PN-ABA-312

87663

FINAL REPORT

8/25/89-12/31/93

Submitted to the Office of the Science Advisor
U.S. Agency for International Development
Washington, D.C. 20523

PHOSPHORUS EQUILIBRIA AND AVAILABILITY IN ACID SULFATE SOILS OF THAILAND

William H. Patrick, Jr.
Aroon Jugsujinda
Wetland Biogeochemistry Institute
Louisiana State University
Baton Rouge, LA 70803-7511

Asadaporn Krairapanond
Office of the National Environment Office
Soi Piboon Watana 7
Rama Road VI Road
Bangkok 10400, Thailand

Senior Scientific Staff
Soil Science Division
Department of Agriculture
Bangkok 10900, Thailand
and
Soil Science Department
Kasetsart University
Bangkok 10900, Thailand

Project Number 9.179

Grant number DHR-5542-G-SS-9027-00

Project Duration: 8/25/89-12/31/93

March 31, 1994

TABLE OF CONTENTS

Executive Summary.....3

Research Objectives.....6

Methods and Results.....8

Research Task No. 1. Phosphorus sorption characteristics in acid sulfate soils of Thailand: Effect of oxidized and reduced soil conditions.....8

Research Task No. 2. Phosphorus sorption characteristics in acid sulfate soils of Thailand: Effect of controlled soil redox potential and pH.....33

Research Task No. 3. P-sorption as influenced by iron, aluminum, manganese, pH, and oxidation-reduction condition in flooded soils.....60

Research Task No. 4. Correlation of soil phosphorus, pH, redox potential, iron, manganese and aluminum contents with yield of rice under flooded conditions in acid sulfate soils.....85

Impact, Relevance and Technology Transfer.....110

Project Activities/Outputs.....112

Project Productivity.....113

Future Work.....114

Addendum 115

EXECUTIVE SUMMARY

Acid sulfate soils are world-wide in distribution and occupy an area of about 12.5 million hectares of actual and potential acid sulfate soils occur in Thailand and approximately 0.8 million hectares of those located in the Bangkok Plain where they are primarily used for rice cultivation. Often production success is very low, less than 0.8 tons per hectare, due to soil acidity, soil salinity, P deficiency, and toxicity of Fe, Al, 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. Several aspects of phosphorus equilibria and availability to rice in acid sulfate soils of Thailand have been investigated. The study of P-sorption by the soils has practical interest but little is known on the P-sorption characteristics of acid sulfate soils of Thailand, particularly under reduced soil conditions. More native insoluble P was released under reduced than oxidized conditions. Para-acid sulfate soils released more native insoluble P than did actual acid sulfate soils under both conditions. Para-acid sulfate soils also sorbed less added P than actual acid sulfate soils. The P-sorption of both actual and para-acid sulfate soils was significantly affected by pH, redox potential and their interactions. The P-sorption increased significantly with increasing pH and decreasing redox potential. Treating soils with NH_4OAc (pH 4.0) and sodium-citrate dithionite solutions reduced P-sorption, and decreased the

differences in P-sorption due to the effects of pH and redox potential. Closely significant correlation between P-sorption parameters and iron-oxides indicated the primary role of iron-oxides to influence P-sorption of the acid sulfate soils of Thailand. Aluminum-oxides seemed to play the secondary role in P-sorption in these soils. Manganese also showed a significant effect on P-sorption.

The results further suggested that soil Al and Fe govern the release of native insoluble P in acid sulfate soils . The actual acid sulfate soils sorbed more P than did the para-acid sulfate soils, and the standard P requirement for normal plant growth, the P-sorption at a concentration of 0.2 ppm in final solution, in the actual acid sulfate soil was higher than the para-acid sulfate soil. The finding also suggested that as the soil pH increased and soil Eh decreased P-sorption increased. Liming the acid sulfate soil which is recommended in Thailand should be considered carefully especially in reduced soil condition. Liming has been recommended in Thailand as an amelioration of acid sulfate soils. Liming increases soil pH. Our study showed that as the soil pH increased, sorption of added P also increased. Use of suitable P sources such as locally available rock phosphate fertilizer to provide the plant nutrient should be considered for successful rice culture in Thailand.

RESEARCH OBJECTIVE

World wide area of acid sulfate soils is estimated to be 12.5 million hectares. In Thailand, one of the major rice production countries in southeast Asia, actual and potential acid sulfate soils occur in approximately 1.5 million hectares. In the Bangkok Plain alone about 0.8 million hectares are acid sulfate soils, 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. In addition, the soils contain the significant amounts of Fe and Al which have been reported to limit the rice growth.

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 effects 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. Acid sulfate soils are soils with pH below 4.0 that is directly caused by sulfuric acid formed by oxidation of pyrite (FeS_2). The soils also have a sulfuric horizon that is composed of mineral or organic soil material with 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).

The soils of Bangkok Plain have been classified 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 Subgroup Typic Tropaquepts. With each suitability classes, 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 soil 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 recently to semi-recent acid sulfate soils which are classified into Sulfic Tropaquepts or Typic Sulfaquepts Subgroups.

The acid sulfate soils in Bangkok Plain of Thailand are generally well developed. Fertility studies of acid sulfate soils, 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 of 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. The maximum P-sorption of acid sulfate soils of Thailand has been reported as high as 1 567 mg kg^{-1} soil.

The overall objective of this research project is to obtain a better understanding of the phosphorus chemistry of acid sulfate soils of Thailand. The oxidation-reduction (redox) and pH

chemistry of these soils determine to a considerable degree the availability of this essential nutrient to crops. The purpose of the research project is to study the basic chemistry of phosphorus, i.e., the redox/sorption-desorption/precipitation-dissolution reactions of acid sulfate soils with other soil constituents, so that phosphorus nutrient management can be made more efficient. Our major trusts are:

1. Determine the P equilibria (meaning precipitation-dissolution, sorption-desorption, and oxidation-reduction) of the acid soils under both drained (aerobic) and flooded (anaerobic) conditions.

2. Study the solubility of different sources of phosphate fertilizer, including rock phosphate, when added to soils under a range of redox and pH conditions.

3. Correlate availability P content of a wide range of acid sulfate soils with growth of plant and yield of rice.

4. Study P uptake by rice under controlled Eh-pH conditions of flooded acid sulfate soils.

METHODS AND RESULTS

Research Task No. 1

Phosphorus sorption characteristics in acid sulfate soils of Thailand: Effect of oxidized and reduced soil conditions [1]

A. KRAIRAPANOND, A. JUGSUJINDA*, and W. H. PATRICK, JR.

Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, La. 70803-7511, U.S.A. * Corresponding author

Key words: redox potential, pH, sorption-desorption, sulfic tropaquepts, typic sulfaquepts, typic tropaquepts

The result of this research task was published in Plant and Soil 157:227-237, 1993, please refer to addendum to this report.

---

[1] Contribution from the Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, Louisiana 70803-7511, U.S.A. The research was supported by USAID Grant No. DHR-5542-G-SS-9027-00, Program in Science and Technology Cooperation, Office of the Science Advisor, U.S. Agency for International Development.

Abstract

A laboratory experiment was conducted to study phosphorus sorption characteristics in acid sulfate soils (para- and actual-acid sulfate soils) of Thailand. The soils were subjected to oxidized and reduced conditions. The results showed that more native insoluble P was released under reduced than oxidized conditions, with more being released from para-acid sulfate soil than from actual acid sulfate soil under both conditions. Apparently, the para-acid sulfate soil has more available P content. Reduction also caused an increase in P-sorption at added P level $>\pm 450$ mg Kg^{-1}. 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 showed that amorphous and possibly crystalline Fe and Al play important roles in P-sorption in acid sulfate soils of Thailand. The classical Langmuir equation provided the best fit of the P-sorption data of acid sulfate soil under both oxidized and reduced conditions.

Introduction

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, 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. Due to the acidic nature of the acid sulfate soils, rice production on these soils in the Bangkok Plain is often severely limited. Kevie 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 unsuitable for rice (PI to PV). 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 Typic Sulfaquepts Subgroups.

One of the major limitations on rice growth in acid sulfate

soils is high P-sorption capacity (Attanandana, 1982). In addition, the excess amount of Fe and Al have been reported to limit rice growth in these soils. Since P-sorption mechanisms in acid sulfate 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 increase. Khalid et al.(1977) reported that more P was sorbed under reduce condition 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 sulphate soils. The results show that the improvement can be achieved by applying rock phosphate (Engelstad et al., 1974), by liming the soils and applying P fertilizer (Charoenchamratcheep et al., 1982; Attanandana and Vacharotayan, 1986). Attanandana and Vacharotayan (1986) found that the application of lime at very high rates reduce the availability of P in the actual acid sulphate soil.

The main objective of this research was to investigate P-sorption characteristics of the acid sulfate soils of Thailand as affected by oxidized and reduced conditions in terms of sorption

models. The effects of Fe and Al on P-sorption behavior under oxidized and reduced condition and at the selected pH levels are also reported.

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. 1.1). 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 where described by Kevie and Yenmanas (1972). Selected soil physical and chemical properties are presented in Table 1.1.

Suspensions of 250 g soil in 1750 ml 0.01 M $CaCl_2$ were incubated in laboratory microcosms under oxidized and reduced conditions for four weeks at 25 °C (4 replications). The microcosm consisted of a 2-L wide mouth flask with rubber stopper. Two platinum electrodes, a salt bridge and a combination glass electrode were permanently inserted through the rubber stopper to measure Eh and pH. The soil solution was kept in suspension by a magnetic stirrer and a stirrer bar. N_2 and O_2 gases bubbled continuously through the soil suspensions through

the gas inlet and gas outlet 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 0.2 % finely ground rice straw 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 equilibrium. After 24 hours equilibration on a reciprocating shaker, the soil suspensions was centrifugated (20 min at 7 000 rpm) and filtered through a 0.45 micro meter 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 solution (20%, 100 mL) on a reciprocating shaken for 18 h. After centrifugation and filtration, the filtrate was analyzed for citrate-dithionite extractable Fe and Al with ICP.

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:

$$x = kxmC/(1+kC) \qquad (1)$$

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 xm is the maximum monolayer sorption capacity. The two constants (k and xm) were determined by fitting the experimental data to linearized form (Lineweaver-Burk form) as given below (Persoff and Thomas, 1988):

$$1/x = 1/xm + (1/kxm)(1/C) \qquad (2)$$

The Freundlich equation is written:

$$x = ac1/n \qquad (3)$$

from which

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

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

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

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

where alpha and beta are constants. A plot of x against lnC 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 <0.005 and

0.001, 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 1.2). 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, increase the solubility of Fe and Al phosphate.

The para-acid sulfate soil (Bk) released more P than actual acid sulfate soils (Ma, Rs, and Rsa) under both oxidized and reduced conditions. Apparently, 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 under both soil conditions, 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 1.2). 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). 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 release 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. 1.2) 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 other actual acid sulfate soils (Rs and Rsa) (Fig. 1.3). 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. This is in consistent with the data in Table 2 which showed that the native P released by the para-acid sulfate soil was more than those by the actual acid sulfate soils under both soil conditions (Table 1.2). Para-acid sulfate soil has low organic matter content, high Bray II P, low exchangeable Al and exchangeable acidity, low citrate-dithionite extractable Fe and Al, and high CEC (Table 1.1). Even though the reduced soil conditions caused an increase in the release of native insoluble P to solution, reduction also led to a very large increase in P sorption capacity of soils at the higher P levels, >450 mg kg^{-1}. 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 study, we

observed that the amount of citrate-dithionite extractable Fe and Al under reduced conditions were considerably higher than under oxidized conditions. This discrepancy needs further studies. Correlation matrices indicated that P sorbed was positively correlated with citrate-dithionite Fe and Al extractable under both oxidized and reduced conditions (r=0.85**, 0.93**, 0.88** and 0.92**, respectively).

Phosphorus sorption in acid sulfate soils in Thailand could be attributed to Fe and Al in both amorphous and crystallire forms. Soil reduced conditions associated with changes of pH have strong effects on P-sorption isotherms. 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 isotherm as depicted in Figs. 1.4 and 1.5. 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 soil 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 value began over estimated.

The goodness of fitness of the three sorption equation was compared by simple linear regression analysis of the actual and predicted sorption 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 by Olsen and Watanabe (1957). According to Olsen and Watanabe (1957), the advantages of the Langmuir equation are that it fit actual P sorption isotherm 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 that other equations under both oxidized and reduced condition. 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 solve P with different sorption energies (Berkheiser et al, 1980). Thus, the classical Langmuir equation has been modified by postulating that there is 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 coefficient for the regression of Lineweaver-Burk

form of classical Langmuir isotherm in eleven western Washington soils are between 0.955-0.996. Barrow (1978) suggested that the simplest model should be preferred unless a more complex one can be shown to improve the measure the 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 for acid sulfate soils of Thailand.

The sorption maximum for each soil under each condition calculated from the Langmuir equation (Table 1.3) indicated that the maximum sorption capacities of para acid sulfate soils 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.

Conclusions

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, in consistent with its Bray II P content.

Although reduced soil conditions resulted in an increase in the amount of native soil P released, reduction also caused an increase in P-sorption at added P level above 450 mg Kg^{-1}. Less P-sorption occurred under both conditions in para-acid sulfate soil than in actual acid sulfate soil.

Significant correlations between the amount of P sorbed and citrate-dithionite extractable Fe and Al showed that amorphous and possibly crystalline Fe and Al played important roles in P-sorption in acid sulfate soils of Thailand.

References

Attanandana T 1982 Fertility problems of acid sulfate soils of Thailand. Ph.D. diss. Kyoto Univ., Kyoto, Japan.

Attanandana T and Vacharotayan 1986 Acid sulfate soils: Their characteristics, genesis, amelioration and utilization. Southeast Asian Studies. 24, 154-180.

Barrow N J 1978 The description of phosphate adsorption curves. J. Soil Sci. 29, 447-462.

Berkheiser V E, Street J J, Rao P S C and Yaun T L 1980 Partitioning of inorganic orthophosphate in soil-water systems. Crit. Rev. Environ. Control. 10, 179-224.

Chang S C and Jackson M L 1958 Phosphorus fraction in some representative soils. J Soil Sci. 9, 109-119.

Charoenchamrathcheep C B, Tantisira B, Chimuson P and Sin-Aiem V 1982 The effects of liming and fertilizer applications to acid sulfate soils for improvement of rice production in Thailand. p. 157-171. *In* H. Dost and N. van Breemen (ed.) Proceedings of the Bangkok symposium on acid sulfate soils. Second International Symposium on Acid Sulfate Soils, Bangkok, Thailand. 18-24 Jan. 1881. ILRI, Wageningen, The Netherlands.

Engelstad O P Jugsujinda A and De Datta S K 1974 Response by rice to phosphate rocks varying in citrate solubility. Soil Sci. Soc Am Proc. 38,524-529.

Gambrell R P, Khalid, Verloo M G and Patrick W H Jr 1975 Transformations of heavy metals and plant nutrients in dredged sediments as affected by oxidation-reduction potential and pH. Part II. Materials and methods, results and discussion. Contract report D-77-4. U.S. Army Engineers Waterways Experiment Station, Vicksburg, MS.

Gambrell R P and Patrick Jr W H 1978 Chemical and microbiological properties of anaerobic soils and sediments. p. 375-423. *In* D.D. Hook and R.M.M. Crawford (ed) Plant life in anerobic environments. Ann Arbor Science Publishers Inc., Ann Arbor, ML.

Haynes R J and Swift R S 1985 Effects of liming and air-drying on the adsorption of phosphate by some acid soils. J. Soil Sci. 36, 513-521.

Holford I C R and Patrick Jr W H 1979 Effects of reduction and pH changes on phosphate sorption and mobility in an acid sulfate soil. Soil Sci. Soc. Am J. 43, 292-297.

Holford I C R, Wedderburn R W M and Mattingly G E G 1974 A Langmuir two-surface equation as a model for phosphate adsorption by soils. J. Soil Sci. 25, 242-255.

Kuo S 1988 Application of a modified Langmuir isotherm to phosphate sorption by some acid soils. Soil Sci. Soc. Am. J. 52, 97-102.

Kevie W van der and Yenmanas B 1972 Detailed reconnaissance soil survey of southern central plain area. Soil Survey Rept. no. 89., Land Dev. Dept., Bangkok, Thailand.

Khalid R A. Patrick W H Jr and DeLaune R D 1977 Phosphorus sorption characteristics of flooded soils. Soil Sci. Soc. Am. J. 41, 305-310.

Lindsay W L 1979 Chemical equilibria in soils. John Willey & Sons, Inc., NY.

Lopez-Hernandez D and Burnham C P 1974 The effect of pH on phosphate adsorption in soils. J. Soil Sci. 25, 207-216.

Low P F and Black C A 1950 Reactions of phosphate with kaolinite. Soil Sci. 70, 273-290.

McKeague J A and Day J H 1966 Dithionite and oxalate Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46,13-22.

Mead J A 1981 A comparison of the Langmuir, Freundlich and Temkin equations to describe phosphate adsorption properties of soils. Aust. J. Soil Res. 19, 333-342.

Mehadi A A and Taylor R W 1988 Phosphate adsorption by two highly-weathered soils. Soil Sci. Soc. Am. J. 52, 627-632.

Mokwunye U 1975 The influence of pH on the adsorption of phosphate by soils from the Guinea and Sudan Savannah zones of Nigeria. Soil Sci. Soc. Am. Proc. 39,1100-1102.

Obihara C H and Russell E W 1972 Specific adsorption of silicate and phosphate by soils. J. Soil Sci. 23, 105-117.

Olsen S R and Watanabe F S 1957 A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. Soil Sci. Soc. Am. Proc. 21, 144-149.

Patrick W H Jr Gotoh S and William B G 1983 Strengite dissolution in flooded soils and sediments. Science 179, 564-565.

Persoff P and Thomas J F 1988 Estimating Michaelis-Menton of Langmuir isotherm constants by weighted nonlinear least squares. Soil Sci. Soc. Am. J. 52, 886-889.

Posner A M and Bowden J W 1980 Adsorption isotherms: Should they be split? J. Soil Sci. 31, 1-10.

Ryden J C, McLaughlin J R and Syers J K 1977 Mechanisms of phosphate sorption by soils and hydrous ferric oxide gel. J. Soil Sci. 28, 72-92.

Satawathananont S 1986 Redox, pH, and ion chemistry of acid sulfate soils in Thailand. Ph.D. diss., Louisiana State Univ., Baton Rouge, LA.

Smyth T J and Sanchez P A 1980 Effects of lime, silicate and phosphorus applications to an Oxisols on phosphate sorption and ion retention. Soil Sci. Soc. Am. J. 44, 500-505.

Tanaka A, Watanabe N and Ishizuke Y 1969 A critical study on the phosphate concentration in the soil solution of submerged soil. J Sci. Soil Manure, Japan. 40, 406-414.

Trana S J, Sposito G, Hesterberg D and Kafkafi U 1986 Effects of pH and organic acids on orthophosphate solubility in an acidic, montmorilloniteic soil. Soil Sci. Soc. Am. J. 50, 45-52.

White R E and Taylor A W 1977 Effects of pH on phosphate adsorption and isotopic exchange in acid soils at low and

high additions of soluble phosphate. J. Soil Sci. 28, 48-61.

