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Phosphorus Sorption Characteristics of Acid Sulfate Soils of Thailand.

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**Phosphorus sorption characteristics of acid sulfate soils of
Thailand**

Krairapanond, Asdaporn, Ph.D.

The Louisiana State University and Agricultural and Mechanical Col., 1989

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Ann Arbor, MI 48106

**Phosphorus Sorption Characteristics
of
Acid Sulfate Soils of Thailand**

A Dissertation

**Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy**

in

The Department of Marine Sciences

by

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December 1989

To my parents
and
my lovely husband

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ABSTRACT

The study of P-sorption by soils has practical interest but little is known on the P-sorption characteristics of acid sulfate soils of Thailand, particularly under reduced soil conditions. The effects of pH, redox potential, and various forms of Fe, Al, and Mn on P-sorption of the actual acid sulfate soils (Sulfic Tropaquept) and the para-acid sulfate soil (Typic Tropaquept) were studied in laboratory microcosms. Soil suspensions with a soil to 0.01 M CaCl₂ solution ratio of 1:7 were incubated under various pH and redox potential conditions. After the incubation period, the soil suspensions were equilibrated with KH₂PO₄ ranging from 0 to 500 mg P kg⁻¹ soil. Some sets of soil suspensions were extracted by 1 N NH₄OAc (pH 4.0) and sodium-citrate dithionite solution (20 %), intended to remove Fe, Al, and probably Mn in the forms of exchangeable and free oxides, before P addition. Three sorption equations were used to describe the P-sorption data.

The classical Langmuir equation provided the best fit of the P-sorption data. More native insoluble P was released under reduced than oxidized conditions. Para-acid sulfate soil released more native insoluble P than did actual acid sulfate soils under both conditions. Para-acid sulfate soil also sorbed less added P than did actual acid sulfate soils. The P-sorption of both actual and para-acid sulfate soils was significantly affected by pH, redox potential, the extracted treatment before P addition, and their interactions. The P-sorption increased significantly with increasing pH and decreasing redox potential. Treating soils with NH₄OAc and sodium-citrate dithionite solutions reduced P-sorption, and decreased the differences in P-sorption due to the effects of pH and redox potential. The treatments did not remove the difference in P-sorption between the actual and para-acid sulfate soils. Closely significant correlation between P-sorption parameters and iron-oxides indicated the primary role of iron-oxides in P-sorption of the acid sulfate soils of Thailand. Aluminum-oxides seemed to play a secondary role in P-sorption of these soils. Manganese also showed a significant effect on P-sorption.

INTRODUCTION

Actual and potential acid sulfate soils are found on an estimated 12.5 million hectares of land throughout the world (FAO/UNESCO, 1979). Geographically, the majority of acid sulfate soils occur on low-lying coastal area, particularly in the tropics (Attanandana and Vacharotayan, 1986). Acid sulfate soils are developed from recent or semi-recent marine sediments where large quantities of pyrite (FeS_2) accumulate. Pyrite accumulation in these sediments is a result of the reduction of sulfate from seawater and iron from the weathering of clay. Pyrite oxidation occurring upon long-time soil drainage produces sulfuric acid. If the acid exceeds the acid neutralizing capacity of the soil, the soil then becomes acidic. This acid condition affects soil physico-chemical properties which are extremely detrimental to plant growth.

Thailand is one of the major rice production countries in southeast Asia. Acid sulfate soils occur mainly in the Bangkok Plain in an area of about 0.8 million hectares (Kevie and Yenmanas, 1972), of which 95 % is used for low land rice production. The remainder of the acid sulfate soils in Thailand, approximately 0.7 million hectares, is located around the coastal areas in the southeastern and southern regions of the country. The Bangkok Plain accounts for nearly half the total rice production of the country. Due to the acidic nature of the acid sulfate soils, rice production on these soils in the Bangkok Plain is often severely limited.

One of the major limitations on rice growth in the acid sulfate soils is high P-sorption capacity (Attanandana, 1982). In addition, the excess amounts of Fe and Al have been reported to limit rice growth in these soils. Since the P-sorption mechanisms in acid soils are greatly influenced by the forms and amounts of Fe and Al compounds, it is probably that soil redox potential and pH condition, which control iron and aluminum reactions, govern the release and sorption of P in the acid sulfate soils. The P-sorption of soil has been reported to either increase (Mokwunye, 1975; White and Taylor, 1977; Haynes and Swift, 1985; Traina et al., 1986) or decrease (Obihara and Russell, 1972;

Lopez-Hernandez and Burnham, 1974; Smyth and Sanchez, 1980) as pH increased. Khalid et al. (1977) mentioned that more P was sorbed under reduced conditions than under oxidized condition at high level of added P.

During the past three decades, several experiments were conducted in an attempt to improve rice production in acid sulfate soils. The results showed that the improvements can be achieved by liming the soils and applying P fertilizer (Charoenchamratcheep et al., 1982; Attanandana and Vacharotayan, 1986). Khouma and Toure (1982) reported that application of 50 kg ha⁻¹ P₂O₅ markedly increased the yield of rice. Attanandana and Vacharotayan (1986) found that the application of lime at very high rates reduced the availability of P in the actual acid sulfate soil.

The main objective of this research was to investigate P-sorption characteristics of the acid sulfate soils of Thailand as affected by pH and redox potential. The P-sorption characteristics under oxidized and reduced conditions without controlled pH are reported in Chapter II. Chapter III examines the P-sorption characteristics under controlled pH and redox potential. The effects of Fe, Al, and Mn on P-sorption behavior under oxidized and reduced condition at the selected pH levels are reported in Chapter IV. Since the chapters are manuscripts prepared for specific journals, subtle differences in format exist.

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CHAPTER ONE

ACID SULFATE SOILS AND PHOSPHORUS SORPTION

INTRODUCTION

The world wide area of acid sulfate soils is estimated to be 12.5 million hectares (FAO/UNESCO, 1979). In Thailand, one of the major rice production countries in southeast Asia, acid sulfate soils occur mainly in the Bangkok Plain in an area of about 0.8 million hectares, of which 95 % is used for lowland rice production. One of the major limitations on rice growth in these soils is the high P-sorption capacity of these soils (Attanandana, 1982). In addition, the soils contain the significant amounts of Fe and Al which have been reported to limit the rice growth (Attanandana, 1982: Attanandana et al., 1982). This review emphasizes on the characteristics of acid sulfate soils of Thailand, the mechanism of P-sorption, and factors affecting P-sorption in these soils.

CHARACTERISTICS OF ACID SULFATE SOILS

Acid sulfate soils occur in all climatic zones of the world, from cold and temperate climates to the humid tropics. Nevertheless, they are most extensive in tropical deltas (Kevie, 1972). These soils have been found in all continents except Australia (Attanandana and Vacharotayan, 1986). Large areas of acid sulfate soils occur in the tropics with at least 7.5 million hectares identified (Kawalec, 1972). In Thailand, about 0.8 million hectares of acid sulfate soils are situated in the Bangkok Plain. The remainder is scattered along the coastal areas and estuaries of the east coast and peninsula (Kevie and Yenmanas, 1972).

The essential feature of acid sulfate soils is the accumulation of pyrite (FeS_2) in intertidal coastal sediments. The accumulation of pyrite is brought about by the combined effect of somewhat unique conditions that occur in tropical coastal areas. Sulfur in pyrite is derived from sulfate in sea water which is biologically reduced to sulfide in the anaerobic zone. An energy source, which is necessary for bacterial sulfate reduction, is usually readily available as a result of high plant growth in these coastal areas. Also, ferrous iron (Fe^{2+}) must be available; it is usually derived from the reduction of insol-

ble ferric compounds that result from the weathering of clay. Thus, the combination of sulfate from sea water, plant organic matter, anaerobic conditions caused by exclusion of atmospheric oxygen by the excess water, and the presence of Fe^{2+} result in the formation and accumulation of pyrite in tropical coastal wetlands (Breemen, 1976).

Acid sulfate soils are soils with pH below 4.0 that is directly or indirectly caused by sulfuric acid formed by oxidation of pyrite (FeS_2) (Attanandana and Vacharotayan, 1986). The soils also have a sulfuric horizon that is composed of mineral or organic soil material with $\text{pH} < 3.5$ and yellow jarosite mottles. Para-acid sulfate soils are soils in which the acid has been leached out or neutralized to the extent that microbiological activation and root development are no longer hampered (generally, pH is not below 4.0) (Attanandana and Vacharotayan, 1986). However, the soils still have jarosite mottles in the profiles, and they also contain high soluble sulfate and high percentage of Al saturation, but not a toxic amount of free or soluble Al.

Keivie and Yenmanas (1972) have classified the soils of the Bangkok Plain into five classes of suitability for rice, ranging from soils very well suited to unsuited for rice (PI to PV), based on the relationship between soil mapping units and soil productivity. The soils in class PI are non-acid marine or para-acid sulfate soils which are in Subgroup Typic Tropaquepts. Within each suitability class, there are subclasses defined by various limitations such as soil acidity (a). According to this classification, the actual acid sulfate soils were classified as PIIa, PIIIa, and PIVa, and the para-acid sulfate soils were classified as PI. The soils in class PIIa are well developed acid sulfate soils whereas the soils in class PIIIa are semi-mature acid sulfate soils. Soils in both classes were mostly classified into Sulfic Tropaquepts Subgroup. The soils in class PIVa are recent to semi-recent acid sulfate soils which are classified into Sulfic Tropaquepts or Typic Sulfaquepts Subgroups.

The criterion used to determine the extent of limitation due to soil acidity of acid sulfate soils for rice is the depth of the jarositic horizon. Jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) is

produced within the soil profile by the reaction of sulfuric acid and aluminosilicate minerals. Jarosite occurs under strongly oxidizing and severely acid conditions ($E_h > +400$ mV and pH 2 to 4). The deeper jarosite occurs in the soil profile, the less effect of acidity on the soil surface. The relationship between the depth of jarositic horizon and suitability class is as follows (Attanandana and Vacharotayan, 1986):

- jarositic horizon within 40 cm from the soil surface; suitability class PIVa
- jarositic horizon between 40 to 100 cm from the soil surface; suitability class PIIIa
- jarositic horizon below 100 cm from the soil surface; suitability class PIIa.

The acid sulfate soils in the Bangkok Plain of Thailand are generally well developed (Breemen, 1976). Fertility studies of acid sulfate soils (Attanandana, 1982), however, indicated that these soils are unproductive. This is due to the high acidity of soil which retards microbiological activity, high P-sorption capacity, and toxicity of Fe, Al, and H_2S . Low availability P and high P-sorption capacity are considered to be the major limiting factor for rice growth on the acid sulfate soils of the Bangkok Plain (Motomura et al., 1975). Imai et al. (1983) reported the maximum P-sorption of acid sulfate soils of Thailand as high as 1 567 mg P kg^{-1} soil.

THE MECHANISM OF P-SORPTION

Adsorption vs Precipitation

The inorganic phosphorus in the soil solution takes part in many equilibria; some of these are within the liquid phase only (homogeneous equilibria) and others occur between the solid and liquid phases (heterogeneous equilibria) (Larsen, 1967). When soluble phosphorus is added to soils, phosphorus will be removed from the solution phases by adsorption and/or precipitation reactions. It is difficult to distinguish between the initial reaction of precipitation and adsorption of P. As a result, these two phenomena are often grouped together as "sorption" (Berkheiser et al., 1980). It has been postulated that

P-adsorption and precipitation are basically the same mechanism (Kittrick and Jackson, 1957; Hsu and Rennie, 1962). Hsu (1965) suggested that P-adsorption is a special case of precipitation in which aluminum or iron remains as the constituent of the original phase but reacts with P by use of residual force on the surface. He noted that whether the process is precipitation or adsorption is dependent on pH and the solution P concentration.

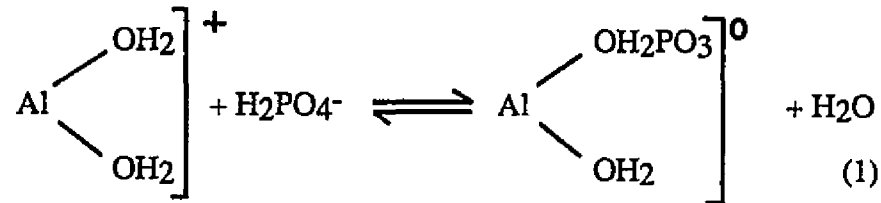
Phosphorus Sorption by Hydrous Oxides of Iron and Aluminum

Aluminum- and iron-oxides and hydrous oxides can occur as discrete compounds in soils or as coating on other soil particles. They can also exist as amorphous Al-hydroxy compounds between the layers of expandable Al-silicates (Sample et al., 1980). The mechanism for P-sorption in soils by Al and Fe compounds has been studied in the past two decades. The amount of P sorbed by these compounds varies with temperature, time of reaction, P concentration, and pH of the system (Berkheiser et al., 1980).

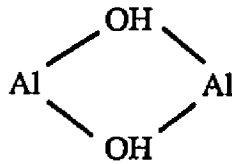
Bache (1964) measured the sorption of P by gibbsite and hydrous ferric oxide at different pH's in buffered solutions and concluded that there were three stages of sorption occurring at different P concentrations of the solution: (i) a high energy chemisorption of small amounts of P; (ii) precipitation of separate P phase; (iii) a low energy sorption of P onto the precipitate. The P-sorption by kaolinite, gibbsite, and pseudoboehmite was studied by Muljadi et al. (1966b). They found three distinct sorption regions: (i) at low P concentrations (10^{-4} M), (ii) at intermediate P concentrations (10^{-4} to 10^{-3} M), and (iii) at medium to high P concentrations (10^{-3} to 10^{-1} M). They suggested that the reaction sites responsible for sorption in region (i) and (ii) were aluminum atoms located on the edge face of the crystal lattice, and that in region (iii), penetration of P into some amorphous region of the crystals occurred.

In acid and neutral solutions, oxides carry a net positive charge with positive and neutral sites on their surface. Rajan et al. (1974) postulated that monovalent phosphate is

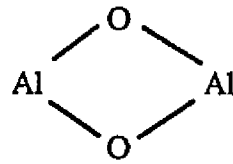
sorbed on positive sites of hydrous aluminum-oxides displacing water molecule that was coordinated to the oxide surface, with neutralization of the positive charge as shown below:



Hydrous aluminum-oxide has a structure in which aluminum atoms are linked by hydroxide or oxide bridges (Hsu, 1965).

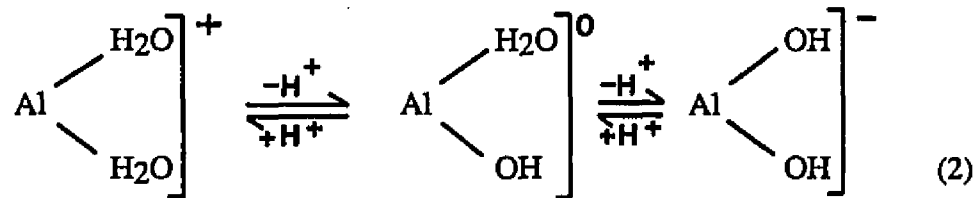


hydroxide

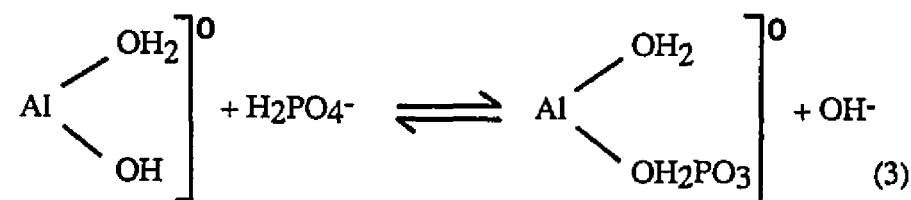


oxide

At the surface of the polymeric structure the coordinate positions of the terminal atoms are occupied by aquo Al-H₂O, and hydroxo Al-OH groups (Hingston et al., 1968). The relative proportion of the aquo and hydroxo groups is determined by the suspension pH and in turn determine the surface charge:



Phosphorus is considered to be sorbed specifically by hydrous aluminum-oxide by ligand exchange with aquo and hydroxo groups, and becoming coordinated to Al ion at the surface (Haynes, 1984). Ligand exchange of phosphate with aquo groups would add negative charge to the surface but would not increase the concentration of the hydroxyl ions in solution (eq. 1). On the contrary, the exchange of P with hydroxo groups would not affect the surface charge, but would release equivalent amounts of hydroxyl ions into the solution, as



When the sorption sites on the surface are saturated, the hydrous oxide carries no net change. Additional sorption evidently occurs by the disruption of hydrous oxide polymers into smaller units with a concomitant increase in sorption sites. The P-sorption on this new surface has been found to make the surface negative (Rajan, 1975a).

Parfitt et al. (1975) studied the mechanism of P-sorption by iron oxides by using infrared spectroscopic techniques and indicated that two surface hydroxyl ions (or water molecules) are replaced by one phosphate ion. Two of the oxygen atoms of the phosphate ion are coordinated, each to a different Fe^{3+} ion, resulting in a binuclear surface complex of the type $\text{Fe-O-P(O)}_2\text{-O-Fe}$. Rajan (1975b) has also suggested that the sorption of P by hydrous aluminum-oxide is due to a binuclear coordination of phosphate ions with two aluminum atoms.

Phosphorus Sorption by Alumino-Silicate Minerals

The principal types of crystalline aluminum silicates are kaolinitic (1:1) and montmorillonitic (2:1) clays. Due to the similarities in the sorption isotherms for alumino-silicates and the hydrous oxides, several researchers have concluded that the sorption mechanism by those minerals are the same (Beek and Riemsdijk, 1979; Berkheiser et al., 1980; Sample et al., 1980). Muljadi et al. (1966a, 1966b, 1966c) concluded that P-sorption was similar for kaolinite, gibbsite, and pseudoboehmite, differing only in the number of sorption sites. Hingston et al. (1972) also noted that the edge faces of kaolinite behave similarly to the hydrous oxides in anion sorption. Rajan and Perrott (1975) demonstrated that synthetic amorphous alumino-silicates sorbed much more P than did kaolinite.

The P-sorption by some tropical soils was studied by Rajan and Fox (1975), suggesting two types of sorption sites. In the first region P-sorption resulted in the release of sulfate and silicate and a rise in pH, which indicated that P was replacing sorbed silicate, sulfate and hydroxyl groups. In the second region, at higher concentrations of P, there was a sharp increase in the release of silicate but with no additional sulfate, suggesting that the silicate clay minerals were being disorganized and the structural silicate displaced, allowing more P to be sorbed.

Phosphorus Sorption by Carbonates

The mechanism of P-sorption by CaCO_3 have been studied intensively during the past two decades. Kuo and Lotse (1972) have suggested that P may replace sorbed water molecules, bicarbonate ions, and hydroxyl ions when it is sorbed by calcite, with sorbing strength depending on the solubility of the compound formed with the surface Ca ions. Nevertheless, P-sorption by CaCO_3 can be ignored on extremely acid soils.

Phosphorus Sorption and Organic Matter

Since organic matter is normally negatively charged, it is not thought to sorb much P by itself. When organic matter is associated with cation such as Fe^{3+} or Al^{3+} , however, it is able to sorb significant amounts of P (Sample et al., 1980). Appelt et al. (1975) found that the amount of P sorbed by hydroxy-Al-humic acid complex increased as the Al:OH ratio decreased. They believed that P was sorbed by ligand exchange of phosphate for hydroxyl groups. Humic acid could react with Al from soil minerals to form hydroxy-Al-humic complex, which would give rise to new surfaces for P-sorption. The effect of an increase in organic content of the soil therefore would increase P-sorption rather than decrease it by competing with P for sorptive sites.

Nevertheless, several researchers have reported that organic acids were capable of reducing the amount of P sorbed by soils and clay mineral (kaolinite) (Nagarajah et al.,

1970; Earl et al., 1979; Lopez-Hernandez et al., 1986). Nagarajah et al. (1970) believed that organic acid competes with P for sorption sites on the surfaces of the hydrated aluminum oxides thereby decreasing their capacity to sorbed P. Earl et al. (1979) reported that the reduction in P-sorption in the presence of citrate, an organic acid commonly occurring in nature, resulted primarily from the elimination of a significant proportion of P-sorbing sites rather than from the competitive specific sorption of citrate. Organic acids also have been reported to perturb the crystallization of aluminum- and iron-oxides and thus enhance P-sorption capacity of soils (Ng Kee Kwong and Huang, 1978).

FACTORS AFFECTING P-SORPTION

Oxidation-Reduction Potential

The P-sorption in anaerobic soils has not yet been extensively studied. However, anaerobic soils have been reported to release more soluble P to soil solution low in soluble P and sorb more P from soil solutions high in soluble P than do aerobic soils (Patrick and Khalid, 1974; Khalid et al., 1977). The differences in characteristics of P-sorption under oxidized and reduced conditions were attributed to the transformation of ferric oxyhydroxide ($\text{Fe}(\text{OH})_3$) to gel-like or amorphous ferrous hydroxide ($\text{Fe}(\text{OH})_2$), which was expected to have higher sorbing surface. Willet and Higgins (1978) found large increases in oxalate extractable Fe and P-sorption when soils were flooded. They also attributed an increase in P-sorption to the reduction of ferric oxyhydroxide to poorly crystalline ferrous hydroxide. The poorly crystalline ferrous compounds would have a greater surface area, and more sites for P-sorption.

Holford and Patrick (1979) studied the effect of redox potential on P-sorption of an acid soil (pH 5.6) and found that reduction to -150 mV caused a very large increase in P-sorption because of increased sorption on freshly precipitated amorphous ferrous hydroxide. At pH 5.0, reduction to -150 mV decreased P-sorption at solution P concentra-

tions below 20 ppm as a result of the reduction and dissolution of ferric hydrous oxides. At higher concentrations, P-sorption increased by ferrous phosphate precipitation due to the very high concentration of soluble Fe under reduced condition. At pH 6.5, reduction to -150 mV caused a very large increase in P-sorption because of increased sorption on freshly precipitated amorphous ferrous hydroxides. At pH 8.0, P-sorption was decreased at P-concentration below 2 ppm as a result of increased surface negative charge, but increased at higher P concentrations due to precipitation of calcium phosphate.

pH

Generally, P-sorption by soils and soil components is maximum in the pH range 2 to 4 (Obihara and Russell, 1972; Bowden et al., 1980). The P-sorption of pure aluminum- and iron-oxides has been reported to decrease as the pH is raised from 3 to 12 (Hingston et al., 1972; Bowden et al., 1980). Lopez-Hernandez and Burnham (1974) did not find a significant correlation between pH and P-sorption for a group of mixed soils, but they did find a highly significant decrease in P-sorption with increasing pH for a group of pedologically similar soils differing mainly in pH. They also found a corresponding decrease in exchangeable Al and acetate extractable Al with increasing pH. Obihara and Russell (1972) showed that P-sorption decreased with increasing pH with two breaks in the curves at about 6.4 and 11.6.

The P-sorption of soils has also been reported to increase with increasing pH (Mokwunye, 1975; White and Taylor, 1977; Haynes and Swift, 1985; Traina et al., 1986a). Mokwunye (1975) found an increase in P-sorption of savannah soils (pH 4.50-5.40) with increasing pH from 3.0 to 7.0. He suggested that high pH increased the activity of hydroxy-aluminum. Phosphorus was sorbed on the surface of the hydroxy-aluminum species when the hydroxy-aluminum-phosphate attraction was strong enough to displace surface OH⁻ ions.

