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THESIS

**DISSOLUTION AND AVAILABILITY OF ROCK
PHOSPHATES FOR RICE CULTIVATION IN ACID
SULFATE SOILS OF THAILAND**

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Phosphorus (P) deficiency in acid sulfate soils of Thailand is often a limiting factor that decreases rice growth and yield. The direct application of rock phosphate (RP) to acid sulfate soils can improve P nutrient status. The efficiency of RP application depends on two reactions: the dissolution of RP and the sorption of dissolved RP. The parameters that used in the Phosphorus Decision Support System (PDSS) calculation such as P critical level, P buffer coefficient (PBC), algorithms for predicting RP dissolution and sorption of dissolved RP were used as a framework to quantify the requirement of RP to supply the P for paddy rice in acid sulfate soils.

This study consists of 6 experiments. 1) A study of PBC of acid sulfate soils. This study was conducted in six important acid sulfate soils and three soil testing methods i.e. Bray 1, Bray 2 and modified iron-oxide impregnated strip test (modified Pi strip test). The PBC obtained by Bray 1 and the modified Pi strip test increased with decreasing effective cation exchange capacity and cation exchange capacity, respectively. Decreases in P retention, oxalate extractable-iron and aluminum increased the PBC as estimated by Bray 2-extraction. 2) A field study was carried out to determine the P critical level which is used in PDSS to estimate the RP requirement for rice cultivation in acid sulfate soils. The study of P critical level was conducted in an Ongkharak (Ok) soil with triple superphosphate (TSP) and two RPs as the P fertilizers. The field-determined P critical levels using TSP as extracted by Bray 2 and modified Pi strip test were 11.97 and 5.12 mg P kg⁻¹, respectively. The P critical levels using RP as extracted by Bray 2 and modified Pi strip test were 13.09 and 5.40 mg P kg⁻¹, respectively. 3) Predicting the individual dissolution of RPs in flooded acid sulfate soils. The experiment was conducted in six acid sulfate soils and two RPs. An individual RP dissolution model for predicting single RP dissolution in six acid sulfate soils was developed from soil properties. The soil acidity was an important property in the RP dissolution model. 4) Incubation study of various RPs with representative soils of acid region of Thailand. The experiment was conducted in six important acid sulfate soils and with four contrasting RP materials. Soil acidity as measured by soil pH and KCl-extractable Al and RP solubility measured by a two extractions of 2-percent citric acid and particle size of RP were the key factors in the generalized RP dissolution model. 5) Incubation studies to determine the availability of dissolved RP in flooded acid sulfate soils for a range of RPs. The sorption or availability of dissolved RP was studied by Bray 1 and Bray 2 extraction in six acid sulfate soils incubated with four contrasting RP materials. Bray 1-extraction can extract a slightly dissolved RP. Bray 2 extracting solution extracted more P than Bray 1. The high acidity of Bray 2-extraction seems to dissolve unavailable RP. The RP dissolution and availability of dissolved RP ratio which was estimated by Bray 1 and Bray 2-extraction was calculated to explain sorption of dissolved RP. 6) Field testing of RP predictions for rice cultivation in two acid sulfate soils. These experiments were conducted in Rangsit and Ongkharak soils. The RP requirement of two RPs, namely Kanchanaburi RP (KRP) and Gafsa RP were predicted for rice cultivation in two soils using PDSS and algorithms which were developed from experiments 1-5. There was no response of rice yield in Rs soil with KRP and Gafsa RP application rates because of initial P in the soil was adequate for rice growth. The field-determined RP requirements for rice in the Ok soil were close to the predicted RP rates, validating the prediction algorithms developed for inclusion into the PDSS software.

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ABBREVIATIONS

Al	=	Aluminum
Al_KCl	=	aluminum extracted by potassium chloride
Al_ox	=	Aluminum extracted by ammonium oxalate
ANOVA	=	Analysis of variance
AOAC	=	Association of Official Analytical Chemists
Ay soil	=	Ayutthaya soil
Bp soil	=	Bang Nam Priao soil
C.V.	=	Coefficient of variance
Ca	=	Calcium
Ca soil	=	Cha-am soil
Cc soil	=	Chachoengsao soil
CCE	=	Calcium carbonate equivalent
CEC	=	Cation Exchange Capacity
Dm soil	=	Don Mueang soil
DMRT	=	Duncan's Multiple Range Test
ECEC	=	Effective Cation Exchange Capacity
Fe	=	Iron
Fe_ox	=	Iron extracted by ammonium oxalate
IFDC	=	International Fertilizer Development Center
KCl	=	Potassium chloride
KRP	=	Kanchanaburi rock phosphate
KRPS	=	Kanchanaburi rock phosphate mixed with soluble phosphate fertilizer
LRP	=	Linear Response Plateau
MAP	=	Mono ammonium phosphate fertilizer
Mn	=	Manganese
N	=	Nitrogen
ns	=	Not significant

