Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	8.39

ed by the solubility product alone because other equilibria besides the solubility equilibrium occur in solution. In the calculation of the so-called solubility product (^{c}Kso), however, all these side reactions are neglected. So that, we will use the conditional solubility product (Ps) that takes account of the effect of the side reactions instead of ^{c}Kso. Taking dicalcium phosphate (DCP) as an example, we'll very briefly look into the relation between Ps and ^{c}Kso. From Table 2,

$$CaHPO_4(DCP) + H^+ = Ca^{2+} + H_2PO_4^-$$
$$^{c*}Kso = [Ca^{2+}][H_2PO_4^-]/[H^+] \quad \cdots\cdots (2)$$

hence, $^{c*}Kso[H^+] = [Ca^{2+}][H_2PO_4^-] = {}^cKso$

Ps is defined as;

$$Ps = {}^{c*}Kso[H^+]/\alpha_{Ca}\alpha_{H,PO_4} \text{ or } Ps = {}^cKso/\alpha_{Ca}\alpha_{H,PO_4} \quad \cdots\cdots (3)^{6,7)}$$

Thus, Ps can be obtained in terms of the solubility product divided by α_i, the ionization fraction. α_i is also called the degree of protolysis, but historically, it has been called the degree of dissociation. The subscript of α refers to the number of protons lost from the most protonated species. For phosphate, $\alpha_0 = [H_3PO_4]/P_T$, $\alpha_1 = [H_2PO_4^-]/P_T$, $\alpha_2 = [HPO_4^{2-}]/P_T$ and so on, where P_T means total phosphate concentration, and hence, is written as;

$$P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

Naturally, $\alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 = 1$

α_0 is also written as $\alpha_{H_3PO_4}$, α_1 as $\alpha_{H_2PO_4^-}$ and so on. α is independent of total concentration and can be expressed as a function of pH alone, so that, $\alpha_{H_2PO_4^-}$ and α_{Ca} used in the calculation of DCP are given as;

$$\alpha_{H_2PO_4^-} = K_1(H^+)/((H^+)^3 + K_1(H^+)^2 + K_1K_2(H^+) + K_1K_2K_3 \quad \cdots\cdots (4)$$

where $\log K_1$, $\log K_2$, $\log K_3$ (I=0.01) are −2.11, −7.07, −12.13, respectively.

$$\alpha_{Ca} = (H^+)/(H^+ + K_1) \quad \cdots\cdots (5)$$

where $\log K_1$ (I=0.01) = −12.83

Applying the equation (3) to the compound, Ca_xP_y,

$$Ca_xP_y + zH^+ = xCa + yP + zH_2O \quad \cdots\cdots (6)$$
$$^{c*}Kso = [Ca]^x[P]^y/[H^+]^z \quad \cdots\cdots (7)$$

hence, $Ps = {}^{c*}Kso[H^+]^z/[Ca]^x[P]^y$ is obtained. Therefore, Ps gives the relationship between the quantities that are of direct interest. The product of actual concentration, Qs_T, can be computed as the product of the concentrations of Ca existing in the soil and phosphate actually added. So that, in a plot of P_T and Qs_T vs. pH, within the pH range where $Qs_T > Ps$ is attained, in principle, a precipitation is possible to occur. Ca concentration in the soil is maintained at a fairly constant level of $10^{-2.5}$ M over a wide range of pH. So that, the following Qs_T values were computed using $\log Ca_T = -2.5$.

Ps values of DCPD*, OCP**, and hydroxyapatite are plotted against pH in Fig. 2 and Qs_T values are also given there for $\log Ca_T = -2.5$ and P_T=1, 10, 100, and 150 ppm P.

In DCPD*, $pQs_T < pPs$ is attained above pH 6.3 when P_T concentration is 50 ppm (shown as the number 3 on pQs_T (DCPD) line). By increasing the P concentration, pH value at which DCPD is precipitated moves toward a more acidic side. At 10 ppm P, the precipitation of DCPD cannot be expected until pH value goes up to 7.5, and at 1 ppm P, Qs_T is undersaturated with respect to DCPD over the pH range of 2 to 9. As the initial pH values, 6.3 and 5.2 were obtained for the precipitation of OCP and hydroxy-

* DCPD = Dicalcium phosphate dihydrate

** OCP = Octa calcium phosphate

apatite, respectively, when 50 ppm of phosphate is added.