Haynes (1984) noted that liming an acid soil from pH 5.0 to 5.5 results in the precipitation of exchangeable Al^{3+} as polymeric hydroxyl-Al cations, which can coat soil colloids and cause a significant decrease in the net negative soil charge. Such polymers may also precipitate independently or be complexed with soil organic matter components. Whatever their exact nature, it is apparent that liming can result in the precipitation of new, positively charged, hydroxyl-Al surfaces which can sorb added P. Haynes (1982) observed that liming increased P-sorption of acid soil (pH 4.2) high in exchangeable Al^{3+} (12.8 meq/100g). The amorphous hydroxy-aluminum compounds had a larger surface area and sorbed approximately 4 to 5 times as much P at pH 6.0 as did the equivalent amount of crystalline aluminum-hydroxide (Ng Kee Kwong and Huang, 1977).

Haynes and Swift (1985) reported that P-sorption by moist-limed soils can be increased, decreased or unaffected, depending on the relative magnitudes of two processes. Firstly, with increasing pH the amphoteric soil surfaces become increasingly negative resulting in greater electrostatic repulsion and a decrease in P-sorption. Secondly, precipitation of exchangeable Al^{3+} as hydroxy-aluminum polymers, as the pH is raised, is thought to result in the formation of new highly-active sorbing surface in the soil and this tends to increase P-sorption.

The P-sorption by aluminum-peat complex has been reported to increase with increasing pH (Bloom, 1981). This would be due to the influence of newly formed surfaces of aluminum-organic matter complex providing a larger P-sorbing surface. Bar-Yosef et al. (1988) found a decrease in P-sorption by kaolinite below the pH of 6.0. They explained this phenomenon as the effect of pH on edge-to face flocculation, which may affect P accessibility to clay mineral sorption sites.

Temperature

The amount of P sorbed by soils and soil constituents is temperature dependent (Berkheiser et al., 1980). The P-sorption in soils has been reported to increase with in-

creasing temperature (Muljadi et al., 1966c; Gardner and Jones, 1973; Sah and Mikkelsen, 1986a; Mehadi and Taylor, 1988). Muljadi et al. (1966c) determined P-sorption by kaolinite, gibbsite, and pseudoboehmite at 2 °, 20 ° and 40 °C, and found the increases in P-sorption with increasing temperature, large because of an irreversible increase in the number of sorption sites. They suggested that when P is sorbed, there is an increase in the entropy of the water surrounding the phosphate ion and the sorption sites. Gardner and Jones (1973) studied P-sorption of two different soils, Aridosol and Spodosol, at 5 ° and 20 °C and found that the sorption rate decreased as the equilibration temperature was lowered. Mehadi and Taylor (1988) reported an increase in P-sorption in two highly-weathered soils, Decatur clay loam and Hartsells sandy loam, with increasing temperature. They also noted that Langmuir sorption constant, related to energy of sorption of P to the soil surface, increased as temperature was raised, indicating that P-sorption was an endothermic process and suggesting that P was held more tightly to the soil surface.

The amount and type of clay

Muljadi et al. (1966a) found that the sorption isotherms for K-kaolinite, gibbsite and pseudoboehmite at constant pH were very similar in shape, and differed only in the amount of P-sorbed. The order of the sorption following the specific surface area is pseudoboehmite > gibbsite > kaolinite. Unlike the uniform metal-oxide surface, clay minerals are characterized by a face of constant negative charge, and edge surface of variable charge on which specific sorption occurs. The study of P-sorption by montmorillonite and kaolinite by Bar-Yosef et al. (1988) showed that maximum P-sorption by montmorillonite was higher than that by kaolinite. They also reported that the effect of pH on P-sorption in calcium-kaolinite was similar to that in montmorillonite with a maximum around pH 6.0. Calcium-montmorillonite, however, sorbed about 10 % more P at a given P solution concentration and pH than the potassium-clay. Significant corre-

lations between P-sorption and the amount of clay have been reported by Pena and Torrent (1984) and Soils and Torrent (1989).

Organic Matter

Organic matter serves as an energy source for obligate and facultative soil microorganisms and is the driving force and source of electrons for soil biological reduction (Ponnamperuma, 1981). In well drained aerobic soils, the application of organic matter has frequently been reported to decrease P-sorption (Reddy et al., 1980; Kuo, 1983). However, in reduced soils, where dissolution and reprecipitation of many soil minerals occur, anaerobic decomposition of organic matter could have opposite effects (Sah and Mikkelsen, 1986b). The added organic matter during flooding significantly increased P-sorption by clay soils of California. Bloom (1981) concluded that the aluminum-organic matter complex in acid surface soils is an important source of P-sorption, particularly in mineral soils of high organic matter contents. Although the influence of organic matter on P-sorption has been debated, organic matter appears to affect P-sorption in an indirect manner. Organically complexed Fe^{3+} and Al^{3+} are the most likely sites for sorption on organic matter surfaces (Berkheiser et al., 1980).

The influence of organic acid production in the rhizosphere on P-sorption remains controversial issues. Ng Kee Kwong and Huang (1978) reported that citric acid, and organic acid commonly occurring in nature, even at very low concentrations, hampers the formation of crystalline aluminum-hydroxides. Due to the hindrance of the crystallization processes, the retention of P by hydrolytic reaction products of aluminum is enhanced and not reduced when they are precipitated in the presence of low concentration of citric acid. On the contrary, the reduction in P-sorption has been reported in the presence of organic acids (Earl et al., 1979; Traina et al., 1986a, 1988b; Lopez-Hernandez et al., 1986; Kafkafi et al., 1988). Earl et al. (1979) found that citrate was markedly effective in reducing P-sorption (50 % reduction), tartrate was only moderately effective (20

% reduction), whereas acetate had little or no effect (1 % reduction). Kafkafi et al. (1988) noted that citrate, bicarbonate, and oxalate decrease, but acetate and amino acid increased P-sorption of kaolinite and montmorillonite.

Iron and aluminum

The P-sorption by acid soils is believed to be due largely to various forms of active Fe and Al. In order to measure the active fraction, several extractants for Fe and Al have been used, but the most popular of which are oxalate and citrate-dithionite (Berkheiser et al., 1980). Bromfield (1965) found that soils sorbed less P after various amount of Fe and Al had been extracted by citrate-dithionite followed by an acid wash. Borggaard (1983) attributed the decrease in P-sorption capacity following dithionite-EDTA extraction to the removal of iron oxides from soils. Soils and Torrent (1989) reported the highly significant correlation between P-sorption and the amount of citrate-dithionite extractable Fe and concluded that iron-oxides, as estimated by citrate-dithionite extractable Fe, were the most active sorbent. Several workers have reported that amorphous or gel-like form of Fe and Al sorbed more P than its crystalline analogues (Ballard and Fiskell, 1974; McLaughlin et al., 1981; Borggaard, 1983; Sah and Mikkelsen, 1986b). On the contrary, crystalline iron-oxides have been reported to be the most important P-sorbing components of soils which provide the most active P-sorbing surfaces (Pena and Torrent, 1984; Torrent, 1987).

The amount of inorganic P sorbed by a range of iron-and aluminum containing components has been reported to vary and decrease in the order: allophane > fresh aluminum gel > iron gel pseudoboehmite > aged aluminum gel > dried iron gel > iron-coated kaolinite > hematite > goethite > akaganite > gibbsite = ground kaolinite > dispersed kaolinite (McLaughlin et al., 1981). Aluminum gel sorbed 30 to 70 times more than gibbsite, and iron gel sorbed approximately 10 times more P than its crystalline analogues (hematite, goethite, and akaganite). Nevertheless, Barron et al. (1988) found

that hematite has low sorption capacity when compared to many natural and synthetic goethites. This gives a reason why red (hematic) soils sorb less P than similar yellow (goethitic) soils.

MODELS FOR P-SORPTION

Three equations, the classical Langmuir, Freundlich, and Temkin, are often used in modeling the sorption of phosphate ions on charged surfaces. By far the most widely used model is the classical Langmuir equation which was originally applied to P-sorption on soils by Olsen and Watanabe (1957). The simple Langmuir equation is written:

$$1/x = 1/x_m + (1/kx_m)(1/C) \quad (4)$$

where x is the amount of sorbed P per unit of soil, C is the final solution P concentration, k is a coefficient which reflects the relative rates of sorption and desorption at equilibrium and is thus an affinity term, and x_m is the maximum monolayer sorption capacity.

Conceptually, equation (4) can be used to measure the amount of P that a soil can sorb. The equation has been utilized in describing the fertility status of soil P, since the parameter k is related to the bonding energy of P to the soil and can be regarded as an intensity factor. Because k is related to the energy of sorption, it may be useful in describing partitioning of P between solid and solution phases. The x_m term has been related to quantity factors and as a measure of the capacity of a soil to retain P. Both terms allow quantitative measures of P availability to agriculture crops (Berkheiser et al., 1980).

Nevertheless, the Langmuir equation can fit P-sorption data for only a limited range of P concentration (Syers et al., 1973; Holford et al., 1974). Syers et al. (1973) used a curve-splitting technique to describe P-sorption by Brazilian soils. Holford et al. (1974) adapted the multisite Langmuir equation to P-sorption by soils. They evaluated both single-surface and two-surface equations and found correlation coefficient of 0.99 for the single-surface and 1.00 for the two-surface models. They postulated that the two-

surface equation was superior to the one-surface model for fitting P-sorption. However, Posner and Bowden (1980) found that the model which is based on a single type of sorption site is closely similar to the experimental isotherms. They, therefore, concluded that it is erroneous to split the isotherms into a series of Langmuir equations. The modified Langmuir isotherm proposed by Kuo (1988) takes into consideration the electrostatic interaction among the phosphate species. The equation was as simple as that for the classical Langmuir isotherm but provided a better estimate of sorption capacity of P by soils than did the latter one.

The Freundlich equation was first applied to P-sorption by Low and Black (1950). The Freundlich equation is written:

$$x = aC^{1/n} \quad (5)$$

where a and $1/n$ are constants. Although the Freundlich parameters have no physico-chemical meaning, this equation can be used as effectively as the Langmuir equation to describe P-sorption by soils (Barrow, 1978). The high correlations ($r = 0.98$) between a and the Langmuir maximum sorption capacity (x_m) indicated that the Freundlich constant gives a relative measure of the soil's sorption capacity (Mead, 1981). The exponent (n) of the Freundlich equation was also significantly correlated with the Langmuir sorption constant (k). Fitter and Sutton (1975), however, found that a slight modification of one parameter of the Freundlich isotherm improved its applicability to soil P-sorption data.

Bache and Williams (1971) proposed the Temkin equation which is obtainable from the Langmuir equation, but which also implies that the energy of sorption decrease linearly with increasing surface coverage. The simplest form of the Temkin equation is stated as (Mead, 1981):

$$x = \alpha + \beta \ln C \quad (6)$$

where α and β are constants. A plot of x against $\ln C$ should give a straight line. Mead (1981) postulated that the Temkin equation can also be used to provide an index of the

soil P-sorption characteristic, as the constant, β , was highly correlated with the Langmuir maximum sorption capacity.

Goldberg and Sposito (1984) proposed the Constant Capacitance Model which is shown to provide a quantitative description of P-sorption by variety of aluminum-and iron-hydrous oxides, including the effect of varying pH values. This complicated model is based on a ligand exchange mechanism for P-sorption. However, Barrow (1978) suggested that the simplest model should be preferred unless a more complex one can be shown to improve the measure of goodness of fit.

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CHAPTER TWO

PHOSPHORUS SORPTION IN ACID SULFATE SOILS UNDER OXIDIZED AND REDUCED CONDITIONS

ABSTRACT

Little is known regarding P-sorption characteristics of the acid sulfate soils of Thailand. This study was conducted to determine the effect of oxidation-reduction status on P-sorption characteristics of these soils. Surface soil samples collected from four different soils in the Bangkok Plain in Thailand were incubated under oxidized and reduced conditions for 4 wk in stirred soil suspension with a soil to 0.01 M CaCl_2 solution ratio of 1:7. After the incubation period the soil suspensions were equilibrated with KH_2PO_4 ranging from 0 to 500 mg P kg^{-1} soil. Major objectives of this study were to investigate the release of native soil P and the sorption of added P. Three sorption equations were used to describe the P-sorption data. The results showed that more native insoluble P was released under reduced than oxidized conditions. Para-acid sulfate soil released more native insoluble P than did actual acid sulfate soils under both conditions. Although reduced soil conditions resulted in an increase in the amount of native soil P released, reduction also caused an increase in P-sorption. Less P-sorption occurred under both conditions in para-acid sulfate soil than in actual acid sulfate soils. Significant correlations between the amount of P sorbed and citrate-dithionite extractable Fe and Al show that amorphous and possibly crystalline Fe and Al play important roles in P-sorption in acid sulfate soils of Thailand, particularly under reduced conditions. The classical Langmuir equation provided the best fit of the P-sorption data of acid sulfate soils under both oxidized and reduced conditions.

Acid sulfate soils are world-wide in distribution and occupy an area of about 12.5 million hectares (FAO/UNESCO, 1979). Approximately 1.5 million hectares of actual and potential acid sulfate soils occur in Thailand (Pons and Kevie, 1969) and approximately 0.8 million hectares of those are located in the Bangkok Plain (Kevie and Yenmanas, 1972) where they are primarily used for rice cultivation. Often production success is low due to soil acidity, soil salinity, P deficiency, and toxicity of Al, Fe, and H_2S . In the absence of Fe and Al toxicity, P deficiency is the most important problem of acid sulfate soils in the Bangkok Plain (Attanandana and Vacharotayan, 1986).

The sorption and release of native and added P are affected by oxidation-reduction potential (Khalid et al., 1977; Holford and Patrick, 1979), pH (Mokwunye, 1975; Bar-Yosef et al., 1988), temperature (Barrow, 1979; Chien et al., 1982; Sah and Mikkelsen, 1986), the amount and type of clay (Muljadi et al., 1966; Fox and Kamprath, 1970; Bar-Yosef et al., 1988), organic matter (Bloom, 1981), and the amounts of Fe and Al (Bromfield, 1965; Khalid et al., 1977; Holford and Patrick, 1979; Bloom, 1981; Torrent, 1987; Lajtha and Bloomer, 1988; Russell et al., 1988).

Several studies have reported that P-sorption increased as acidity increased in some soils and clay systems (Syers et al., 1973; Mokwunye, 1975; Holford and Patrick, 1979). Lopez-Hernandez and Burnham (1974) reported a decrease in P-sorption with increasing pH in some soils from England (Typic Hapludalf and Typic Quartzipsamment). Bar-Yosef et al. (1988) also reported a decrease in P sorption by Ca- and K-montmorillonite and kaolinite with increasing pH. Imai et al. (1983) found that the maximum sorption of P in oxidized acid sulfate soil occurs at pH 5.0. Khalid et al. (1977) observed that P sorption increased only in reduced soils whose pH is near neutral. Holford and Patrick (1979) reported similar results, but they noted a decrease of P sorption in reduced soils at a pH of 5.0.

The classical Langmuir, Temkin, and Freundlich equations are often used to describe the quantity and intensity relationship between solid and solution phases of P in

soils (Olsen and Watanabe, 1957; Bache and Williams, 1971), but normally fit sorption data for only a limited range of P concentration (Syers et al., 1973; Holford et al., 1974). The lack of agreement between P-sorption data and these equations caused many scientists to develop more complicated models such as the Langmuir two-surface equation (Holford et al., 1974), the applied constant capacitance model (Goldberg and Sposito, 1984), and the modified Langmuir equation (Kuo, 1988). The classical Langmuir and Freundlich isotherms, which require the determination of only two parameters, are much simpler than the complicated models mentioned above. Mead (1981) and Polyzopoulos et al. (1985) reported that the Freundlich isotherm fitted P-sorption data better than the classical Langmuir and Temkin isotherms. However, the Freundlich equation has limited usefulness because it cannot predict a maximum sorption capacity (Bohn et al., 1985). Bache and Williams (1971) noted that the Temkin equation is convenient for two reasons: (i) the wide concentration range that is of interest in soils is most conveniently represented on a logarithmic scale; (ii) the intensity factor that is of fundamental importance in soil P studies is a chemical potential and therefore a logarithmic function of concentrations.

The objective of this study was to determine the characteristics of P-sorption of acid sulfate soils as affected by oxidation-reduction status in the terms of sorption models.

MATERIALS AND METHODS

The surface layer (0-15 cm) of the acid sulfate soils used in this study were collected from the Bangkok Plain of Thailand (Fig. 2.1.). Soils were air-dried, sieved (<2 mm), and thoroughly mixed prior to chemical analysis. In this study one para-acid sulfate soil, Bangkok (Bk) (pH 4.9), and three actual acid sulfate soils, Maha-Phot (Ma)

(pH 4.5), Rangsit (Rs) (pH 4.3), and Rangsit very acid (Rsa) (pH 3.9) were used. These soils represent those where rice is produced on the Bangkok Plain. General morphology and chemical characteristics of the soils were described by Kevie and Yenmanas (1972). Selected soil physical and chemical properties are presented in Table 2.1.

Suspensions of 250 g soil in 1750-mL 0.01 M CaCl_2 were incubated in laboratory microcosms (Fig. 2.2.) under oxidized and reduced conditions for 4 wk at 25 °C (4 replications). N_2 and O_2 gases were bubbled continuously through the soil suspensions at a slow rate of flow to promote reduced and oxidized conditions, respectively. The redox potential and pH of the system were monitored. Prior to the incubation, the soils were amended with finely ground rice straw (40 mesh, 0.2 % on oven-dried soil weight basis) which provided an energy source to promote microbial activity. At the end of the incubation period, the soil suspensions (50 mL) were then transferred to 250-mL polycarbonate centrifuge bottles and P in concentrations ranging from 0 to 500 mg P kg^{-1} soil as KH_2PO_4 was then added to the soil suspensions. For the reduced condition treatment, the centrifuge bottles were flushed with O_2 -free N_2 prior to adding the soil suspensions to maintain a reduced atmosphere during the equilibration. After 24-h equilibration on a reciprocating shaker, the soil suspension was centrifuged (20 min at 7 000 rpm (8 000 \times g), Sorvall GSA-400 rotor, DuPont co., Wilmington, DE) and filtered through a 0.45- μm membrane filter, under an O_2 -free N_2 atmosphere to maintain a reduced condition (Gambrell et al., 1975). The filtrate was analyzed for P, soluble Fe and Al using an ICP (Inductively Coupled Argon Plasma Atomic Emission Spectrometer). The P that disappeared from solution was considered as sorbed P.

The residual soil samples were shaken with 100-mL sodium citrate-dithionite solution (20%) on a reciprocating shaker for 18 h. After centrifugation and filtration, the filtrate was analyzed for citrate-dithionite extractable Fe and Al with the ICP.

Table 2.1. Selected physical and chemical properties of the actual and para-acid sulfate soils

Soil Properties	Bangkok (Bk)	Maha-Phot (Ma)	Rangsit (Rs)	Rangsit very acid (Rsa)
Great Soil Group	Typic Tropaquept	Sulfic Tropaquept	Sulfic Tropaquept	Sulfic Tropaquept
Acidity class	Non-acid	Moderately acid	Severely acid	Extremely acid
pH (1:1 water)	4.9	4.5	4.3	3.9
Organic matter (%) ^a	1.3	1.9	3.3	4.4
Available Pb	19.2	3.2	5.5	6.5
Exchangeable Al (cmol kg ⁻¹) ^c	1.1	2.3	2.0	10.1
Exchangeable acidity (cmol kg ⁻¹) ^d	1.2	3.2	2.9	10.5
CEC (cmol kg ⁻¹) ^e	24.9	19.9	20.8	21.8

^a Walkely-Black (Allison, 1965)

^b modified Bray II; soil:extractant = 1:10

^c 1 M KCl

^d BaCl₂-Triethanolamine (Peech, 1965)

^e Ammonium saturation-distillation (Chapman, 1965)

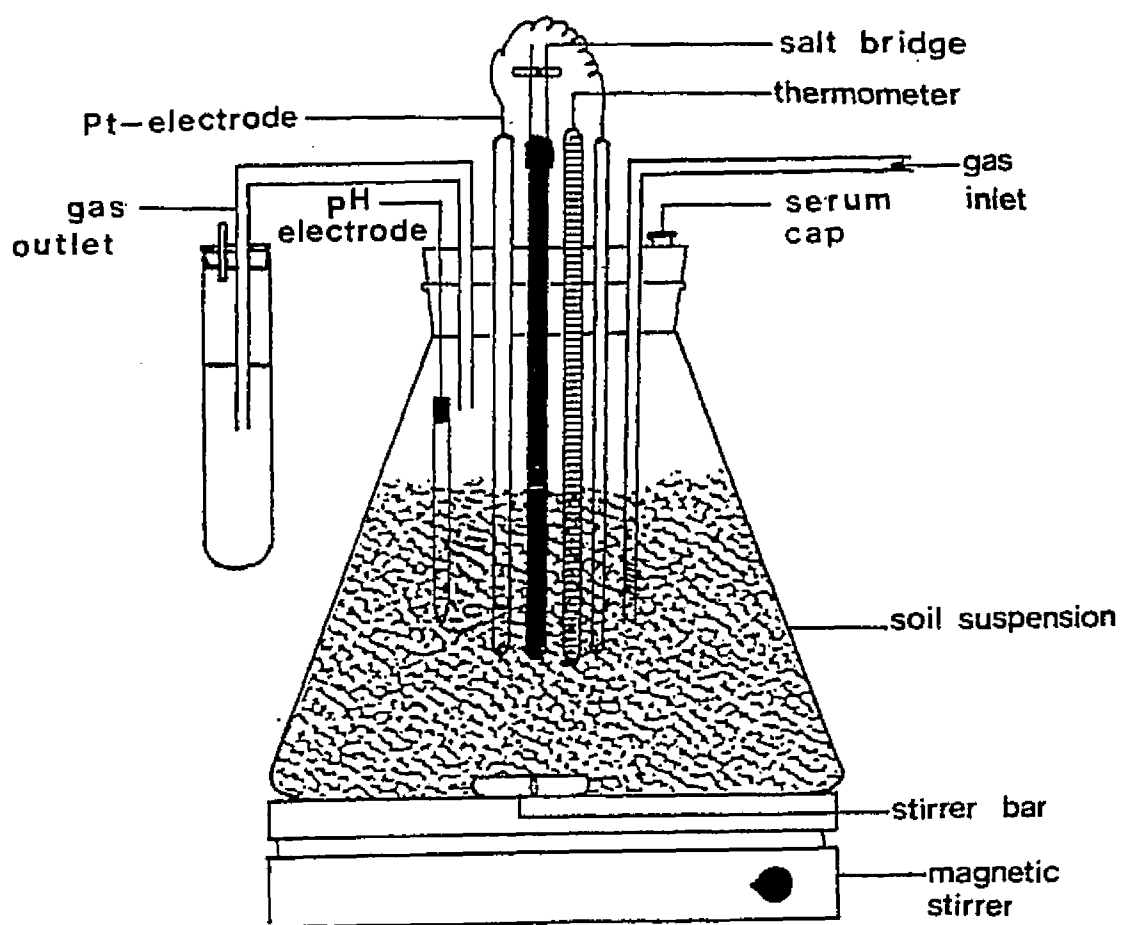


Figure 2.2. The system used to study the P-sorption characteristics under oxidized and reduced conditions

Sorption data for the soils were fitted to the classical Langmuir (Olsen and Watanabe, 1957), Freundlich (Low and Black, 1950) and Temkin (Mead, 1981) equations.