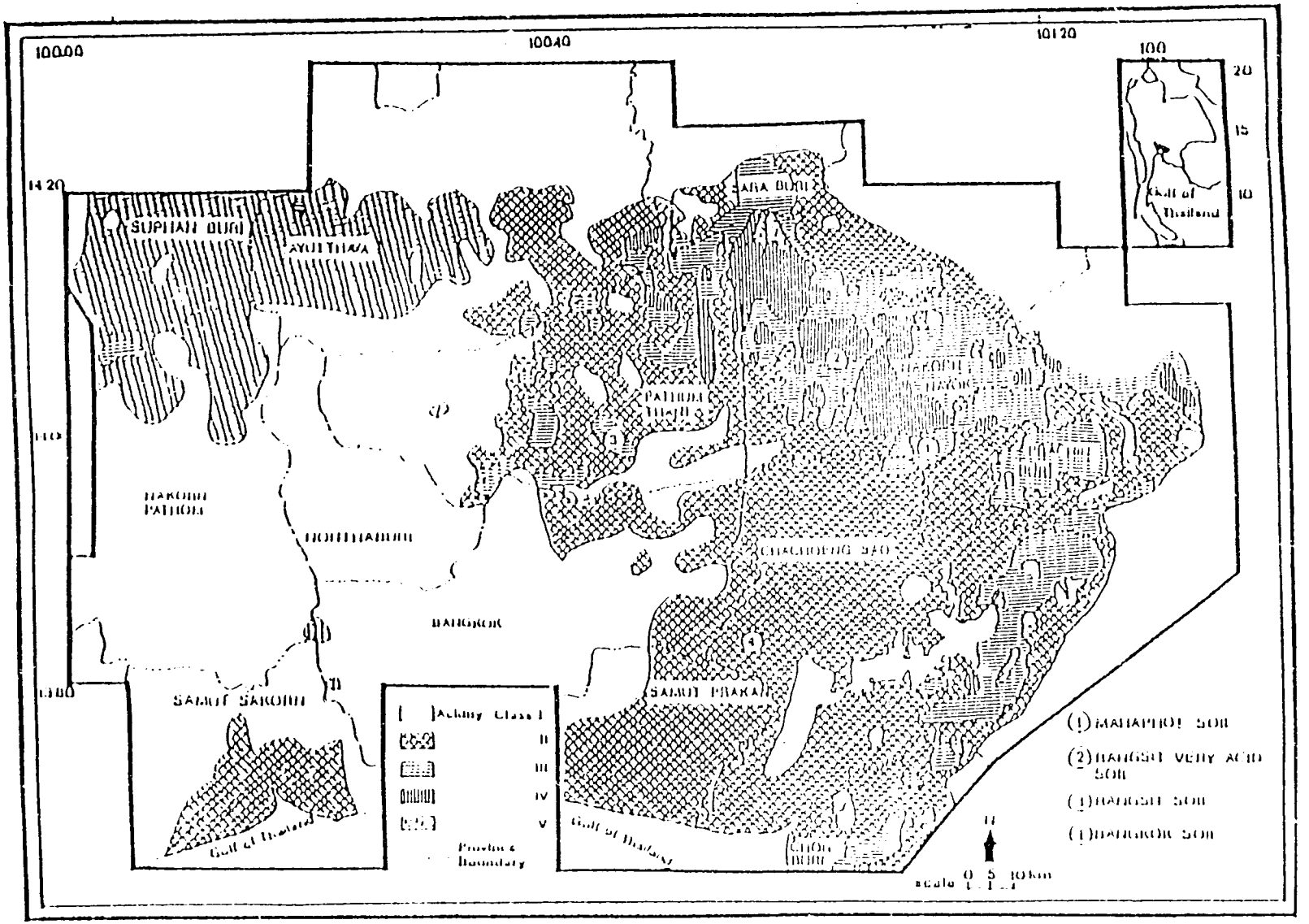


Fig. 1.1 Map showing location of soil sampling sites in the Bangkok Plain of Thailand

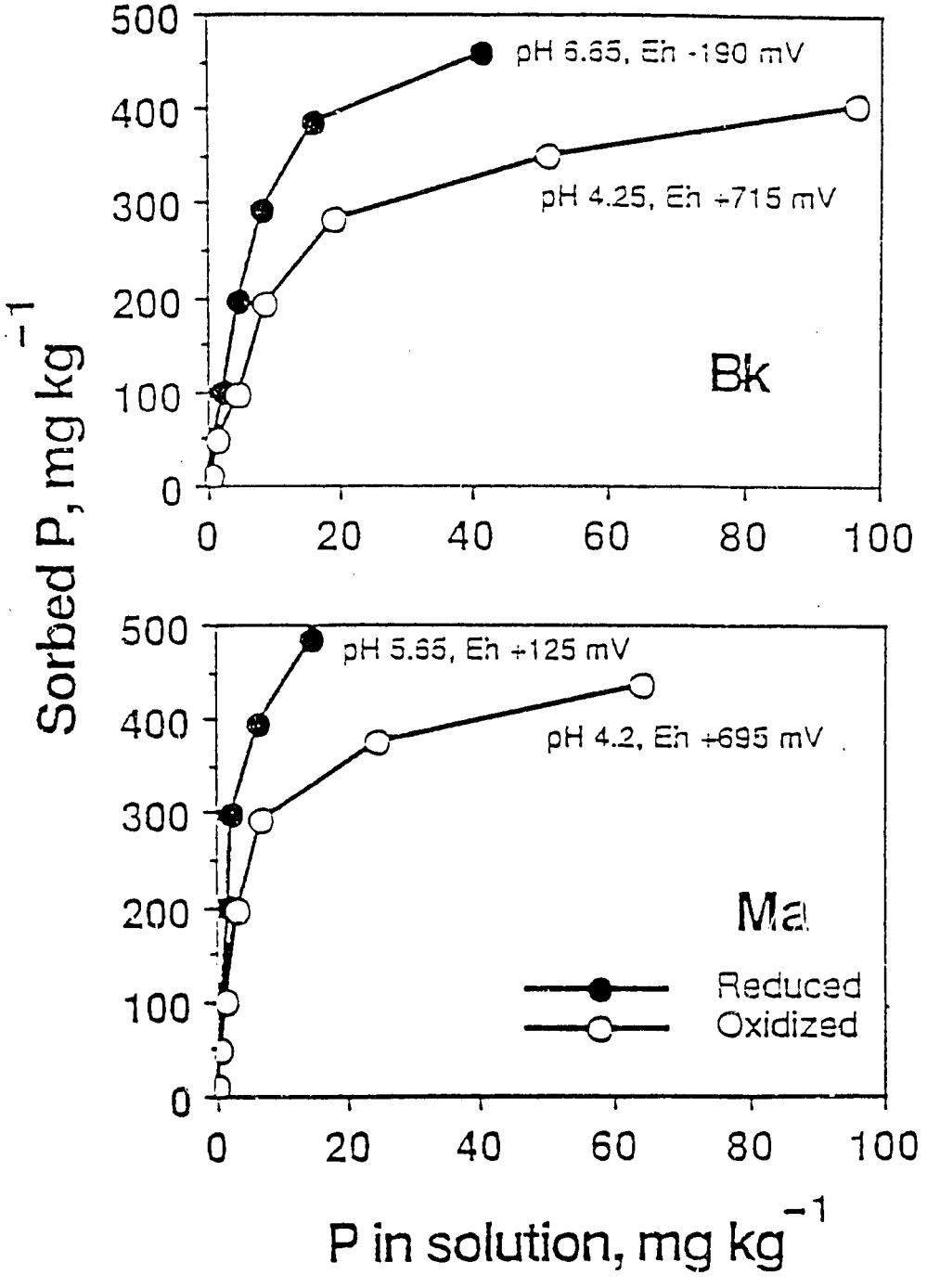


Fig. 1.2. The actual P-sorption isotherms in Bangkok soil (Bk) and Maha-Phot soil (Ma) as affected by oxidation-reduction status

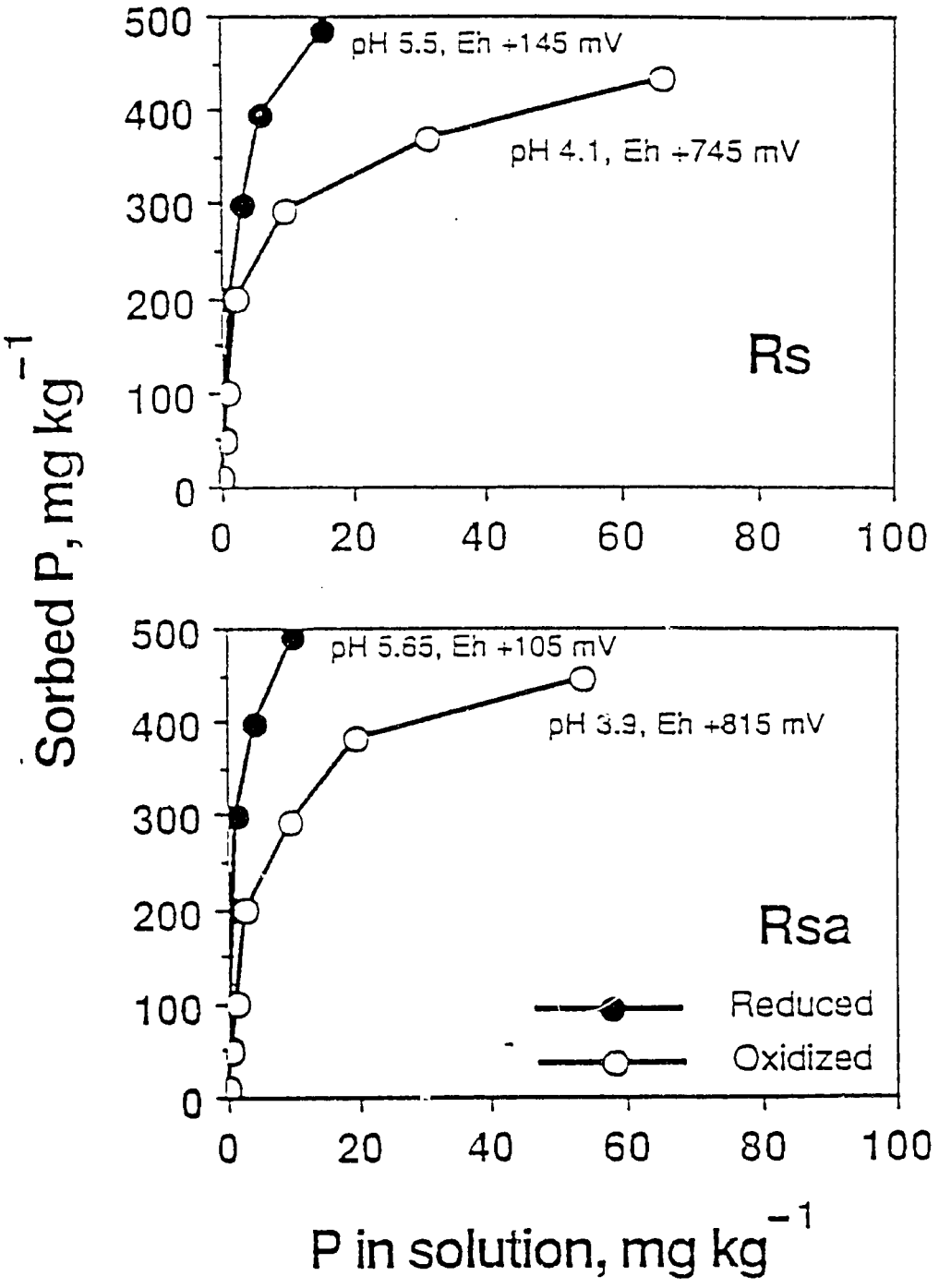


Fig. 1.3. The actual P-sorption isotherms in Rangsit soil (Rs) and Rangsit very acid soil (Rsa) as affected by oxidation-reduction status

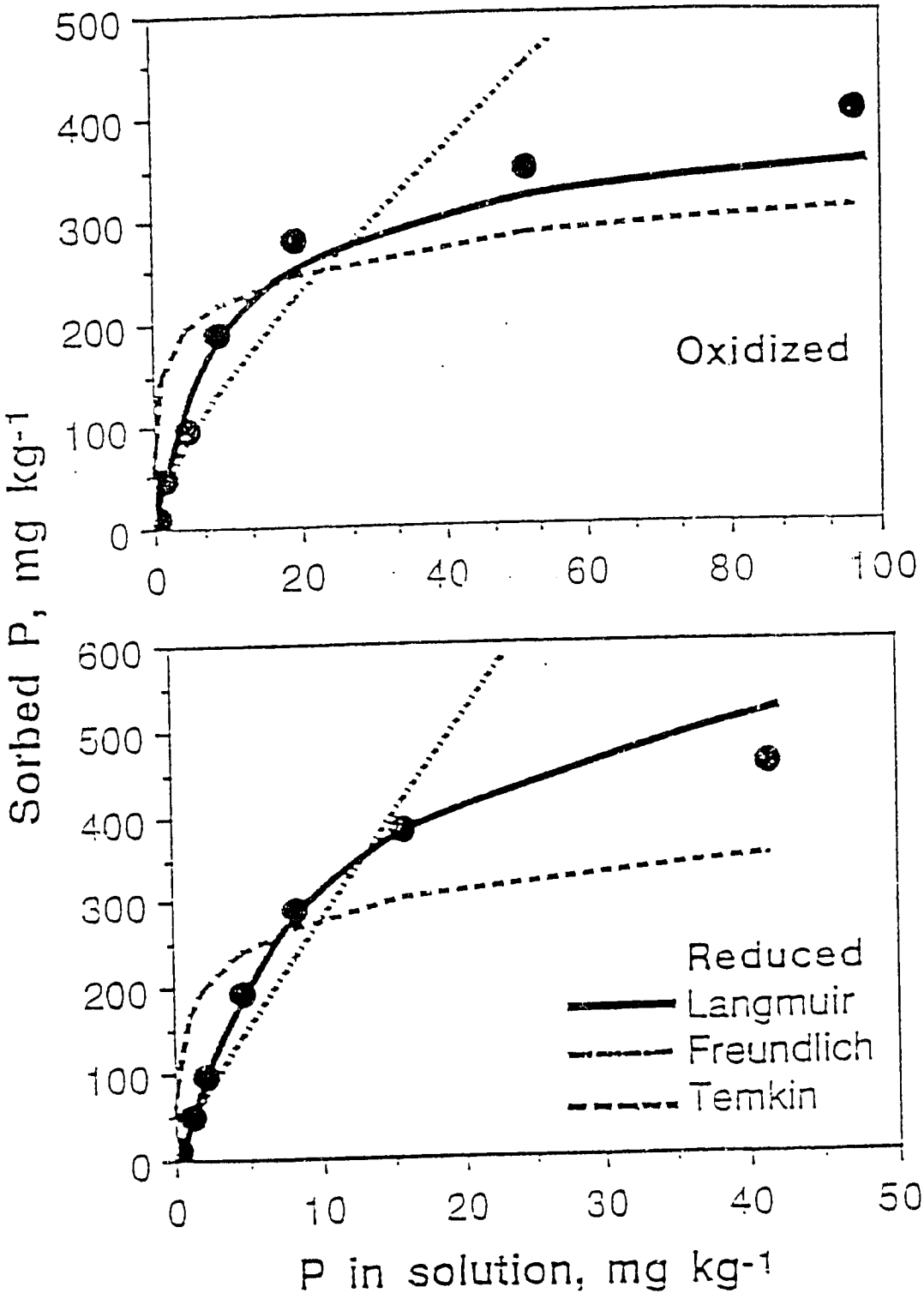


Fig. 1.4. Comparison of observed and predicted P-sorption in the para-acid sulfate soil (Bk) under oxidized and reduced conditions using three different sorption equations

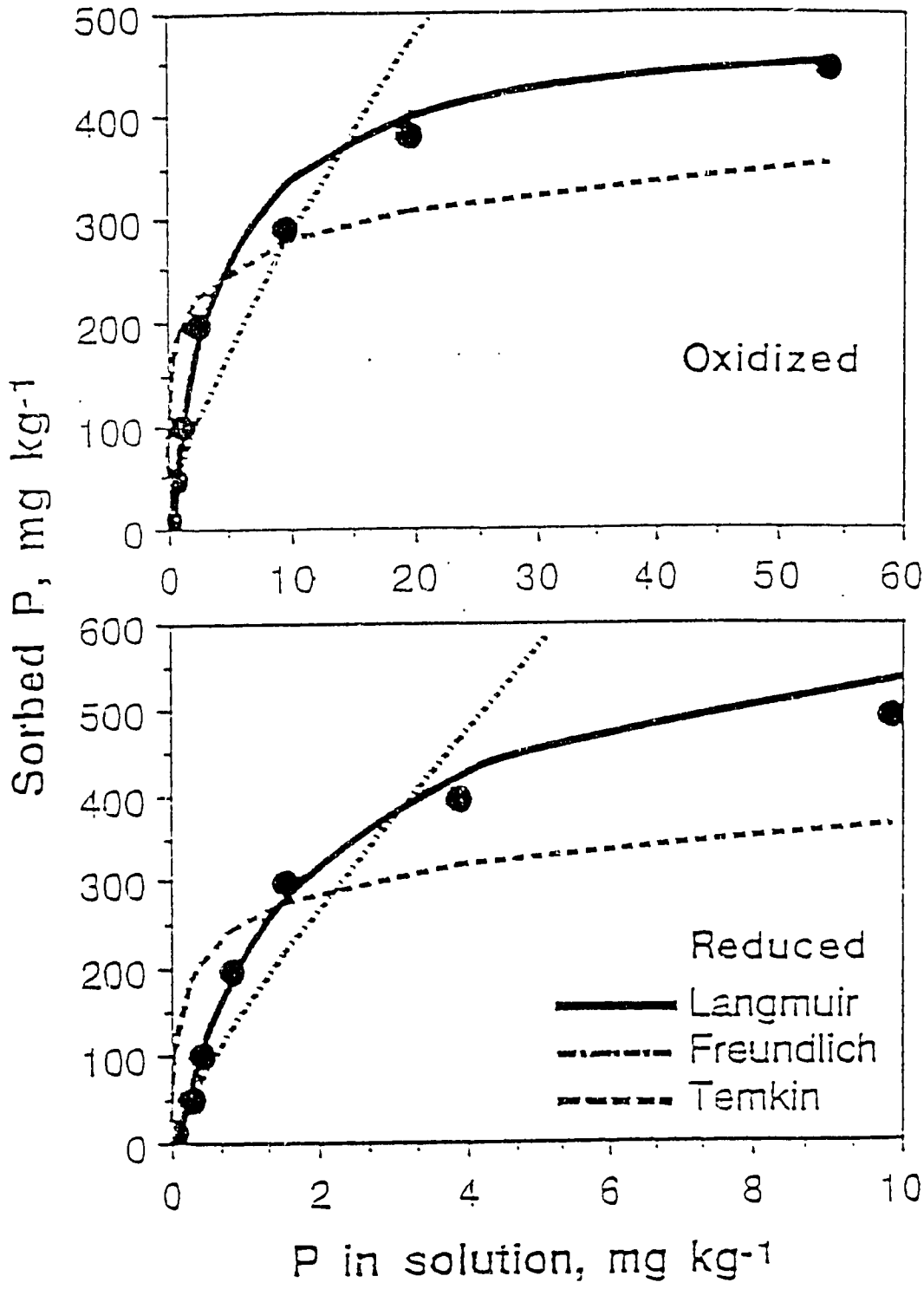


Fig. 1.5. Comparison of observed and predicted P-sorption in the acual acid sulfate soil (Rsa) under oxidized and reduced conditions using three different sorption equations

Table 1.1. 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 P[b]	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] $BaCl_2$-Triethanolamine (Peech, 1965)

[e] Ammonium saturation-distillation (Chapman, 1965)

Table 1.2. Concentrations of P released, soluble Fe, Al, and citrate-dithionite extractable Fe and Al

Soil	pH	Eh		native P	soluble		citrate-dithionite extractable	
		actual	corrected to pH 7	released	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

Table 1.3. 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

Research Task No. 2

Phosphorus sorption characteristics in acid sulfate soils of Thailand: Effect of controlled soil redox potential and pH[2]

A. KRAIRAPANOND, A. JUGSUJINDA*, and W. H. PATRICK, JR.

Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, La. 70803-7511, U.S.A. * Corresponding author.

Key words: redox potential, pH, sorption-desorption, sulfic tropaquepts, typic sulfaquepts, typic tropaquepts

The result of this research task was published in Plant and Soil 157:227-237, 1993, please refer to addendum to this report.

---

[2] Contribution from the Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, Louisiana 70803-7511, U.S.A. The research was supported by USAID Grant No. DHR-5542-G-SS-9027-00, Program in Science and Technology Cooperation, Office of the Science Advisor, U.S. Agency for International Development.

Abstract

The influences of soil pH and redox potential on P-sorption characteristics of acid sulfate soils of Thailand were studied. Surface soil samples of the para- and actual-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 $CaCl_2$ 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. Sorption isotherms were described by the classical Langmuir equation. It was found that 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 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. Significant correlation between P-sorption parameters and 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 a significant effect on P-sorption.

Introduction

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 low land 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 from 500 to 1 500 Kg^{-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 response to P fertilizer unless the soil pH was raised by liming.

Kevie 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 unsuitable for rice (PI to PV). 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 Typic Sulfaquepts Subgroups.

One of the major limitations on rice growth in acid sulfate soils is high P-sorption capacity (Attanandana, 1982). In addition, the excess amount of Fe and Al have been reported to limit rice growth in these soils. Since P-sorption mechanisms in acid sulfate 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, 1984; Traina et al., 1986) or decrease (Obihara and Russell, 1972; Lopez-Hernandez and Burnham, 1974; Smyth and Sanchez, 1980) as pH increase. Khalid et al.(1977) reported that more P was sorbed under reduce condition 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 sulphate soils. The results show that the improvement can be achieved by applying rock phosphate (Engelstad et al., 1974), by liming the soils and applying P fertilizer (Charoenchamratcheep et al., 1982; Attanandana and Vacharotayan, 1986). Attanandana and Vacharotayan (1986) found that the application of lime at very high rates reduce the availability of P in the actual acid sulphate soil. The sorption of P by aerobic soils and pure iron- or aluminum -oxide 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 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. In our previous study (Research Task No. 1) where the acid sulfate soils were subjected to oxidized and reduced conditions without changes of redox potential and pH, more native insoluble P was released under reduced than oxidized conditions, with being more released from para-acid sulfate soil than from actual acid sulfate soil under both conditions. The effects of redox potential 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. 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 different controlled levels of pH and redox potential.

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 (see Fig. 1.1). Soils were air-dried, sieved (<2 mm), and thoroughly mixed prior to chemical analysis. In this study one para-acid sulfate soil, Bangkok (Bk), and one actual acid sulfate soils, Maha-Phot (Ma), were used. General morphology and chemical characteristics of soils were described by Kevie and Yenmanas (1972). Selected soil physical and chemical properties are presented in Table 1.1.