Before comparing the Qs_T values with the experimental points presented in Fig. 1, however, we must bear in mind that this sort of thermodynamical information cannot give any kinetical prediction. In P retention by soils, adsorption reaction is much faster than the formation of precipitation and there is a great difference in the rate of precipitation among the calcium-phosphate compounds thus formed.

Therefore, instead of initial P concentration, equilibrium concentration was used for recalculation of Qs_T. Here, P concentration at which the formation of precipitation was safely neglected on a graph of Langmuir plots, was chosen as the equilibrium P concentration. Initial P concentration, 150, 100, 75, 50 and 10 ppm, corresponds to 113, 68, 33, 25, 1 and 0 ppm of the equilibrium concentration, respectively. The results are plotted in Fig. 2.

When 100, 75, 50, 30 and 10 ppm P as the initial concentrations are added, the precipitation of DCPD can be expected at pH 6.0, 6.4, 6.5, 7.5, respectively. In the formation of OCP, these pH values are 6.1, 6.1, 6.4, 6.5 and 6.7, respectively, when the same amounts of P are added. Both compounds are very similar to each other in the pH values of precipitation. The formation of hydroxyapatite begins at more acidic pH values, but, this compound has an ordered structure with respect to DCPD and OCP, hence it takes a longer time to be formed. Under the condition of this experiment, monocalcium phosphate such as brushite (DCPD) and monetite is firstly formed, and followed by OCP. These compounds are gradually converted to such more stable compounds as hydroxyapatite and fluoroapatite.

The results of these computations fitted fairly well to those of the experiment shown in Fig. 1.

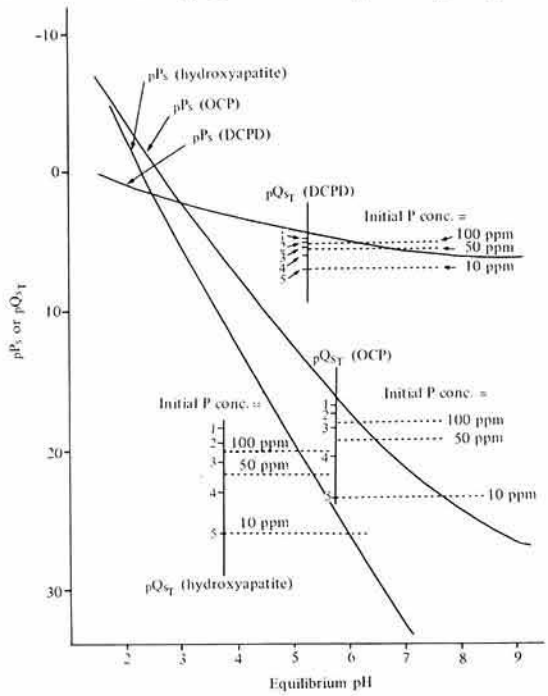

Fig. 2. Change in Ps and Qs_T with pH and P concentration
The conditional solubility product $Ps = c^*Kso \times (H^+)^z/(\alpha_{Ca})^x(\alpha_{H_2PO_4})^y$ and the product of actual concentration.
$Q = (Ca_T)^x \times (P_T)^y$ were calculated using $Ca_T = 10^{-2.5}$ M and $P_T = 1$ to 150 ppm. The numbers given on the left hand side of the pQ line of each compound indicate the P_T level. The numbers 1 to 5 correspond to 1, 10, 50, 100 and 150 ppm P, respectively. Dotted lines indicate the equilibrium P concentration when 100, 50 and 10 ppm of P solution was added to Grumusol.