The Langmuir equation is written:

$$x = kx_m C / (1 + kC) \quad (1)$$

where x is the amount of sorbed P per unit of soil, C is the final solution P concentration, k is a coefficient which reflects the relative rates of sorption and desorption at equilibrium and is thus an affinity term, and x_m is the maximum monolayer sorption capacity. The two constants (k and x_m) were determined by fitting the experimental data to linearized form (Lineweaver-Burk form) as given below (Persoff and Thomas, 1988):

$$1/x = 1/x_m + (1/kx_m)(1/C) \quad (2)$$

The Freundlich equation is written:

$$x = ac^{1/n} \quad (3)$$

from which

$$\ln x = \ln a + (1/n) \ln C \quad (4)$$

(Mead, 1981) gives a linear test plot where a and $1/n$ are constants.

The simplest form of Temkin equation (Mead, 1981) was used:

$$x = \alpha + \beta \ln C \quad (5)$$

where α and β are constants. A plot of x against $\ln C$ should give a straight line.

The constants in equation (2), (4), and (5) were calculated by linear regression techniques using the procedures available with Statistical Analysis System (SAS Institute Inc., 1985). An asterisk (*) and double asterisks (**) were used to represent significant correlations at the probability levels < 0.05 and 0.01 , respectively.

RESULTS AND DISCUSSION

Effects of Reduced and Oxidized Conditions on Release of Native P

Under reduced conditions (Eh -190 to +145 mV) more native insoluble P was released from soils than under oxidized conditions (Eh +695 to +815 mV) (Table 2.2.). The concentrations of Fe and Al in solution as well as the citrate-dithionite extractable Fe and Al were higher under the reduced conditions than that under the oxidized conditions. The increase in P concentration of the soil solutions is generally attributed to the reduction and dissolution of ferric phosphate, particularly in acid soils (Patrick et al., 1973) and the release of P occluded in previous insoluble ferric hydrous oxides (Chang and Jackson, 1958). Tanaka et al. (1969) attributed most of the increase in P solubility under reduced conditions to the increase in pH which usually occurs along with reduction in acid soils. Lindsay (1979) also reported that the pH of reduced soil, which generally rises toward neutrality, increases the solubility of Fe and Al phosphate. On the contrary, Patrick et al. (1973) noted that an increase in pH results in a release of smaller amount of P under reduced condition. They also found that the dissolution of strengite increases as both pH and redox potential decrease.

The para-acid sulfate soil (Bk) released more P than actual acid sulfate soils (Ma, Rs, and Rsa) under both oxidized and reduced conditions. The para-acid sulfate soil had a much higher amount of Bray II P than the actual acid sulfate soils. Among the actual acid sulfate soils, Ma and Rs released more P than Rsa, while Rsa had a higher Bray II P concentration than Rs and Ma. The results showed that Rsa had higher amounts of citrate-dithionite extractable Fe and Al than Rs and Ma, respectively (Table 2.2.). Correlation matrices computed between the amount of native insoluble P released into solution and some chemical soil properties indicated that the concentration of native P released under oxidized conditions was negatively correlated with both soluble Al and citrate-dithionite extractable Al and Fe ($r = -0.90^{**}$, -0.84^{**} , and -0.80^{*} , respectively).

Table 2.2. Concentrations of P released, soluble Fe, Al, and citrate-dithionite extractable Fe and Al

Soil	pH	Eh		native P released	soluble		citrate-dithionite extractable	
		actual	corrected to pH 7		Fe	Al	Fe	Al
		-----mV-----		-----mg kg ⁻¹ soil-----				
Bangkok (Bk)								
Oxidized	4.25	+715	+553	2.6	0.6	2.8	1049	815
Reduced	6.65	-190	-211	4.8	477	26.2	4694	749
Maha-Phot (Ma)								
Oxidized	4.20	+695	+530	1.2	0.8	32.6	1378	1273
Reduced	5.65	+125	+45	2.7	579	47.8	6092	1801
Rangsit (Rs)								
Oxidized	4.10	+745	+574	1.2	0.9	51.1	1933	1942
Reduced	5.50	+145	+57	2.7	905	53.1	7727	2351
Rangsit very acid (Rsa)								
Oxidized	3.90	+815	+632	0.9	1.8	52.5	2255	2331
Reduced	5.45	+105	+14	2.2	1103	56.8	8834	2962

Under reduced conditions, native P released was also negatively correlated with both soluble Al and Fe and citrate-dithionite extractable Al and Fe ($r = -0.97^{**}$, -0.78^{**} , -0.90^{**} , and -0.87^{**} , respectively). The results suggest that Al (trivalent aluminum ion, amorphous and crystalline forms) and Fe (ferrous and ferric ions, amorphous and crystalline) are important in affecting the released of native insoluble P in acid sulfate soils under both oxidized and reduced conditions. It should be pointed out that citrate-dithionite extraction dissolves Fe and Al from both amorphous materials, weathering products, and some crystalline primary oxides (McKeague and Day, 1966).

Phosphorus Sorption Characteristics Under Oxidized and Reduced Conditions

The experimental P-sorption isotherms constructed for the para-acid sulfate soil (Bk) and one of the actual acid sulfate soils (Ma) (Fig. 2.3.) indicated that the amount of P sorbed differed for soils with different acidity classes. Furthermore, the sorption behavior was influenced by soil oxidation-reduction status. Similar patterns were also observed in the other actual acid sulfate soils (Rs and Rsa) (Fig. 2.4.). The amounts of P sorbed by the para-acid sulfate soil was less than those by the actual acid sulfate soils under both oxidized and reduced conditions. Considerable lower citrate-dithionite extractable Fe and Al concentrations in para-acid sulfate soil were observed under both oxidized and reduced conditions (Table 2.2.).

Even though the reduced soil conditions caused an increase in the release of native insoluble P to solution, they also led to a very large increase in P sorption capacity of soils at the higher P levels. Khalid et al. (1977) reported similar results, while Holford and Patrick (1979) demonstrated that the reduced conditions led to a decrease in P sorption of the soil at pH 5.0, but induced an increase of P sorption of the soil at pH 6.5. In our experiment, we observed that the amounts of citrate-dithionite extractable Fe and Al under reduced conditions were considerably higher than under oxidized conditions. Correlation matrices indicated that P sorbed was positively correlated with citrate-

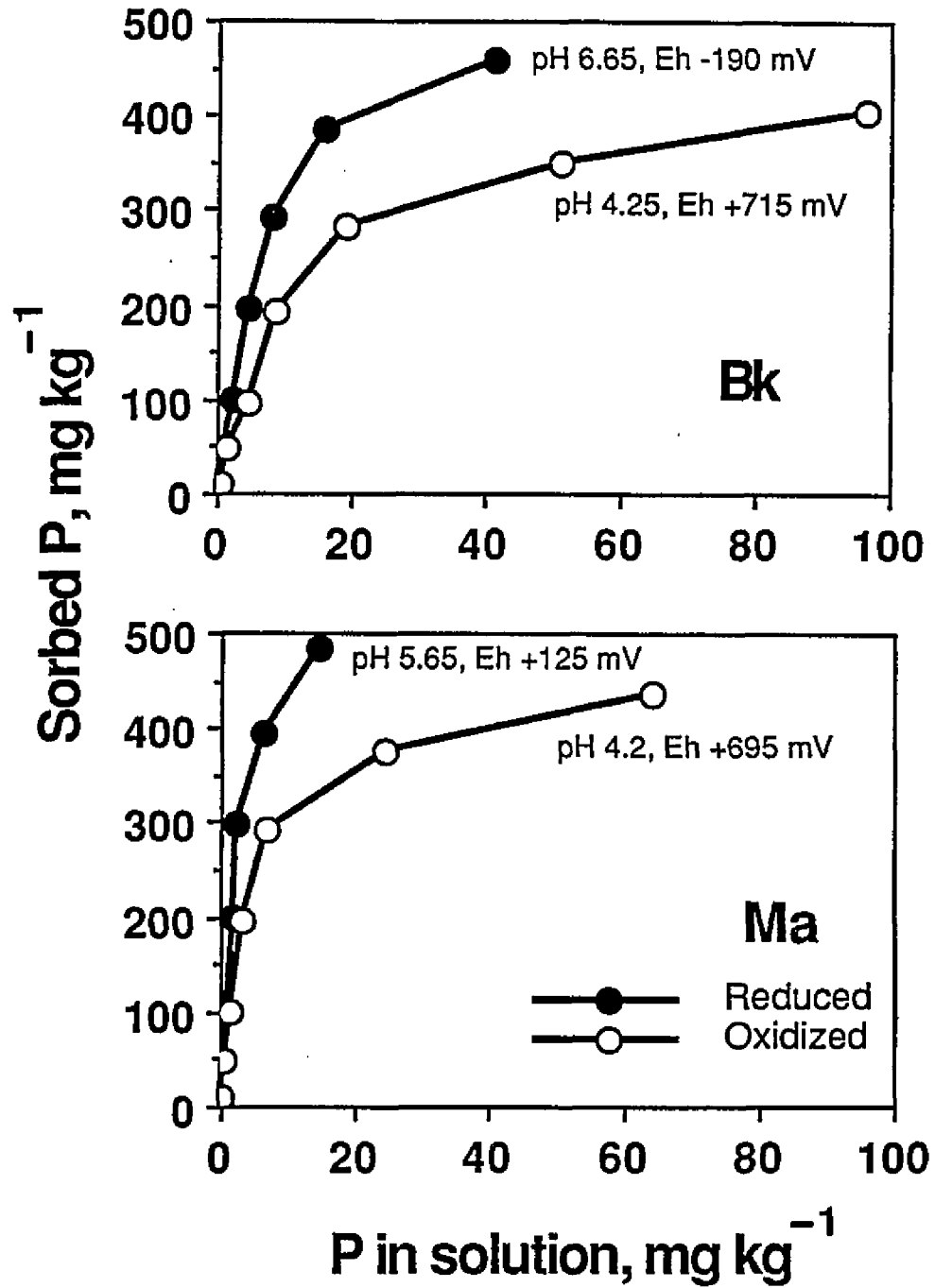


Figure 2.3. The actual P-sorption isotherms in Bangkok soil (Bk) and Maha-Phot soil (Ma) as affected by oxidation-reduction status

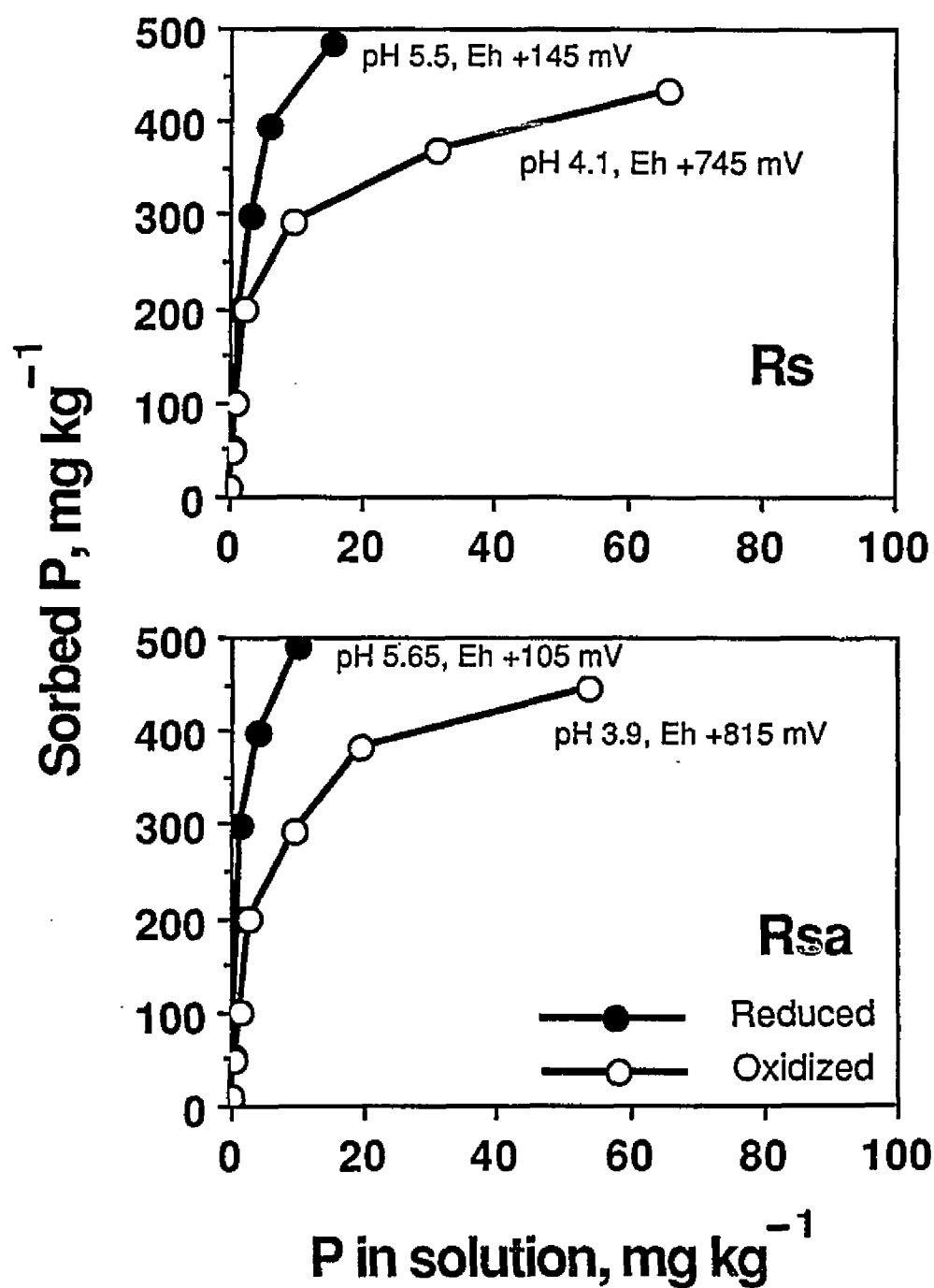


Figure 2.4. The actual P-sorption isotherms in Rangsit soil (Rs) and Rangsit very acid soil (Rsa) as affected by oxidation-reduction status

dithionite Fe and Al extractable under both oxidized and reduced conditions ($r = 0.85^{**}$, 0.93^{**} , 0.88^{**} and 0.92^{**} , respectively).

Patrick and Khalid (1974) noted that the difference in P sorption between oxidized and reduced soils is very likely due to the difference in the capacity of oxidized and reduced forms of iron-oxides to sorb orthophosphate ions. Ferric oxyhydroxide is apparently capable of binding orthophosphate ions more firmly than the ferrous form, but probably has less surface area exposed to the solution P than the gel-like hydrated ferrous oxide or ferrous hydroxide. Holford and Patrick (1979) also reported that ferrous ion in reduced soils can reprecipitate as ferrous hydroxide which is more reactive and has a greater sorption capacity than ferric hydrous oxide. Poorly crystalline, amorphous, and crystalline iron oxides provide the active P-sorbing surfaces (Khalid et al., 1977; Torrent, 1987). Our results suggest that amorphous and crystalline iron, as extracted by citrate-dithionite extraction, play an important role in the increase of P sorption capacity of acid sulfate soils under reduced conditions.

Large quantities of iron compounds in soils, when incompletely reduced as a result of flooding, also encourage resorption of P (Patrick and Mahapatra, 1968). In a review by Gambrell and Patrick (1978) ferric iron is noted to be stable until redox potential decreases to around +120 mV and sulfate reduction is initiated when redox potential fell to approximately -150 mV, assuming pH 7.0 conditions and a redox potential/pH slope of -60 mV/pH unit. They also noted that one redox component is not always completely reduced before reduction of the next most easily reduced component begins. The Eh value (+14 to +57 mV, corrected to pH 7) of the three actual acid sulfate soils under reduced conditions indicated that incomplete reduction of Fe in these soils may have caused the increase in P-sorption. For the para-acid sulfate soil, whose pH and Eh under reduced condition were 6.65 and -190 mV, the cause of the increase in P sorption could be attributed to the secondary precipitation of reduced iron as $\text{Fe}(\text{OH})_2$, which is expected to have high sorption capacity (Holford and Patrick, 1979).

Reduced conditions resulted in pH increasing from 4.25 to 6.65 for the para-acid sulfate soil and from 3.90-4.20 to 5.45-5.65 for the actual acid sulfate soils. At pH 5 and above, the trivalent aluminum ion does not interfere with the hydroxy-aluminum forms, whose activity increases with increasing pH (Mokwunye, 1975). The low activity of hydroxy-aluminum forms at low pH could help explain the lower P sorption in the oxidized soil conditions whose pH were below 5. Imai et al. (1983) also reported the maximum P sorption of acid sulfate soils in Thailand at a pH of approximately 5. They suggested that P was initially sorbed on the surface of acid sulfate soils and formed chelating compounds with hydroxy-aluminum existing as a dominant species above pH 5.0.

Phosphorus sorption by hydroxy aluminum species was explained by Hsu and Rennie (1962) and Berkheiser et al. (1980). The strong affinity of the trivalent aluminum ion for OH^- ions accounts for its hydrolysis in aqueous solutions. The hydrolyzed Al ion species is then polymerized through a hydroxyl bridge. Polymerization is encouraged by an increase in pH, which provides the OH^- units for the bridge. However, as the polymer increases in size, the average net positive charge for each aluminum ion decreases and consequently its attraction for additional OH^- units becomes weaker. Therefore, the last OH^- ion attached to the hydroxy-aluminum polymer is very weakly attached. Once attached, the last OH^- ion should be capable of being readily displaced by other anions. The weakly-held hydroxyl units, which have become attached as a result of an increase in pH, do not function as an hydroxyl bridge. Rather, they are located on the surface. Phosphorus will be sorbed on the surface when the hydroxyl-aluminum-phosphate attraction is strong enough to displace these weakly held surface hydroxyl ions.

Phosphorus sorption in acid sulfate soils in Thailand could be attributed to Fe and Al in both amorphous and crystalline forms. Soil reduced conditions associated with changes of pH have strong effects on P-sorption isotherms. A decrease in redox potential led to an increase in amorphous and possible poorly crystalline Fe, which have high active P-sorbing surfaces. As the pH increased upon reduction, the increased activity of

the amorphous hydroxy-aluminum species probably also supported the increase in P sorption.

Comparison of sorption equations

The experimental P-sorption data for the para-acid sulfate soil (Bk) and one of the actual acid sulfate soils (Rsa) under both oxidized and reduced conditions were fitted with the classical Langmuir, Freundlich, and Temkin isotherms as depicted in Fig. 2.5. and 2.6. A similar pattern was also observed in Ma and Rs soils. The classical Langmuir equation showed the best fit with the actual P-sorption data in all soils under both oxidized and reduced conditions. The Temkin equation closely predicted the actual P-sorption as well. The Freundlich equation, however, provided the closely predicted values of P-sorption only up to P added level of 400 mg P kg⁻¹ soil. Beyond that level the predicted values began to be overestimated.

The goodness of fit of the three sorption equations was compared by simple linear regression analysis of the actual and predicted sorptions for each soil under each condition.

By far the most widely used model for describing P-sorption is the Langmuir equation (Berkheiser et al., 1980), which was originally applied to P-sorption on soil by Olsen and Watanabe (1957). According to Olsen and Watanabe (1957), the advantages of the Langmuir equation are that it fits actual P sorption isotherm data for soils better, and that the sorption maximum can be calculated. Our results also indicated that the classical Langmuir equation fitted the actual P-sorption better than other equations under both oxidized and reduced conditions (Table 2.3.). The Langmuir equation is applicable to uniform energy sorption. However, sorption potential energies of surfaces in soil systems are not usually uniform in distribution. Each mineral and type of organic matter can be expected to sorb P with different sorption energies (Berkheiser et al., 1980). Thus, the classical Langmuir equation has been modified by postulating that there is

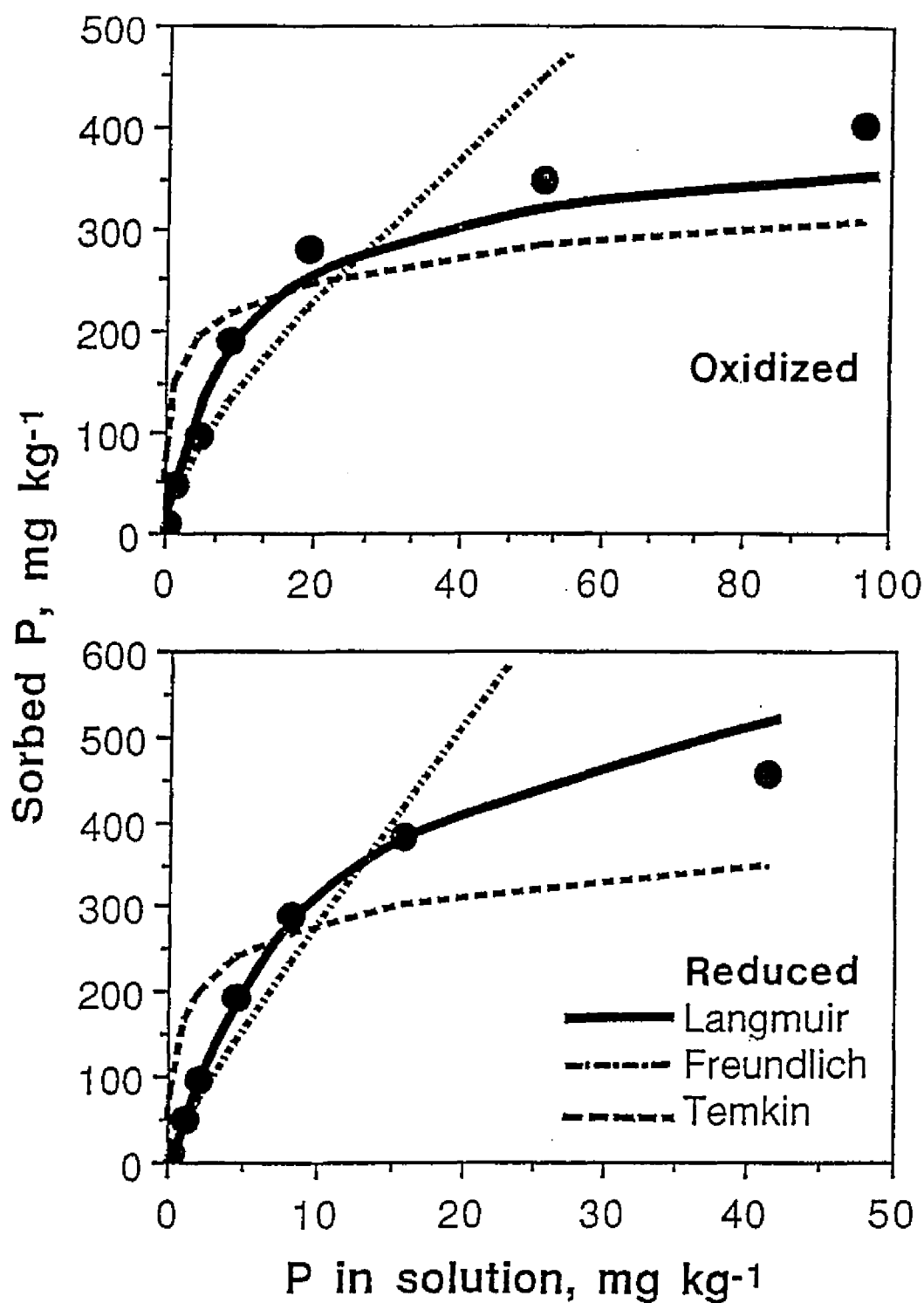


Figure 2.5. Comparison of observed and predicted P-sorption in the para-acid sulfate soil (Bk) under oxidized and reduced conditions using three different sorption equations