ABBREVIATIONS (cont'd)

Ok soil	=	Ongkharak soil
P	=	Phosphorus
P _{retention}	=	Phosphorus retention
P ₀	=	Phosphorus in the soil
PBC	=	Phosphorus buffer coefficient
P _c	=	Phosphorus critical level
PDSS	=	Phosphorus Decision Support System
PI	=	Panicle Initiation
Pi strip test	=	Iron-oxide impregnated strip test
P _{init}	=	Initial level of extractable phosphorus
P _{req}	=	Phosphorus requirement
RP	=	Rock phosphate
Rs soil	=	Rangsit soil
Rsa soil	=	Rangsit very acid soil
RMS	=	Residual mean square
SAS	=	Statistical Analysis System
Se soil	=	Sena soil
Tan soil	=	Thanyaburi soil
Tq soil	=	Tha Khwang soil
TSP	=	Triple superphosphate
$\Delta P_{\text{Bray 1}}$	=	Change in Bray 1-extractable phosphorus
$\Delta P_{\text{Bray 2}}$	=	Change in Bray 2-extractable phosphorus
ΔP_{NaOH}	=	Change in sodium hydroxide-extractable phosphorus

DISSOLUTION AND AVAILABILITY OF ROCK PHOSPHATES FOR RICE CULTIVATION IN ACID SULFATE SOILS OF THAILAND

INTRODUCTION

Acid sulfate soils occur widely in the Tropics, including South East Asia, West Africa, and selected coastal regions of South America. They occur in Thailand mainly in the Central Plain. Most of the acid sulfate soils are used for rice cultivation (Department of Agriculture, 2004). Rice yields are often low as a result of the low potential productivity in acid sulfate soils (Land Development Department, 2002). The low potential productivity is often due to low phosphorus (P) availability (Attanandana and Vacharotayan, 1984). Rock phosphate (RP) can be applied directly to rice and the residual effect from the first application can provide adequate available P for three crops of rice (Sassanarakkit, 1982). The extreme acidity of acid sulfate soils, in which soil pH can be less than 3 to 4, is a logical choice because high acidity is required for the dissolution of RP. The choice of paddy rice for acid sulfate soils is also logical because the flooded conditions prevent even further acidification that would be caused by oxidation of the sulfur-containing jarosite. Soil pH is typically increased due to the reduced condition of flooded soil. With acid sulfate soils, however, even submergence may still only increase the soil pH to around 4.5-5 (Kyuma, 2004), which is sufficiently acid to dissolve most RP.

Acid sulfate soils in the Central Plain of Thailand were classified into three categories of paddy suitability based on acidity of soils (Kevie and Yenmanyas, 1972). This classification is useful for nutrient management in acid sulfate soils. The P status in acid sulfate soils of each category can be approximately forecast from this classification. Soluble phosphate fertilizer such as mono ammonium phosphate (16-20-0) and RP have been recommended for rice grown in P deficient acid sulfate soils at the rate of 16.3 kg P ha⁻¹ (Department of Agriculture, 2004). The current recommendations are extensively used for all acid sulfate soils but do not consider the categories of paddy suitability nor soil or rock phosphate properties. The efficiency of RP for direct application depends on the crop, soil, RP properties, climate and management (Sidibé-Diarra *et al.*, 2004).

One of the first reactions that occurs when RP is added to soils is dissolution, which depends on chemical and physical properties of the RP and soil characteristics. The RP dissolution in particular soils were modeled and predicted by soil properties. MacKay *et al.* (1986) described the dissolution of RP by a modified Mitscherlich's equation; $Y = A(1 - e^{-CX})$ in which Y = amount of RP dissolved at time x ; A = asymptote; C = curvature coefficient and X = time. This equation describes an initially rapid dissolution of the rock with a gradually slowing to a plateau which represents the maximum dissolution unless disturbance occurs. MacKay *et al.* (1986) proposed a stepwise regression between the A coefficient in a modified Mitscherlich's equation and soil properties. Coefficient C was independent of soil type. Calcium saturation, P sorption capacity, calcium exchange capacity and organic carbon were the important soil properties that control the dissolution of Sechura RP in New Zealand soils. The following equation was proposed, $A = 176 - 156\text{calcium saturation} + 0.97\text{P sorption capacity} - 0.033\text{calcium exchange capacity} + 6.67\text{ organic carbon}$. However, the algorithms can only be used to estimate the dissolution of Sechura RP in soils.