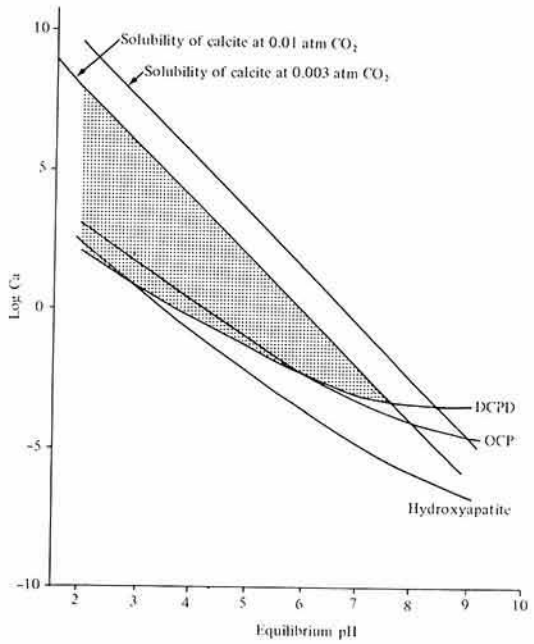

Fig. 3. Change in Ca concentration necessary to precipitate DCPD, OCP and hydroxyapatite with pH when P_T is fixed at 50 ppm.
In the dotted area the solution becomes oversaturated with respect to DCPD.

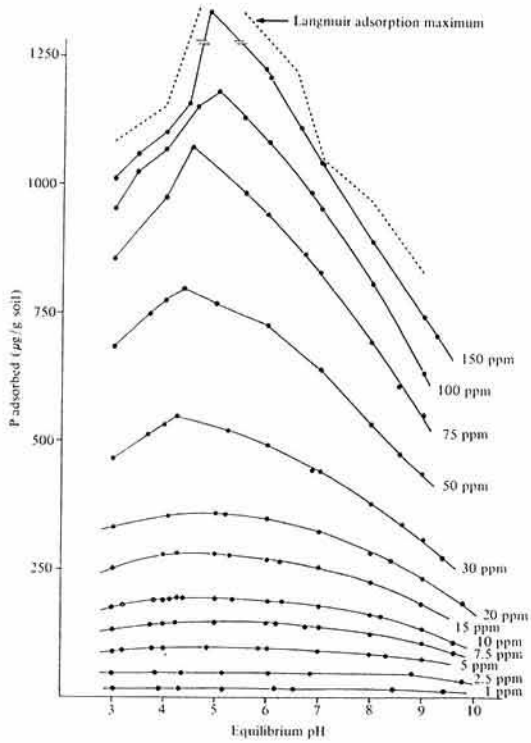

Fig. 4. The effect of equilibrium pH on P adsorption by Acid Sulfate soil

At pH above 6, P is easily precipitated as DCPD and/or OCP when more than 50 ppm P is added. This is responsible for a steep increase in P retention by Grumusol in alkaline pH region.

P adsorption in Grumusol also increases to more than 50 ppm as the pH is lowered below 5. This is also due to the formation of calcium phosphates. So far, Ca concentration is fixed at $10^{-2.5}$ M in all the solubility computations. Ca concentration in Grumusol, however, increases as the pH decreases because of an increase in the solubility of calcite contained in a great amount in acidic pH region. If Ca concentration in Grumusol varies in equilibrium with calcite, the precipitation is possible to occur at pH below 5 and is accelerated as the pH lowers. Change in Ca concentration in equilibrium with calcite and with equilibrium pH is presented in Fig. 3. This result shows that the precipitation of calcium phosphate may occur in the acidic region.

Acid Sulfate soil (ASS)

P adsorption reached its maximum at the pH around 5 (Fig. 4). This corresponds to the formation of aluminium phosphate compounds. Hofstee plotting of these results, however, shows that the precipitation of aluminium phosphate is not so significant at any pH values (Fig. 5). Change in Ps values with pH are given for variscite and K-taranakite in Fig. 6. The Qs_T values for the respective compound are also plotted at 10, 50 and 100 ppm P on the same graph. The constants and equations used for illustrating Fig. 6 are given by reactions 6 to 8 of Table 2.

$$\alpha_{Al} = (1/Al^{3+} + 10^{-5.02}/AlOH^{2+}(H^+) + 10^{-9.30} /Al(OH)_2^+(H^+)^2 + 10^{-14.99}/Al(OH)_3^0(H^+)^3 + 10^{3.20} (SO_4^{2-})/AlSO_4^+)^{-1} \quad \cdots\cdots (5)$$

In addition to these equations, the equations (1), (2) and (3) were used for the conversion of the concentrations of ion species to the activities, the computations of Ps and $\alpha_{H_2PO_4^-}$, respectively.