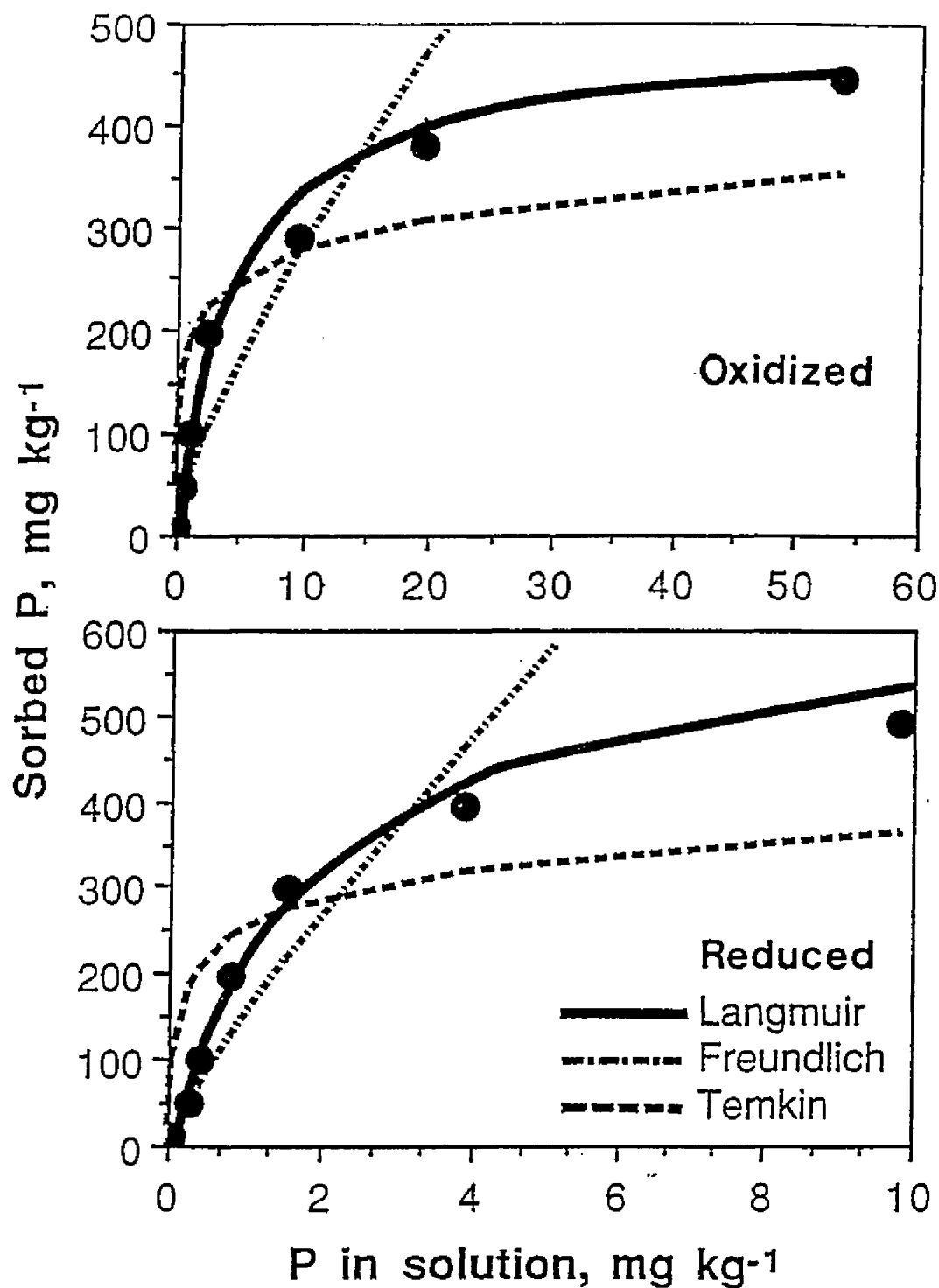


Figure 2.6. Comparison of observed and predicted P-sorption in the actual acid sulfate soil (Rsa) under oxidized and reduced conditions using three different sorption equations

more than one sorption surface (Holford et al., 1974; Ryden et al., 1977). However, Posner and Bowden (1980) reported that the model, which is based on a single type of adsorption site, is very similar to their experimental isotherms. Kuo (1988) found that the correlation coefficients for the regression of Lineweaver-Burk form of classical Langmuir isotherms in eleven western Washington soils are between 0.955 to 0.996. Barrow (1978) suggested that the simplest model should be preferred unless a more complex one can be shown to improve the measure of goodness of fit. In this experiment, we concluded that because of its better fit to the experiment data the classical Langmuir equation should be preferred for describing P-sorption in acid sulfate soils of Thailand.

The sorption maximum for each soil under each condition calculated from the Langmuir equation (Table 2.3.) indicated that the maximum sorption capacities of para-acid sulfate soil were less than those of actual acid sulfate soils under both oxidized and reduced conditions. The sorption maxima of all soils under oxidized conditions were less than under reduced conditions. This prediction is in good agreement with the experimental data.

Table 2.3. Regression data for relationship between actual and predicted P-sorption for the three sorption equations and the maximum sorption capacity for the Langmuir equation

Soil	Langmuir		Freundlich	Temkin
	R-square	X_m	R-square	R-square
mg kg ⁻¹ soil				
Bangkok (Bk)				
oxidized	0.99	432	0.88	0.78
reduced	0.99	566	0.81	0.78
Maha-Phot (Ma)				
oxidized	1.00	488	0.76	0.84
reduced	0.99	652	0.84	0.78
Rangsit (Rs)				
oxidized	0.99	454	0.81	0.86
reduced	1.00	659	0.85	0.77
Rangsit very acid (Rsa)				
oxidized	0.99	496	0.82	0.81
reduced	0.99	648	0.83	0.77

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CHAPTER THREE

PHOSPHORUS SORPTION IN ACID SULFATE SOILS UNDER CONTROLLED pH AND REDOX POTENTIAL

ABSTRACT

The influences of pH and redox potential on P-sorption characteristics of acid sulfate soils of Thailand were studied. Surface soil samples of the actual and para-acid sulfate soils collected from the Bangkok Plain in Thailand were incubated under controlled pH (4.0, 5.0, and 6.0) and redox potential (+600, +400, +300, +200, +100, and 0 mV) conditions for 6 wk in stirred soil suspensions with a soil to 0.01 M CaCl₂ solution ratio of 1:7. After the incubation period, the soil suspensions were equilibrated with KH₂PO₄ ranging from 0 to 500 mg P kg⁻¹ soil. Sorption isotherms were described by the classical Langmuir equation. The P-sorption of both actual and para-acid sulfate soils was significantly affected by pH, redox potential, and interaction between pH and redox potential. The effects of redox potential on P-sorption changed as pH level changed. This was primarily due to the influence of Fe reduction at the particular redox potential on P-sorption. The P-sorption increased significantly with increasing pH and decreasing redox potential. The actual acid sulfate soil sorbed more P than did para-acid sulfate soil. Closer correlation between P-sorption parameter and iron-oxides than aluminum-oxides indicated the primary role of iron oxides on P-sorption of both actual and para-acid sulfate soils even though the soils contain the considerable amount of aluminum oxides. Manganese also showed a significant effect on P-sorption, but the mechanism is unclear.

The worldwide area of acid sulfate soils is estimated to be 12.5 million hectares (FAO/UNESCO, 1979). In Thailand, one of the major rice production countries in southeast Asia, acid sulfate soils occur mainly in the Bangkok Plain in an area of about 0.8 million hectares, of which 95 % is used for lowland rice production. The Bangkok Plain accounts for nearly half the total rice production of the country. During the rice growing season, the Bangkok Plain is inundated by river floods and rain water, and water levels in dry seasons are predominantly 100 cm below the soil surface. Furthermore, irrigation water is rarely available during the dry season. Under this condition, one crop per year is a rule, and rice production is low to very low, ranging between 500 to 1 500 kg ha⁻¹ (Attanandana et al., 1982). Fertility studies of acid sulfate soils (Attanandana, 1982) indicated that the high acidity of these soils retards microbiological activity, and the P-sorption coefficient is high. In addition, the excess amounts of Fe and Al have been reported to limit rice growth. Charoenchamratcheep et al. (1982) noted that rice did not respond to P fertilizer unless the soil pH was raised by liming.

The sorption of P by aerobic soils and pure iron- or aluminum-oxides have been studied intensively during the last two decades. However, few attempts have been made to simulate effects of pH on P-sorption of anaerobic soils, particularly in acid sulfate soils of Thailand. The P-sorption capacity of pure aluminum- and iron-oxides has been reported to decrease as the pH is raised from 3 to 12 (Hingston et al., 1972; Bowden et al., 1980). Unlike the pure oxides, the P-sorption of oxidized soils has been reported to increase (Mokwunye, 1975; White and Taylor, 1977; Haynes and Swift, 1985; Traina et al., 1986) or decrease (Obihara and Russell, 1972; Lopez-Hernandez and Burnham, 1974; Smyth and Sanchez, 1980) as pH is raised. The effect of pH on P-sorption of oxidized acid sulfate soils of Thailand studied by Imai et al. (1983) showed that P-sorption capacity increased with increasing pH and reached its maximum around pH 5 to 6.

Khalid et al. (1977) found that more P was sorbed under reduced conditions than under oxidized conditions in most soils at high level of added P. The effects of redox po-

tential and pH changes on P-sorption had been studied by Holford and Patrick (1979). They found that changes in P-sorption varied depending on both redox potential and pH. At pH 5.0, reduction to Eh -150 mV decreased P-sorption whereas reduction (same Eh) caused a very large increase in P-sorption at pH 6.5.

Little information is available on P-sorption of acid sulfate soils of Thailand as affected by pH and redox potential changes have been available. Knowledge of P-sorption phenomena when pH and redox potential change will aid in developing a program for lime and P usage for improving the rice production in the Bangkok Plain.

The objective of the present work was to obtain more information on P-sorption of acid sulfate soils of Thailand as affected by pH and redox potential.

MATERIALS AND METHODS

The surface layer (0-15 cm) of acid sulfate soils used in this study were collected from the Bangkok Plain of Thailand (see Fig. 2.1.). Soils were air-dried, sieved (< 2 mm), and thoroughly mixed prior to analysis. In this study, one para-acid sulfate soil, Bangkok (Bk), and one actual acid sulfate soil, Maha-Phot (Ma), were used. General morphology and chemical characteristics of soils were described by Kevie and Yenmanas (1972). Selected soil properties are presented in Table 2.1.

The experiment was conducted to determine P-sorption of each soil under six different levels of redox potential (+600, +400, +300, +200, +100, and 0 mV, respectively) at three levels of pH (4.0, 5.0, and 6.0, respectively). The experimental design was 6*3 factorial in a randomized complete block design with two replications.

The suspensions of 250 g soil in 1 750-mL 0.01 M CaCl_2 were incubated in laboratory microcosms at various redox potential and pH (as mentioned above) using a modification of the redox control system developed by Patrick et al. (1973) (Fig. 3.1.) for 6 wk at 25 °C. Prior to incubation, the soils were amended with finely ground rice straw (40 mesh, 0.2 % on oven-dried soil weight basis) which provided an energy source to pro-

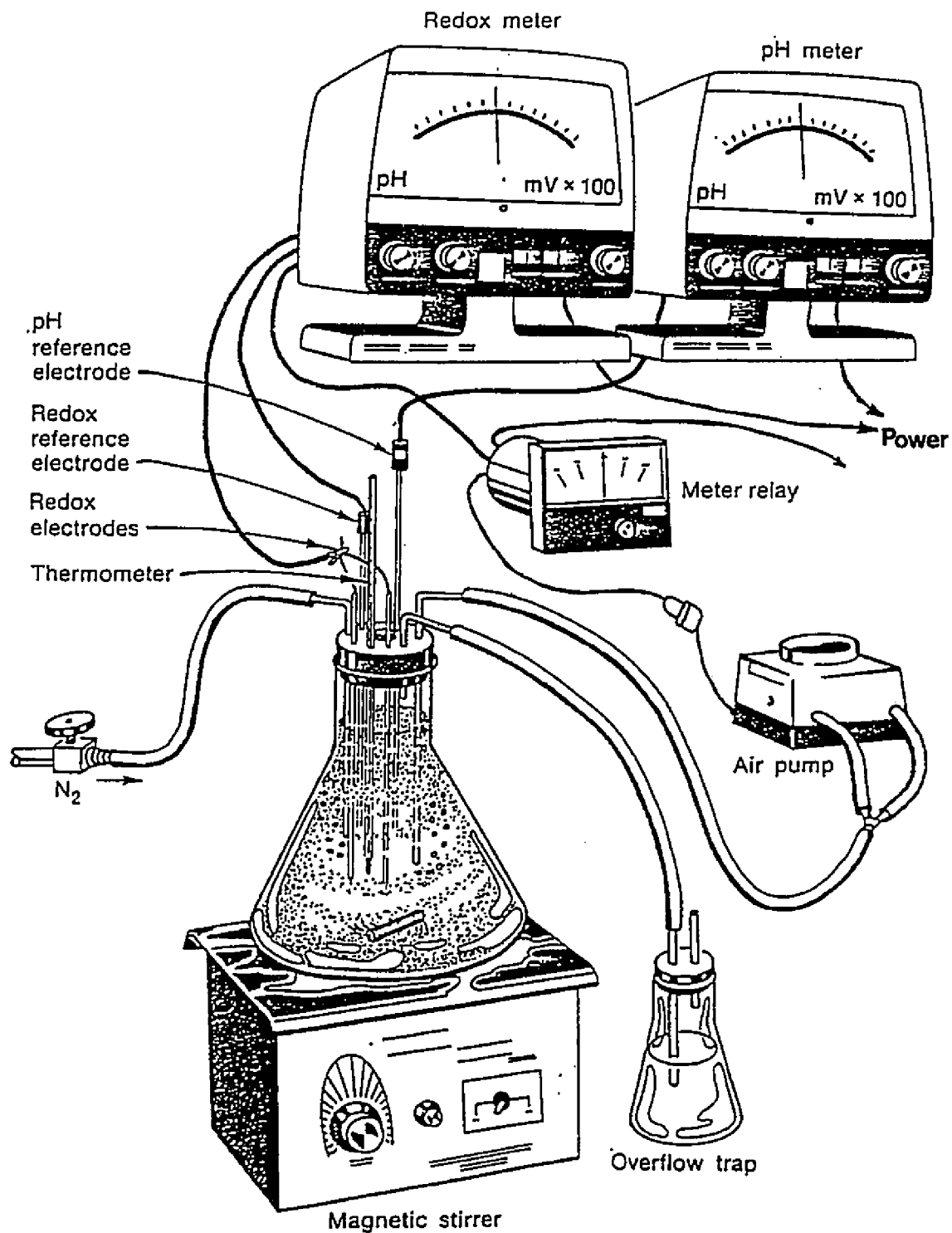


Figure 3.1. The system used to study the P-sorption under controlled pH and redox potential

mote microbial activity. In the redox control system, pH of soil suspensions was controlled at the desired pH values by manual additions of either 2 *N* HCl or 2 *N* NaOH daily or as required. The redox potential was maintained at aforementioned levels automatically. The two platinum electrodes in each microcosms were connected to millivolt meters to give continuous measurement of redox potential of the soil suspensions. The recorder output of the millivolt meter sent a signal to a meter relay which, in turn, activated an air pump to supply a small amount of air into the system to maintain the desired redox potential whenever the redox potential dropped below the selected level. Nitrogen gas was bubbled continuously through the soil suspensions at a slow rate to purge excessive O₂ from the additional air to control redox potential of the system. Using this system with the ability to provide a slow flow rate of air by virtue of a capillary tubing in conjunction with continuous N₂ flow resulted in maintaining redox potential within ± 5 mV.

At the end of the incubation period, the soil suspensions (50 mL) were transferred to 250-mL polycarbonate centrifuge bottles and P concentrations ranging from 0 to 500 mg P kg⁻¹ soil as KH₂PO₄ was then added to the soil suspensions. For the reduced condition treatment, the centrifuge bottles were flushed with O₂-free N₂ prior to filling with soil suspensions to maintain a reduced atmosphere during the equilibration. After 24-h equilibration on a reciprocating shaker, the soil suspensions were centrifuged (20 min at 7 000 rpm (8 000 \times g), Sorvall GSA-400 rotor, DuPont Co., Wilmington, DE) and filtered through a 0.45- μ m membrane filter, under an O₂-free N₂ atmosphere for reduced conditions (Gambrell et al., 1975). A shaking time of 24 h was chosen because this period was considered adequate for the fast reactions as well as the initiation of the slow reactions to take place during P retention in the soils (Mehadi and Taylor, 1988). The filtrate was immediately analyzed for P, soluble Fe, Al, and Mn using an ICP (Inductively Coupled Argon Plasma Atomic Emission Spectrometer). The P that disappeared from solution was considered as sorbed P.

Fifty mL of soil suspension was shaken with 100 mL of 1 N NH_4OAc , pH 4.0 on a reciprocating shaker for 1 h. The suspension was centrifuged (20 min at 7 000 rpm or 8 000 x g) and filtered through a 0.45- μm membrane filter. The filtrate was analyzed for exchangeable Fe, Al, and Mn using the ICP. Another 50 mL of soil suspension was shaken with sodium-citrate dithionite solution (20 %, 100 mL) on a reciprocating shaker for 18 h. The suspension was also centrifuged and filtrated. The filtrate was analyzed for free oxides of Fe, Al, and Mn with the ICP.

To compare the results, P-sorption data for all samples were fitted to the classical Langmuir equation (Olsen and Watanabe, 1957). The Langmuir equation is written:

$$x = kx_m C / (1 + kC) \quad (1)$$

where x is the amount of sorbed P per unit of soil, C is the final solution P concentration, k is a coefficient which reflects the relative rates of sorption and desorption at equilibrium and is thus an affinity term, and x_m is the maximum monolayer sorption capacity. The two constants (k and x_m) were determined by fitting the experimental data to linearized form (Lineweaver-Burk form) as given below (Persoff and Thomas, 1988):

$$1/x = 1/x_m + (1/kx_m)(1/C) \quad (2)$$

The buffer capacity (BI), a mixed quantity-intensity parameter, was calculated from kx_m (Holford, 1979). The standard P requirement (SPR), P-sorption at a concentration of 0.2 ppm P in final solution, was also calculated. The analysis of variance (ANOVA), Duncan Multiple Range Test (DMRT), and Pearson's correlation coefficients were processed using the procedures available with Statistical Analysis System (SAS Institute Inc., 1985).

RESULTS AND DISCUSSION

Effects of Redox Potential and pH on The Release of Native P

The release of native P measured from soluble P concentrations at the levels of 0 mg P kg^{-1} soil P added was present in Table 3.1. and 3.2. The concentration of soluble P

increased with decreasing soil redox potential and pH. Redox potential had greater effect on soluble P than did soil pH. The concentrations of soluble Fe also increased as redox potential and pH decreased (Table 3.1. and 3.2.). Level of soluble Fe sharply increased as Eh decreased from +400 to +300 mV at pH 4.0, from +300 to +200 mV at pH 5.0, and from +300 to +200 mV at pH 6.0, respectively, illustrating the reduction of Fe in ferric forms (Fe^{3+}) to ferrous forms (Fe^{2+}), which is more soluble. In a review by Gambrell and Patrick (1978), ferric reduction begins when redox potential decrease to around +120 mV, assuming pH 7.0 conditions and a redox potential/pH slope of -59 mV/pH units. The concentrations of soluble Mn slightly increased with decreasing redox potential and pH (Table 3.1. and 3.2.). There was no clear pattern between the concentration of soluble Al and redox potential, however, the concentration of soluble Al increased with decreasing pH (Table 3.1. and 3.2.) Satawathananont (1986) also reported the similar patterns of increasing soluble P and Fe in acid sulfate soils of Thailand. Major contributions to increasing in the concentration of soluble P with decreasing redox potential and pH would be the reduction and dissolution of ferric phosphate (strengite, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), which releases Fe^{2+} and phosphate ions (Patrick et al., 1973), the release of P occluded in previous insoluble ferric hydrous oxides (Chang and Jackson, 1958), and a greater dissolution at low pH of ferrous phosphate as well as ferric phosphate (Patrick et al., 1973).

Although Mn^{2+} in soils is redox dependent (Lindsay, 1979), the concurrent increase in the concentration of soluble Mn may not contribute to the increase in the amount of soluble P due to the solubility of manganese phosphates (MnHPO_4 and $\text{Mn}_3(\text{PO}_4)_2$) which are likely stable under the condition of this experiment. The increase in the amount of soluble Al may not contribute to the increase in the amount of soluble P due to the solubility of aluminum phosphate (variscite, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$). Lindsay (1979) noted that when soils are reduced until $pe + pH$ drops below 4.96, variscite, which is considered to be stable beyond this $pe + pH$ levels, can be converted to vivianite

Table 3.1. Concentrations of soluble (s) P, Fe, Al, and Mn, and concentrations of Fe, Al, and Mn extracted by 1 N NH₄OAc (pH 4.0) (a), and sodium-citrate dithionite solution (d) in Bangkok soil

pH	Redox	P	Fe			Al			Mn		
	potential	s	s	a	d	s	a	d	s	a	d
mV		-----mg kg ⁻¹ soil-----									
4.0	+600	2.9	1.3	42	5203	41	576	6123	58	51	49
	+400	2.7	4.1	52	5497	39	574	6338	62	51	52
	+300	5.7	832	3105	7129	42	568	6327	66	53	55
	+200	6.2	951	3561	7844	46	573	6359	70	59	48
	+100	6.3	1190	3817	8384	38	570	6364	74	60	47
	0	6.1	1455	4008	8906	43	562	6369	84	64	50
5.0	+600	2.4	1.1	38	5344	38	535	6398	46	44	39
	+400	2.2	5.2	50	5805	34	546	6492	42	42	41
	+300	2.9	23	74	6057	38	547	6547	50	53	42
	+200	5.3	894	3254	7726	36	540	6542	47	62	45

Table 3.1. (Continued)

pH	Redox	P	Fe			Al			Mn		
	potential	s	s	a	d	s	a	d	s	a	d
mV		-----mg kg ⁻¹ soil-----									
5.0	+100	5.6	1058	3654	8269	39	538	6532	53	64	44
	0	5.7	1274	3779	8663	40	535	6547	66	64	44
6.0	+600	1.7	1.1	32	5512	36	575	6646	37	31	51
	+400	1.9	5.0	46	5807	39	520	6688	44	30	46
	+300	1.9	19	65	6138	34	525	6740	48	35	43
	+200	4.5	837	3003	8243	38	521	6773	42	41	44
	+100	4.9	965	3382	8502	37	514	6794	50	48	48
	0	5.1	1121	3559	8967	39	505	6826	54	52	48

Table 3.2. Concentrations of soluble (s) P, Fe, Al, and Mn, and concentrations of Fe, Al, and Mn extracted by 1 *N* NH₄OAc (pH 4.0) (a), and sodium-citrate dithionite solution (d) in Maha-Phot soil

pH	Redox	P	Fe			Al			Mn		
	potential	s	s	a	d	s	a	d	s	a	d
mV		-----mg kg ⁻¹ soil-----									
4.0	+600	2.3	1.4	38	5904	65	755	14775	185	223	243
	+400	2.5	4.3	36	6197	67	744	14842	202	230	263
	+300	3.8	1188	2315	9603	64	747	14908	207	231	266
	+200	3.9	1717	2546	9935	60	765	14914	219	233	265
	+100	4.2	2245	2819	10254	61	748	14935	217	231	265
	0	4.2	2659	3122	10763	64	746	14963	228	235	269
5.0	+600	1.7	1.2	30	5245	45	637	15047	156	202	236
	+400	1.9	3.7	31	6427	41	621	15153	162	215	235
	+300	2.0	7.6	44	7643	43	626	15164	174	218	242
	+200	3.1	1381	1854	9802	49	631	15205	182	220	243

Table 3.2. (Continued)

pH	Redox	P	Fe			Al			Mn		
	potential	s	s	a	d	s	a	d	s	a	d
mV		-----mg kg ⁻¹ soil-----									
5.0	+100	3.3	2039	2362	10164	46	626	15194	186	223	240
	0	3.2	2367	2821	10599	48	622	15242	191	224	248
6.0	+600	1.2	1.0	28	6429	39	603	15484	127	195	230
	+400	1.1	2.9	33	6801	37	612	15502	138	209	244
	+300	1.3	4.7	39	8785	37	596	15514	154	215	246
	+200	2.8	1246	1573	10064	34	597	15616	166	219	246
	+100	2.7	1809	2107	10359	36	580	15627	172	224	246
	0	2.9	2227	2648	10854	42	584	15654	180	224	253

($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$). In the presence of vivianite, lowering redox potential lowers the solubility of P (Lindsay, 1981).