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 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) for 6 wk at 25 °C. Prior to incubation, the soil were amended with 0.2 % finely ground rice straw which provided an energy source to promote 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 O_2 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 N_2 flow resulted in maintaining redox potential within $\pm$ 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 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 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) and filtered through a 0.45-um membrane filter, under an O_2-free N_2 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 reaction 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 1N 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-um 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 filtered. The filtrate was analyzed for free oxides of Fe, Al, and Mn with 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):

$$1/x = 1/xm + (1/kxm)(1/c) \quad (2)$$

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 when no P was added in para-acid sulfate, Bangkok (Bk) soil was

presented in Table 2.1 and in actual acid sulfate, Maha-Phot (Ma) soil in Table 2.2. 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 2.1 and 2.2). 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 unit. The concentrations of soluble Mn slightly increased with decreasing redox potential and pH. 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 2.1 and 2.2). Satawathananont (1986) also reported in 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 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 $Mn_3(PO_4)_2$) 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, $AlPO_4.2H_2O$). Lindsay (1979) noted that when soils are reduced until pe + pH levels drops below 4.96, variscite, which is considered to be stable beyond this pe + pH levels, can be converted to vivianite ($Fe_3(PO_4)_2.8H_2O$). 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 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. 2.1 and 2.2. Langmuir maximum sorption capacity (*xm*) and Langmuir sorption constant (*k*) of both soils were shown in Fig. 2.3 and 2.4. 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 constantly in solution culture, will

provide adequate P to many plants.

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 2.3 and 2.4). 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 pH 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. 2.2 and 2.3). At pH 4.0, standard P requirement considerably increased with increasing 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 kg^{-1} soil was classified as low (10-100 mg kg^{-1} soil) to medium (100-500 mg kg^{-1} soil) level, whereas that of para-acid sulfate soil (Bangkok, Bk) ranging from 34 to 59 mg 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 2.1 and 2.2).

Like standard P requirement, Langmuir maximum sorption capacity (*xm*) was significantly affected by redox potential, pH, and interaction between redox potential and pH in both actual and para-acid sulfate soils (Table 2.3 and 2.4). A significant interaction 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.

2.1 and 2.2) 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 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 soil ranging from 508 to 699 mg kg^{-1} soil, and from 458 to 618 mg 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 determined the maximum sorption capacity. Imai et al. (1983) used air-dried acid sulfate soils, and they used two layers Langmuir equation to determine the maximum sorption capacity.

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. 2.3 and 2.4). 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 different 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 induces 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.

Conclusions

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 mV to +200 mV. This would be mainly due to the reduction of Fe at particular redox and pH levels. 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 solubilization of ferric compounds, the role of organic matter and 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. 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.

References

Attanandana T 1982 Fertility problems of acid sulfate soils of Thailand. Ph.D. diss. Kyoto Univ., Kyoto, Japan.

Attanandana T and Vacharotayan 1986 Acid sulfate soils: Their characteristics, genesis, amelioration and utilization. Southeast Asian Studies. 24, 154-180.

Chang S C and Jackson M L 1958 Phosphorus fraction in some representative soils. J Soil Sci. 9, 109-119.

Charoenchamrathcheep C B, Tantisira B, Chimuson P and Sin-Aiem V 1982 The effects of liming and fertilizer applications to acid sulfate soils for improvement of rice production in Thailand. p. 157-171. *In* H. Dost and N. van Breemen (ed.) Proceedings of the Bangkok symposium on acid sulfate soils. Second International Symposium on Acid Sulfate Soils, Bangkok, Thailand. 18-24 Jan. 1881. ILRI, Wageningen, The Netherlands.

Engelstad O P Jugsujinda A and De Datta S K 1974 Response by rice to phosphate rocks varying in citrate solubility. Soil Sci. Soc Am Proc. 38,524-529.

Haynes R J and Swift R S 1985 Effects of liming and air-drying on the adsorption of phosphate by some acid soils. J. Soil Sci. 36, 513-521.

Gambrell R P, Khalid, Verloo M G and Patrick W H Jr 1975 Transformations of heavy metals and plant nutrients in dredged sediments as affected by oxidation-reduction

potential and pH. Part II. Materials and methods, results and discussion. Contract report D-77-4. U.S. Army Engineers Waterways Experiment Sttation, Vicksburg, MS.

Gambrell R P and Patrick Jr W H 1978 Chemical and microbiological properties of anaerobic soils and sediments. p. 375-423. *In* D.D. Hook and R.M.M. Crawford (ed) Plant life in anerobic environments. Ann Arbor Science Publishers Inc., Ann Arbor, ML.

Kevie W van der and Yenmanas B 1972 Detailed reconnaissance soil survey of southern central plain area. Soil Survey Rept. no. 89., Land Dev. Dept., Bangkok, Thailand.

Khalid R A. Patrick Jr W H and DeLaune R D 1977 Phosphorus sorption characteristics of flooded soils. Soil Sci. Soc. Am. J. 41, 305-310.

Lindsay W L 1979 Chemical equilibria in soils. John Willey & Sons, Inc., NY.

Lopez-Hernandez D and Burnham C P 1974 The effect of pH on phosphate adsorption in soils. J. Soil Sci. 25, 207-216.

McKeague J A and Day J H 1966 Dithionite and oxalate Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46,13-22.

Mehadi A A and Taylor R W 1988 Phosphate adsorption by two highly-weathered soils. Soil Sci. Soc. Am. J. 52, 627-632.

Mokwunye U 1975 The influence of pH on the adsorption of phosphate by soils from the Guinea and Sudan Savannah zones of Nigeria. Soil Sci. Soc. Am. Proc. 39,1100-1102.

Obihara C H and Russell E W 1972 Specific adsorption of silicate and phosphate by soils. J. Soil Sci. 23, 105-117.

Patrick Jr W H Gotoh S and William B G 1983 Strengite dissolution in flooded soils and sediments. Science 179, 564-565.

Satawathananont S 1986 Redox, pH, and ion chemistry of acid sulfate soils in Thailand. Ph.D. diss., Louisiana State Univ., Baton Rouge, LA.

Smyth T J and Sanchez P A 1980 Effects of lime, silicate and phosphorus applications to an Oxisols on phosphate sorption and ion retention. Soil Sci. Soc. Am. J. 44, 500-505.

Tanaka A, Watanabe N and Ishizuke Y 1969 A critical study on the phosphate concentration in the soil solution of submerged soil. J Sci. Soil Manure, Japan. 40, 406-414.

Trana S J, Sposito G, Hesterberg D and Kafkafi U 1986 Effects of pH and organic acids on orthophosphate solubility in an acidic, montmorilloniteic soil. Soil Sci. Soc. Am. J. 50, 45-52.

White R E and Taylor A W 1977 Effects of pH on phosphate adsorption and isotopic exchange in acid soils at low and high additions of soluble phosphate. J. Soil Sci. 28, 48-61.

Table 2.1. Concentrations of soluble (s) P, Fe, Al, and Mn, and concentrations of Fe, Al, and Mn extracted by 1 *N* NH_4OAc (pH 4.0) (a), and sodium-citrate dithionite solution (d) in Bangkok soil

pH	Redox potential	P	Fe			Al			Mn		
		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 2.1. (Continued)

pH	Redox potential	P	Fe			Al			Mn		
		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 2.2. Concentrations of soluble (s) P, Fe, Al, and Mn, and concentrations of Fe, Al, and Mn extracted by 1 *N* NH_4OAc (pH 4.0) (a), and sodium-citrate dithionite solution (d) in Maha-Phot soil

pH	Redox potential	P	Fe			Al			Mn		
		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 2.2. (Continued)

pH	Redox potential	P	Fe			Al			Mn		
		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

Table 2.3. 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 2.4. 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		

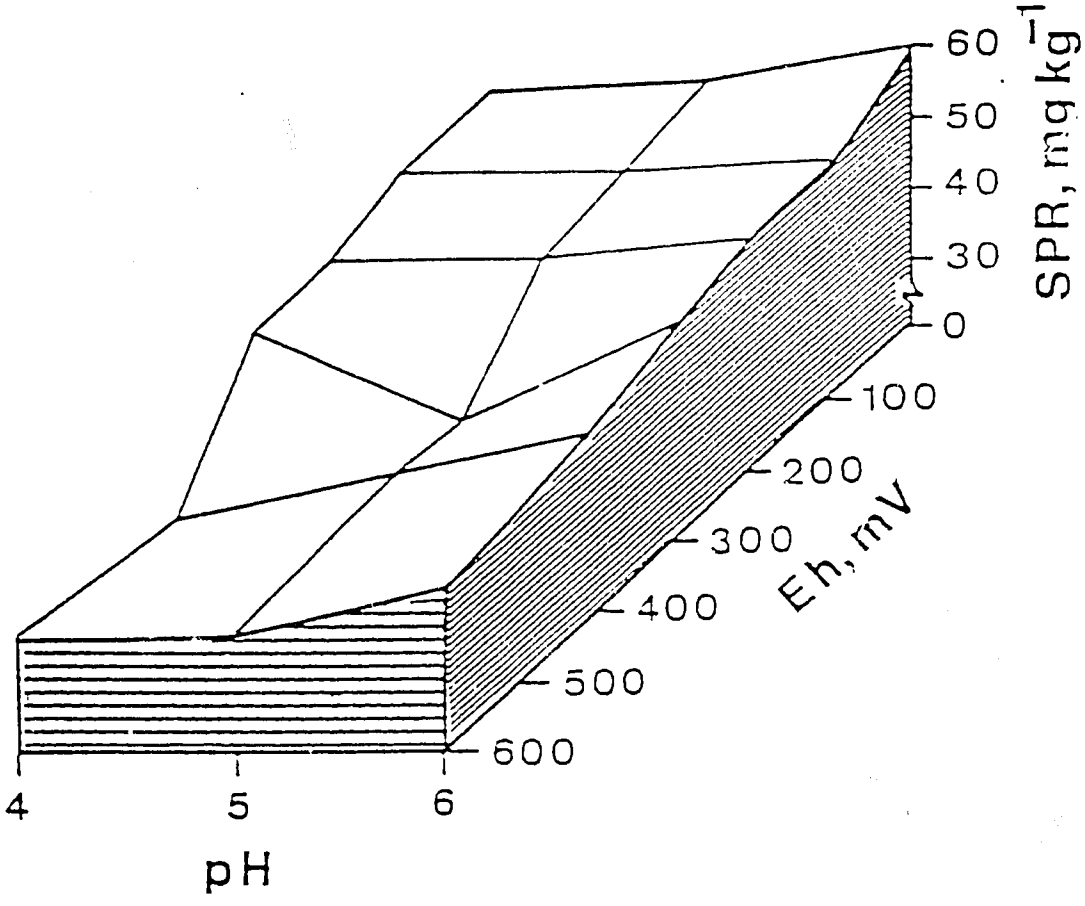


Fig. 2.1 Effects of pH, redox potential, and their interaction on standard P requirement (SPR) (mg kg^{-1}) in Bangkok soil

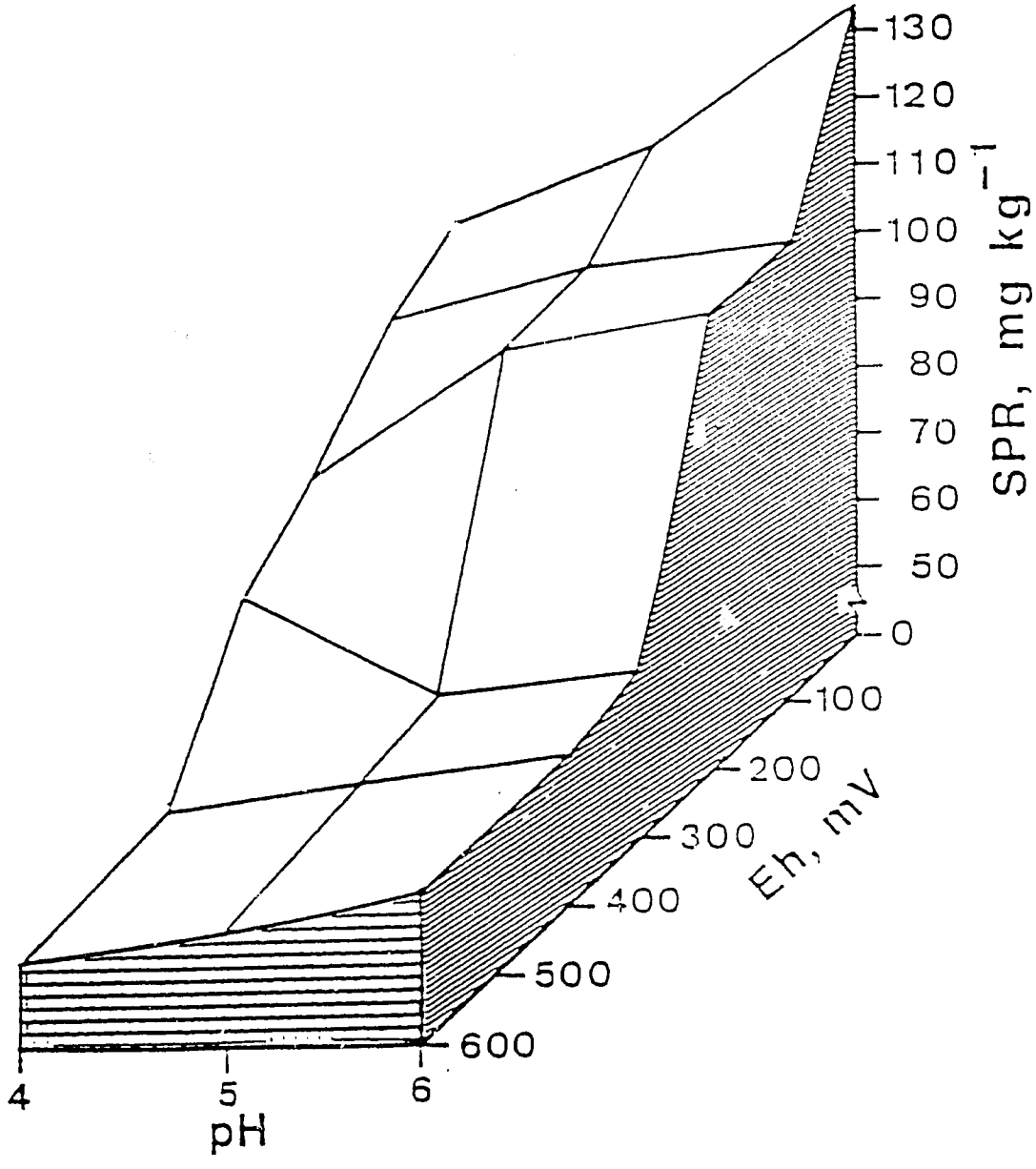


Fig. 2.2. Effects of pH, redox potential, and their interaction on standard P requirement (SPR) (mg kg^{-1}) in Maha-Phot soil

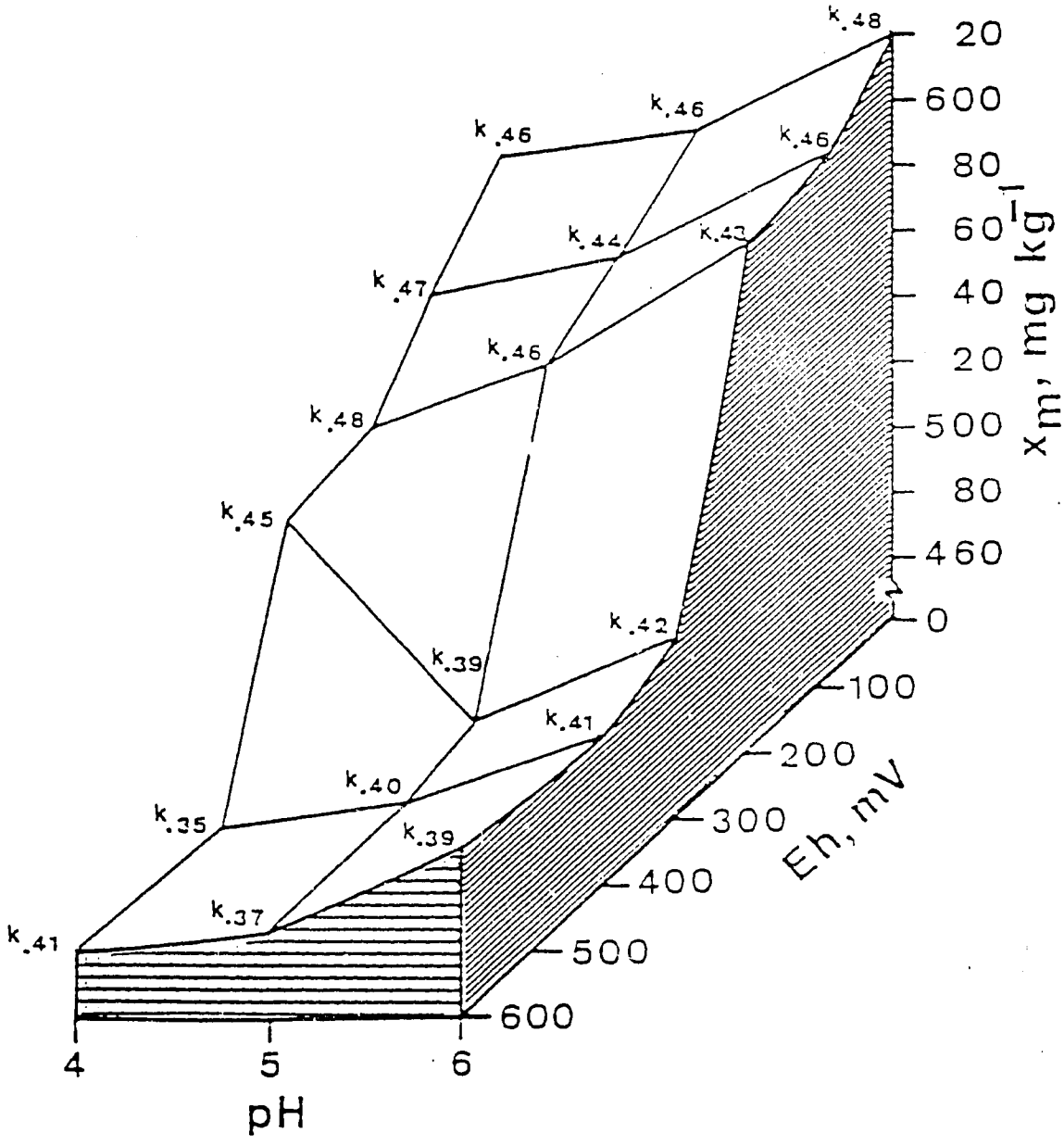


Fig. 2.3 Effects of pH, redox potential, and their interaction on Langmuir maximum sorption capacity (x_m) (mg kg^{-1}) and Langmuir sorption constant (k) (mg^{-1} kg) in Bangkok soil

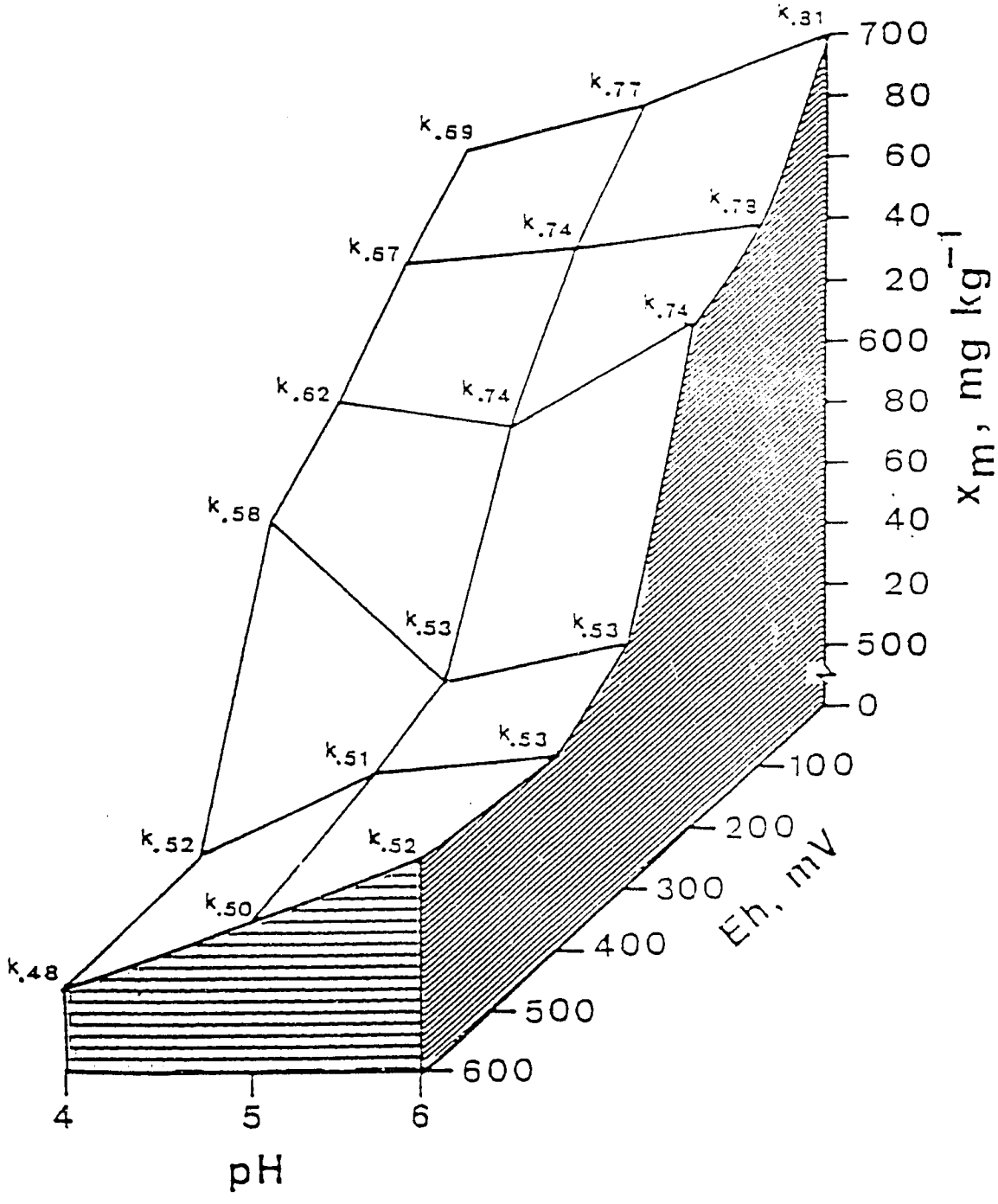


Fig. 2.4 Effects of pH, redox potential, and their interaction on Langmuir maximum sorption capacity (x_m) (mg kg^{-1}) and Langmuir sorption constant (k) (mg^{-1} kg) in Maha-Phot soil

Research Task No 3.