The Ps curves of variscite and K-taranakite have their minimum at around pH 5, and this is in good agreement with the optimum pH values of P adsorption in ASS. In comparison with the respective Qs_T values, however, it is very clear that the precipitation of aluminium-phosphate compounds are favored in an acidic pH region, and above pH 5, they become less important due to a steep decrease in aluminium concentration in solution. Lindsay et al.[5] showed that the initial reaction products of phosphate fertilization were 10 to 30 times more soluble than variscite and during the ensuing 18 months, the phosphate solubility decreased and approached that of variscite. This facts indicate that amorphous aluminium phosphate is firstly formed and then gradually changed to more stable compounds such as variscite with aging. Under the condition of this experiment, therefore, P may be initially adsorbed on the surface of ASS and form chelating compounds there with hydroxy-aluminium existing as a dominant species above pH 5.0. Since the ZPC of ASS lies in around pH 4.5, P adsorption decreases steeply with increasing pH to above 5.0. These results indicate that rock phosphate with high content of Ca is highly recommendable as a phosphate fertilizer to ASS.

Fresh Water Alluvial soils (FWA)

P adsorption decreased smoothly with the increase of the equilibrium pH (Fig. 7). This is a typical adsorption pattern which is seen in the adsorption of polybasic acids like phosphate, and