Effects of Redox Potential and pH on P-sorption Characteristics

The experimental P-sorption data were described by the classical Langmuir equation. Standard P requirement (SPR) of actual and para-acid sulfate soils were plotted in varying redox potential and pH field as presented in Fig. 3.2. and 3.3. Langmuir maximum sorption capacity (x_m) and Langmuir sorption constant (k) of both soils were shown in Fig. 3.4. and 3.5. Standard P requirement, P-sorption at a concentration of 0.2 ppm P in final solution, was selected following the suggestion of Beckwith (1965) that this concentration, if maintained continuously in solution culture, will provide adequate P to many plants. Although P concentration required by plants may vary among the group of plants, this value can provide a useful information about P fertilizer requirements. Fox and Kang (1978) recorded data on the external P concentration requirements of numerous agronomic and horticultural crops grown in Hawaii. The requirements were reasonably constant within a given species growing on dissimilar soils. Nonetheless, the standard P requirement has been used by many workers (Juo and Fox, 1977; Khalid et al., 1977; Loganathan et al., 1987). Langmuir sorption constant and buffering index have been used in P-sorption studies by several workers (Mehadi and Taylor, 1988; Soils and Torrent, 1989). Soils and Torrent (1989) found that buffering capacity measured from P quantity and intensity changes produced by cropping was similar in magnitude and correlated with buffer capacity calculated from sorption equations in the laboratory. Thus, sorption equation can provide a rough estimation of the field phosphate buffer capacity in the soil studies. However, the estimation is not precise under natural condition due to a multiplicity of factors affecting changes in labile and soluble P.

Standard P requirement was significantly affected by redox potential, pH, and interaction between redox potential and pH in both actual and para-acid sulfate soils (Table

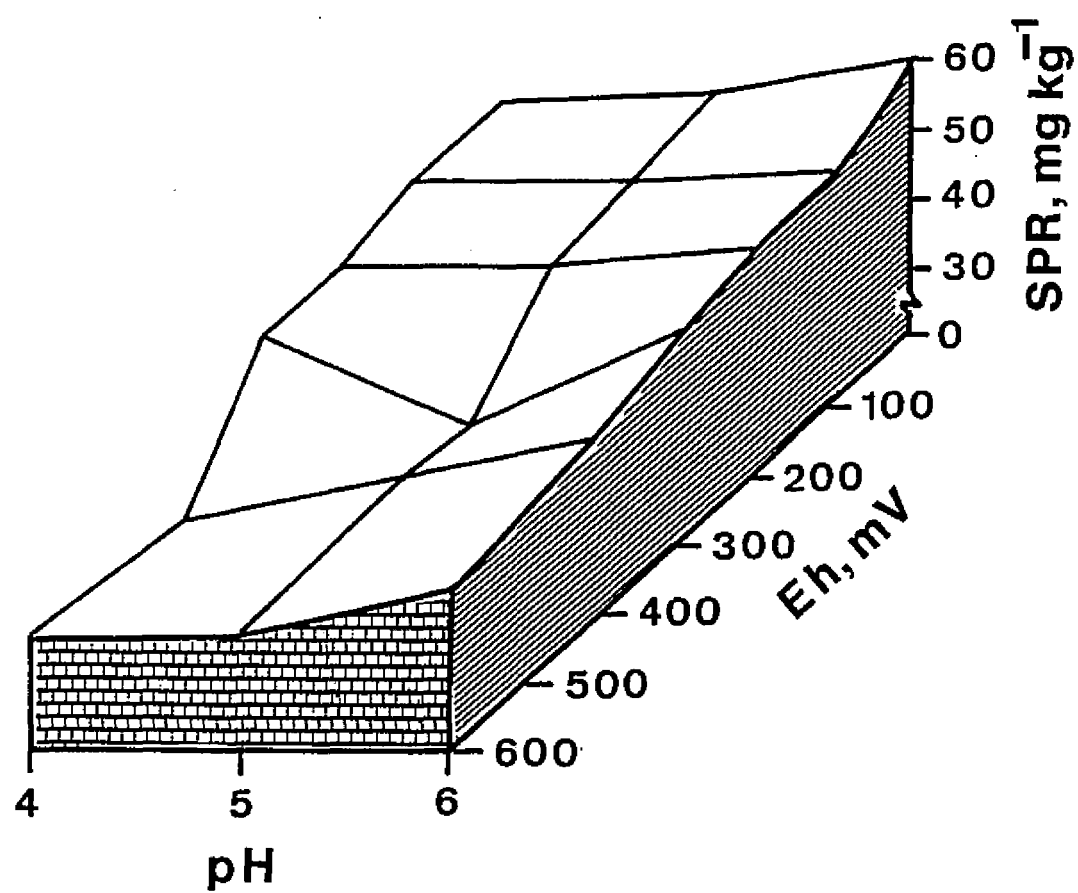


Figure 3.2. Effects of pH, redox potential, and their interaction on standard P requirement (SPR) (mg kg^{-1}) in Bangkok soil

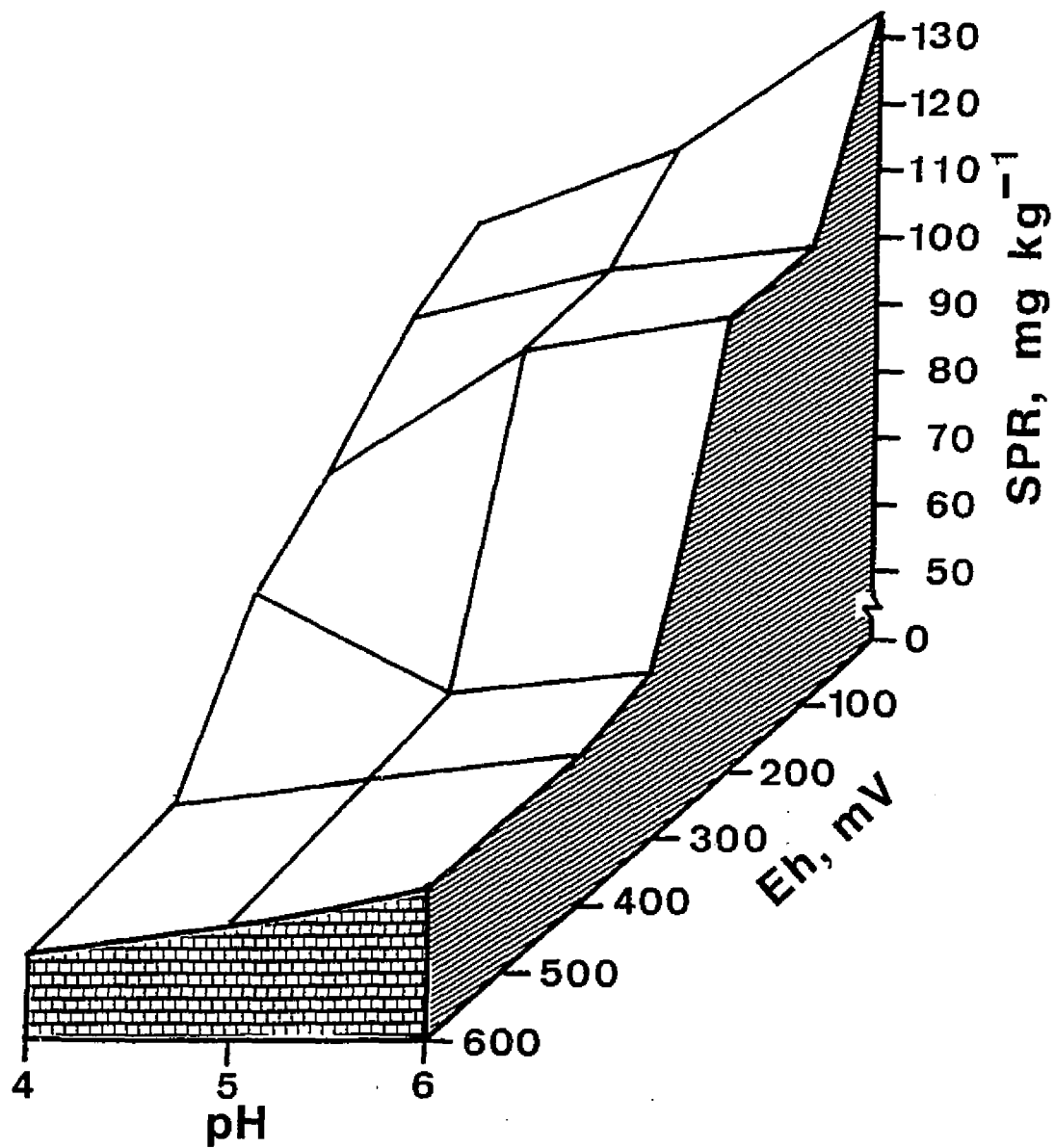


Figure 3.3. Effects of pH, redox potential, and their interaction on standard P requirement (SPR) (mg kg^{-1}) in Maha-Phot soil

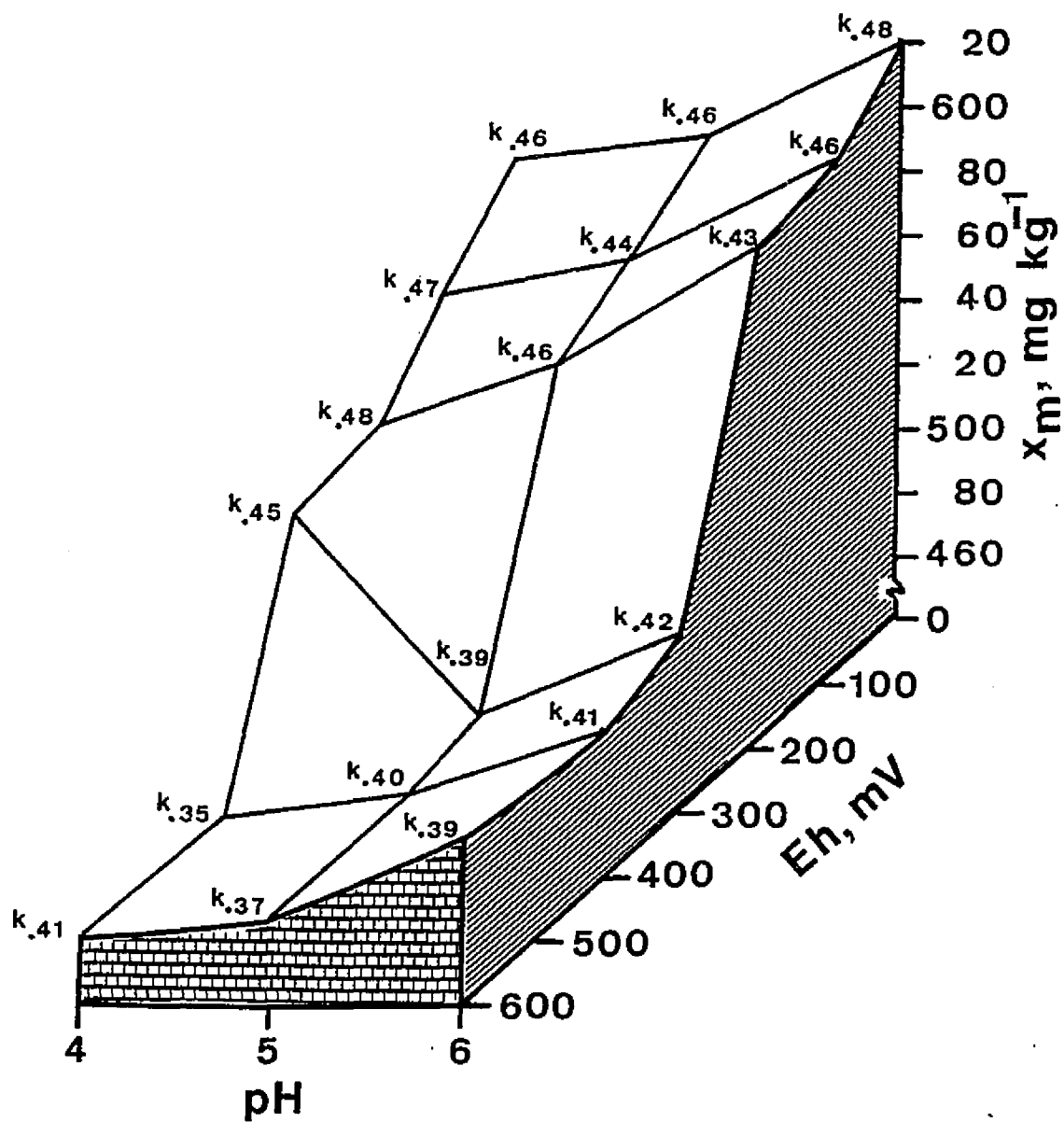


Figure 3.4. Effects of pH, redox potential, and their interaction on Langmuir maximum sorption capacity (x_m) (mg kg^{-1}) and Langmuir sorption constant (k) ($\text{mg}^{-1} \text{kg}$) in Bangkok soil

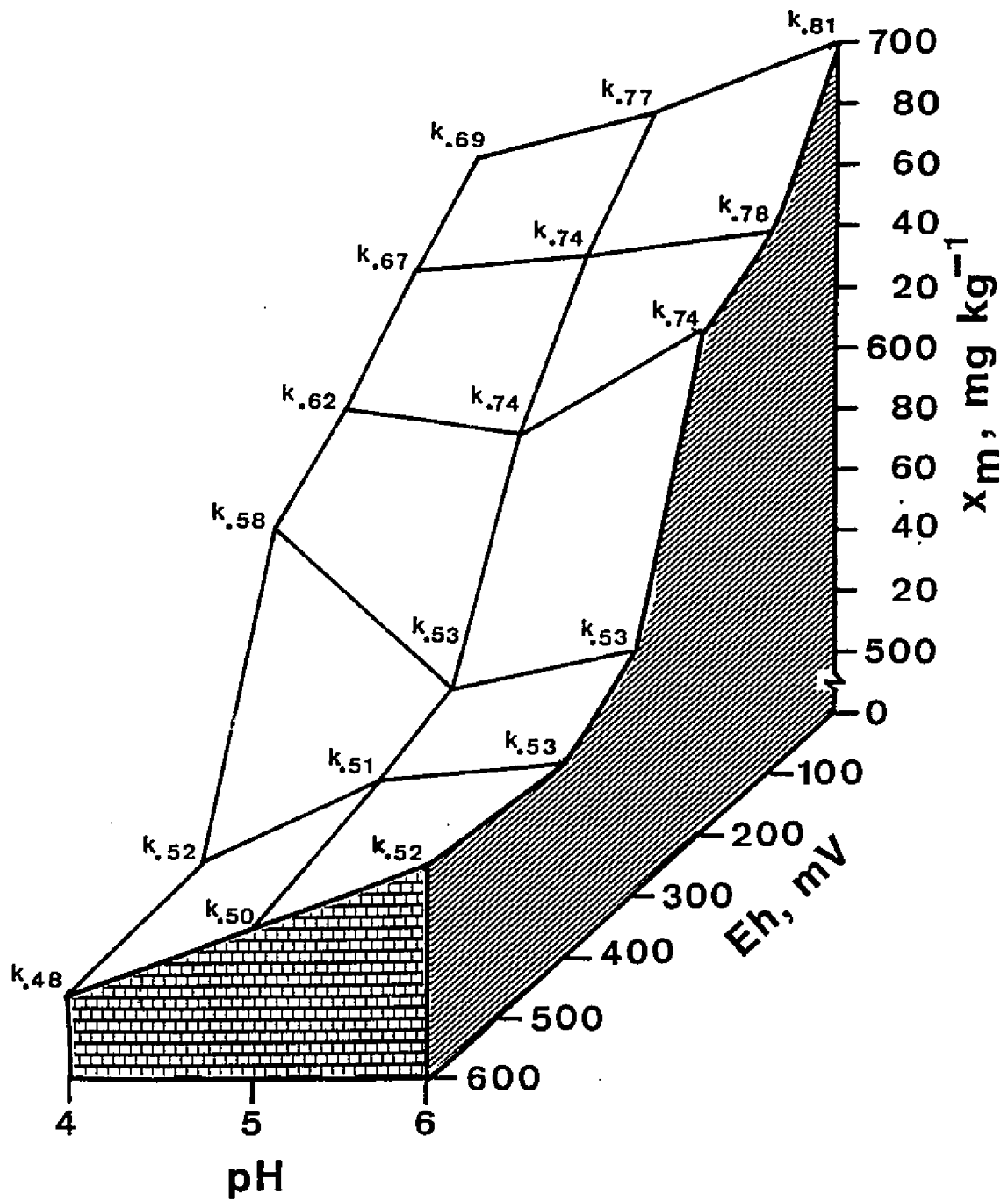


Figure 3.5. Effects of pH, redox potential, and their interaction on Langmuir maximum sorption capacity (x_m) (mg kg^{-1}) and Langmuir sorption constant (k) ($\text{mg}^{-1} \text{kg}$) in Maha-Phot soil

3.3. and 3.4.). A significant interaction indicated that the effect of redox potential changed as the level of pH changed. The graphical factorial comparison between treatment means showed that the significant interaction was due to the different effect of redox potential between pH 4.0, and pH 5.0 and 6.0 (graph not shown). At every pH level, standard P requirement slightly increased or did not change as redox potential decreased from +600 to +400 mV in both actual and para-acid sulfate soils (Fig. 3.2. and 3.3.). At pH 4.0, standard P requirement considerably increased with decreasing redox potential from +400 to +300 mV, whereas at pH 5.0 and 6.0, it gradually increased. As redox potential continued to decrease from +300 to 0 mV, standard P requirement at pH 4.0 continued to gradually increase. At pH 5.0 and 6.0, the patterns of standard P requirement were likely the same. As redox potential declined from +300 to +200 mV, standard P requirement steeply increased, particularly in the actual acid sulfate soil. Below the redox potential of +200 mV, standard P requirement continued to increase, particularly in the actual acid sulfate soil.

The comparison between treatment means using Duncan's Multiple Range Test (DMRT) indicated that standard P requirement increased significantly as pH increased (SPR at pH 6.0 > 5.0 > 4.0, respectively). The standard P requirement also increased significantly with decreasing redox potential (SPR at Eh 0 > +100 > +200 > +300 > +400 mV, respectively). Nevertheless, an increase in standard P requirement as redox potential decreased from +600 to +400 mV was not significant. The standard P requirement of the actual acid sulfate soil (Maha-Phot, Ma) ranging from 52 to 132 mg P kg⁻¹ soil was classified as low (10-100 mg P kg⁻¹ soil) to medium (100-500 mg P kg⁻¹ soil) level, whereas that of the para-acid sulfate soil (Bangkok, Bk) ranging from 34 to 59 mg P kg⁻¹ was classified as low level on the scale proposed by Juo and Fox (1977). The materials classified as low level were 2:1 clays, quartz, and 1:1 clays, and materials classified as medium level were 1:1 clays with oxides. This is in good agreement with the properties of soils under study. Both actual and para-acid sulfate soils comprised more than 60 %

of kaolinite (Breemen, 1976) which is 1:1 type clay. However, the amount of free iron oxides (citrate-dithionite extractable Fe) of actual acid sulfate soil was higher than that of para-acid sulfate soil (Table 3.1. and 3.2.).

Like standard P requirement, Langmuir maximum sorption capacity (x_m) was significantly affected by redox potential, pH, and interaction between redox potential and pH in both actual and para-acid sulfate soils (Table 3.3. and 3.4.). A significant interaction between redox potential and pH resulted from the similar reason as standard P requirement. The effects of redox potential and pH on Langmuir maximum sorption capacity of both soils (Fig. 3.4. and 3.5.) showed the similar trend with those on standard P requirement. The obvious change in Langmuir maximum sorption capacity at pH 4.0 occurred when redox potential decreased from +400 to +300 mV, but at pH 5.0 and 6.0 this phenomenon occurred when redox potential declined from +300 to +200 mV. Although the pattern of Langmuir maximum sorption capacity of the actual acid sulfate soil was not quite different from that of the para-acid sulfate soil, the Langmuir maximum sorption capacity of the actual acid sulfate soil was higher than that of the para-acid sulfate soil at the same redox potential and pH levels.

Duncan's Multiple Range Test indicated that an increase in pH significantly increased the Langmuir maximum sorption capacity. The Langmuir maximum sorption capacity also significantly increased with decreasing redox potential except when redox potential declined from +600 to +400 mV. The maximum sorption capacity of the actual and para-acid sulfate soils ranging from 508 to 699 mg P kg⁻¹ soil, and from 458 to 618 mg P kg⁻¹ soil, respectively, was somewhat lower than that reported by Imai et al. (1983). This may be due to the differences in soil conditions, soil series, and equations used to determine the maximum sorption capacity. Imai et al. (1983) used air-dried acid sulfate soils which were not state the series, and they used two layers Langmuir equation to determine the maximum sorption capacity.