When RP is applied to soils and dissolved, another important reaction is the sorption of the dissolved P in the soil (Sample *et al.*, 1980). The two processes, RP dissolution and sorption of dissolved RP, characterize the most important reactions that control rock phosphate availability and served as the basis for this study. The sorption of the dissolved RP can be expressed by RP dissolution and P availability. Sidibé-Diarra *et al.* (2004) proposed the ratio of RP dissolution and availability of dissolved RP by Olsen and Bray 1-extracting solution, to represent the sorption of dissolved Tilemsi RP in Mali soils. The availability of dissolved RP can be measured by P soil test methods but some P extracting solution may cause overestimation or underestimation of available dissolved RP. New P soil test methods such as iron-oxide impregnated paper strip test have been recommended to estimate available P in soil fertilized with RP.

Many P decision-aids have been developed to assist P nutrient management. The Phosphorus Decision Support System (PDSS) was designed to assist in the diagnosis and correction of P deficiencies in soils and crops, with emphasis on tropical conditions (Yost *et al.*, 1992). However, PDSS was developed for water-soluble P fertilizer and primarily estimates P requirement based on P sorption by soils. Sidibé-Diarra *et al.* (2004) revised

the structure of PDSS for predicting the amount of Tilemsi RP addition for upland crops in West Africa soils. Sidibé-Diarra *et al.* (2004) used the P critical level, extractable P in soil, the equation for predicting RP dissolution (modified Mitscherlich equation) and the ratio between RP dissolution and extractable P of dissolved RP to estimate amount of Tilemsi RP addition for crops. Rock phosphate deposits in West Africa differ widely in their properties. Software for predicting the rock phosphate requirement for crop will be very useful if the user can select the type of rock phosphate that is suited for their area and crops.

A hypothesis of this study is that the dual processes of dissolution and sorption of RP, measured by the plant availability of RP, can provide a useful structure to estimate the amount of RP that should be added to the soil to correct P deficiencies. An associated hypothesis is that the PDSS structure can be revised to estimate the RP requirement in acid sulfate soils of Thailand based on widely used soil P extraction methods. The P critical level and P buffer coefficient which are the important variables in the model must be estimated for each extractant to be used in the model. This approach to estimating RP requirement may be useful for researchers, extension workers and farmers.

Objectives

1. estimate P buffer coefficients, which is the soil parameter in PDSS, necessary to estimate RP requirement for rice cultivation in acid sulfate soils of Thailand.
2. estimate the P critical level, which is a plant parameter in PDSS, necessary to estimate RP requirement for rice cultivation in acid sulfate soils of Thailand.
3. investigate, measure, and model the factors controlling the dissolution and availability of rock phosphate in acid sulfate soils.
4. develop algorithms that predict rock phosphate dissolution and sorption of RP in acid sulfate soils.
5. test the prediction of rock phosphate requirement for rice cultivation in acid sulfate soils under field conditions.

LITERATURE REVIEW

1. Acid sulfate soils

Acid sulfate soils are soils that contain acid forming substances (mainly iron sulfides) as the minerals that can be oxidized causing acid sulfate soils to become acid. The acidity of the soils depends on the balance between the acid forming substances and the substances (minerals) that neutralize acidity, most commonly calcium carbonate minerals (Andriesse and Mensvoort, 2002). The conditions that lead to acid forming substance are i) the presence of marine or brackish water as the source of sulfate, ii) the stagnation of water, such as that found in lagoons and bays, and iii) a supply of decomposable organic matter (Kyuma, 2004). Acid sulfate soils occur in many coastal areas in the tropics and are characterized by high acidity with a pH of 4 or less within 50 cm depth from the soil surface (Attanandana and Vacharotayan, 1991). The oxidation of pyrite results in sulfuric acid which is usually the cause of high acidity in acid sulfate soils. Acid sulfate soils are recognized as three kinds based on the genetic distinction i.e. potential acid sulfate soils, active acid sulfate soils and post active acid sulfate soils (Andriesse and Mensvoort, 2002).