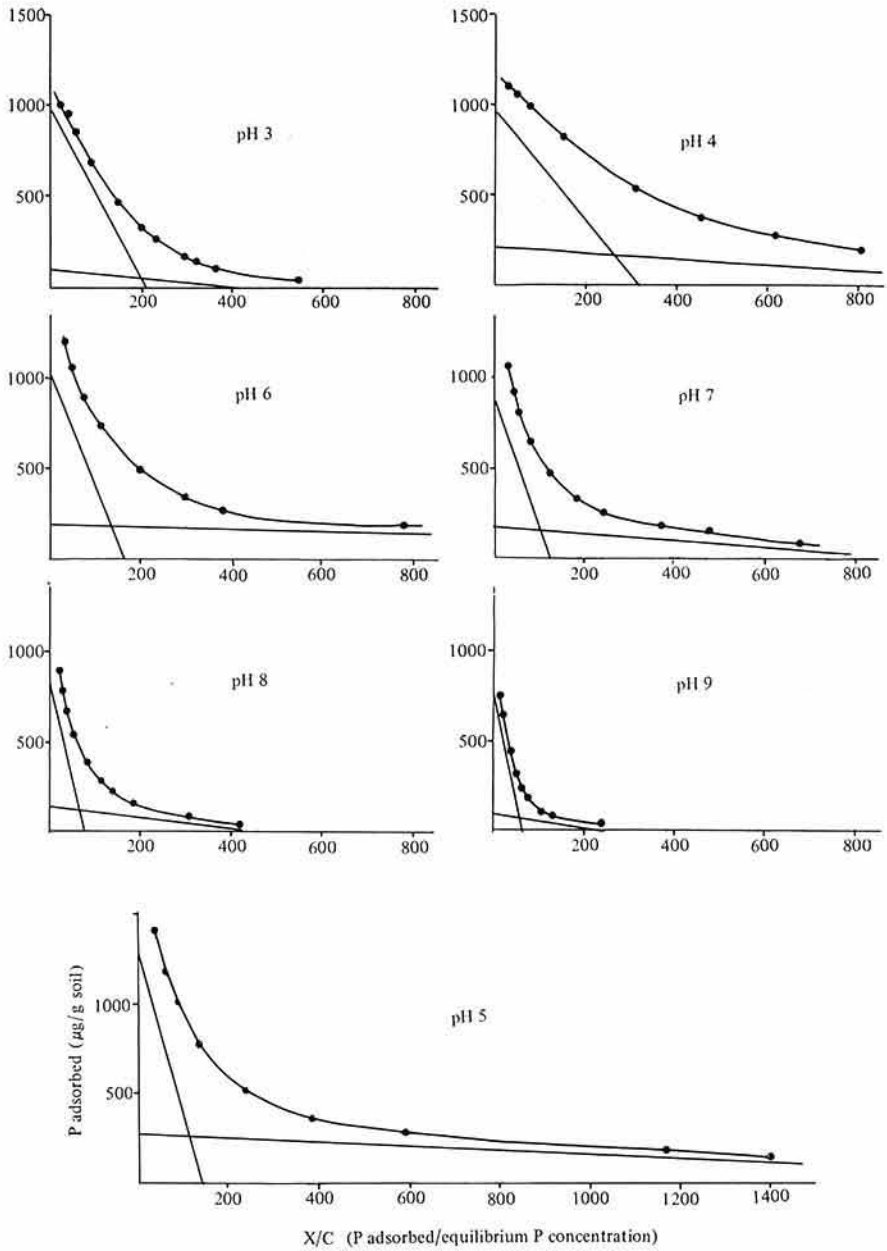

Fig. 5. Hofstee plot (X vs. X/C) for P adsorption by Acid Sulfate soil at various pH values

carbonate onto soil surface, especially, amorphous materials such as allophane, and synthetic gels.[2] With the increase of the pH, the amount of positive charges decreases continuously, and then the reverse of surface charge comes to occur above the pH corresponding to ZPC, causing a steep decrease in P adsorption.

Above 15 ppm P, a shoulder appeared in the adsorption curve around pH 7. The dissociation of phosphate ion increases with pH towards the pK and becomes almost constant at about two pH units above the pK.[1] On the other hand,

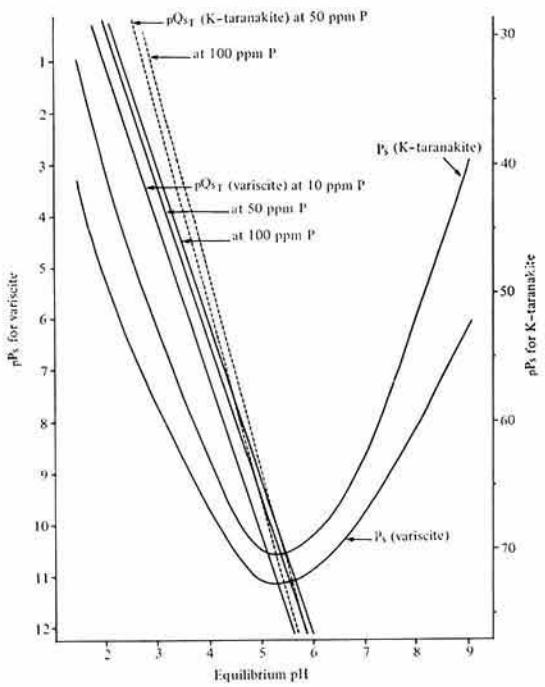

Fig. 6. Change in Ps and Qs_T values of variscite and K-taranakite with equilibrium pH and P concentration

positive charges on the soil surface decreases continuously as the pH increases. This decrease may be compensated with an increase in the dissociation of P ion, hence a shoudler appears around the pH corresponding to the pK (pK_2= 7.1).

P adsorption in FWA increased greatly in acidic pH region when P of high concentrations is added. As already mentioned before, this soil is considered to be fragile to some extent in its structure, deriving from the characters of the clay itself or amorphous materials. Phosphate is known to be a strong ligand, so, reacts continuously with breaking the structure of the clays and amorphous materials in acidic pHs.