Table 3.3. Analysis of variance of P-sorption data in Bangkok soil

Source	Degrees of Freedom	Sum of Squares	F Values	Probability of a Greater F
SPR				
Block	1	1.8	3.7	0.0722
pH	2	354	366	0.0001
Redox Potential	5	1241	513	0.0001
pH*Redox Potential	10	291	60	0.0001
Error	17	8.2		
x_m				
Block	1	2.3	3.0	0.6562
pH	2	15526	708	0.0001
Redox Potential	5	122203	2230	0.0001
pH*Redox Potential	10	13261	121	0.0001
Error	17	282		

Table 3.4. Analysis of variance of P-sorption data in Maha-Phot soil

Source	Degrees of Freedom	Sum of Squares	F Values	Probability of a Greater F
SPR				
Block	1	1.8	0.86	0.3673
pH	2	978	236	0.0001
Redox Potential	5	20381	1967	0.0001
pH*Redox Potential	10	1287	62	0.0001
Error	17	35		
x_m				
Block	1	17	1.4	0.2512
pH	2	5121	208	0.0001
Redox Potential	5	102988	1674	0.0001
pH*Redox Potential	10	7176	58	0.0001
Error	17	209		

The Langmuir sorption constant (k), related to the energy bonding of sorption of P to soil surface, and buffering capacity (BI) were significantly affected by redox potential, pH, and interaction between redox potential and pH as well (data not shown). Both parameters of the actual acid sulfate soil were higher than those of the para-acid sulfate soil at the same level of redox potential and pH (Fig. 3.4. and 3.5.). These P-sorption parameters significantly increased with increasing pH in both soils, and significantly increased with decreasing redox potential in the actual acid sulfate soil. For the para-acid sulfate soil, there was no significant increase in Langmuir sorption constant as redox potential declined from +600 to +400 mV, and from +300 to 0 mV. However, there was a significant difference in Langmuir constant when redox potential decreased from +400 to +300 mV. Phosphorus was more loosely bounded to well oxidized soil than reduced soil. The buffering indices at redox potential +600 and +400 mV were not significantly different, but they increased significantly as redox potential decreased from +400 to +300 mV, from +300 to +200 mV, and from +100 to 0 mV, respectively. Nonetheless, there was no significant increase in buffering index with decreasing redox potential from +200 to +100 mV.

The changes in P-sorption parameters as mentioned above may result from the reaction of redox elements with changing in redox potential and pH levels. At redox potential of +600 and +400 mV, soils were defined as well oxidized soils (Patrick and Mahapatra, 1968). Therefore, the changes in P-sorption parameters at every pH level were not significant. In a review by Gambrell and Patrick (1978), ferric iron is reported to be stable until redox potential decreases to around +120 mV (corrected to pH 7.0 by -59 mV per unit pH changes). This may explain the discrepancies of the effect of redox potential on standard P requirement and Langmuir maximum sorption capacity at different levels of pH. As redox potential of soils at pH 4.0 decreased from +400 to +300 mV (+123 mV, corrected to pH 7.0 by -59 mV per unit pH change), standard P requirement and Langmuir maximum sorption capacity increased considerably. Unlike

the condition at pH 4.0, the obvious increase in those parameters at pH 5.0 and 6.0 did not occur until redox potential declined to +200 mV (+82 and +141 mV at pH 5.0 and 6.0, corrected to pH 7.0).

The considerable increases in the amount of soluble Fe, exchangeable Fe, and citrate-dithionite extractable Fe were observed at the aforementioned redox potential (Table 3.1. and 3.2.). Willet and Higgins (1978) also reported an increase in the amounts of exchangeable Fe (1 *M* ammonium acetate, pH 4.8) and amorphous-iron oxides (0.2 *M* ammonium oxalate, pH 3.0) upon flooding (decreased redox potential). On the contrary, the concentration free iron-oxides (citrate-dithionite extractable Fe) were reported to decrease while the concentration of ferrous iron increased (Munch and Ottow, 1980). For this experiment, the increase in the amount of soluble Fe was due to the dissolution of ferric-hydrous oxides and possibly ferric phosphates. Subsequently to this reaction, secondary reaction can lead to the formation of ferroso-ferric hydroxide compounds ($\text{Fe}_3(\text{OH})_8$) (Ponnamperuma et al., 1967; Lindsay, 1979). The freshly precipitated $\text{Fe}_3(\text{OH})_8$ would be expected to be more amorphous, have a greater surface area, and more sites for P-sorption, giving high sorption capacity than original ferric hydrous oxides, and thus sorbed much more P (Willet and Higgins, 1978; Holford and Patrick, 1979). The increase in the amount of citrate-dithionite extractable Fe may be due to an increase of iron-oxides in the form of amorphous and poorly crystalline. Considerably more amorphous iron oxides under reduced condition than under oxidized condition were reported by Patrick and Khalid (1974), and Willet and Higgins (1978). It should be pointed out that the oxalate extraction dissolved much of the Fe and Al from the amorphous materials but very little from crystalline oxides, whereas the dithionite extraction dissolved a large proportion of the crystalline-oxides as well as much of the amorphous materials (McKeague and Day, 1966).

The significant correlations between P-sorption parameters and all forms of Fe were established in both actual and para-acid sulfate soils (Table 3.5.). Each form of Fe

was also significant correlated to each other. Of all forms, free iron oxides (citrate-dithionite extractable) was the most closely correlated with P-sorption parameters. Phosphate-fractionation following P additions and work correlating P-sorption with various soil properties have shown that various forms of Fe were largely responsible for P-sorption in acid soils (Smith, 1965). Several workers reported that amorphous or gel like form of Fe sorbed more P than its crystalline analogues (Ballard and Fiskell, 1974; McLaughlin et al., 1981; Borggaard, 1983; Sah and Mikkelsen, 1986). Ballard and Fiskell (1974) also noted that on a per unite weight basis, exchangeable Fe sorbed more P than amorphous Fe. On the contrary, crystalline iron oxides have been reported to be the most important P-sorbing components of soils which provide the most active P-sorbing surfaces (Pena and Torrent, 1984; Torrent, 1987). The P-sorption was highly correlated with crystalline iron-oxides but not with amorphous iron oxides due to the very low amount of amorphous form which could not be expected to contribute significantly to P-sorption. In most acid sulfate soils of Thailand, most iron-oxides are present in the form of free ferric-oxides which can be extracted by citrate-dithionite solution. Amorphous ferric-oxides or oxalate extractable Fe is relatively low and does not change much with depth in well developed acid sulfate soils and para-acid sulfate soils (Breemen, 1976). For this experiment, we, however, could not conclude that crystalline or amorphous iron oxide was the most important component in P-sorption even though we have found the highly significant relationship between citrate-dithionite extractable Fe and P-sorption parameters. As discussed earlier, the amount of citrate-dithionite which increased as redox potential decreased may come from an increase in the amounts of amorphous and poorly crystalline forms which, led to an increase in P-sorption. This would contribute to the high correlation between citrate-dithionite extractable Fe and P-sorption parameters.

As the solubility of Fe changed with decreasing redox potential, this, in turn, would affect the solubility of iron phosphate (Williams and Patrick, 1973). In the well oxidized acid sulfate soil with P addition, the iron phosphate mineral would be strengite

Table 3.5. Pearson's correlation coefficients between P-sorption parameters and various forms (soluble, s; extracted by 1 N NH₄OAc (pH 4.0), a; and sodium citrate-dithionite solution, d) of Fe, Al, and Mn

P-sorption parameters	Fe			Al			Mn		
	s	a	d	s	a	d	s	a	d
Bangkok									
SPR	0.783***	0.788***	0.841***	0.257	-0.356*	0.545**	0.185	0.230	0.154
x_m	0.851***	0.856***	0.928***	0.239	-0.409*	0.501***	0.224	0.394*	0.120
k	0.376*	0.374*	0.346*	0.231	-0.071	0.146	0.203	0.069	0.193
BI	0.833***	0.834***	0.867***	0.248	-0.308	0.416*	0.301	0.352*	0.196
Maha-Phot									
SPR	0.898***	0.856***	0.906***	0.139	-0.245	0.402*	0.340*	0.449**	0.399*
x_m	0.923***	0.904***	0.946***	0.224	-0.142	0.359*	0.409*	0.449**	0.386*
k	0.872***	0.827***	0.886***	0.121	-0.273	0.401*	0.317	0.381*	0.208
BI	0.897***	0.857***	0.910***	0.142	-0.243	0.403	0.343*	0.404*	0.262

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively

due to the high redox potential, low pH, and high P concentration condition which appropriated for the formation strengite (Nriagu, 1972). A decreasing redox potential does not affect P solubility at $pe + pH > 12.0$ ($Eh = 59.2 pe$) (Lindsay, 1981). As redox potential continues to decrease below $pe + pH < 8.34$, vivianite becomes the stable phosphate phase, and strengite can convert to vivianite (Lindsay, 1979). In the presence of vivianite, lowering redox potential lowers the solubility of added P reflecting higher P-sorption. This may in part explain an increase in P-sorption parameters with decreasing redox potential.

The application of organic matter to the well oxidized soil has been frequently reported to decrease P-sorption (Reddy et al., 1980; Kuo, 1983). Nevertheless, the dissolution and reprecipitation of many soil minerals may occur as redox potential of soils decreased, and anaerobic decomposition of organic matter under this condition can have opposite effects on P-sorption (Willet and Higgins, 1978; Sah and Mikkelsen, 1986). In the present study, we added 0.2 % organic matter to soil suspensions to provide an energy source for microbial activity during the incubation period. This could enhance the increase in P-sorption as redox potential decreased.

The significant correlations between P-sorption parameters, and soluble and exchangeable Mn were observed in actual acid sulfate soil but not in para-acid sulfate soil (Table 3.5.). This may be due to the lower concentrations of those fractions in para-acid sulfate soil when compared to actual acid sulfate soil (Table 3.1. and 3.2.). There was no significant relationship between citrate-dithionite extractable Mn and P-sorption parameters in both actual and para-acid sulfate soils except the relationships between citrate-dithionite extractable Mn, and standard P requirement and Langmuir maximum sorption capacity in the actual acid sulfate soil. In acid sulfate soils of Thailand, Mn^{2+} may be present mainly in soluble and exchangeable forms (Breemen, 1976). This would in part explain a lack of significant relationship between manganese oxide (citrate-dithionite extractable) and P-sorption parameters. Since there is a lack of information on the effect

of Mn on P-sorption, the mechanism of P-sorption by Mn is still unclear. However, this mechanism may concern the stability and solubility of manganese phosphates (MnHPO_4 and $\text{Mn}_3(\text{PO}_4)_2$). Lindsay (1979) reported that $\text{Mn}_3(\text{PO}_4)_2$ is more soluble than strengite at $pe + pH$ value > 15 but less soluble below this redox potential, whereas MnHPO_4 is more stable than strengite at all $pe + pH$ value > 19 . Lowering redox potential would lower the solubility of manganese phosphate reflecting higher P-sorption.

The further increase in P-sorption parameters, particularly standard P requirement and Langmuir maximum sorption capacity, as redox potential continued to decrease toward the level of 0 mV (Fig. 3.2., 3.3., 3.4., and 3.5., respectively) would be due to the effect of sulfate. Harter and McLean (1965) reported that sulfate reducing organisms were active around -75 mV, whereas Cornell and Patrick (1968) found that sulfate reduction occurred when redox potential dropped to approximately -150 mV (corrected to pH 7.0 by -59 mV per unit pH change). In the well oxidized soil, sulfate is sorbed by both crystalline and amorphous iron oxides (Gebhardt and Coleman, 1974; Ponnamperna, 1981). Sulfate is less strongly sorbed than P (Gebhardt and Coleman, 1974), and can exchange with P (Rajan and Watkinson, 1976). When lowering redox potential, sulfate was desorbed into soil solution following the reduction of the iron oxides (Ponnamperna, 1981). Dissolved sulfate would be utilized by sulfate reduction. As sulfate reduction occurred, added P may displace the sulfate sorption sites reflecting the higher P-sorption at low redox potential.

At the same redox potential, P-sorption increased with increasing pH as mentioned above. The P-sorption capacity of acid soils has been reported to either increase (Mokwunye, 1975; Haynes and Swift, 1985) or decrease (Obihara and Russell, 1972; Smyth and Sanchez, 1980) as pH increased. Mokwunye (1975) postulated that the increase in P-sorption with an increase in pH (from pH 3 to 7) in the savannah soils (pH 4.5-5.4) can be largely attributed to the increased activity of amorphous hydroxy-aluminum species from the increased pH of the systems. At low pH, trivalent aluminum

(Al^{3+}) is the dominant species in solution. The activity of trivalent aluminum in equilibrium with aluminum-oxide and hydroxide minerals decreases with increasing pH (Lindsay, 1979). As pH increases, the relative importance of the hydroxy complexes increases (Drever, 1988). In the present experiment, the concentrations of soluble Al and exchangeable Al decreased as pH increased, whereas the concentration of citrate-dithionite extractable Al (aluminum oxides) increased with increasing pH corresponding to an increase in P-sorption. The increase in P-sorption with increasing pH may be contributed from the precipitation of exchangeable Al as hydroxyl-Al polymers which results in a formation of new highly-active sorbing surfaces in the soils (Haynes and Swift, 1985; Traina et al., 1986). Loganathan et al. (1987) also reported that in strongly acid soils, an increase in pH up to about 5.0 was shown to reduce exchangeable Al and increase the extent of formation of hydrous Al polymers, resulting in increasing P-sorption.

The mechanism of this sorption process was explained by Hsu and Rennie (1962). The strong affinity of the trivalent aluminum ion for OH^- ions accounts for its hydrolysis in aqueous solutions. The hydrolyzed aluminum ion species is then polymerized through a hydroxyl bridge. Polymerization is encouraged by an increase in pH which provides the OH^- units for the bridge. As the polymer increases in size, however, the average net positive charge for each aluminum ion decreases and consequently, its attraction for additional OH^- units becomes weaker. Therefore, the last OH^- ion attached to the hydroxyl-aluminum polymer is very weakly attached. Once attached, the last OH^- ion should be capable of being readily displaced by other ions. The weakly-held hydroxyl units, which have become attached as a result of an increase in pH, do not function as an hydroxyl bridge. Rather, they are located on the surface. Phosphorus will be sorbed on the surface when the hydroxyl-aluminum-phosphate attraction is strong enough to displace these weakly held surface hydroxyl ions.

Using 2 N NaOH to raise pH of the system may enhance the reprecipitation of gel-like $\text{Fe}(\text{OH})_2$, which is expected to have high P-sorption capacity (Holford and Patrick, 1979), resulting in increasing P-sorption with increasing pH. White and Taylor (1977) also observed increases in P-sorption when soil pH was raised with NaOH.

Bloom (1981) found that P-sorption in Al-peat, which has an Al-saturation that may be quite similar to that of many acid mineral soils, increased with increasing pH. He concluded that the Al-organic matter complexes in acid surface soils is an important source of P-sorption.

Another explanation for an increase in P-sorption with increasing pH may be attributed to sulfate-sorption. As discussed above, sulfate is less strongly sorbed than P and can exchange with P. Opposite to P-sorption, sulfate-sorption increases with decreasing pH in the range of 6.5 to 4.0 (Gebhardt and Coleman, 1974). As sulfate sorption decreases along with increasing pH, P may displace the sorption site on iron- or aluminum-oxides resulting in increasing P-sorption. Bar-Yosef et al. (1988) used P concentration in the solution phase stabilized within 24 h after introducing P into the system to study P-sorption. They found that P solution concentration as a function of pH was minimal in kaolinite around pH 6.0. They attributed the decrease in P-sorption below pH of 6.0 to the effect of pH on edge-to face flocculation, which may affect P accessibility to clay mineral sorption sites.

There were significant correlations between P-sorption parameters and citrate-dithionite extractable Al in both actual and para-acid sulfate soils (Table 3.5.). Nevertheless, P-sorption parameters were more closely correlated with citrate-dithionite extractable Fe than Al suggesting the dominant role of iron oxides in P-sorption characteristics of acid sulfate soils even though the soil contained considerable amount of aluminum oxides (Table 3.1. and 3.2.). These results agree with previous investigations, which showed good correlations between P-sorption capacity and the contents of free

iron oxides in soils (Lopez-Hernandez and Burnham, 1974; Borggaard, 1983; Pena and Torrent 1984; Loganathan et al., 1987; Soils and Torrent, 1989).

CONCLUSION

The P-sorption of both actual and para-acid sulfate soils was affected by pH, redox potential, and interaction between pH and redox potential. The effect of redox potential on P-sorption changed as pH level changed. At pH 4.0, a considerable increase in P-sorption occurred as redox potential decreased from +400 to +300 mV, whereas at pH 5.0 and 6.0 an obvious change in P-sorption occurred when redox potential decreased from +300 to +200 mV. This would be mainly due to the reduction of Fe at particular redox level (corrected to pH 7.0). The P-sorption increased significantly with decreasing redox potential and increasing pH. The increase in P-sorption with decreasing redox potential may be attributed to the reduction and reprecipitation of Fe, the role of organic matter, the effect of Mn on P-sorption, and the relationship between sulfate-sorption and P-sorption by amorphous or crystalline iron- and aluminum-oxides. The increase in P-sorption with increasing pH would be mainly contributed from the activity of amorphous hydroxy-aluminum species which increases with increasing pH. The actual acid sulfate soil sorbed more P than did para-acid sulfate soil. Closer correlation between P-sorption parameters and iron-oxides than aluminum-oxides indicated the primary role of iron-oxides in P-sorption of both actual and para-acid sulfate soils. Manganese seemed to have an important effect on P-sorption, but further study on the effect of Mn on P-sorption is needed. In the present experiment, it is inconclusive that amorphous or crystalline forms of Fe and Al plays a major role in P-sorption of acid sulfate soils. Further investigation on the different effects of amorphous and crystalline forms of iron- and aluminum-oxides on P-sorption should be done. Although we reported that P-sorption increased with increasing pH from 4.0 to 6.0, a study on the effect of further increase in

pH beyond 6.0 on P-sorption should be done to make a better possibility in liming and P fertilizer recommendation.

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CHAPTER FOUR

EFFECTS OF IRON, ALUMINUM, MANGANESE, pH, AND OXIDATION- REDUCTION CONDITIONS ON PHOSPHORUS SORPTION IN ACID SULFATE SOILS

ABSTRACT

The effects of pH, oxidation-reduction conditions, and various forms of Fe, Al, and Mn on P-sorption characteristics of acid sulfate soils of Thailand were investigated. Surface soil samples collected from the Bangkok Plain in Thailand were incubated under oxidized and reduced conditions at three different levels of pH (4.0, 5.0, and 6.0) for 6 wk in stirred soil suspensions with a soil to 0.01 M CaCl₂ solution ratio of 1:7. After the incubation period the soil suspensions were treated with 1 N NH₄OAc (pH 4.0) and sodium-citrate dithionite solution (20 %) intended to remove Fe, Al, and possibly Mn in the forms of exchangeable, and free oxides, respectively. Then the soil suspensions were then equilibrated with KH₂PO₄ ranging from 0 to 500 mg P kg⁻¹ soil. Sorption isotherms were described by the classical Langmuir equation. The actual acid sulfate soil sorbed more P than did the para-acid sulfate soil. The P-sorption capacity of soils under reduced conditions was higher than that under oxidized conditions, and increased with increasing pH. Treating soils with NH₄OAc and sodium-citrate dithionite solution reduced P-sorption, and also decreased the differences in P-sorption due to the effects of pH and oxidation-reduction conditions. These treatments did not remove the differences in P-sorption between the actual and para-acid sulfate soils. Significant correlations between P-sorption and the amount of free iron-oxides indicated the primary role of iron-oxides in P-sorption of acid sulfate soils of Thailand. Aluminum-oxides seemed to play a secondary role in P-sorption of these soils. Manganese also showed an important effect on P-sorption, but the mechanism is ambiguous.

Acid sulfate soils, in Thailand, occupy an area of about 1.5 million hectares (Pons and Kevie 1969) and they are considered to be deficient in P available to crops (Attanandana and Vacharotayan 1986). Phosphorus content in rice plants is relatively low even under submerged conditions in which soil P is assumed to become available (Uwasawa et al. 1988). The low content of P in acid sulfate soils is considered to be one of the most important factors responsible for the low productivity of rice plant. In addition, the low productivity of rice plant is due to Al and Fe toxicity as well (Attanandana and Vacharotayan 1986).

The sorption of P by aerobic soil has been extensively studied. It has been found that pH (Mokwunye 1975; Bar-Yosef et al. 1988), temperature (Barrow 1979; Sah and Mikkelsen 1986a), the amount and type of clay (Muljadi et al. 1966; Bar-Yosef et al. 1988), organic matter (Bloom 1981), and the amount of Fe and Al (Bromfield 1965; Torrent 1987; Lajtha and Bloomer 1988; Russell et al. 1988) influence P-sorption. In contrast, P-sorption in anaerobic soils has not yet been extensively studied. However, it has been reported that oxidation-reduction potential, pH, and the amount of iron-oxides affected P-sorption under reduced conditions (Khalid et al. 1977; Holford and Patrick 1979).

Phosphorus sorption by acid soils is believed to be due largely to various forms of active Fe and Al (Bromfield 1965). Imai et al. (1983) claimed that P was initially sorbed on the surface of acid sulfate soils and formed chelating compounds there with hydroxy-aluminum. Uwasawa et al. (1988) also reported that added P was sorbed as Al-P and Fe-P in acid sulfates soils of Thailand. A marked decrease in P-sorption following the chemical removal of Fe-oxides from soils and clay minerals was reported (Bromfield 1965; Borggaard 1983; Sah and Mikkelsen 1986b). Various sorption equations have been used to describe P-sorption in soils, but the classical Langmuir equation is most frequently employed. A previous work (Krairapanond and Patrick in prep.) indicated that

P-sorption data of acid sulfate soils of Thailand conform well to the classical Langmuir equation.

The present study was undertaken to investigate P-sorption of actual and para-acid sulfate soils from Thailand and relationship with various forms of Fe, Al, and Mn under both oxidized and reduced conditions at various pH levels.

MATERIALS AND METHODS

The surface layer (0-15 cm) of acid sulfate soils collected from the Bangkok Plain of Thailand (see Fig. 2.1.) were used in this study. Soils were air-dried, sieved (< 2 mm), and thoroughly mixed prior to analysis. In this study, one para-acid sulfate soil, Bangkok (Bk), and one actual acid sulfate soil, Maha-phot (Ma), were used. General morphology and chemical characteristics of soils were described by Kevie and Yenmanas (1972). Selected soil properties are presented in Table 2.1.

The experiment was conducted to determine P-sorption of each soil treated and untreated with two different extractants (1 *N* NH₄OAc, pH 4.0 and sodium citrate-dithionite solution, 20 %) intended to remove different forms of Fe, Al, and Mn from soils under oxidized and reduced conditions at three different pH levels (4.0, 5.0, and 6.0, respectively). The experimental design was 3*2*3 factorial in a randomized complete block design with two replications.

Suspension of 250 g soil in 1,750-mL 0.01 *M* CaCl₂ (1:7) were incubated in laboratory microcosms (see Fig. 2.2.) under oxidized and reduced conditions for 6 wk at 25°C. Prior to the incubation, the soils were amended with finely ground rice straw (40 mesh, 0.2 % on oven-dried soil weight basis) which provided an energy source to promote microbial activity. Nitrogen and oxygen gases were bubbled continuously through the soil suspensions at a slow rate of flow to promote reduced and oxidized conditions, respectively. The redox potential and pH of the system were monitored. The

pH of the soil suspensions was controlled at the desired pH values by manual additions of either 2 *N* HCl or 2 *N* NaOH daily or as required.