P-sorption as influenced by iron, aluminum, manganese, pH, and oxidation-reduction condition in flooded soils[3*]

A. Jugsujinda[1,4], A. Krairapanond [2], and W.H. Patrick, Jr. [1]

[1] Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, LA 70803-7511, U.S.A.

[2] Office of the National Environment Office, Soi Piboon Watana 7, Rama VI Road, Bangkok 10400, Thailand;

[4] Corresponding author

Key word: buffer index - Langmuir maximum sorption capacity - standard P requirement - Sufic Tropaquepts - Typic Tropaquepts

The manuscript of this paper has been submitted for publication in Biology and Fertility of Soils Journal.

[3*] Contribution from the Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, Louisiana 70803-7511, U.S.A. The research was supported by USAID Grant No. DHR-5542-G-SS-9027-00, Program in Science and Technology Cooperation, Office of the Science Advisor, U.S. Agency for International Development.

Abstract

P-sorption in soils are controlled by many factors. The objective of the present study was to evaluate the effect of various forms of soil Fe, Al, and Mn on P-sorption of flooded Typic Tropaquepts and Sulfic Tropaquepts under different soil oxidation-reduction and pH conditions. We used Bangkok soil and Maha-phot soil from Bangkok Plain Thailand to represent Typic Tropaquepts and Sulfic Tropaquepts and incubated them 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* $CaCl_2$ solution ratio of 1:7. After the incubation period the soil suspensions were treated with 1*N* NH_4OAc (buffered to pH 4.0) and sodium-citrate dithionite solution (20%) to remove Fe, Al, and Mn in the forms of exchangeable, and free oxides, respectively. The soil residues were then equilibrated with KH_2PO_4 ranging from 0 to 500 mg P kg^{-1} soil. Sorption isotherms were described by the classical Langmuir equation. The P-sorption capacity (x_m) of soil under reduced conditions was higher than under oxidized conditions and increased with increasing pH. Treating soils with NH_4OAc reduced x_m by 15 to 42% and with sodium-citrate dithionite solution by 32 to 55%, and also decreased the differences in P-sorption due to the effects of pH and oxidation-reduction conditions. Significant correlations between P-sorption and Fe, Al, and Mn extracted by sodium-citrate dithionite indicated that Fe, Al, and Mn oxides

controlled P-sorption of these soils.

Introduction

Many factors influence P-sorption including 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; Jajtha and Bloomer 1988; Russell et al. 1988). These P-sorption studies were conducted in aerobic soil. In contrast, P-sorption in anaerobic soils has not been extensively studied. However, it has been reported that oxidation-reduction potential, pH, and the amount of iron-oxides affect P-sorption under reduced conditions (Khalid et al. 1977; Holford and Patrick 1981).

Soil oxidation-reduction condition and pH influence P-sorption characteristics of acid sulfate soils of Thailand (Krairapanond et al. 1993), however, factors controlling P-sorption in these soils have not yet been extensively investigated. Imai et al.(1983) claimed that P was initially sorbed on the surface of acid sulfate soils and formed chelating compounds with hydroxy-aluminum. Uwasawa et al. (1988) also reported that added P was sorbed as Al-P and Fe-P in acid sulfate 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).

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). The poor growth and low yield of rice grown in acid sulfate soils in Thailand due to high P-sorption capacity is well knowr (Jugsujinda et al. 1978: Attanandana 1982).

Various equations have been used to describe P-sorption in soils, but the classical Langmuir equation is most frequently employed. Here, we report the effect of soil Fe, Al, and Mn on P-sorption under both oxidized and reduced conditions of flooded acid sulfate soils from Thailand at various pH levels. The identification of the factors affecting P-sorption in the soils will be important in determining the most effective mitigation to prevent increasing P-sorption.

Materials and methods

The surface layer (0-15 cm) of Bangkok soil (Typic Tropaquepts), and Maha-Phot soil (Sulfic Tropaquepts) collected from the Bangkok Plain of Thailand were used in the study. According to U.S. soil taxonomy classification (Soil Survey Staff 1975), the Typic Tropaquepts are para-acid sulfate soils which are non-acid

marine soils, and the Sulfic Tropaquepts are actual acid sulfate soils. Attanandana and Vacharotayan (1986) described the non-acid marine 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), and the actual acid sulfate soils are soils which have pH values below 4.0 that is directly or indirectly caused by sulfuric acid formed by oxidation of pyrite (FeS_2). We brought the soils to our laboratory and they were air-dried, sieved ($\leq$2 mm), and thoroughly mixed prior to analyses. General morphology and chemical characteristics of soils were described by Kevie and Yenmanas (1972). Selected soil properties are presented in Table 3.1.

Experimental design

The experiment was conducted to determine P-sorption characteristics of each soil treated with either of two extractants (1*N* NH_4OAc, pH 4.0 and sodium citrate-dithionite solution (20% weight/volume basis) to remove different forms of Fe, Al, and Mn from soils under oxidized and reduced conditions at three pH levels (4.0, 5.0, and 6.0). The experiment was arranged as a 3*2*3 factorial in a randomized complete block design with two replications.

Soil incubation

Suspensions of 250 g soil in 1,750 mL 0.01 *M* $CaCl_2$(1:7, soil to $CaCl_2$ solution ratio) were incubated in laboratory microcosms (Patrick et al. 1973) under oxidized and reduced conditions for six weeks at 25 °C. Prior to the incubation, the soils were amended with 0.2% (weight/weight on dry soil basis) ground rice straw (C/N ratio = 29) which provided an energy source to promote microbial activity. Nitrogen and oxygen gases were bubbled continuously through the soil suspensions in the microcosms to promote reduced and oxidized conditions, respectively. The redox potential and pH of the system were monitored for a 6-week period. 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.

Soil washing

After 6 weeks, the soil suspensions (50 mL) from each of the oxidized and reduced conditions were transferred to 250-mL polycarbonate centrifuge bottles. For the reduced condition treatment, the centrifuge bottles were flushed with O_2-free N_2 gas to maintain a reduced atmosphere. For the oxidized condition treatment, the centrifuge bottles were flushed with air. In the first treatment (control), the soil suspensions were not washed or pretreated with any extractants. For the second treatment

(II), the soil suspensions were pretreated with 100 mL of 1 *N* NH_4OAc, pH 4.0 For the third treatment (III), the soil suspensions were pretreated with 100 mL of a sodium-citrate dithionite solution (20%, w/v solution basis). In the washing procedures, the soil suspensions from both the first and the second treatments were shaken on a reciprocating shaker for 18 hour, centrifuged for 20 min at 7 000 rpm (Sorvall GSA-400 rotor, DuPont Co., Wilmington, DE) and filtered through a 0.45 μm membrane filter. The reduced soil suspensions only were centrifuged and filtered under O_2-free N_2 atmosphere (Gambrell et al., 1975). The soil residues from both the second and the third treatments were washed twice with 100 mL distilled water. All solutions and distilled water added to soils under reduced conditions were free of O_2. After each washing the soil 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).

Phosphorus sorption isotherm

Fifty mL of 0.01 *M* $CaCl_2$ containing P as KH_2PO_4 in concentrations ranging from 0 to 500 mg kg^{-1} was added to all samples in the first, second and third treatments. For reduced condition treatment, the samples were flushed again with O_2-free N_2 prior to adding the diluted $CaCl_2$-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 interpret the results, P-sorption data for the soils were fitted to the classical Langmuir equation (Olsen and Watanabe 1957).

$$x = kx_mC/(1+kC) \qquad (1)$$

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)7 were determined by fitting the experimental data to the linearized Lineweaver-Burk form as given below (Persoff and Thomas 1988):

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

The buffering index (BI), a mixed quantity-intensity parameter, was calculated from kx_m (Holdford 1979). The standard P requirement (SPR), P-sorption at a concentration of 0.2 ppm P in final solution, was also calculated as outlined by Beckwith (1965). The analysis of variance (ANOVA), Duncan Multiple Range Test (DMRT), and Pearson's correlation coefficients were calculated using the procedures available with Statistical Analysis System (SAS Institute Inc. 1985).

Results and discussion

P-sorption characteristics

The P-sorption isotherms constructed for each treatment are shown in Fig.3.1 (for Bangkok soil) and Fig. 3.2 (for Maha-Phot soil). Reduced conditions (Eh -165 to +225 mV) caused mark rise in P-sorption of untreated soil (control treatment) at every pH level when compared with oxidized condition (Eh +635 to +765 mV). Standard P requirement (SPR), Langmuir maximum sorption capacity (x_m), Langmuir sorption constant (k), and buffering index (BI) for Bangkok soil are presented in Table 3.2 and for Maha-Phot soil in Table 3.3. 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 provided adequate P to many plants. All P-sorption parameters (SPR, xm, k, and BI) in Bangkok soil were higher under reduced conditions than those under oxidized condition (Table 3.2). 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 3.3). Several studies have also been reported a higher P-sorption under reduced conditions than under oxidized conditions (Khalid et al. 1977; Willett and Higgins 1978; Holdford and Patrick 1979; Krairapanond et al. 1993). 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.

SPR obviously increased as pH increased in control treatment. For the second and third treatments, SPR slightly increased and almost steady with increasing pH, respectively. SPR under reduced condition was significantly higher than that under oxidized condition in control treatment, whereas in the second and third treatments this value under oxidized and reduced conditions was almost the same.

Like SPR, Langmuir maximum sorption capacity (x_m) was significantly affected by all factors and all of their interactions in both soils (Table 3.2 and 3.3). The significant interactions were resulted from the similar reasons as SPR. The amount of P sorbed by the Bangkok soil was less than those by Maha-Phot soil under both conditions at every pH level.

The Langmuir sorption constant (k) related to the energy bonding of sorption of P to soil surface, was smaller under oxidized than under reduced conditions (Table 3.2 and 3.3). This indicated that P was more tightly bounded to the soil surface under reduced conditions than under oxidized conditions.

Another P-sorption parameter, the buffering index (BI) also diminished after washing the soils with these extractions (Table 3.2 and 3.3).

P-sorption characteristics as influenced by Fe, Al, Mn, oxidation-reduction condition, and pH.

The amounts of Fe, Al and Mn dissolved by NH_4OAc (Fe_a, Al_a, and Mn_a) and by sodium-citrate dithionite (Fe_d, Al_d, and Mn_d) are presented in Table 4.4. Reduced conditions caused enormous increases in the amount of Fe_a. But, oxidized 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. Higher amounts of Fe_d, Al_d, and Mn_d were removed from soil under reduced conditions than under oxidized conditions.

Pretreatment of soil with 1*N* NH_4OAc and sodium-citrate dithionite solution followed by washing with distilled water reduced P-sorption by 15 to 42% and 32 to 55% according to the Langmuir maximum sorption capacity (x_m), and 7 to 34% and 68 to 84% based on the SPR, respectively (Table 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. 3.1 and 3.2). 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 Bangkok and Maha-Phot soils 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.

Correlation of P-sorption and soil Fe, Al, and Mn

Phosphorus sorption parameters of pretreated soils were significantly correlated with Fe_d, Al_d, and Mn_d (Table 3.5). 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. There were significant correlations between P-sorption parameters (except x_m) and Mn_a (Table 3.5) indicating the importance of exchangeable Mn on P-sorption of acid sulfate soils.

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 3.5). The reduction of SPR was also significantly correlated with Fe_d, Al_d, and Mn_d, whereas the reduction of x_m was significantly correlated with Fe_d only. The reduction of SPR was more closely correlated with Fe_d than any other fractions, while the reduction of the x_m 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 crystalline iron-oxides, and vice versa at low concentration of added P.

Conclusion

P-sorption of both Bangkok soil (Typic Tropaquepts) and Maha-Phot soil (Sulfic Tropaquepts) was significantly affected by soil Fe, Al, and Mn. Pretreatment of the soils with 1*N* NH_4OAc (pH 4.0) and sodium-citrate dithionite solution (20%) to remove exchangeable, and amorphous and crystalline forms of Fe, Al, and Mn, reduced P-sorption of soils. 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 Typic Tropaquepts and Sulfic Tropaquepts were not eliminated by these treatments.

P-sorption of the soils was greatly affected by both pH and oxidation-reduction conditions. The P-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.

Significant correlations between P-sorption parameters and the reductions in P-sorption after the treatments, and the free iron-oxides indicated the primary role of iron-oxides in P-

sorption of 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.

As the results indicated the increase in P-sorption with increasing soil pH, liming the soils should be carefully taken into consideration for successfully rice culture.

References

Attanandana T (1982) Fertility problems of acid sulfate soils of Thailand.Ph.D. diss. Kyoto Univ., Kyoto, Japan.

Attanandana T and Vacharotayan S (1986) Acid sulfate soils: Their characteristics, genesis, amelioration and utilization. Southeast Asian Studies. 24: 154-180.

Barrow NJ (1979) Three effects of temperature on the reactions between inorganic phosphate and soils. J. Soil Sci. 30:271-279.

Bar-Yosef BU, Kafkafi R, Rosenberg R, and Sposito G (1988) Phosphorus adsorption by kaolinite and montmorillonite: I. Effect of equilibration time, ionic strength, and pH. Soil Sci. Soc. Am. J. 52:1580-1585.

Beckwith RS (1965) Sorbed phosphate at standard supernatant concentration as an estimate of the phosphate needs of soils. Aust. J. Exp. Agric. Anim. Husb. 5:52-58.

Bloom PR (1981) Phosphorus adsorption by an aluminum-peat complex. Soil Sci. Soc. Am. J. 45:267-272.

Borggaard OK (1983) The influence of iron oxides on phosphate adsorption by soil. J. Soil Sci. 34:333-341.

Bromfield SM (1965) Studies of the relative importance of iron and aluminum in the sorption of phosphate by some Australian soils. Aust. J. Soil Res. 3:31-44.

FAO/UNESCO (1979) Soil map of FAO/UNESCO 1979. Soil Map of the World, Scale 1:5,000,000. Volume I-X, UNESCO, Paris.

Gambrell RP, Khalid KA, Verloo MG, Patrick WH Jr (1975) Transformation of heavy metals and plant nutrients in dredged sediments as affected by oxidation-reduction potential and pH. Part II. Materials and methods, results and discussion. Contract report D-77-4. U.S. Army Engineers Waterways Experiment Station, Vicksburg, Mississippi.

Holford ICR (1979) Evaluation of soil phosphate buffering indices. Aust. J. Soil Res. 17,495-504.

Holford ICR, Patrick WH Jr (1979) Effects of reduction and pH changes on phosphate sorption and mobility in an acid soil. Soil Sci. Soc. Am. J. 43, 292-297.

Holford ICR, Patrick WH Jr (1981) Effects of duration of anaerobiosis and reoxidation on phosphate sorption characteristics of an acid soil. Aust. J. Soil res. 19:69-78.

Imai HP, Sangtong P, Cholitkul W (1983) Characteristics in phosphate adsorption of major soil groups of Thailand. JARQ 17:59-68.

Jugsujinda A, Breemen N van, Yaki T (1978) Aluminum toxicity and phosphate deficiency in acid sulfate soils of Thailand. International Rice Research Newsletter 3 (1),9-10.

Kevie W van der, Yenmanas B (1972) Detailed reconnaissance soil survey of southern central plain area. Soil Survey Rept. No. 89., Land Dev. Dept., Bangkok, Thailand.

Khalid RA, Patrick WH Jr, DeLaune RD (1977) Phosphorus sorption characteristics of flooded soils. Soil Sci. Soc. Am. J.

41:305-310.

Krairapanond A, Jugsujinda A, Patrick WH Jr (1993) Phosphorus sorption characteristics in acid sulfate soils of Thailand: Effect of uncontrolled and controlled soil redox potential (Eh) and pH. Plant and Soil 157: 227-237.

Lajtha K, Bloomer SH (1988) Factors affecting phosphate sorption and phosphate retention in a desert ecosystem. Soil Sci. 146:160-167.

Mehadi AA, Taylor RW (1988) Phosphate adsorption by two highly-weather soils. Soil Sci. Am. J. 52:627-632.

Mokwunye U (1975) The influence of pH on the adsorption of phosphate by soils from the Guinea and Sudan Savannah zones of Nigeria. Soil Sci. Soc. Amer. Proc. 39,1100-1102.

Muljadi D, Posner AM, Quirk JP (1966) The mechanism of adsorption by kaolinite, gibbsite, and pseudoboehmite. I. The isotherms and the effect of pH on adsorption. J. Soil Sci. 17:212-229.

Olsen SR, Watanabe FS (1957) A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir sotherm. Soil. Sci. Soc. Proc. 21,144-149.

Patrick WH Jr, Williams BG, Morghan JT (1973) A simple system for controlling redox potential and pH in soil suspensions. Soil Sci. Soc. Am. J. 37:331-332.

Persoff P, Thomas JF (1988) Estimating Michaelis-Menton of Langmuir isotherm constants by weighted nonlinear least squares. Soil Sci. Soc. Am. J. 52:886-889.

Pons LJ, Kevie W van der (1969) Acid sulfate soils in Thailand. Soil Survey Rept. no. 81, Land Dev. Dept., Bangkok, Thailand.

Russell JS, Kamprath EJ, Andrew CS (1988) Phosphorus sorption of subtropical acid soils as influenced by the nature of the cation suite. Soil Sci. Soc. Am. J. 52:1407-1410.

Sah, RN, Mikkelsen DS (1986a) Effects of temperature and prior flooding on intensity and sorption of phosphorus in soil. II. Effects on P sorption. Plant Soil 95:163-171.

Sah, RN, Mikkelsen DS (1986b) Effects of anaerobic decomposition of organic matter on sorption and transformations of phosphate in drained soils: I. Effects on phosphate sorption. Soil Sci. 142:267-274.

SAS Institute Inc (1985) SAS User's guide: Statistic. Cary, North Carolina.

Soil Survey Staff (1975) Soil Taxonomy US Dept. of Agriculture Handbook 436.

Torrent J (1987) Rapid and slow phosphate sorption by mediterranean soils: Effect of iron oxides. Soil Sci. Soc. Am. J. 51:78-82.

Uwasawa M, Sangtong P, Cholitkul W (1988) Behavior of phosphorus in paddy soils of Thailand. Soil Sci. Plant Nutr. 34:183-194.

Willett IR, Higgins ML (1978) Phosphate sorption by reduced and reoxidized rice soils. Aust. J. Soil Res. 16:319-326.

Table 3.1. Selected physical and chemical properties of the actual and para-acid sulfate soils

Soil Properties	Bangkok	Maha-Phot
Great Soil Group	Typic Tropaquept	Sulfic Tropaquept
Acidity class	Non-acid	Moderately acid
pH (1:1 water)	4.9	4.5
Organic matter (%)[a]	1.3	1.9
Available P[b]	19.2	3.2
Exchangeable Al (cmol kg^{-1})[c]	1.1	2.3
Exchangeable acidity (cmol kg^{-1})[d]	1.2	3.2
CEC (cmol kg^{-1})[e]	24.9	19.9

[a] Walkley-Black
[b] modified Bray II; soil:extractant ratio = 1:10
[c] 1*M* KCl
[d] $BaCl_2$-Triethanolamine
[e] Ammonium saturation-distillation

Table 3.2. Phosphorus sorption parameters for Bangkok soil

Condition	pH	Treatment	SPR	x_m	k	BI
			—mg kg^{-1}—			
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

II=NH_4OAc

III=Citrate dithionite

SPR=Standard P requirement

xm=Langmuir maximum sorption capacity

k=Langmuir sorption constant

BI=Buffering index

Table 3.3. Phosphorus sorption parameters for Maha-Fhot soil

Condition	pH	Treatment	SPR	x_m	k	BI
			—mg kg^{-1}—			
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

II=NH_4OAc

III=Citrate dithionite

SPR=Standard P requirement

xm=Langmuir maximum sorption capacity

k=Langmuir sorption constant

BI=Buffering index

Table 3.4. The amounts of Fe, Al, and Mn removed from soils by 1 *N* NH_4OAc (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	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	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 in *xm* *a*=(*xm* in control treatment-*xm* in NH_4OAc treatment) x 100/*xm* in control treatment

Reduction in SPR *a*=(SPR in control treatment-SPR in NH_4OAc treatment) x 100/SPR in control treatment

Table 3.5. Pearson's correlation coefficients between P-sorption parameters and various forms of Fe, Al, and Mn (extracted by 1 *N* NH_4OAc (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.

SPR = Standard P requirement

x_m = Langmuir maximum sorption capacity

k = Langmuir sorption constant

BI = Buffering index

Fig. 3.1. Phosphorus sorption isotherm for Bangkok soil.