Reddish Brown Lateritic soils (RBL)

P adsorption in RBL is much less than Grumusol and ASS and effect of pH on P adsorption is not significant (Fig. 8). The titration curve of RBL indicates that this soil has rather rigid structure than FWA. Though RBL contains about 8% of iron, the Fe seems to be inactive in P adsorption unless P concentration is high and pH is very low. With increasing P added, a peak appeared around pH 4. This may be due to iron-phosphate complex. But, there is no

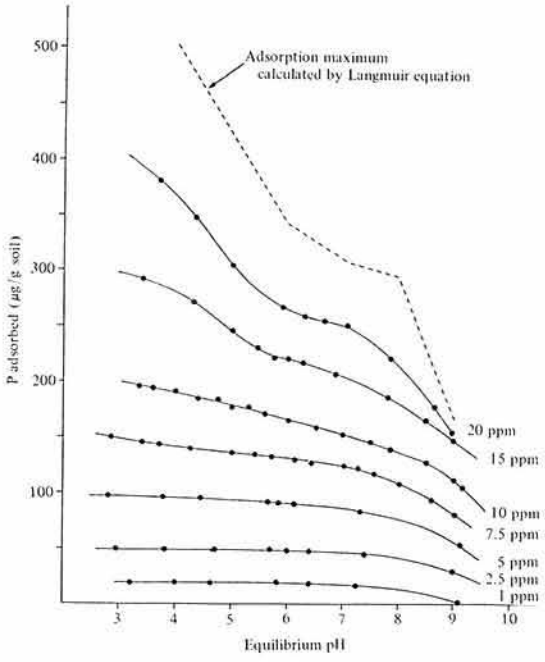

Fig. 7. Effect of equilibrium pH on P adsorption by Fresh Water Alluvial soil

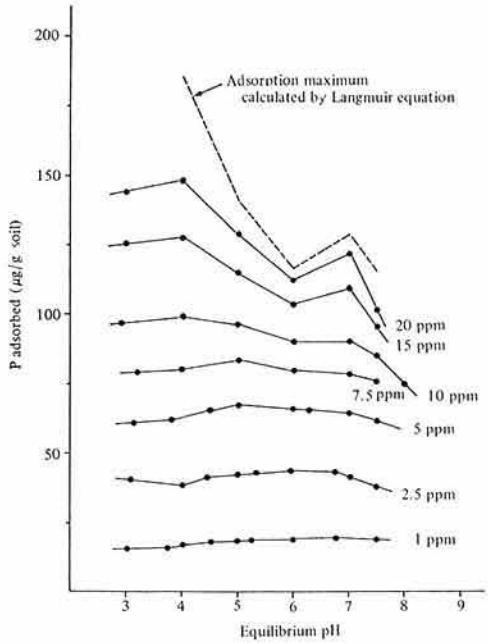

Fig. 8. Effect of equilibrium pH on P adsorption by Reddish Brown Lateritic soil

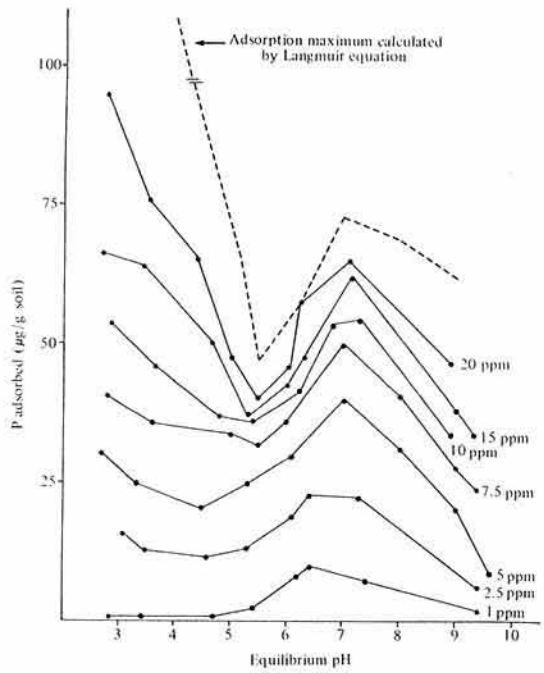

Fig. 9. The effect of equilibrium pH on P adsorption by Noncalcic Brown soil

need to consider P fixation by this soil in usual phosphate fertilization.

Noncalcic Brown soils (NCB)

The optimum pH of P adsorption came to around 7 (Fig. 9). This may be due to the formation of Ca-phosphate like brushite. At low pH, P adsorption increased again. However, the amount of P adsorbed in NCB is as little as in RBL, so that there is no need to pay special attention in ordinary phosphate fertilization.