At the end of the incubation period, the soil suspensions (50 mL) were then transferred to 250-mL polycarbonate centrifuge bottles. For the reduced condition treatment, the centrifuge bottles were flushed with O₂-free N₂ prior to filling the soil suspensions to maintain a reduced atmosphere. Phosphorus in concentrations ranging from 0 to 500 mg P kg⁻¹ soil as KH₂PO₄ was then added to the soil suspensions for the control treatment, not treated with any extractants. For the second treatment, the soil suspensions were shaken with 1 *N* NH₄OAc, pH 4.0 (100 mL), on a reciprocating shaker for 1 h. The suspensions were centrifuged (20 min at 7 000 rpm (8 000 × *g*), Sorvall GSA-400 rotor, DuPont Co., Wilmington, DE) and filtered through a 0.45-μm membrane filter, under O₂-free N₂ atmosphere for reduced conditions (Gambrell et al. 1975). For the third treatment, the soil suspensions were shaken with sodium-citrate dithionite solution (20 %, 100 mL) on a reciprocating shaker for 18 h. The suspensions were then centrifuged and filtered. The soil residues from both second and third treatments were washed twice with distilled water (100 mL). The soil residues were flushed with O₂-free N₂ before washing for reduced conditions. All solutions and distilled water added to soils under reduced conditions were free of O₂. After each wash the suspensions were centrifuged and filtered. All filtrates were analyzed for P, Fe, Al, and Mn using an ICP (Inductively Coupled Argon Plasma Atomic Emission Spectrometer).

Fifty mL of 0.01 *M* CaCl₂ containing P in concentrations ranging from 0 to 500 mg P kg⁻¹ soil as KH₂PO₄ was added to all samples pretreated with the second and third treatments. For reduced treatment, the samples were flushed with O₂-free N₂ prior to adding diluted CaCl₂-P solution. After 24-h equilibration on a reciprocating shaker, all samples were centrifuged and filtered. A 24-h period was chosen because this period was considered adequate for the fast reactions as well as the initiation of the slow reactions to take place during P retention in the soils (Mehadi and Taylor 1988). The filtrates were

analyzed for P, Fe, Al, and Mn using the ICP. The P that disappeared from solution was considered as sorbed P.

To compare the results, P-sorption data for all samples were fitted to the classical Langmuir equation (Olsen and Watanabe 1957). The Langmuir equation is written:

$$x = kx_m C / (1 + kC) \quad (1)$$

where x is the amount of sorbed P per unit of soil, C is the final solution P concentration, k is a coefficient which reflects the relative rates of sorption and desorption at equilibrium and is thus an affinity term, and x_m is the maximum monolayer sorption capacity. The two constants (k and x_m) were determined by fitting the experimental data to linearized form (Lineweaver-Burk form) as given below (Persoff and Thomas 1988):

$$1/x = 1/x_m + (1/kx_m)(1/C) \quad (2)$$

The buffer capacity (BI), a mixed quantity-intensity parameter, is calculated from kx_m (Holford 1979). The standard P requirement (SPR), P-sorption at a concentration of 0.2 ppm P in final solution, was also calculated. The analysis of variance and Pearson's correlation coefficients were processed using the procedures available with Statistical Analysis System (SAS Institute Inc. 1985).

RESULTS AND DISCUSSION

Effects of Oxidation-Reduction Conditions and pH on The Release of Native P in Untreated soils

Under reduced conditions (Eh -165 to +225 mV), more native insoluble P was released from untreated soils (both actual and para-acid sulfate soils) than under oxidized conditions (Eh +635 to +765 mV) at every pH level. The amounts of native soil P released also increased with decreasing pH under both oxidized and reduced conditions. The concentrations soluble Fe were considerably higher under reduced conditions than that under oxidized conditions, and increased with decreasing pH as well (Table 4.1. and 4.2.). The concurrent increase in P and Fe concentrations as soil redox potential and pH

Table 4.1. Concentrations of soluble P, Fe, Al, and Mn in Bangkok soil

Conditions	Eh		pH	Treatment	Soluble			
	actual	corrected to pH 7			P	Fe	Al	Mn
	-----mV-----				-----mg kg ⁻¹ -----			
Oxidized	+675	+498	4.0	Control	2.8	1.6	44.0	55.5
				II	1.2	0.6	2.2	5.3
				III	1.0	0.9	1.3	1.1
	+685	+567	5.0	Control	2.2	1.2	24.6	31.3
				II	1.2	0.8	2.2	4.3
				III	0.9	1.0	1.1	1.0
	+635	+576	6.0	Control	1.9	1.1	7.6	19.3
				II	1.2	0.7	2.1	4.2
				III	0.9	0.9	1.0	1.0
Reduced	-15	-192	4.0	Control	6.3	946.6	30.8	86.9
				II	1.8	1.0	2.3	5.5
				III	1.1	1.0	1.4	1.2
	-125	-243	5.0	Control	5.5	572.1	13.7	52.9
				II	1.6	0.8	2.5	3.9
				III	1.0	0.9	1.7	1.0
	-165	-225	6.0	Control	4.9	439.2	4.6	33.3
				II	1.3	0.8	2.3	3.7
				III	1.0	0.8	1.2	1.0

Table 4.2. Concentrations of soluble P, Fe, Al, and Mn in Maha-Phot soil

Conditions	Eh		pH	Treatment	Soluble			
	actual	corrected to pH 7			P	Fe	Al	Mn
	-----mV-----				-----mg kg ⁻¹ -----			
Oxidized	+765	+588	4.0	Control	2.5	1.7	50.2	225.3
				II	0.7	0.4	2.1	17.5
				III	0.9	0.8	1.8	3.4
	+725	+607	5.0	Control	2.0	1.4	37.8	112.5
				II	0.5	0.9	1.6	19.0
				III	0.9	0.8	0.9	5.1
	+660	+601	6.0	Control	1.2	1.1	10.5	82.3
				II	0.5	0.7	1.3	13.4
				III	0.9	0.7	0.8	4.2
Reduced	+225	+48	4.0	Control	3.9	1065.5	39.8	243.4
				II	0.8	0.8	2.2	16.4
				III	1.0	0.8	1.2	3.5
	+70	-48	5.0	Control	3.2	652.5	22.9	205.2
				II	0.9	0.8	2.5	19.8
				III	0.9	0.7	1.2	5.1
	-35	-94	6.0	Control	2.8	321.5	6.5	102.2
				II	0.7	0.8	2.1	15.8
				III	0.9	0.7	1.1	4.4

decreased could be due to reduction and dissolution of ferric phosphate (strengite), which releases Fe^{2+} and phosphate ions (Patrick et al. 1973), the release of P occluded in previous insoluble ferric hydrous oxides (Chang and Jackson 1958), and a greater dissolution at low pH of ferrous phosphate as well as ferric phosphate (Patrick et al. 1973). Satawathananont (1986) also reported similar results in acid sulfate soils of Thailand.

Effects on P-sorption Characteristics

The experimental P-sorption isotherms constructed for every treatment are shown in Fig. 4.1. (Bangkok soil) and Fig. 4.2. (Maha-phot soil). Standard P requirement (SPR), Langmuir maximum sorption capacity (x_m), Langmuir sorption constant (k), and buffering index (BI) are presented in Table 4.3. and 4.4. Standard P requirement, P-sorption at a concentration of 0.2 ppm P in final solution, was selected following the suggestion of Beckwith (1965) that this concentration, if maintained continuously in solution culture, will provide adequate P to many plants. Although P concentration required by plants may vary among the group of plants, this value can provide useful information about P fertilizer requirements. Fox and Kang (1978) recorded data on the external P concentration requirements of numerous agronomic and horticultural crops grown in Hawaii. The requirements were reasonably constant within a given species growing on dissimilar soils. Nevertheless, the standard P requirement has been used by many workers (Juo and Fox 1977; Khalid et al. 1977; Loganathan et al. 1987). Langmuir sorption constant and buffering index have been used in P-sorption studies by several workers (Mehadi and Taylor 1988; Soils and Torrent 1989). Soils and Torrent (1989) found that buffer capacity measured from P quantity and intensity changes produced by cropping was similar in magnitude and correlated with buffer capacity calculated from sorption equations in the laboratory. Thus, sorption equation can provide a rough estimation of the field phosphate buffer capacity in the soil studies. However, the

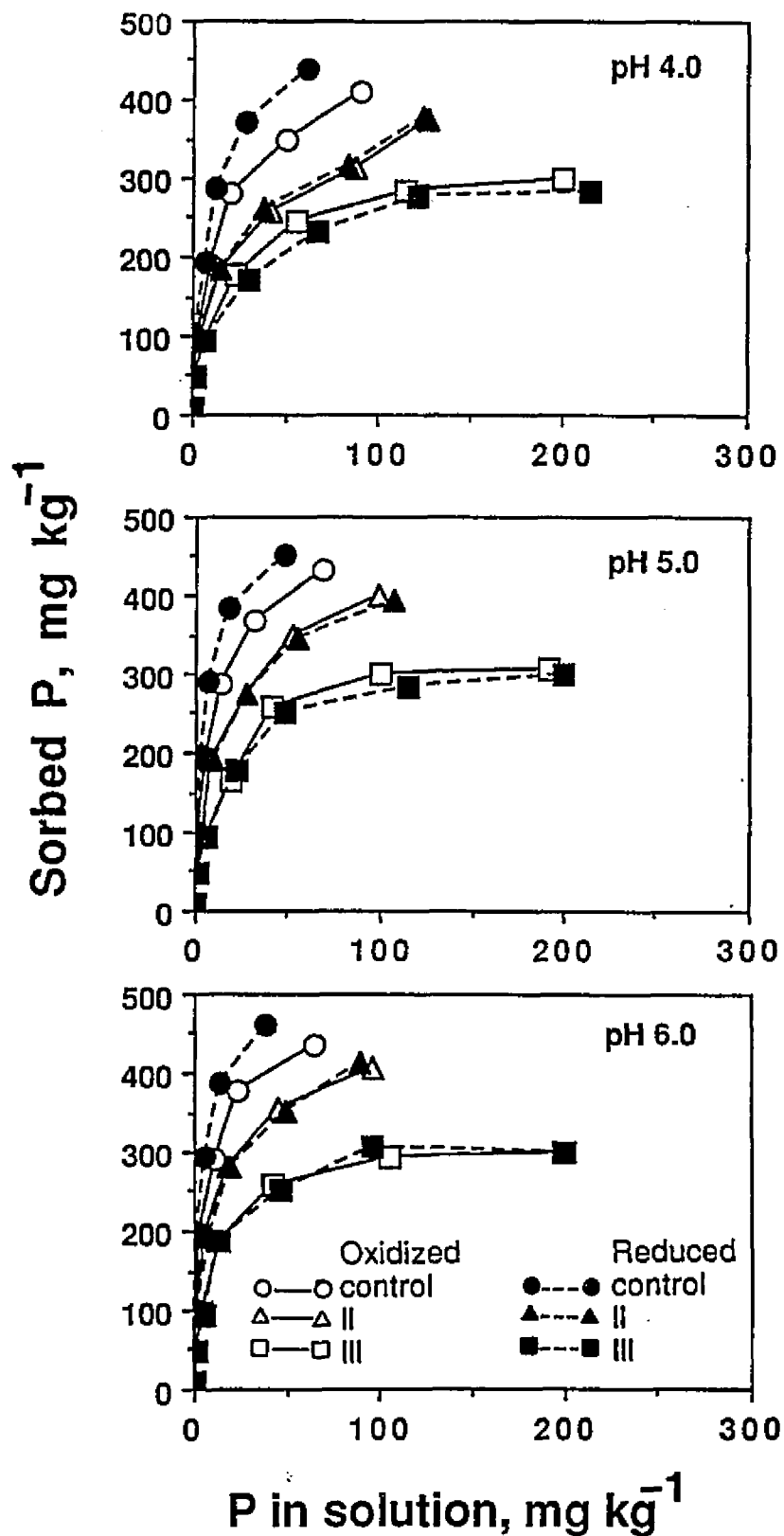


Figure 4.1. Phosphorus sorption isotherms for Bangkok soil

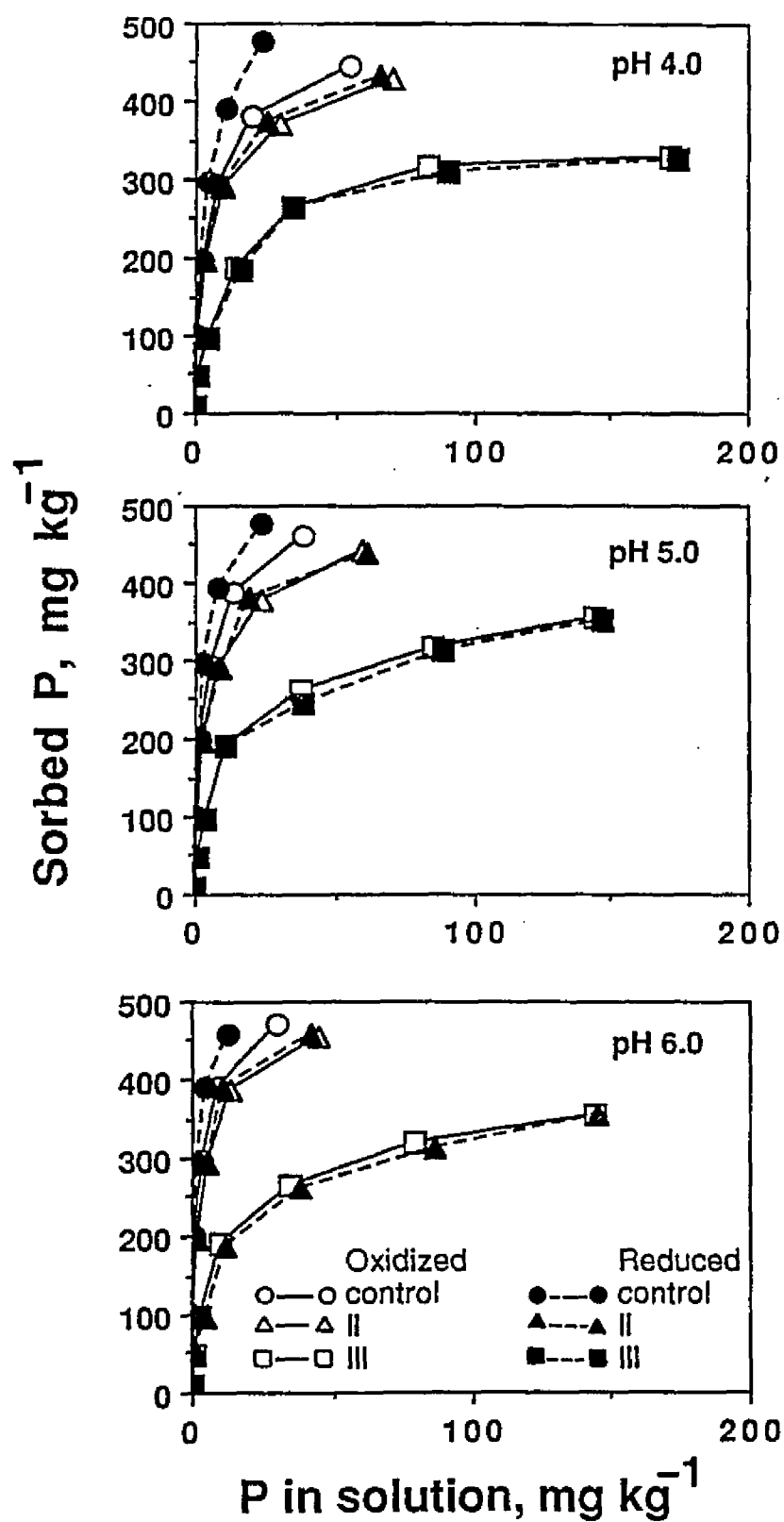


Figure 4.2. Phosphorus sorption isotherms for Maha-Phot soil

Table 4.3. Phosphorus sorption parameters for Bangkok soil

Condition	pH	Treatment	SPR	x_m	k	BI
			-----mg kg ⁻¹ -----		mg ⁻¹ kg	
Oxidized	4.0	Control	34	410	0.515	208
		II	30	352	0.353	122
		III	11	255	0.181	45
	5.0	Control	39	437	0.515	227
		II	34	347	0.460	162
		III	11	296	0.210	61
	6.0	Control	51	491	0.635	305
		II	40	403	0.543	214
		III	12	305	0.216	63
Reduced	4.0	Control	48	521	0.551	286
		II	37	338	0.545	185
		III	12	238	0.209	66
	5.0	Control	52	583	0.565	321
		II	41	346	0.610	209
		III	12	266	0.319	83
	6.0	Control	58	668	0.632	414
		II	44	396	0.615	241
		III	12	299	0.281	82

Table 4.4. Phosphorus sorption parameters for Maha-Phot soil

Condition	pH	Treatment	SPR	x_m	k	BI
			-----mg kg ⁻¹ -----		mg ⁻¹ kg	
Oxidized	4.0	Control	51	461	0.633	290
		II	47	382	0.634	245
		III	13	306	0.251	76
	5.0	Control	68	610	0.659	403
		II	48	397	0.587	253
		III	13	302	0.316	94
	6.0	Control	58	516	0.615	315
		II	51	416	0.645	270
		III	14	312	0.288	86
Reduced	4.0	Control	76	673	0.696	464
		II	53	403	0.604	244
		III	13	303	0.344	100
	5.0	Control	63	589	0.639	382
		II	55	419	0.635	272
		III	14	318	0.286	88
	6.0	Control	88	696	0.725	501
		II	58	408	0.664	273
		III	13	315	0.348	110

estimation is not precise under natural condition due to a multiplicity of factors affecting changes in labile and solution P.

Standard P requirement was significantly affected by all factors and their interactions in both actual and para-acid sulfate soils (Table 4.5. and 4.6.). Significant interaction between oxidation-reduction conditions and pH indicated that the effect of pH on standard P-requirement changed as the conditions changed. The graphical factorial comparison between treatment means showed that degree of increasing in standard P requirement with increasing pH under oxidized condition was more than that under reduced condition (graph not shown). Significant interactions between pH and treatment, and between oxidation-reduction conditions and treatment were due to the different effects of pH and conditions at the different levels of treatment. Standard P requirement obviously increased as pH increased in control treatment. For the second and the third treatments, standard P requirement slightly increased and almost steady with increasing pH, respectively. Standard P requirement under reduced condition were significantly higher than that under oxidized condition in control treatment, whereas in the second and the third treatments, this value under oxidized and reduced conditions was almost the same. The significant interaction among pH, oxidation-reduction conditions, and treatment was due to the completely different effect of treatment on standard P-requirement the different level of both pH and oxidation-reduction conditions.

Khalid et al. (1977) indicated that the effect of oxidized and reduced conditions on the amount of P needed to maintain a solution concentration of 0.2 ppm P was greatly dependent on soil type. The standard P requirement of the acid sulfate soils (untreated soils), ranging from 48 to 87 mg P kg⁻¹ soil under reduced conditions, and from 34 to 63 mg P kg⁻¹ soil under oxidized conditions, was classified as low level (10-100 mg P kg⁻¹ soil) on the scale proposed by Juo and Fox (1977). The materials classified as low level were 2:1 clays, quartz, and 1:1 clays. Although these values of the acid sulfate soils have been classified as low level, they were higher than that of other soils reported by Khalid

Table 4.5. Analysis of variance of P-sorption data in Bangkok soil

Source	Degrees of Freedom	Sum of Squares	F Values	Probability of a Greater F
SPR				
Block	1	1.2	1.2	0.2883
Condition	1	310	304	0.0001
pH	2	343	168	0.0001
Treatment	2	8515	3986	0.0001
Condition*pH	2	20	10	0.0012
Condition*Treatment	2	171	84	0.0001
pH*Treatment	4	169	41	0.0001
Condition*pH*Treatment	4	13	3.3	0.0368
Error	17	17		
x_m				
Block	1	85	3.0	0.0994
Condition	1	14292	506	0.0001
pH	2	34247	607	0.0001
Treatment	2	360855	6369	0.0001
Condition*pH	2	1204	21	0.0001
Condition*Treatment	2	499992	885	0.0001
pH*Treatment	4	6006	53	0.0001
Condition*pH *Treatment	4	1387	12	0.0001
Error	17	479		

Table 4.6. Analysis of variance of P-sorption data in Maha-Phot soil

Source	Degrees of Freedom	Sum of Squares	F Values	Probability of a Greater F
SPR				
Block	1	0.76	0.79	0.3862
Condition	1	443	229	0.0001
pH	2	482	498	0.0001
Treatment	2	18468	9557	0.0001
Condition*pH	2	22	11	0.0007
Condition*Treatment	2	243	63	0.0001
pH*Treatment	4	704	364	0.0001
Condition*pH*Treatment	4	18	4.7	0.0001
Error	17	16		
<i>x_m</i>				
Block	1	50	3.0	0.0995
Condition	1	13559	408	0.0001
pH	2	16608	1000	0.0001
Treatment	2	492039	14820	0.0001
Condition*pH	2	782	24	0.0001
Condition*Treatment	2	10749	161	0.0001
pH*Treatment	4	40205	1211	0.0001
Condition*pH*Treatment	4	1184	18	0.0001
Error	17	282		

et al. (1977). They reported these values of Inceptisols (Sharky clay and Harris silt loam soils) ranging from -29.5 to 25.1 mg P kg⁻¹ soil under reduced conditions, and from 25.0 to 53.6 mg P kg⁻¹ soil under oxidized conditions whereas those of Alfisols (Crowley silt loam and Midland silt loam soils) ranging from -2.5 to 73.4 mg P kg⁻¹ soil, and from 2.7 to 43.3 mg P kg⁻¹ soil, respectively. Loganathan et al. (1987) reported the standard P-requirements of ten Inceptisols soils of the Nigeria delta in southern Nigeria ranging from 50 to 200 mg P kg⁻¹ soil (low to medium level), whereas the maximum sorption capacity ranging from 220 to 667 mg P kg⁻¹ soil. The maximum sorption capacity of acid sulfate soils reported in Table 4.3. and 4.4. was higher than that reported by Loganathan et al. (1987). This suggested that the classification of soils based on the scale proposed by Juo and Fox (1977) may not definitely indicate the sorption capacity level of the soils.

Like standard P requirement, Langmuir maximum sorption capacity was significantly affected by all factors and all of their interactions in both actual and para-acid sulfate soils (Table 4.5. and 4.6.). The significant interactions were resulted from the similar reasons as standard P-requirement. The amounts of P sorbed by para-acid sulfate soil was less than those by actual acid sulfate soil under both oxidized and reduced conditions at every pH level. All P-sorption parameters of the actual acid sulfate soil were higher than those of the para-acid sulfate soil (Table 4.3. and 4.4.).

Reduced conditions (Eh -165 to + 225 mV) caused mark rises in P-sorption of untreated soils at every pH level when compared with oxidized conditions (Eh +635 to +765 mV) (Fig. 4.1. and 4.2.). All P-sorption parameters in Bangkok soil were higher under reduced conditions than those under oxidized conditions (Table 4.3.). The P-sorption parameters in Maha-Phot soil under reduced condition were also higher than those under oxidized condition, except at pH 5.0 (Table 4.4.). Several studies have been reported higher P-sorption under reduced conditions than under oxidized conditions (Khalid et al. 1977; Willett and Higgins 1978; Holford and Patrick 1979; Sah and Mikkelsen 1986b). Holford and Patrick (1981) reported an increase in P-sorption at pH

5.0 during reduction which may be due to some precipitation of ferrous phosphate. When the soil was undergone reoxidation, there was a large decrease in P-sorption capacity at pH 6.6, but little change at pH 5.0.