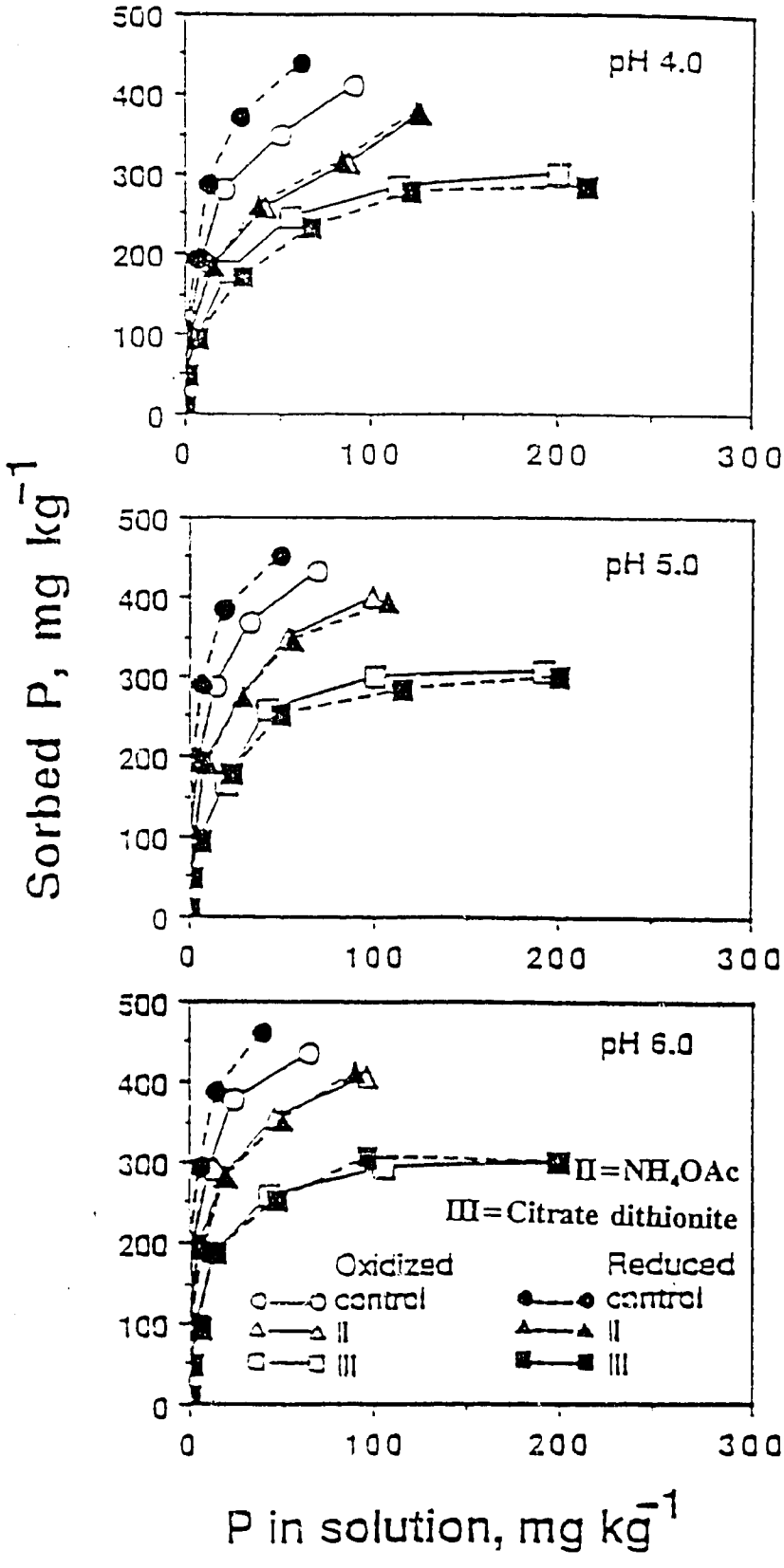
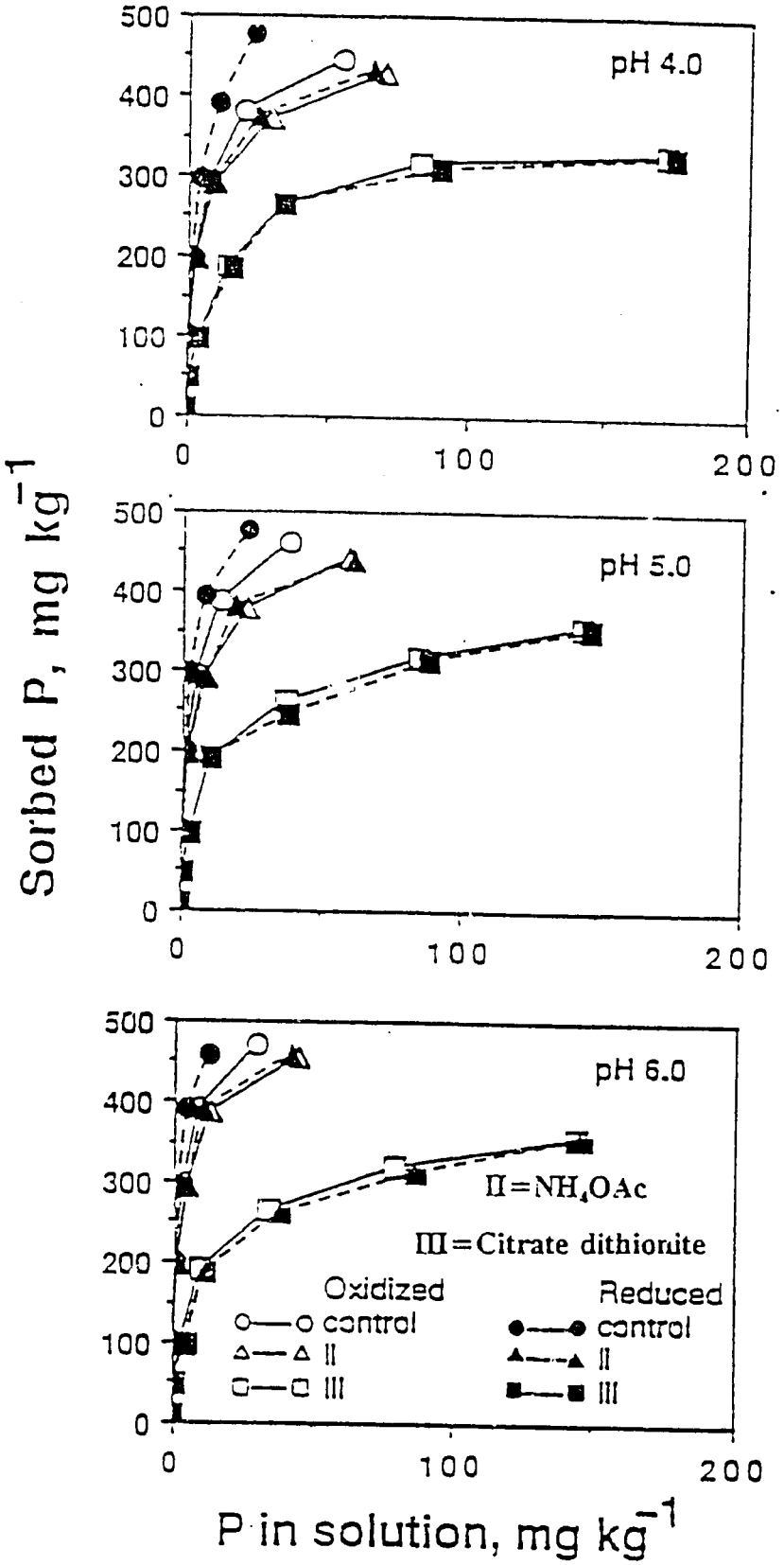


Fig. 3.2. Phosphorus sorption isotherm for Maha-phot soil.



Research Task No. 4.

Correlation of soil phosphorus, pH, redox potential, iron, manganese, and aluminum contents with yield of rice under flooded acid sulfate soils [4]

A. JUGSUJINDA* and W.H. PATRICK, JR

Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, LA 70803-7511, USA. * Corresponding author

Key words: oxidation-reduction potential (Eh), sulfic tropaquepts, typic tropaquepts

The manuscript of this paper is *In Preparation* for publication

---

[4] Contribution from the Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, Louisiana 70803-7511, U.S.A. The research was supported by USAID Grant No. DHR-5542-G-SS-9027-00, Program in Science and Technology Cooperation, Office of the Science Advisor, U.S. Agency for International Development.

Abstract

Sodium acetate (NaOAC, buffered to pH 4.0) extractable Fe in twenty-five flooded acid sulfate soils averaged 4 000 mg kg^{-1}, 4-fold higher than the NaOAC extractable Al, Mn, and P. Similar trend was observed with water-soluble extractable forms of these elements, but the magnitude was lower than the NaOAC extractable fractions. Water-soluble Fe under flooded soil condition was greater than 100 mg kg^{-1}. An uptake of 100 mg Fe $plant^{-1}$ was observed in the plant growing under flooded soil condition. Dry matter weight of rice plant under this condition was 0.04 g. Uptake of Al, Mn, and P by rice growing under flooded soil condition was also high. Uptake of these elements by rice was in the following order: Fe > P > Mn > Al. Based on these results, rice growing under flooded soil conditions suffer Fe, and Al toxicity since their average tissue concentrations were greater than reported toxicity threshold level of 300 mg for Fe and 300 mg for Al kg^{-1}. Rice plant growing in the flooded condition would also perhaps suffered from P deficiency since level are lower than rice phosphorus requirement reported in literature. The results obtained also suggest that the rice plant may suffer from Mn toxicity since Mn concentration in the tissue was greater than reported threshold toxicity value of 2 500 mg Mn kg^{-1} of plant tissue. There was a significant correlation between soil pH and NaOAc extractable Fe, Al, Mn, and P, and between soil Eh and all of these NaOAc extractable forms except Mn in soils. No

significant correlation was observed between soil pH and water soluble forms of these nutrients except P. P released and P absorbed in soils and concentration and uptake of Fe, Al, Mn and P by rice also showed no significant correlation in this study.

Introduction

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). The poor growth and low yield of rice grown in acid sulfate soils in Thailand due to high P-sorption capacity is well known. Many factors influence P-sorption. 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; Jajtha and Bloomer, 1988; Russell et al., 1988) influence P-sorption. These P-sorption studies were conducted in aerobic soil. 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; Holdford and Patrick, 1981).

It has recently been reported that soil oxidation-reduction condition and pH influenced phosphorus sorption characteristics of acid sulfate soils of Thailand (Krairapanond et al., 1993). Factors controlling phosphorus sorption in acid

sulfate soils has not yet been extensively investigated. P-sorption in soils is generally 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 with hydroxy-aluminum. Uwasawa et al. (1988) also reported that added P was sorbed as Al-P and Fe-P in acid sulfate 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. Here, we report the effect of both oxidized and reduced soil conditions on Fe, Al, Mn and P solubility and their uptake by rice in acid sulfate soils from Thailand. The identification of the soil conditions affecting nutrient solubility and uptake by rice in the soils will be important in determining the most effective method to prevent increasing P-sorption based on agricultural practices and scientific knowledge.

Materials and method

Twenty-five soil samples representing five acidity classes: I, II, III, IV, and V were used in our studies. Each acidity class consisted of different soil series: Bk, Rs, Ma, Rsa. These soils

were identified as Tropic Tropaquepts and Sulfic Tropaquepts collected from Central Plain Thailand [5]. Range in soil organic matter content and pH of airdried are shown in Table 4.1.

Redox potential (Eh) and pH measurement

Special platinum electrode tubes were used to measure changes in redox potential in the soils. The tubes were constructed by sealing 12.5 millimeter pieces of 18-gauge platinum wire on both sides near the bottom of 40x138-millimeter Pyrex test tubes similar to the ones used by Jugsujinda and Patrick, (1993). Sixty grams of air-dry soils were weighed, in duplicate, and uniformly mixed with 0.1% ground rice straw as an energy source for microbial activities before transferring into the electrode tubes. The soils were flooded with an excess of high purity deionized distilled water, and incubated at 30 °C. An overlying layer of flood water depth of about 2 cm was maintained throughout the incubation period. Eh and pH measurements were made immediately after flooding followed by daily measurements for 30 days, and then weekly through 60 days. Eh measurements were made with a Beckman Zeromatic pH meter using a platinum electrode and a saturated calomel half-cell. pH measurements of the top 1 cm soil layer were made with a Beckman Zeromatic pH

---

[5] The soil samples were collected by Dr. Philip A. Moore, Jr. in 1984 when the field had been flooded for 6 to 10 weeks. They were air-dried ground with a stainless steel mortar & pestle and sieved through a 20 mesh sieve.

meter using a calibrated combination glass electrode.

At the end of 60 days period, water-soluble and NaOAc extractable ions (0.1 N sodium acetate buffered to pH 4.0 because acid sulfate soils pH is acidic in reaction) were determined by the following procedures. Excess floodwater was decanted from the redox tubes and then a core extending vertically through the soil was removed from the electrode tube to insure that both the oxidized and reduced soil zones were sampled. The samples were immediately transferred to preweighed centrifuge bottles and weighed to determine water and soil contents. The bottles were immediately purged with N_2 gas. Twenty-five ml of oxygen-free deionized water was added to the wet soil samples with a hypodermic syringe and the bottles were shaken for 30 minutes. The soil solutions were centrifuged under N_2 atmosphere at 7000 rpm for 20 minutes. The supernatant were filtered through 0.45 micron membrane under an N_2 atmosphere. The aliquot were acidified to pH 2 by adding 12 N HCL and stored for analysis. One hundred ml of oxygen free 1N sodium acetate (pH 4.0) was added to the residual moist soil from water-soluble fraction with the help of a hypodermic syringe and the centrifuge bottles were purged with N_2. The mixture was shaken for 1 h on a mechanical shaker and centrifuged at 7000 rpm for 20 minutes. The supernatant were filtered through 0.45 micron membrane filter as described earlier. The extract was acidified to pH 2 and stored for analysis of selected nutrients on ICAP.

In a parallel incubation two or three rice plants were grown

in each of the flooded soils, and after 60 days incubation the rice plants were harvested and the plant tissue analyzed for total analyses.

P Fixation experiment

The objective of this experiment is to study phosphorus fixation capacity of the soils. Five g of soils each of the 25 soils and 10 mL of deionized water were preincubated under anaerobic conditions in 50 mL Nalgene centrifuge bottle. This was accomplished by sealing the bottle with serum cap and immediately purged with oxygen-free N^2 gas and keep under the laboratory condition for three weeks. In one treatment 100 ppm PO_4-P on soil basis was added, in another treatment no P was added. In both treatments the soils were shaken on reciprocal shaker for 48 hours to obtain equilibrium. The soils was allowed to settle for 48 hours, and repurged with N_2 gas then centrifuged at 7 000 rpm for 20 min. The clear supernatant was filtered through a 0.45 millipore filter, acidified with *N* HCl and stored in refrigerator till analysis. P in the soil solution was analyzed by ICP. P in solution was considered to be P released in the soils, and P added less P released was P sorbed in the soils.

Results

Changes in soil Eh and pH

Average soil Eh decreased as time of flooding increased. There was a sharp decrease during the first 10 days after flooding. The decrease was gradual from 11 days until 30 days of flooding. There was no further decrease in soil Eh thereafter and soil Eh was stabilized at -100 mV until 60 days after flooding (Fig.4.1). Soil pH on the other hand was increased very sharply during the first 10 days of flooding, and was gradually increased from 11 days until 20 days of flooding, and then level off thereafter till 60 days of flooding.

Solubility of Fe, Al, Mn and P in soils

Under flooded soil condition, the concentrations of NaOAC extractable Fe, Al, Mn and P were presented in Fig. 4.2, and water-soluble forms were presented in Fig. 4.3. The data showed that flooded soil conditions resulted in a forty-fold increases in the amount of NaOAc extractable Fe over the water soluble form. Al, Mn, and P also showed the same trend.

Dry matter weight

Dry matter weights of the rice plant tissue are shown in Fig. 4.6. The growth of the rice plant under flooded soil condition varied according to soils. No significant correlation between the dry matter weight and soil organic matter content, redox, pH level, P release and P sorbed in these soils was observed.

Concentration and uptake of Fe, Al, Mn, and P

Under flooded soil condition, concentration of Fe, Al, Mn, and P in the plants are shown in Fig.4.4 and the uptake of these nutrients by rice are shown in Fig. 4.5. More Fe found its way through the plant tissue than Al, Mn, and P under flooded soil conditions. More P was taken up by rice flooded soil condition than Al, and Mn. Aluminum was the least taken up by the plants. The concentration and uptake of these nutrients are in the following order: Fe > P > Mn > Al.

P fixation capacity

Large amount of P added was fixed in the soils under flooded condition (Table 4.1). In our previous study (Krairapanond et al. 1993) found also that soil reduction led to a very large increase in P sorption capacity of soils at higher P levels added (Table 4.1).

Correlation coefficient among the chemical soil test of Fe, Al, Mn, P with growth and soil pH-Eh, and among P released and P sorbed with their concentration and uptake by rice.

There was a significant correlation between soil pH and soil Eh with extractable Fe, Al, Mn, and P in the soils (Table 4.2). No significant correlation was found between P released and P in the plants nor between P absorbed and P in the plants (Table 4.3).

Conclusion

The findings in the present study suggested that the flooding condition of acid sulfate soils of Thailand caused an increase in soil pH and a decrease in soil Eh and release of extractable Fe, Al, Mn, and P in the soils, flooding also increased P fixation. Liming which is recommended in Thailand as an amelioration method of acid sulfate soils should be considered in flooded soil condition. Liming increased soil pH and as soil pH increased, sorption of added P is also increased. Liming should be considered only when soils need Ca or Mg for normal plant growth. In this case soils need P, use of the fertilizer P sources such as locally available rock phosphate to provide the plant nutrient should be considered for successful rice culture in Thailand.

References

Barrow N J 1979 Three effects of temperature on the reactions between inorganic phosphate and soils. J. Soil Sci. 30,271-279.

Bar-Yosef B U, Kafkafi R, Rosenberg R and Sposito G 1988 Phosphorus adsorption by kaolinite and montmorillonite: I. Effect of equilibration time, ionic strength, and pH. Soil Sci.Soc. Am. J. 52,1580-1585.

Beckwith R S 1965 Sorbed phosphate at standard supernatant concentration as an estimate of the phosphate needs of soils. Aust. J. Exp. Agric. Anim. Husb. 5,52-58.

Bloom P R 1981 Phosphorus adsorption by an aluminum-peat complex. Soil Sci. Soc. Am. J. 45,267-272.

Borggaard O K 1983 The influence of iron oxides on phosphate adsorption by soil. J. Soil Sci. 34,333-341.

Breemen N van 1976 Genesis and solution chemistry of acid sulfate soils in Thailand. Center for Agricultural Publishing and Documentation, Wageningen, Netherlands.

Bromfield S M 1965 Studies of the relative importance of iron and aluminum in the sorption of phosphate by some Australian soils. Aust. J. Soil Res. 3,31-44.

FAO/UNESCO 1979 Soil map of FAO/UNESCO 1979. Soil Map of the World, Scale 1:5,000,000. Volume I-X, UNESCO, Paris.

Gambrell R P, Khalid R A, Verloo M G and Patrick W H Jr 1975 Transformation of heavy metals and plant nutrients in dredged sediments as affected by oxidation-reduction potential and pH. Part II. Materials and methods, results and discussion. Contract report D-77-4. U.S. Army Engineers Waterways Experiment Station, Vicksburg, Mississippi.

Holford I C R 1979 Evaluation of soil phosphate buffering indices. Aust. J. Soil Res. 17,495-504.

Holford I C R and Patrick W H Jr 1981 Effects of duration of anaerobiosis and reoxidation on phosphate sorption characteristics of an acid soil. Aust. J. Soil res. 19:69-78.

Imai H, Sangtong P, and Cholitkul W 1983 Characteristics in phosphate adsorption of major soil groups of Thailand. JARQ 17,59-68.

Jugsujinda, A. and W. H. Patrick, Jr. 1993. Evaluation of toxic conditions associated with oranging symptoms of rice in a flooded Oxisol in Sumatra, Indonesia. Plant and Soil 152, 237-243.

Kevie W van der and Yenmanas B 1972 Detailed reconnaissance soil survey of southern central plain area. Soil Survey Rept. No. 89., Land Dev. Dept., Bangkok, Thailand.

Khalid R A, Patrick W H Jr, and DeLaune R D 1977 Phosphorus sorption characteristics of flooded soils. Soil Sci. Soc. Am. J. 41,305-310.

Krairapanond A, Jugsujinda A and Patrick W H Jr 1993 Phosphorus

sorption characteristics in acid sulfate soils of Thailand: Effect of uncontrolled and controlled soil redox potential (Eh) and pH. Plant and Soil 157:227-237.

Lajtha K and Bloomer S H 1988 Factors affecting phosphate sorption and phosphate retention in a desert ecosystem. Soil Sci. 146,160-167.

Loganathan P, Isirimah N O and Nwachuku D A 1987 Phosphorus sorption by Ultisols and Inceptisols of the Niger delta in southern Nigeria. Soil Sci. 144,330-338.

Lopez-Hernandez D and Burnham C P 1974 The covariance of phosphate sorption with other properties in some British and tropical soils. J. Soil Sci. 25,196-206.