3) Langmuir adsorption maximum and energy constant

In Langmuir model, adsorption sites on the soil surface have the same adsorption energy to phosphate each other, so it is also called "homogeneous adsorption sites model." According to this model, therefore, P adsorption may be in proportion to the numbers of adsorption sites and P concentration. Langmuir equation is expressed as,

$$1/x=(1+KC)/KCx_m \quad \cdots\cdots(8)$$

where x_m: adsorption maximum, x: P adsorbed, C: equilibrium P concentration. Multiplying C

Table 3. Langmuir adsorption maximum and energy constants

Reddish Brown Lateritic soil

pH	X_m^I μg g^{-1}	K^I ml μg^{-1}	X_m^{II} μg g^{-1}	K^{II} ml μg^{-1}	$X_m^I+X_m^{II}$ μg g^{-1}
4	32.0	5.48	153.5	0.16	185.5
5	43.8	5.69	97.2	0.24	141.0
6	39.0	8.29	77.5	0.35	116.5
7	37.3	7.41	91.0	0.26	128.3
7.5	35.0	4.35	80.0	0.32	115.0

Acid Sulfate soil

pH	X_m^I μg g^{-1}	K^I ml μg^{-1}	X_m^{II} μg g^{-1}	K^{II} ml μg^{-1}	$X_m^I+X_m^{II}$ μg g^{-1}
3	90.0	2.09	987.5	0.10	1077.5
4	201.0	3.73	956.0	0.16	1157.0
5	275.0	4.46	1292.5	0.06	1567.5
6	190.5	7.13	1030.0	0.09	1220.5
7	171.0	2.55	880.0	0.07	1051.0
8	135.5	1.56	820.0	0.05	955.5
9	65.0	1.68	757.5	0.04	822.5

Grumusol

pH	X_m^I μg g^{-1}	K^I ml μg^{-1}	X_m^{II} μg g^{-1}	K^{II} ml μg^{-1}	$X_m^I+X_m^{II}$ μg g^{-1}
4.5	312.0	0.29	395.0	0.08	707.0
5.0	226.5	0.41	531.0	0.05	757.5
6.0	191.0	0.92	456.5	0.09	647.5
7.0	145.5	2.59	650.0	0.05	795.5
7.5	140.5	1.95	697.5	0·05	838.0
8.0	127.5	0.98	885.0	0.04	1012.5

Fresh Water Alluvial soil

pH	X_m^I μg g^{-1}	K^I ml μg^{-1}	X_m^{II} μg g^{-1}	K^{II} ml μg^{-1}	$X_m^I+X_m^{II}$ μg g^{-1}
4	140.0	6.82	361.5	0.84	501.5
5	102.5	15.25	317.5	0.30	420.0
6	65.0	11.13	277.5	0.34	342.5
7	58.5	11.93	250.0	0.28	308.5
8	—	—	292.5	0.29	292.5

Noncalcic Brown soil

pH	X_m^I μg g^{-1} soil	XK^I ml μg^{-1}
4.0	166.7	0.05
5.0	72.5	0.12
5.5	46.9	0.34
6.0	51.6	0.36
7.0	72.6	0.41
8.0	68.2	0.25
9.0	61.9	0.13

to both sides of equation (8)

$$C/x = 1/Kx_m + C/x_m \quad \cdots\cdots (9)$$

In the equation (9), when C/x is plotted against C, a straight line should be obtained if P adsorption follows Langmuir model. From the slope of the line, x_m can be calculated, and K from y interception. If there are more than two adsorption sites with different adsorption energy in the soil the adsorption maximum (x_m) of the soil is simply the summation of x_m^I of each adsorption site.

$$x = K^I C x_m^I/(1+K^I C) + K^{II} C x_m^{II}/(1+K^{II} C) + \quad \cdots (10)$$

Equation (8) can be rearranged as follows.

$$x = x_m - x/KC \quad \cdots\cdots (11)$$

A plot of x vs. x/C gives a straight line, from which x_m can be evaluated directly and K from the reciprocal of the slope. For more than two adsorption sites,

$$x = x_m^I - x^I/K^I C + x_m^{II} - x^{II}/K^{II} C + \quad \cdots\cdots (12)$$

A plot of x vs. x/C is also called "Hofstee Plot," being used for evaluation of K_m, V_m of enzymes.