The soluble Fe concentrations under reduced conditions were tremendously higher than under oxidized conditions at every pH level (Table 4.1. and 4.2.). Increases in concentration of Fe in soil solution can come from the dissolution of ferric-hydrous oxides and possibly ferric phosphates, and these reactions can also increase the release of native insoluble P (as mentioned above) due to its release from compounds, occluded or sorbed forms. Subsequent to these initial reactions, secondary reactions can lead to the precipitation of ferroso-ferric hydroxide compounds ($\text{Fe}_3(\text{OH})_8$), ferrous phosphate, and changes in the P-sorption properties of the soils. Under reduced conditions, ferric compounds containing phosphate must have been reduced to poorly crystalline ferrous hydroxides, ferroso-hydroxide, and soluble Fe^{2+} , and consequent increase in Fe^{2+} concentration. The solid, poorly crystalline ferrous compounds or newly precipitated $\text{Fe}(\text{OH})_2$ which would be expected to be more amorphous, have a greater surface area, and more sites for P-sorption, giving higher sorption capacity and bonding index than original ferric hydrous oxides, and thus sorbed much more P (Willett and Higgins 1978; Holford and Patrick 1979, 1981). The Langmuir sorption constant, k , related to the energy bonding of sorption of P to soil surface, was smaller under oxidized conditions than under reduced conditions (Table 4.3. and 4.4.). This indicated that P was more tightly bounded to the soil surface under reduced conditions than under oxidized conditions.

The application of organic matter to soil under oxidized condition has frequently been reported to decrease P-sorption (Reddy et al. 1980; Kuo 1983). However, in reduced soil, where dissolution and reprecipitation of many soil minerals occur, anaerobic decomposition of organic matter could have opposite effects (Willett and Higgins 1978; Sah and Mikkelsen 1986b). Lopez-Hernandez and Burnham (1974a) found a positive

correlation between organic matter content and P-sorption in poorly drained British soils. Sah and Mikkelsen (1986b) reported that reduced soils, even without added organic matter, increased P-sorption significantly over oxidized soils. Added organic matter (0.5-1 % organic matter) during flooding, however, further significantly increased P-sorption. They suggested that the increase in dissolution of Al and Fe minerals and the reprecipitation of amorphous Fe due to anaerobic decomposition of organic matter are possibly responsible for the increased P-sorption capacity of soil. For the present experiment, we added 0.2 % organic matter to soil suspensions to provide an energy source for microbial activity during the incubation period. This could partly explain the discrepancy difference between P-sorption under reduced and oxidized conditions. Organic matter content of actual acid sulfate soil is higher than that of para-acid sulfate soil (Table 2.1.). The P-sorption isotherms shown in Fig. 4.1. and 4.2. were in good agreement with the organic matter contents. This suggests that organic matter is possibly partial responsible for P-sorption.

Phosphorus sorption of untreated soils increased with increasing pH under both oxidized and reduced conditions (Fig. 4.1. and 4.2., and Table 4.3. and 4.4.). The P-sorption capacity of acid soils has been reported to increase (Mokwunye 1975; Haynes and Swift 1985) or decrease (Obihara and Russell 1972; Lopez-Hernandez and Burnham 1974b; Smyth and Sanchez 1980) as pH increased. Mokwunye (1975) postulated that the increase in P-sorption with an increase in pH (from pH 3 to 7) in the savannah soils (pH 4.5-5.4) can be largely attributed to the increased activity of amorphous hydroxy-aluminum species resulting from the increased pH of the systems. At low pH, trivalent aluminum (Al^{3+}) is the dominant species in solution. As pH increases, the relative importance of the hydroxy complexes increases (Drever 1988). In this experiment, the concentrations of soluble Al and exchangeable Al decreased as pH increased, whereas P-sorption increased with increasing pH. Furthermore, the concentrations of those two fractions were higher under oxidized conditions than under reduced conditions (Table

4.1., 4.2., and 4.7.). Loganathan et al. (1987) noted that in strongly acid soils, an increase of pH up to about 5 was shown to reduce exchangeable Al and increase the extent of formation of hydroxy Al polymers, resulting in increased P-sorption. The mechanism of this sorption process was explained by Hsu and Rennie (1962) and was discussed in the previous study.

Haynes and Swift (1985) also explained that the increase in P-sorption with increasing pH was contributed from the precipitation of exchangeable Al as hydroxyl-Al polymers which results in a formation of new highly-active sorbing surfaces in the soils. Traina et al. (1986) found an increase in P-sorption as pH increase from 5.5 to 7. As pH increased, the hydrolysis of exchangeable Al^{3+} increased and subsequently reacted with P in solution enhancing the increase of P-sorption. Bloom (1981) found that P-sorption in Al-peat, which has an Al-saturation that may be quite similar to that of many acid mineral soils, increased with increasing pH. They concluded that the Al-organic matter complexes in acid surface soils is an important source of P-sorption.

An obvious decrease of soluble Fe concentrations as pH increased under reduced conditions may result from the reprecipitation of gel-like $Fe(OH)_2$, which is expected to have high P-sorption capacity (Holford and Patrick 1979). Furthermore, we used 2 N NaOH to raise pH of the system. This may enhance Fe reprecipitation process resulting in increasing P-sorption with increasing pH. White and Taylor (1977) also observed increases in P-sorption when soil pH was raised with NaOH. Aluminum was also considered to precipitate as hydroxy-Al polymers as the pH was raised, which results in the formation of new sorbing surfaces as mentioned above (Haynes and Swift 1985).

The concentrations of soluble Mn were higher under reduced conditions than those under oxidized conditions, and increased with decreasing pH (Table 4.1. and 4.2.) due to the stability and solubility of Mn-minerals. Satawathananont (1986) also reported similar results in acid sulfate soils of Thailand. Manganese becomes very soluble under acid and low redox conditions (Lindsay 1979). The increase in soluble Mn upon

Table 4.7. The amounts of Fe, Al, and Mn removed from soils by 1 *N* NH₄OAc (pH 4.0) (a), and sodium-citrate dithionite solution (d) and their effects on Langmuir maximum sorption capacity (x_m) and Standard P requirement (SPR)

Soil	Condition	pH	Fe		Al		Mn		Reduction in x_m		Reduction in SPR	
			a	d	a	d	a	d	a	d	a	d
			-----mg kg ⁻¹ -----						-----%-----			
Bangkok (Bk)	Oxidized	4.0	51	8129	564	9415	57	71	15	38	13	68
		5.0	46	8097	543	9414	45	60	20	32	13	72
		6.0	42	7982	530	9675	39	54	18	38	22	77
	Reduced	4.0	5190	8900	557	10123	73	74	35	55	24	76
		5.0	4808	8637	540	10168	53	64	40	55	22	77
		6.0	4445	8826	528	10404	46	61	41	55	23	79
Maha-Phot (Ma)	Oxidized	4.0	41	8930	823	18528	292	351	17	34	7	74
		5.0	36	8783	787	18679	286	344	19	40	12	77
		6.0	28	8720	742	18743	274	343	29	46	13	78
	Reduced	4.0	2225	9669	745	18767	305	371	35	51	30	80
		5.0	1916	9784	698	18796	281	369	40	55	28	82
		6.0	1689	9600	674	18931	272	365	42	55	34	84

reduction may be due to the release of exchangeable Mn^{2+} or the release of Mn^{2+} incorporated in ferric oxides, because Mn-oxides are considered to be unstable in acid sulfate soils of Thailand (Breemen 1976). The increases in soluble Mn concentration under reduced conditions were corresponded to the increases in P-sorption (Fig 4.1. and 4.2.). Since there is a lack of information about the effect of Mn on P-sorption, the mechanism of P-sorption by Mn is still unclear. However, this mechanism may concern the stability and solubility of manganese phosphates (MnHPO_4 and $\text{Mn}_3(\text{PO}_4)_2$). Lindsay (1979) mentioned that $\text{Mn}_3(\text{PO}_4)_2$ is more soluble than strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) at $pe+pH$ value > 15 but less soluble below this redox, whereas MnHPO_4 is more stable than strengite at all $pe+pH$ values < 19 . The $pe+pH$ values in this experiment, ranging from 2.9 to 7.8 under reduced conditions and from 10.7 to 17.2 under oxidized conditions, indicated that manganese phosphates would be less soluble under reduced conditions reflecting higher P-sorption under these conditions.

Pretreatment of soils with 1 N NH_4OAc (pH 4.0) and sodium-citrate dithionite solution (20 %) followed by washing with distilled water reduced P-sorption by 15 to 42 % and 32 to 55 % according to the Langmuir maximum sorption capacity, and 7 to 34 % and 68 to 84 % based on the standard P requirement, respectively (Table 4.7.). Other P-sorption parameters (k and BI) also diminished after these extractions (Table 4.3. and 4.4.). The differences in P-sorption under oxidized and reduced conditions that were observed in untreated soils were decreased after either NH_4OAc or sodium-citrate dithionite extractions. Soil pH had less effect on P-sorption of pretreated soils than that of untreated soils (Fig. 4.1. and 4.2.). This implies that the increase in P-sorption due to reduced conditions and increasing pH is related to the components of soil extractable by these extractions. The differences in P-sorption between actual and para-acid sulfate soils, however, were not removed by these treatments. There are other soil components (organic matter and/or clay minerals) besides the components which had been removed

by the extractions, that participate in P-sorption. The extractions, therefore, did not eliminate the difference in P-sorption between the soils.

Neutral 1 *N* NH₄OAc is known to extract exchangeable Fe which consists of both water-soluble and exchangeable Fe (Olson and Ellis 1982). Nevertheless, Satawathananont (1986) used 1 *N* NH₄OAc, pH 4.0, to extract exchangeable Fe, Al, and Mn from acid sulfate soils of Thailand. The amounts of Fe, Al and Mn dissolved by NH₄OAc (Fe_a, Al_a, and Mn_a) were presented in Table 4.7. Reduced conditions caused enormous increases in the amount of Fe_a. Meanwhile, oxidation-reduction conditions had less effect on the amounts of Al_a and Mn_a than that of Fe_a. The amount of Fe_a, Al_a, and Mn_a increased as pH decreased. This was probably due to the hydrolysis of exchangeable Fe to Fe(OH)₃ under oxidized condition at high pH, and incomplete extraction of the latter (Olson and Ellis 1982). Satawathananont (1986) also reported similar results for acid sulfate soils of Thailand. Willett and Higgins (1978) reported the corresponding increase of 1.0 *M* NH₄OAc (pH 4.8) extractable Fe and P-sorption capacity upon flooding conditions.

Sodium-citrate dithionite solution dissolved a large proportion of the crystalline iron-oxides as well as much of the amorphous materials (McKeague and Day 1966). Aluminum oxides were extracted at least partly together with iron-oxides (Borggaard 1983). The extractant also partly dissolved manganese-oxides from amorphous material. The amounts of Fe, Al, and Mn dissolved by sodium-citrate dithionite (Fe_d, Al_d, and Mn_d) were presented in Table 4.7. Higher amounts of Fe_d, Al_d, and Mn_d were removed from soil under reduced conditions than under oxidized conditions. Willett and Higgins (1978) mentioned an increase in the amount of Fe_{ox} (iron extracted by 0.2 *M* ammonium oxalate at pH 3.0), which is considered to be Fe in the form of amorphous (McKeague and Day 1966), when soil were undergone flooding. In highly reduced soils ferric hydrous oxides are reduced to poorly crystalline ferrous hydroxides, ferrosoferric hy-

droxides, ferrous carbonate and soluble Fe^{2+} (Ponnamperuma et al. 1967). These compounds may be expected to be extractable in dithionite extraction.

The decreases in P-sorption capacity following NH_4OAc extraction and sodium-citrate dithionite extraction could be attributed to the removal of the different forms of Fe, Al, and possibly Mn. Several workers reported reductions of P-sorption by soils after various amounts and forms of Fe and Al had been extracted chemically (Bromfield 1965; Borggaard 1983; Sah and Mikkelsen 1986*b*; Torrent 1987; Loganathan et al. 1987). Sah and Mikkelsen (1986*b*) reported that extracting amorphous Fe by 0.2 *M* ammonium oxalate, which decreased the surface area for P-sorption, significantly reduced P-sorption. Furthermore, the difference in P-sorption due to flooding was eliminated after this extraction. Ammonium oxalate (0.2 *M*) at pH 3.0 extracted amorphous Fe selectively (Borggaard 1981). Torrent (1987) found a decrease in P-sorption when soils were treated with citrate-bicarbonate-dithionite to dissolved Fe-oxides. Pretreatment of some soils from the Niger delta in southern Nigeria with citrate-bicarbonate-dithionite and ammonium oxalate, followed by washing with CaCl_2 reduced P-sorption by 21 to 46 % and 31 to 57 %, respectively (Loganathan et al. 1987).

Phosphorus sorption parameters (SPR, x_m , k and BI) of untreated soils were significantly correlated with Fe_d , Al_d , and Mn_d (Table 4.8.). However, P-sorption parameters (except k) were more closely correlated with Fe_d than Al_d and Mn_d suggesting the dominant role of amorphous and poorly crystalline iron-oxides or free iron-oxides in P-sorption characteristics of acid sulfate soils. These results agree with previous investigations, which showed good correlations between P-sorption capacity and the contents of free iron-oxides in soils (Lopez-Hernandez and Burnham 1974*a*; Borggaard 1983; Pena and Torrent 1984; Loganathan et al. 1987; Soils and Torrent 1989). Soils and Torrent (1989) found the close correlation between BI and Fe_d , and postulated that crystalline iron-oxides are the primary role in P-sorption by calcareous Vertisols and Inceptisols of Spain.

Table 4.8. Pearson's correlation coefficients between P-sorption parameters and various forms of Fe, Al, and Mn (extracted by 1 N NH₄ OAc (pH 4.0), a; and sodium-citrate dithionite solution, d)

	Fe _a	Al _a	Mn _a	Fe _d	Al _d	Mn _d
SPR	0.120	-0.208	0.677***	0.854***	0.735***	0.721***
x_m	0.364	-0.104	0.369	0.711***	0.441*	0.421*
k	0.268	0.112	0.573**	0.570**	0.629**	0.629**
BI	0.027	0.031	0.549**	0.733***	0.616**	0.607**
Reduction in SPR	0.492*	-0.234	0.047	0.667***	0.516**	0.486*
Reduction in x_m	0.746***	-0.128	0.112	0.520**	0.115	0.096

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

There were significant correlations between P-sorption parameters (except x_m) and Mn_a (Table 4.8.) indicating the importance of exchangeable Mn on P-sorption of acid sulfate soils. Since there is a lack of information about the effect of Mn on P-sorption, it is difficult to explain these anomalous results. Nevertheless, Breemen (1976) noted that Mn in acid sulfate soils may be present primarily in exchangeable form. This may explain these significant relationships.

Although there was a lack of significance in correlation between P-sorption parameters of untreated soils and the amounts of Fe_a and Al_a , significant correlations between the reduction in P-sorption (SPR and x_m) and the amounts of Fe_a were established (Table 4.8.). The reduction of standard P requirement was also significantly correlated with Fe_d , Al_d , and Mn_d , whereas the reduction of Langmuir maximum sorption capacity was significantly correlated with Fe_d only. The reduction of standard P requirement was more closely correlated with Fe_d than any other fractions, while the reduction of the Langmuir maximum sorption capacity was more closely correlated with Fe_a than Fe_d . This indicated that at high concentrations of added P, exchangeable Fe had more effect on P-sorption than did amorphous and poorly crystalline iron-oxides, and vice versa at low concentration of added P.

Bromfield (1965) found that the decrease in P-sorption by some acid soils from Australia following the various extraction tended to relate to the amount of Al removed rather than the amount of Fe removed. On the contrary, we found that Fe appeared to be more important on P-sorption of acid sulfate soils than did Al even though the soils contained the significant amount of Al. Free iron-oxides were shown to be the primary role controlling P-sorption of acid sulfate soils of Thailand, particularly within the range that is important to P-availability to many plants.

Earl et al. (1979) found a close, linear relationship between the reduction in the amount of P sorbed and the amounts of Fe and Al removed from soils. He claimed that reduction in the amount of P sorbed results primarily from the elimination of a significant

proportion of P-sorbing sites on the sorbent. Close correlations ($P < 0.001$) were established (i) between amorphous iron-oxides and the decrease in P-sorption capacity after these compounds were removed from the soils and (ii) between crystalline Fe-oxides and the further decrease in P-sorption capacity following the extraction of these compounds (Borggaard 1983). Pena and Torrent (1984) concluded that crystalline Fe-oxides are the most important P-sorbing components of Alfisols soils from a river terrace sequence of mediterranean Spain. Crystalline Fe-oxides provide the most active P-sorbing surfaces (Torrent 1987; Soils and Torrent 1989).

CONCLUSION

The P-sorption of acid sulfate soils was greatly affected by both pH and oxidation-reduction conditions. Phosphorus sorption under reduced conditions was higher than that under oxidized conditions, and it increased as pH increased. The effects of pH and oxidation-reduction conditions on P-sorption could be attributed to (i) the reduction and dissolution of Fe, (ii) the role of organic matter, (iii) the activity of amorphous hydroxy-aluminum species which increases with increasing pH. Pretreatment of soil with 1 *N* NH₄OAc (pH 4.0) and sodium-citrate dithionite solution (20 %), intended to remove exchangeable, and amorphous and crystalline forms of Fe, Al, and Mn, reduced P-sorption of soils. Furthermore, the treatments also decreased the differences in P-sorption due to the effects of pH and oxidation-reduction conditions. However, the differences in P-sorption between the actual and para-acid sulfate soils were not eliminated by these treatments. Significant correlations between P-sorption parameters and the reductions in P-sorption after the treatments, and free iron-oxides indicated the primary role of iron-oxides in P-sorption of acid sulfate soils of Thailand. Aluminum-oxides seemed to play a secondary role in P-sorption. Manganese appeared to have the important effect on P-sorption, but further study is needed to determine the effect of Mn on P-sorption in these soils.

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SUMMARY AND CONCLUSIONS

The effects of pH, redox potential, and various forms of Fe, Al, and Mn on P-sorption of acid sulfate soils of Thailand were investigated in laboratory microcosms using three actual acid sulfate soils (Sulfic Tropaequept), which are in the different acidity class, and one para-acid sulfate soil (Typic Tropaequept). Soil suspensions with a soil to 0.01 M CaCl₂ solution ratio of 1:7 were incubated under various pH (natural, 4.0, 5.0, and 6.0) and redox potential conditions (oxidized and reduced conditions without controlling Eh, and controlled Eh at +600, +400, +300, +200, +100, and 0 mV, respectively). After the incubation period, the soil suspensions were equilibrated with KH₂PO₄ ranging from 0 to 500 mg P kg⁻¹ soil. Some sets of soil suspensions were extracted by 1 N NH₄OAc (pH 4.0) and sodium-citrate dithionite solution (20 %) intended to remove Fe, Al, and probably Mn in the forms of exchangeable and free oxides before P addition. Three sorption equations were used to describe the P-sorption data.

The result indicated that the P-sorption data conformed well to the classical Langmuir equation. More native P was released to the soil solution under reduced than oxidized conditions. Para-acid sulfate soil released more native P than did actual acid sulfate soils under both conditions. Para-acid sulfate soil also sorbed less added P than did actual acid sulfate soils.

The P-sorption of both actual and para-acid sulfate soils was significantly affected by pH, redox potential, the extracted treatment before P addition, and their interactions. Significant interactions indicated that the effect of one factor changed as the level of other two factors changed. At pH 4.0, a considerable increase in P-sorption occurred as redox potential decreased from +400 to +300 mV, whereas at pH 5.0 and 6.0 a significant change in P-sorption occurred when redox potential decreased from +300 to +200 mV. This was mainly due to the change in iron solubility at a particular *pe* + pH value.

Significant interactions between pH and treatments, and between redox conditions and treatments were due to the different effects of pH and redox conditions at the diffe-

rent levels of treatments. The P-sorption of untreated soils increased significantly with increasing pH and decreasing redox potential, while there was no significant changes in P-sorption with changing pH and redox potential of soils pretreated with NH_4OAc and sodium-citrate dithionite solution. The increase in P-sorption with decreasing redox potential of untreated soils would be attributed to the reduction and reprecipitation of Fe, the role of organic matter, the effect of Mn on P-sorption, and the relationship between sulfate sorption and P-sorption by amorphous or crystalline iron- and aluminum-oxides. The increasing in P-sorption with increasing pH would be mainly contributed from the activity of amorphous hydroxy-aluminum species which increased with increasing pH.

Treating soils with NH_4OAc and sodium-citrate dithionite solution reduced P-sorption of the soils, and also decreased the differences in P-sorption due to the effects of pH and redox conditions. Treating soils with sodium-citrate dithionite obviously reduced more P-sorption than did NH_4OAc . The treatments, however, did not remove the differences in P-sorption between the actual and para-acid sulfate soils.

Significant correlations between P-sorption parameters and iron-oxides, and between the reduction of P-sorption after treatments and iron oxides indicated the primary role of iron-oxides in P-sorption of the acid sulfate soils of Thailand. Aluminum-oxides were also significantly correlated with P-sorption parameters and the reduction of P-sorption after treatments, but in a lower degree of significance when compared with iron-oxides. This illustrated the secondary role of aluminum-oxides on P-sorption in these soils. Nevertheless, it is inconclusive that amorphous or crystalline form of Fe and Al plays a major role in P-sorption of acid sulfate soils. Manganese also showed an important effect on P-sorption, but the mechanism is unclear.

As the results indicated the increase in P-sorption with increasing pH, liming the acid sulfate soils which is recommended in Thailand should be taken into account.

VITA

Asdaporn Krairapanond was born on April 13, 1961, in Bangkok, Thailand. In 1982, I graduated cum laude from Khon-Kaen University in Khon-Kaen, Thailand with a Bachelor of Science degree in Soil Science. I returned to Bangkok to work on Soil Loss Equation Project at the Department of Land Development. I received my Master of Science degree in Soil Science from Kasetsart University in Bangkok, Thailand, in 1985. I attended Louisiana State University in August 1986. I studied P-sorption characteristics of Thai coastal soils under the direction of Dr. William H. Patrick, Jr. I am presently candidate for the doctorate of Marine Sciences.

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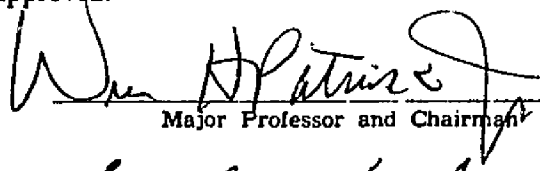
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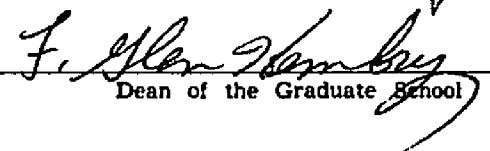
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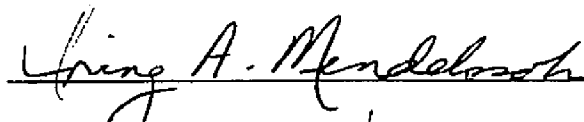

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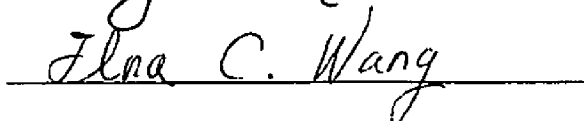

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