Mehadi A A and Taylor R W 1988 Phosphate adsorption by two highly-weather soils. Soil Sci. Am. J. 52,627-632.

McKeague J A and Day J H 1966 Dithionite and oxalate extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46,13-22.

Mokwunye U 1975 The influence of pH on the adsorption of phosphate by soils from the Guinea and Sudan Savannah zones of Nigeria. Soil Sci. Soc. Amer. Proc. 39,1100-1102.

Muljadi D, Posner A M, and Quirk J P 1966 The mechanism of adsorption by kaolinite, gibbsite, and pseudoboehmite. I. The isotherms and the effect of pH on adsorption. J. Soil Sci. 17,212-229.

Olsen S R and Watanabe F S 1957 A method to determine a phosphorus adsorption maximum of soils as measured by the

Langmuir isotherm. Soil. Sci. Soc. Proc. 21,144-149.

Olsen S R and Ellis R Jr 1982 Iron. *In* Methods of Soil Analysis: Part 2 Chemical and Microbiological Properties. 2nd Ed. A.L. Pace, R.H. Miller, and D.R. Keeney. Am. Soc. Agron., Inc. Madison, Wisconsin.

Pena F and Torrent J 1984 Relationships between phosphate sorption and iron oxides in Alfisols from a river terrace sequence of mediterranean Spain. Geoderma 33,283-296.

Persoff P and Thomas J F 1988 Estimating Michaelis-Menton of Langmuir isotherm constants by weighted nonlinear least squares. Soil Sci. Soc. Am. J. 52,886-889.

Pons L J and Kevie W van der 1969 Acid sulfate soils in Thailand. Soil Survey Rept. no. 81, Land Dev. Dept., Bangkok, Thailand.

Prasittiket J, Patrick W H Jr, Gambrell R P, Breeman N van, Jugsujinda A and Kanareugsa C 1991 Iron and manganese availability to rice in acid-sulfate soils under controlled redox potential and pH conditions. Soil management for sustainable rice production in the tropics. International Board for Soil Research and Management. IBSRAM Monograph no. 2.

Russell J S, Kamprath E J and Andrew C S 1988 Phosphorus sorption of subtropical acid soils as influenced by the nature of the cation suite. Soil Sci. Soc. Am. J. 52,1407-1410.

Sah R N and Mikkelsen D S 1986a Effects of temperature and

prior flooding on intensity and sorption of phosphorus in soil. II. Effects on P sorption. Plant Soil 95,163-171.

Sah R N and Mikkelsen D S 1986b Effects of anaerobic decomposition of organic matter on sorption and transformations of phosphate in drained soils: I. Effects on phosphate sorption. Soil Sci. 142,267-274.

SAS Institute Inc 1985 SAS User's guide: Statistic. Cary, North Carolina.

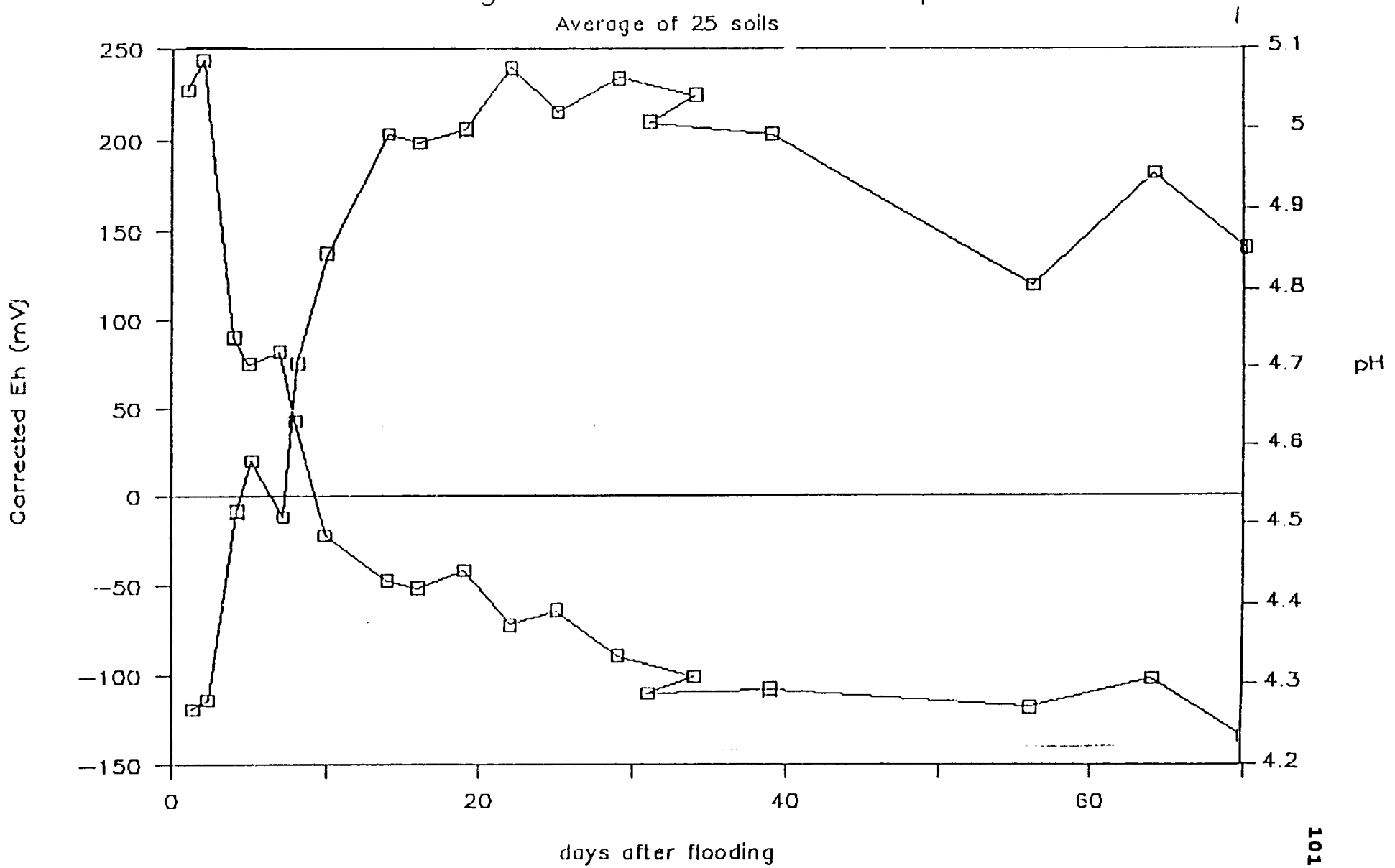
Soils P and Torrent J 1989 Phosphate sorption by calcareous Vertisols and Inceptisols of Spain. soil Sci. Soc. Am. J. 53,456-459.

Torrent J 1987 Rapid and slow phosphate sorption by mediterranean soils: Effect of iron oxides. Soil Sci. Soc. Am. J. 51,78-82.

Uwasawa M, Sangtong P and Cholitkul W 1988 Behavior of phosphorus in paddy soils of Thailand. Soil Sci. Plant Nutr. 34,183-194.

Willett I R and Higgins M L 1978 Phosphate sorption by reduced and reoxidized rice soils. Aust. J. Soil Res. 16,319-326.

Fig. 4.1. Changes in soil Eh and pH



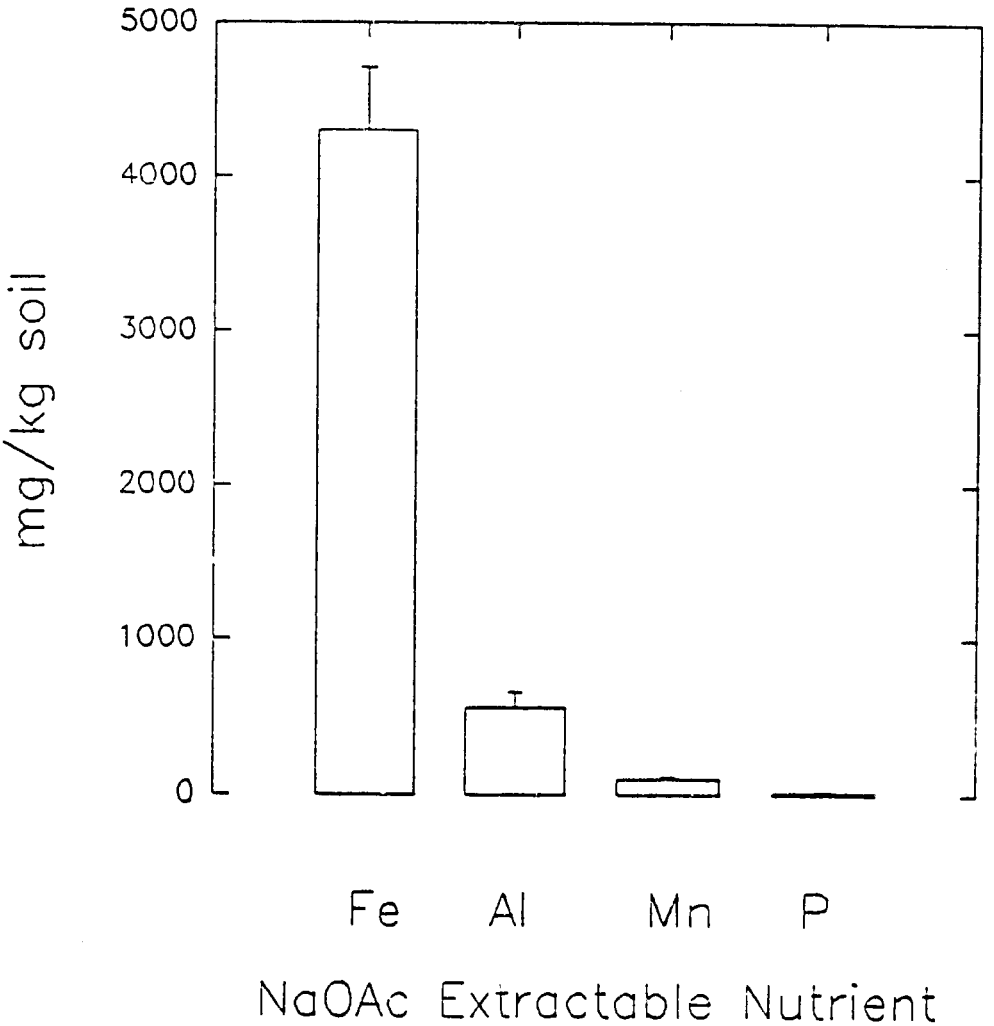


Fig. 4.2. NaOAc extractable nutrients in soils under anaerobic conditions.

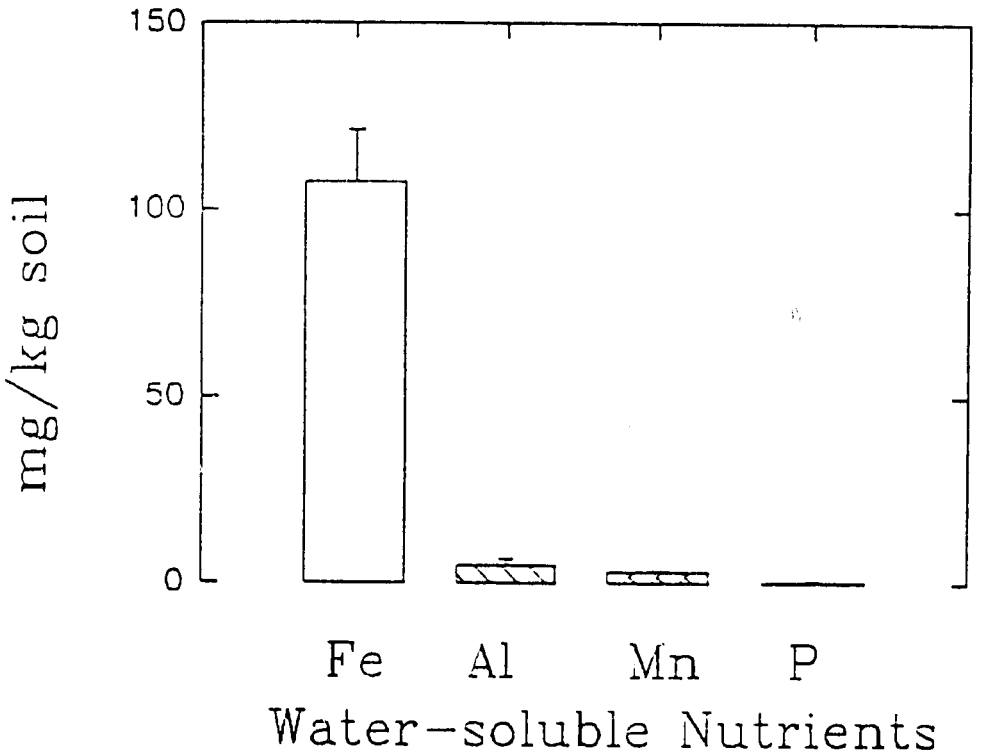


Fig. 4.3. Water-soluble nutrients in soils under anaerobic conditions.

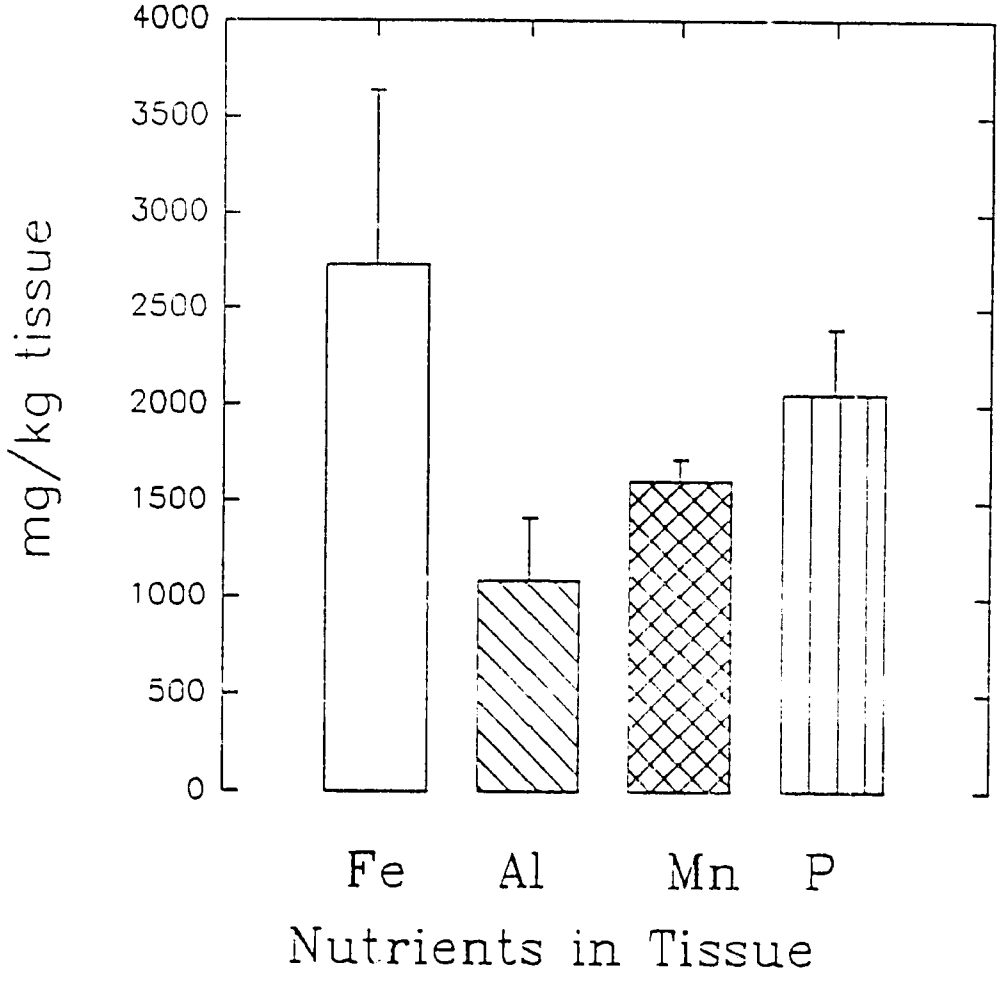


Fig. 4.4. Concentrations of nutrients in the rice plants tissue under anaerobic conditions.

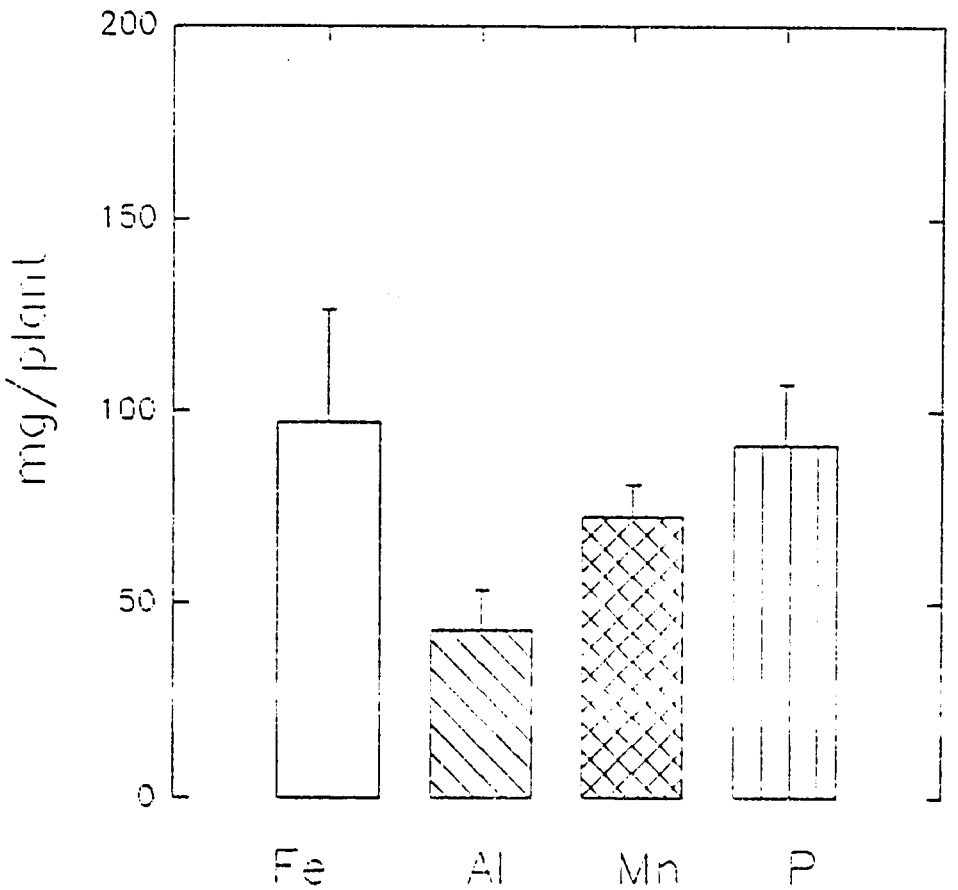


Fig. 4.5. Uptake of nutrients by the rice tissues under anaerobic conditions

Fig. 4.6. Weight of rice plant tissue in 25 soils under flooded condition

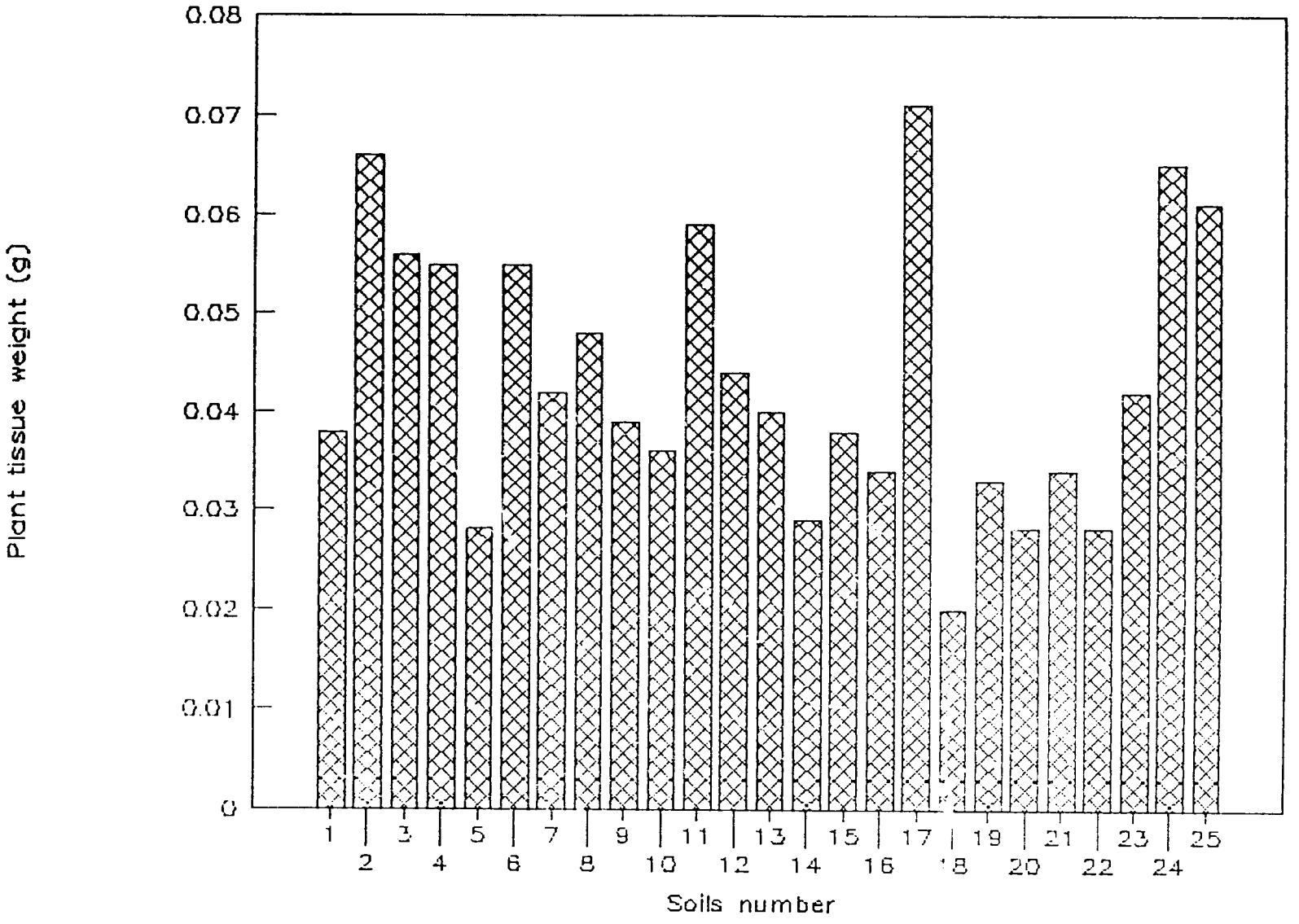


Table 4.1. Range in soil organic matter content, redox condition, pH level, P released and P sorbed of the twenty five soils.