Langmuir adsorption maximum and energy constant for the five Thai soils are summarized in Table 3. All the soils except NCB provide P with more than two adsorption sites. Generally, x_m^I decreases with increasing the pH, meaning that the numbers of adsorption site I is closely related to the amount of positive charge on soil surface. The variation of x_m^{II} with pH corresponds to dominant cation species contained in the respective soils. In Grumusol, for example, x_m^I decreases with increasing pH, reflecting a decrease in the positive charges, while inversely, x_m^{II} increases with pH due to the formation of calciumphosphate compounds. x_m^I and x_m^{II} in ASS reached their maximums at the same pH of 5, and x_m^I decreases greatly both in very acidic and alkaline pH regions while a decrease in x_m^{II} is not so significant even at pH 3. At pH 3, aluminium adsorbed on soil surface is dissolved into the solution bulk and reacts to P there, thus, resulting in a decrease in x_m^I and in part, an increase in x_m^{II}. Actually, however, it is impossible to separate adsorption from precipitation, hence x_m^I represents the sum of adsorption onto the site II and the precipitation of aluminium-phosphate complex.

Summary

Phosphate adsorption in the major soil groups in Thailand was examined over the wide range of pH and equilibrium P concentration, and the characteristics of these soils in P adsorption were discussed in terms of Langmuir adsorption model and equilibrium diagrams for phosphate compounds.

P adsorption increased steeply at pH values where buffer intensity of the soils was at its maximum. Thus, P adsorption is greatly affected by kinds and amounts of soil components responsible for H^+ or OH^- acceptance.

P adsorption by Grumusol increased steeply due to precipitation of calcium phosphate compounds above pH 6 when more than 75 ppm of phosphate was added. The product of actual ion concentration, $Qs_T = (Ca_T)^x \times (P_T)^y$, also exceeded conditional solubility product, $Ps = {}^c{*}Kso(H^+)^z/(\alpha_{Ca})^x(\alpha_{H_2PO_4})^y$, around 6, and adsorption isotherm indicated that phosphate was precipitated as calcium phosphates.

P adsorption by ASS reached its maximum around pH 5, but adsorption isotherm at this pH value showed that the precipitation of alumino-phospho compounds in the bulk solution was not significant even at 150 ppm, therefore, this is due to the formation of surface chelating compounds with hydroxy-aluminium. Rock phosphate with high content of Ca is highly recommendable as a phosphate fertilizer to ASS. P adsorption in FWA increased greatly in acidic pH region when high concentration of P was added and then decreased smoothly with increasing the equilibrium pH. This reflects structural fragility of the soil, and indicates that clay with ill-defined structure and amorphous materials are responsible for P adsorption in this soil.

P adsorption in RBL and NCB is much less than in Grumusol and ASS. Fe contained in RBL seems to be inactive unless P concentration is high and pH is very low. So that there is no need to pay much attention in ordinary levels of phosphate fertilization.

References

1) Bowden, J. W., et al.: Generalized model for anion and cation adsorption at oxide surfaces. *Nature*, **245**, 81–83 (1973).
2) Hingston, F. J., Posner, A. M., & Quirk, J. P.: Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *J. Soil Sci.*, **23**, 177–192 (1972).
3) Inoue, T. et al.: Potentiometric titration of some upland soils in Thailand. *JARQ*, **15**, 286–290 (1982).
4) Lindsay, W. L.: Chemical equilibria in soils, Wiley-Interscience, New York (1979).
5) Lindsay, W. L., Lehr, J. R., & Stephenson, H.F.: Nature of the reactions of monocalcium phosphate monohydrate in soils. III. Studies with metastable triple-point solution. *Soil Sci. Soc. Am. Proc.*, **23**, 342–345 (1959).
6) Ringbon, A.: Complexation in analytical chemistry. Wiley-Interscience, New York (1963).
7) Schwarzenbach, G.: Complexometric titrations. Interscience, New York (1957).

(Received for publication, July 15, 1982)