Soil No	Soil Series	pH airdried	OM airdried %	pH flooded	Eh flooded mV	P Released ppm	P Sorbed ppm
1	Bk	4.1	3.4	6.2	-240	0.768	99.232
2	Bk	4.2	3.8	6.4	-210	0.776	99.224
3	Bk	4.2	3.2	6.5	-265	1.596	98.404
4	Bnp	3.9	4.5	5.5	-150	8.416	91.584
5	Sb	3.5	4.5	5.8	-140	14.636	85.364
6	Ma	4.2	3.0	6.2	-210	0.000	100.000
7	Ma	4.0	2.0	5.7	-120	1.260	98.740
8	Sn	3.8	3.3	4.0	-40	1.008	98.992
9	Rs	3.5	2.3	3.9	160	0.000	100.000
10	Rs	3.6	3.4	6.0	-200	2.480	97.520
11	Ay	4.0	1.6	4.5	40	0.388	99.612
12	Bk	4.6	3.2	6.3	-240	2.220	97.780
13	Rs	4.3	2.7	6.1	-300	0.996	99.004
14	Rs	3.8	3.9	4.3	0	0.332	99.668
15	Rs	3.9	3.5	4.1	0	0.684	99.316
16	Tb	4.0	2.1	4.8	-110	1.108	98.892
17	Sn	4.3	3.6	6.2	-200	0.868	99.132
18	Sn	4.1	2.3	4.1	50	0.000	100.000
19	Rsa	3.6	2.8	3.8	60	0.000	100.000
20	Rsa	3.8	2.0	6.1	-240	2.436	97.564
21	Rsa	3.7	2.6	4.2	-50	0.000	100.000
22	Rsa	3.3	3.0	3.3	10	0.520	99.480
23	Ok	3.8	3.6	4.4	-60	0.816	99.184
24	Ok	3.4	3.9	3.7	-50	0.440	99.560
25	Rs	3.5	5.0	3.8	-60	0.548	99.452
AVG		3.9	3.2	5.0	-103	1.692	98.308
STD		0.3	0.8	1.1	119	3.111	3.111

Bk=Bangkok, Bnp=Bang Nam Preo, Sr=Saraburi, Ma=Mahaphot,
Sn=Sena, Rs=Rangsit, Ay=Ayuthaya, Tb=Tanyabu
Rsa=Rangsit Very Acid, Ok=Ongkarak Sb=Saraburi

'able 4.2. Correlations of chemical tests for soil phosphorus, iron, manganese, aluminum content, pH, redox potential with yield of rice under flooded soil condition in the growth chamber.

	A.NaOAc Extractable nutrient in soils				P released in soils
	Fe	Al	Mn	P	
pH (flooded)	0.730**	-0.750**	0.510**	0.530**	0.090ns
Eh (flooded)	-0.660**	0.540**	0.380ns	0.500*	0.060ns
Growth (dry matter)	0.030ns	0.001ns	0.005ns	0.062ns	0.02ns
	B. Water soluble nutrient in soils				**P sorbed in soils**
	Fe	Al	Mn	P	
pH (flooded)	-0.180ns	0.339ns	0.256ns	0.418*	0.090ns
Eh (flooded)	0.109ns	0.414ns	0.148ns	0.331ns	0.060ns
Growth (dry matter)	0.054ns	0.006ns	0.011ns	0.070ns	0.020ns

n=25

ıble 4.3. Correlations of chemical tests for phosphorus, iron, manganese, aluminum concentration and uptake by rice and P released and P sorbed in flooded soils condition.

A. Concentration of nutrient in rice

	Fe	Al	Mn	P
P Released in soils	0.001ns	0.032ns	0.071ns	0.027ns
P sorbed in soils	0.001ns	0.032ns	0.071ns	0.027ns

B. Uptake of nutrient by rice

	Fe	Al	Mn	P
P Released in soils	0.000ns	0.038ns	0.001	0.010ns
P sorbed in soils	0.000ns	0.038ns	0.001	0.010ns

ı=25

IMPACT, RELEVANCE AND TECHNOLOGY TRANSFER

As higher yield of rice are sought from land resources now in production and as more marginal lands are put into cultivation fertility and toxicity problems become greater factors in achieving and maintaining high yields of the crop. These problems have been identified through the cooperative research. One of the significant problems we found in our study in acid sulfate soils of Thailand is P-sorption and the finding has been described and published (see addendum to this report: Plant and Soil 157:227-237, 1993). The published result is one of the best ways to bring about the technology transfer and shorten this time gap. The Thai Department of Agriculture has the responsibility of improving utilization of plant nutrients, both native and applied, in all land areas of the country, including acid sulfate soils areas. Utilizing their locally available sources in ongoing field conditions will make the results of this study immediately applicable to Thai conditions. The Soil Science Department of Kasetsart University carries on active research, including both staff research and graduate research. The collaboration of the basic results carried out in the Wetland Biogeochemistry Institute (Formerly called Laboratory for Wetland Soils and Sediments) with the two Thai research program benefited both groups. Giving a Thai graduate student the opportunity to complete her Ph.D. work in the U.S. laboratory and support for a Thai scientist to conduct post-doctoral research in our

laboratory that has close connections with Thai institutions enhanced the technology transfer between the two countries.

In addition to this research project, the Institute recently completed a project that dealt with toxic soil chemical conditions in acid sulfate soils that limit the growth of rice. The program was very successful both in terms of the research carried out and the exchange between American and Thai laboratories. Two Thai graduate students received Ph.D. degree carrying out research projects that examined the redox chemistry of acid sulfate soils with the objective of identifying the significant toxic components in the soils that cause adverse growing conditions. One American student spent one year in Thailand doing field work of his Ph.D. thesis which he has also completed. Four Thai scientist spent a total of over two years in the Institute's laboratory learning new research techniques that could be applied to Thai soils problems as well as carrying out research on acid sulfate soils.

PROJECT ACTIVITIES/OUTPUTS

The principal investigator spent several weeks each year in Thailand during the active part of the project interacting with staff members of the Kasetsart University's Department of Soils and the Thai Department of Agriculture and Land Development. One of main objective was to give a seminar pertaining to the research program and to select candidates from the Thai counterparts for further training in the U.S. laboratory.

Publications

A. Krairapanond, A. Jugsujinda and W.H. Patrick, Jr. 1993. Phosphorus sorption characteristics in acid sulfate soils of Thailand: Effect of uncontrolled and controlled soil redox potential (Eh) and pH. Plant and Soil 157: 227-237.

A. Jugsujinda, A. Krairapanond and W.H. Patrick, Jr. 1994. P-absorption and iron, aluminum, manganese, pH and oxidation-reduction in flooded acid soils. *Submitted* Biol and Fert. Soils 00:000-000.

A. Jugsujinda and W.H. Patrick, Jr. 1994. Correlation of soil phosphorus, pH, redox potential, iron, manganese, and aluminum contents with yield of rice under flooded acid sulfate soils. *In Prep.*

PROJECT PRODUCTIVITY

The program was very successful both in terms of the research carried out and the exchange between American and Thai laboratories. One Thai student received the Ph.D. degree carrying out part of this research project. This student examined the P-sorption characteristics of acid sulftae soils of Thailand with the objective of identifying the significant P-sorption characteristics in the soils that cause poor growing conditions and lower rice yield. The principal investigator made several trips to Thailand and spent several weeks there to interact with senior scientific staff of the Kasetsart University's Department of Soils and the Thai Department of Agriculture and Land Development. One of his main objectives was to select candidates from the Thai counterparts for further training in the U.S. laboratory. One American student spent one year in Thailand doing field work for his Ph.D. thesis which he has also completed. Several Thai scientists spent a total of over several months in the Institute's laboratory learning new research techniques that could applied to Thai soils problems as well as carrying out research on acid sulfate soils. As a result of this program several publications have been published in Thai and American journals.

FUTURE WORK

Worldwide attention was focused on factors controlling methane production in flooded soils. Methane is an important greenhouse gas and may account for 15 to 20% of the current increase in commitment to global warming and tropospheric concentrations are increasing about 1% yr^{-1}. Flooded rice paddies are a major source of CH_4 and contribute 60 to 170 Tg to the atmosphere per year that is approximately 25% of total global CH_4 emissions. To keep up with population increases over the next 20 to 30 yr it is estimated that about 50 x 10^6 ha of land including acid sulfate soils will have to be converted to flooded rice production, which may increase CH_4 emission by 20% in the next decade. Flooded systems are conducive to the production of CH_4 due to the presence of methanogenic bacteria that decompose organic materials under anaerobic soil conditions. Methane production in flooded rice soils is strongly influenced by soil factors such as; redox potential, temperature, pH, organic matter, soil type and addition of chemicals or fertilizers. For a better understanding of why atmospheric methane is increasing globally, improved estimate of rice field emissions and soil factors governing emissions are needed to order to stabilize or reduce future CH_4 emissions from flooded rice fields. Such information hopefully will lead to field management practices that will reduce CH_4 emissions while maintaining or increasing the productivity of lowland acid sulfate soils growing to rice.

ADDENDUM

Plant and Soil 157: 227-237, 1993

Plant and Soil 157: 227–237, 1993.
© 1993 *Kluwer Academic Publishers. Printed in the Netherlands.*
PLSO 3103

Phosphorus sorption characteristics in acid sulfate soils of Thailand: Effect of uncontrolled and controlled soil redox potential (Eh) and pH

A. KRAIRAPANOND, A. JUGSUJINDA[1] and W.H. PATRICK, Jr.
Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, LA 70803-7511, USA;
[1]*Corresponding author*

Received 9 March 1993. Accepted in revised form 5 July 1993

Key words: Oryza sativa L., phosphorus deficiency, rice, sorption isotherm, sulfic tropaquepts

Abstract

Two laboratory experiments were conducted to study phosphorus sorption characteristics in acid sulfate soils (para- and actual-acid sulfate soils) of Thailand. In one experiment the soils were subjected to oxidized and reduced conditions, in another they were maintained under different controlled pH (4.0, 5.0, and 6.0) and Eh (−600, −400, −300, −200, −100, and 0 mV) conditions. In both experiments the soils were kept in stirred suspensions with a soil to 0.01 *M* $CaCl_2$ solution ratio of 1:7 for 6 weeks. After the incubation period, the soil suspensions were equilibrated with KH_2PO_4 ranging from 0 to 500 mg P kg^{-1} soil. Sorption isotherms were described by the classical Langmuir equation. The results from the first experiment showed that more native insoluble P was released under reduced than oxidized conditions, with more being released from para-acid sulfate soil than from actual acid sulfate soils. Soil 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. In the second experiment, the P-sorption of both actual and para-acid sulfate soils was significantly affected by soil Eh, pH, and their interactions. The P-sorption increased significantly with increasing pH and decreasing Eh. At pH 4.0, a considerable increase in P-sorption occurred as Eh decreased from −400 to −300 mV, whereas at pH 5.0 and 6.0 an obvious change in P-sorption occurred when Eh decreased from −300 mV to −200 mV. The actual acid sulfate soil sorbed more P than did para-acid sulfate soil. Significant correlation between P-sorption parameters and 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 a significant effect on P-sorption.

Introduction

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, of which 95% is used for lowland rice production. Due to the acidic nature of the acid sulfate soils, rice production on these soils in the Bangkok Plain is often severely limited (Kevie and Yenmanas, 1972).

The major limitations on rice growth in acid sulfate soils are high P-sorption capacity (Attanandana, 1982) resulting in P deficiency and Fe and Al toxicity (Jugsujinda et al., 1978). Since P-sorption mechanisms in acid sulfate soils are greatly influenced by the forms and amounts of Fe and Al compounds, it is probably that soil Eh

Contribution from the Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, LA 70803-7511, USA. The research was supported by USAID Grant No. DHR-5542-G-SS-9027-00.

116

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 (Haynes and Swift, 1985; Trana et al., 1986) or decrease (Lopez-Hernandez and Burnham, 1974; Smyth and Sanchez, 1980) as pH increase. Khalid et al. (1977) reported that more P was sorbed under reduced condition than under oxidized condition at high level of added P.

Rice is grown under a wide range of oxidized and reduced soil conditions with varied Eh and pH levels. P-sorption characteristics under the different Eh and pH levels in acid sulfate soils of Thailand have not been thoroughly investigated.

The objectives of this research were to investigate P-sorption characteristics of the acid sulfate soils of Thailand under uncontrolled or oxidized and reduced soil conditions., and under different controlled Eh and pH levels of the soils. Relationships between P-sorption parameters and Fe, Mn and Al in these soil conditions are also reported.

Materials and methods

Experiment 1. P-sorption in acid sulfate soils under oxidized and reduced conditions

The surface layer (0–15 cm) of the acid sulfate soils used in this study were collected from the Bangkok Plain of Thailand. Soils were air-dried, sieved (<2 mm), and thoroughly mixed prior to chemical analysis. In this study one para-acid sulfate soil (Typic Tropaquepts), Bangkok (Bk) (pH 4.9), and three actual acid sulfate soils (Sulfic Tropaquepts Typic Sulfaquepts), Maha-Phot (Ma) (pH 4.5), Rangsit (Rs) (pH 4.3), and Rangsit very acid (Rsa) (pH 3.9) were used. These soils represent sites 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 1.

Suspensions of 250 g soil in 1750 mL 0.01 *M* $CaCl_2$ were incubated in laboratory microcosms under oxidized and reduced conditions for four weeks at 25 °C (4 replications). The microcosm consisted of a 2-L widemouth flask with rubber stopper. Two platinum electrodes, a salt bridge and a combination glass electrode were permanently inserted through the rubber stopper to measure Eh and pH. The soil solution was kept in suspension by a magnetic stirrer and a stirring bar. N_2 and O_2 gases bubbled continuously through the soil suspensions through the gas inlet and gas outlet 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 0.2% finely ground rice straw 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 bot-

Table 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 P[b]	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]$BaCl_2$-Trelthanolamine (Peech, 1965).
[e]Ammonium saturation-distillation (Chapman, 1965).

117

tles were flushed with O_2-free N_2 prior to adding the soil suspensions to maintain a reduced atmosphere during the equilibrium. After 24 hours equilibration on a reciprocating shaker, the soil suspensions was centrifugated (20 min at 7000 rpm) 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). A shaking time of 24 h was chosen because this period was considered adequate for the fast reaction 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 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 sodium citrate-dithionite solution (20%, 100 mL) on a reciprocating shaken for 18 h. After centrifugation and filtration, the filtrate was analyzed for citrate-dithionite extractable Fe and Al with ICP.

Sorption data for the soils were fitted to the classical Langmuir (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):

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

Experiment 2. P-sorption in acid sulfate soils under controlled Eh and pH

In the previous experiment Eh and pH of the oxidized and reduced soil conditions were not controlled. In this experiment, to know more precisely the P-sorption characteristics at each Eh and pH combination, the soil Eh was controlled at six different levels (−600, −400, −300, +200, +100, and 0 mV, respectively) each at three levels of the soil pH (4.0, 5.0, and 6.0, respectively). The experimental design was 6×3 factorial in randomized complete block design with two replications.

Previous soil samples, one para-acid sulfate soil, Bangkok (Bk), and one actual acid sulfate soil, Maha-Phot (Ma), were used. The soil suspensions as mentioned in the first experiment were incubated in laboratory microcosms at the above Eh and pH combinations using a modification of the redox control system developed by Patrick et al. (1973) for 6 wk at 25 °C.

At the end of the incubation period, the soil suspensions (50 mL) were treated with different P concentrations, extracted and filtered the same method as mentioned in the first experiment. Another 50 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 7000 rpm or 8000 × g) and filtered through a 0.45-μm membrane filter. The filtrate was analyzed for exchangeable Fe, Al, and Mn using the ICP. Again, 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 filtered. The filtrate was analyzed for free oxides of Fe, Al, and Mn with ICP.

To compare the results, P-sorption data for all samples were fitted to the classical Langmuir equation as described in the first experiment.

The buffer capacity (BI), a mixed quantity-intensity parameter, was calculated from kx_m (Holdford, 1979). The standard P requirement (SPR), P-sorption at a concentration of 0.2 mg kg^{-1} P in final solution, was also calculated following the suggestion of Beckwith (1965). 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

Release of native insoluble P

Under reduced soil conditions (Eh −190 to −145 mV) more native insoluble P was released

from soils than under oxidized soil conditions (Eh +695 to −815 mV) (Table 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.

Among the actual acid sulfate soils, Ma and Rs released more P and 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). 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). Likewise, 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).

Under controlled redox potential and pH conditions, the release of native P measured from soluble P concentrations when no P was added in para-acid sulfate, Bangkok (Bk) soil and in actual acid sulfate, Maha-Phot (Ma) soil, the concentration of soluble P increased with decreasing soil redox potential and pH (data not shown). Redox potential had greater effect on soluble P than did soil pH. The concentrations of soluble Fe also increased as Eh and pH decreased. 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.

Sorption characteristics of added P

The experimental P sorption isotherms constructed for the para-acid sulfate soil (Bk) and one of the actual acid sulfate soils (Ma) (Fig. 1) 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 other actual acid sulfate soils (Rs and Rsa) (Fig. 2). 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.

Sorption of added P was predicted by using Langmuir P-sorption isotherm since it showed the best fit with actual P sorption from the first experiment (data not shown). The effect of Eh and pH on sorption of added P are observed in term of their effects on Langmuir equation parameters.

Standard P requirement (SPR)

Analysis of variance of P-sorption data in Bangkok soil (para-acid sulfate) and in Maha-Phot soil (actual acid sulfate) (data not shown) indicated that SPR was significantly affected by Eh, pH, and interaction between Eh and pH in both actual and para-acid sulfate soils. A significant interaction indicated that the effect of Eh changed as the level of pH changed.

At every pH level, SPR slightly increased or did not change as Eh decreased from −600 to +400 mV in both actual and para-acid sulfate soils (Figs. 3 and 4). At pH 4.0, SPR considerably increased with decreasing Eh from −400 to −300 mV, whereas at pH 5.0 and 6.0, it gradually increased. As Eh continued to decrease from 300 to 0 mV, SPR at pH 4.0 continued to gradually increase. At pH 5.0 and 6.0, the patterns of SPR were likely the same. As Eh declined from −300 to −200 mV, standard P requirement steeply increased, particularly in the actual acid sulfate soil. Below the Eh of −200 mV, SPR continued to increase, particularly in the actual acid sulfate soil (Fig. 4).

The comparison between treatment means using Duncan's Multiple Range Test (DMRT) indicated that SPR increased significantly as pH increased (SPR at pH 6.0 > 5.0 > 4.0, respectively). SPR also increased significantly with decreasing Eh from −400 to 0 mV. An increase in SPR as Eh decreased from −600 to −400 mV was not significant.

Langmuir maximum sorption capacity (x_m)

Like SPR, Langmuir maximum sorption capacity (x_m) was significantly affected by Eh, pH, and

Table 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	1039	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)								
Oxidised	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

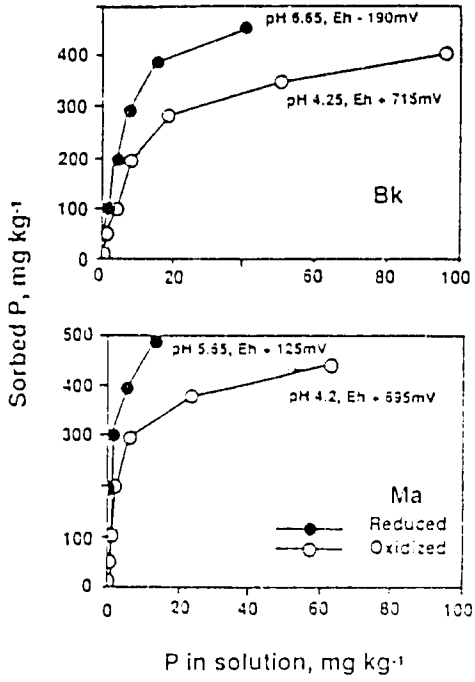


Fig. 1. The actual P-sorption isotherm in Bangkok soil (Bk) and Maha-Phot soil (Ma) as affected by oxidation-reduction status.

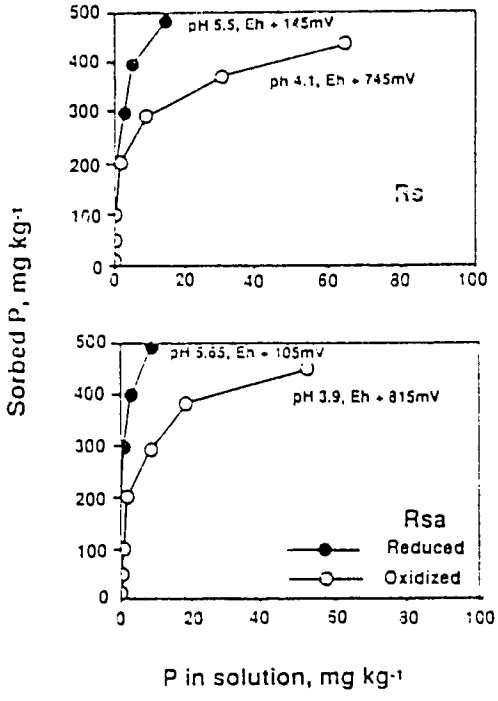


Fig. 2. The actual P-sorption isotherm in Rangsit (Rs) and Rangsit very acid soil (Rsa) affected by oxidation-reduction status.

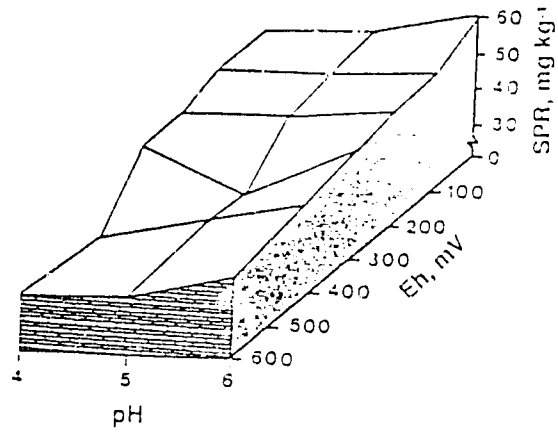


Fig. 3. Effects of pH, redox potential and their interactions on standard P requirement (SPR) (mg kg^{-1}) in Bangkok soil.

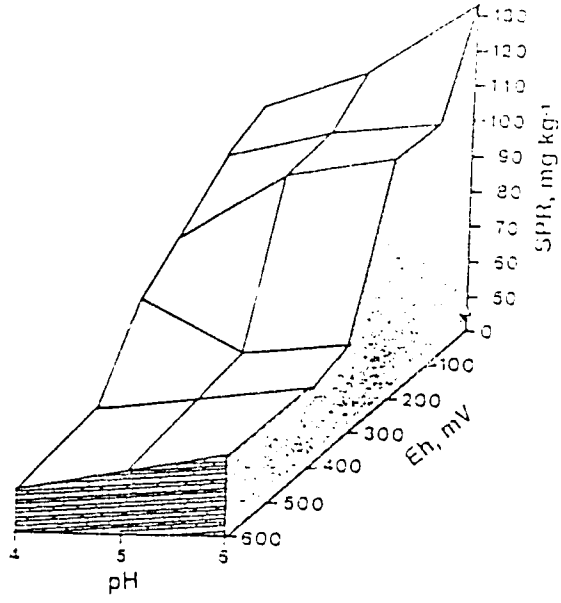


Fig. 4. Effects of pH, redox potential and their interactions on standard P requirement (SPR) (mg kg^{-1}) in Maha-Phot soil.

their interactions in both actual and para-acid sulfate soils (data not shown). The effects of Eh and pH on x_m of both soils (Figs. 5 and 6) showed the similar trend with those on SPR. The obvious change in x_m at pH 4.0 occurred when Eh decreased from −400 to −300 mV, but at pH 5.0 and 6.0 this phenomenon occurred when Eh declined from −300 to −200 mV. But the pattern of x_m of the actual acid sulfate soil was not different from that of the para-acid sulfate soil at the same Eh and pH levels.

121

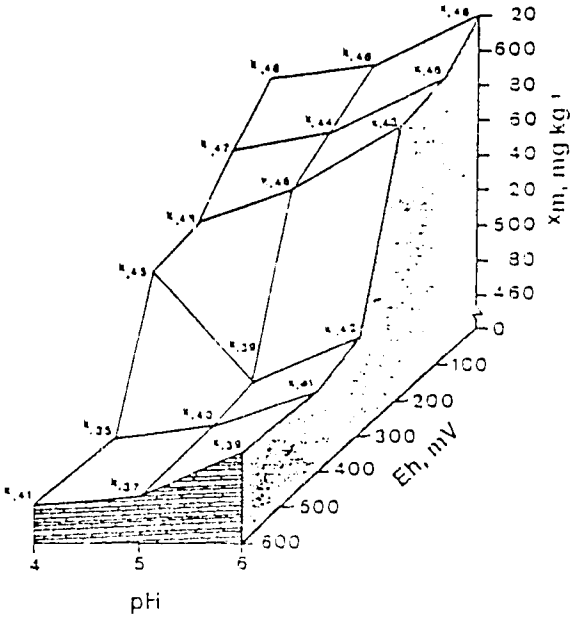


Fig. 5. Effects of pH, redox potential, and their maximum sorption capacity (x_m) (mg kg^{-1}) and Langmuir sorption constant (k) (mg kg^{-1}) in Bangkok soil.

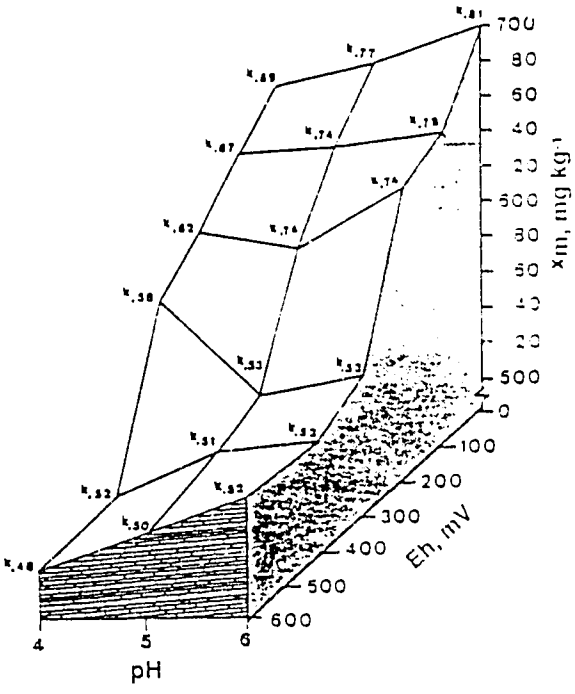


Fig. 6. Effects of pH redox potential, and their maximum sorption capacity (x_m) (mg kg^{-1}) and Langmuir sorption constant (k) (mg kg^{-1}) in Maha-Phot soil.

DMRT indicated that an increased in pH significantly increased the x_m. x_m also significantly increased with decreasing Eh except when Eh declined from +600 to +400 mV.

Langmuir sorption constant (k) and buffering capacity (BI)

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 Eh, pH, and interaction between Eh 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 Eh and pH (Figs. 5 and 6). These P-sorption parameters significantly increased with increasing pH in both soils, and significantly increased with decreasing Eh in the actual acid sulfate soil. For the para-acid sulfate soil, there was no significant increase in k as Eh declined from +600 to +400 mV, and from +300 to 0 mV. However, there was a significant difference in k when Eh decreased from +400 to +300 mV. Phosphorus was more loosely bounded to well oxidized soil than reduced soil.

The buffering capacity (BI) at Eh +600 and +400 mV were not significantly different, but they increased significantly as Eh 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 BI with decreasing Eh from +200 to +100 mV.

Relationships between P-sorbed and soil Fe, Al and Mn

The relationships between P-sorbed and soil Fe and Al, in our study, we observed that the amount of citrate-dithionite extractable Fe and Al under reduced conditions were considerably higher than under oxidized conditions (Table 2). Correlation matrices indicated that P sorbed was positively correlated with citrate-dithionite Fe and Al extractable under both oxidized and reduced conditions ($r = 0.85^{**}$, 0.93^{**}, 0.88^{**} and 0.92^{**}, respectively).

Pearson's correlation coefficients indicated significant correlations between P-sorption parameters and all forms of Fe in both acid sulfate soils

Table 3. Pearson's correlation coefficients between P-sorption parameters and various forms (soluble, s, extracted by 1 N NH_4OAc (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**	0.300*
x_m	0.923***	0.904***	0.926***	0.224	−0.142	0.359*	0.409*	0.449**	0.356*
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*	0.402*	0.262

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

(Table 3). Of all forms, free iron oxides (citrate-dithionite extractable) was the most correlated with P-sorption parameters. Similar relationships were also observed with Mn in actual acid sulfate soil but not in para-acid sulfate soil. This may have been due to the lower concentrations of those fractions in para than actual acid sulfate soils. Significant correlation between P sorption parameters and citrate-dithionite extractable Al were observed in both soils. 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 soils contained considerable amount of aluminum oxide (data not shown).

Discussion

Rice grown in acid sulfate soils in Thailand is limited by high P-sorption in the soils (Attanandana, 1982) resulting in P deficiency and Fe and Al toxicity (Jugsujinda et al., 1978). Liming as an amelioration method has been practiced in acid soils of Thailand for flooded rice culture. Liming increases soil pH, while flooding increases soil pH and decreases soil Eh. The suitability of liming flooded acid sulfate soils is questionable. It is probably that soil oxidation-reduction or redox potential (Eh) and pH conditions, which control Fe and Al reactions, govern the release and sorption of P in the acid sulfate soils. In the present experiments, the effect of oxidized and reduced soil conditions and the effect of Eh and pH on P-sorption characteristics in acid sulfate soils of Thailand were investigated in the laboratory. More native insoluble P was released under reduced than oxidized conditions, soil reduction also caused an increase in P-sorption of added P. The para-acid sulfate soil (Bk) released more P than actual acid sulfate soils (Ma, Rs, and Rsa) under both oxidized and reduced conditions. This can be attributed to a higher quantity of Bray II P in para-acid sulfate soil than in the actual acid sulfate soils. Results suggest that Al (trivalent aluminum ion, amorphous and crystalline forms) and Fe (ferrous and ferric ions, amorphous and crystalline) govern the release 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). Even though the reduced soil conditions caused an increase in the release of native insoluble P into solution, reduction 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 Holdford and Patrick (1979) demonstrated that reduced soil conditions can lead to a decrease in P sorption in soil at pH 5.0, but an increase of P sorption in soil at pH 6.5.

Phosphorus sorption in acid sulfate soils in

Thailand is 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 compounds, which have high active P-sorbing surfaces. As the pH increased upon reduction, the increased activity of the amorphous hydroxy-aluminum species resulted in increased P-sorption.

Major contributions to the increased concentration of soluble P with decreasing Eh and pH are the reduction and dissolution of ferric phosphate 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) report similar patterns of increasing soluble P and Fe in acid sulfate soils of Thailand. The concentrations of soluble Mn increased slightly with decreasing Eh and pH. 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 $Mn_3(PO_4)_2$) which are likely stable under the condition of this experiment. There was no clear pattern between the concentration of soluble Al and soil Eh, however, the concentration of soluble Al increased with decreasing soil pH. The increase in the amount of soluble Al likely does not contribute to the increase in the amount of soluble P as a result of the low solubility of aluminium phosphate in soils.

The standard P requirement (SPR) is P-sorption at a concentration of 0.2 mg kg^{-1} P in final solution for normal growth of most plants (Beckwith, 1965). The significant increase of SPR for both actual and para-acid sulfate soil can be attributed to marked release of iron and aluminium into solution at those Eh ranges (below +300 mV at pH 4; and below −200 mV at pH 5 and 6. The greater increase of SPR in actual acid sulfate soil indicated that more P sorbed than release as compared with a less steep slope of SPR in para-acid sulfate soil. This was attributed to more iron ad aluminium present in the actual acid sulfate soil than in para-acid sulfate soil. The critical Eh value for transformation of ferric to ferrous is about +300 mV (Gotoh and Patrick, 1974). Reduced Fe in acid sulfate soil increased as the Eh decreased (Attanandana et al., 1985; Charoenchamratcheep et al., 1987; Satawathananont et al., 1991). Moreover, at pH 4 most of aluminum ions stay in the soil solution. More ferrous and aluminum ions in the soil solution caused more P sorbed by formation of ferrous and aluminum phosphate compounds (McKeague and Day, 1966). SPR of the actual acid sulfate soil (Maha-Phot, Ma) ranging from 52 to 132 mg kg^{-1} soil was classified as low (10–100 mg kg^{-1} soil) to medium (100–500 mg kg^{-1} soil) level, whereas that of para-acid sulfate soil (Bangkok, Bk) ranging from 34 to 59 mg kg^{-1} was classified as low level on the scale proposed by Juo and Fox (1977).

The adsorption of phosphorus by soils from dilute solution was calculated from the Langmuir maximum sorption capacity (x_m) and can be related to various soil properties including information on the nature of reactions between soil and fertilizer phosphorus. The reaction of fertilizer phosphorus in soils depends upon the nature and amount of adsorbing surface as well as pH and redox potential (Eh). The obvious change in x_m at pH 4.0 and Eh between +400 to +300 mV in both actual and para-acid sulfate soils is likely attributed to more ferrous and aluminum ions in the soil solution causing more P being sorbed as ferrous and aluminum phosphate. At pH 5.0 and 6.0 ferrous and aluminum ions still existed at the lower Eh values of +300 to +200 mV. Although the pattern of x_m of the actual and the para-acid sulfate soils was not different at the same Eh and pH levels the magnitude of x_m in the actual acid sulfate soil was greater because actual acid sulfate soil had higher contents of water soluble and NaOAc extractable Fe and Al than the para-acid sulfate soils at the same Eh and pH levels. x_m of the actual acid sulfate soil ranging from 508 to 699 mg kg^{-1}, and of the para-acid sulfate soil from 458 to 618 mg kg^{-1} soil, respectively, was somewhat lower than that reported by Imai et al. (1983). This is attributed to the differences in

124

soil conditions, soil series, and equations used to determine the x_m. Imai et al. (1983) used air-dried acid sulfate soils, and two layers Langmuir equation to determine the x_m.

The x_m is the maximum value of P sorption capacity while the SPR is the minimum value of P requirement of the soil. So P fertilizer application rates should be derived using these two values. From an economic consideration P fertilizer could be added more than the SPR value but should not exceed the x_m value. Therefore, the maximum amount of P fertilizer to be added should be calculated from x_m in order to achieve the best fertilizer efficiency.

The findings of this study suggested that the reduced soil conditions not only caused an increase in the release of native insoluble P to solution, reduction also led to a very large increase in P sorption capacity of soils at the higher P levels. The para-acid sulfate soil releases more P than the actual acid sulfate soils, and among the acid sulfate soils, Ma and Rs released more P than Rsa. The results further suggested that soil Al and Fe govern the release of native insoluble P in acid sulfate soils of Thailand. The actual acid sulfate soils sorbed more added P than did the para-acid sulfate soil, and the standard P requirement for normal plant growth in the actual acid sulfate soil was higher than the para-acid sulfate soil. The findings also suggested that as the soil pH increased and soil Eh decreased P-sorption increased. Liming the acid sulfate soil which is recommended in Thailand should be considered especially in reducing soil condition. Liming has been recommended in Thailand as an amelioration method of acid sulfate soils. Liming increases soil pH and as the soil pH is increased, sorption of added P is also increased. Without liming use of suitable P sources such as locally available rock phosphate sources to provide the plant nutrient should be considered for successful rice culture in Thailand. These sources are lower in price than acidulated phosphates and can represent a means of reducing fertilizers cost. Greenhouse (TVA) and field data (Thailand) showed that a close relationship was found to exist between first-crop yield response to applied P (as triple superphosphate) and citrate solubility in a series of phosphate rocks (Engelstad et al., 1974).

Acknowledgements

We acknowledge the assistance of Dr R D DeLaune, Professor, Wetland Biogeochemistry Institute, Louisiana State University, Baton Rouge, Louisiana, for his valuable comments on the preparation of the manuscript and of Mr. Sulaeman, Soil Scientist, Center for Soil and Agro-climate Research, Bogor, Indonesia, for taking his valuable time in reviewing the manuscript.

References

Attanandana T 1982 Fertility problems of acid sulfate soils of Thailand. Ph.D. Diss. Kyoto Univ., Kyoto, Japan

Attanandana T, Pechayapist J and Patrick W H Jr 1985 Factors affecting Amelioration of the oxidized potential acid sulfate soil for rice cultivation. Proceedings of International Seminar on Environmental Factors in Agricultural Production, Thailand, pp 413–421.

Beckwith R S 1965 Sorbed phosphate at standard supernatant concentrations as an estimate of phosphorus needs of soils. Aust. J. Exp. Agric. Anim. Husb. 5, 52–58.

Chang S C and Jackson M L 1958 Phosphorus fraction in some representative soils. J Soil Sci. 9, 109–119.

Charoenchamratcheep C, Smith C J, Satawathananont and Patrick W H Jr 1987 Reduction and oxidation of acid sulfate soils of Thailand. Soil Sci. Soc. Am. J. 51, 630–634.

Gambrell R P, Khalid R, Verloo M G and Patrick W H Jr 1975 Transformations of heavy metals and plant nutrients in dredged sediments as affected by oxidation-reduction potential and pH. Part II. Materials and methods, results and discussion. Contract report D-75-4. U.S. Army Engineers Waterways Experiment Station, Vicksburg, MS.

Engelstad O P, Jugsujinda A and DeDatta S K 1974 Response by flooded rice to phosphate rocks varying in citrate solubility. Soil Sci. Soc. Am. Proc. 38, 524–529.

Haynes R J and Swift R S 1985 Effects of liming and air-drying on the adsorption of phosphate by some acid soils. J. Soil Sci. 36, 513–521.

Holdford I C R 1979 Evaluation of soil phosphate buffering indices. Aust. J. Soil Res. 17, 495–504.

Holdford I C R and Patrick W H Jr 1979 Effect of reduction and pH changes on phosphate sorption and mobility in an acid soil. Soil Sci. Soc. Am. J. 43, 292–297.

Imai H, Sangtong P and Cholitkul W 1983 Characteristics in phosphate adsorption of major soil groups of Thailand. JARQ. 17, 59–68.

Jugsujinda A, van Breemen N and Yaki T 1978 Aluminum toxicity and phosphate deficiency in acid sulfate soils of Thailand. International Rice Research Newsl. 3, 9–10.

Juo A S R and Fox R L 1977 Phosphate sorption characteristics of some bench-mark soil of West Africa. Soil Sci. 124, 370–376.

125

Kevie W van der and Yenmanas B 1972 Detailed reconnaissance soil survey of southern central plain area. Soil Survey Rept. no. 89., Land. Dev. Dept., Bangkok, Thailand.

Kevie W van der and Yenmanas B 1972 Detailed reconnaissance soil survey of southern central plain area. Soil Survey Rept. no. 89. Land Dev. Dept., Bangkok, Thailand.

Khalid R A, Patrick W H Jr and DeLaune R D 1977 Phosphorus sorption characteristics of flood soils. Soil Sci. Soc. Am. J. 41, 305–310.

Lindsay W L 1979 Chemical Equilibria in Soils. John Wiley & Sons, Inc., NY.

Lopez-Hernandez D and Burnham C P 1974 The effect of pH on phosphate adsorption in soils. J. Soil Sci. 25, 207–216.

McKeague J A and Day J H 1966 Dithionite and oxalate Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46, 13–22.

Mehadi A and Taylor R W 1988 Phosphate adsorption by two highly-weathered soils. Soil Sci. Soc. Am. J 52, 627–632.

Olsen S R and Watanabe F S 1957 A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. Soil Soil Sci. Soc. Am. Proc. 21 144–149.

Patrick W H Jr, Gotoh S and William B G 1973 Strengite dissolution in flooded soils and sediments. Science 179, 564–565.

Persoff P and Thomas J F 1988 Estimating Michaelis-Menton of Langmuir isotherm constants by weighted nonlinear least square. Soil Sci. Soc. Am J. 52, 886–889.

SAS Institute, Inc. 1985 SAS User's Guide: Statistics. Cary, NC.

Satawathananont S 1986 Redox, pH, and ion chemistry of acid sulfate soils in Thailand. Ph.D. Diss., Louisiana State Univ., Baton Rouge, LA.

Satawathananont S, Patrick W H Jr and Moore P A 1991 Effect of controlled redox conditions on metal solubility in acid sulfate soils. Plant and Soil 133, 281–290.

Smyth T J and Sanchez P A 1980 Effects of lime, silicate and phosphorus applications to an Oxisols on phosphate sorption and ion retention. Soil Sci. Soc. Am. J 44, 500–505.

Trana S J, Sposito G, Hesterberg D and Kafkafi U 1986 Effects of pH and organic acids on orthophosphate solubility in an acidic, montmorillonitic soil. Soil Sci. Soc. Am. J. 50, 45–52.

Section editor: B E Clothier

126