Potential acid sulfate soils are anaerobic soils, commonly occurring in coastal sedimentary environments affected by sulfidization, the process which leads to the formation of iron sulfide minerals (Andriesse and Mensvoort, 2002). Potential acid sulfate soils contain sulfide minerals in near surface horizons that are expected to generate, upon exposure to oxidizing conditions, sufficient sulfuric acid to drive the pH of these horizons to low levels. Under these conditions, most plants would be unable to grow and an active acid sulfate soil would then be recognized. Active acid sulfate soils form where sulfide minerals (most typically iron sulfides and the mineral pyrite) are oxidized in the near surface horizons and have formed enough sulfuric acid, with insufficient neutralization, result in the low pH. Usually a soil horizon with a pH of 3.5, as measured in water, is recognized as a sulfuric horizon. In post active acid sulfate soils, weathering and pedogenesis have proceeded beyond the active stage such that sulfide minerals are no longer present in surface soil horizons. The pH in these horizons has risen to levels above

that which would cause them to be recognized as sulfuric horizons (Andriesse and Mensvoort, 2002).

Estimates of the total area of potential and actual acid sulfate soils in the world are in the order of 12–13 million ha (FAO, 1974). Approximately 10 million ha occur in tropical regions and a half of them occur in Asia. Potential acid sulfate soil materials occur under thick covers of peat (mainly in Indonesia and Malaysia) or under nonpyritic alluvial sediments. Andriesse and Mensvoort (2002) have updated the extent of acid sulfate soil in the world, based on new information and on expert knowledge, and have included an accuracy assessment of the existing information. Their new estimate increases the estimated world total to over 17 million ha (Table 1). This higher figure is mainly due to the discovery of acid sulfate soils in Australia since the 1980s.

Table 1 World distribution and extent of potential and actual acid sulfate soils.

Region	Area (1 000 ha)
Africa	4 490
Asia	6 515
Australia	3 000
Latin America and the Caribbean	2 800
North America (Unites States and Canada)	100
Europe	235
World Total	17 100

Source : Andriesse and Mensvoort (2002)

1.1 Acid sulfate soils in Thailand

Acid sulfate soils in Thailand cover an area of 0.84 million ha (Andriesse and Mensvoort, 2002) and mostly occur in the Central Plain of Thailand which is suitable for rice cultivation. Most of the acid sulfate soils in the Central Plain of Thailand are “active”

acid sulfate soils. Acid sulfate soils in the Central Plain of Thailand are classified into three categories of paddy suitability (Kevie and Yenmanyas, 1972). Soil acidity is one of the criteria used for this classification and depth of jarosite mottles is a visual acidity index. The three categories are: i) PIIa soils, with an estimated area of 0.32 million ha and jarosite mottles are only found deeper than 100 cm. ii) PIIIa soils, with an approximate area of 0.38 million ha and jarosite mottles are found within the 50-100 cm depth and iii) PIVa soils, with an estimated area of 0.06 million ha and jarosite mottles are found within 50 cm of the soil surface. The series of acid sulfate soils in the three categories and the average rice yield are shown in Table 2.

Table 2 Soil suitability classification for paddy rice of acid sulfate soils of the Central Plain of Thailand.

Soil series	Soil suitability class for paddy rice
Mahaphot (Ma), Bang Nam Priao (Bp) Ayutthaya (Ay), Tha Khwang (Tq) Chachoengsao (Cc)	PIIa: (jarosite deeper than 1 meter) soil well suited for paddy with moderate limitations due to soil acidity, average yield 1.2-2.2 t/ha
Sena (Se), Don Mueang (Dm) Thanyaburi (Tan) Rangsit (Rs)	PIIIa: (jarosite found within 0.5-1.0 meter depth) soil moderately suited for paddy with some limitations due to soil acidity, average yield 0.9-1.2 t/ha
Ongkharak (Ok) Cha-am (Ca) Rangsit very acid (Rsa)	PIVa: (jarosite found within 0.5 meter of surface) soil poorly suited for paddy with severe limitations due to soil acidity, average yield 0.9 t/ha

Source: Kevie and Yenmanyas (1972)

1.2 Fertility problems of acid sulfate soils

A low pH is a characteristic feature in acid sulfate soils. Sulfur occurs mainly in the form of sulfide. On the other hand, low pH enhances solubility of aluminum (Al) and trace elements such as iron (Fe), and manganese (Mn). Acid sulfate soils are generally unproductive. Their low productivity may be due to soil acidity, salinity, aluminum toxicity, iron toxicity, low content of major nutrients, low base status and hydrogen sulfide toxicity. Phosphorus deficiency is the most important problem of acid sulfate soils. The abundance of Al, Fe and Mn promotes precipitation of soluble P in acid sulfate soils, thus P is unavailable to plants and hence, P deficiency is observed. Raising soil pH with frequent liming and applying P fertilizer has been suggested to enhance P uptake by plants. Liming of acid sulfate soils increases soil pH and another important effect of liming is increased availability of plant nutrient such as phosphorus, potassium, calcium, and magnesium (Kyuma, 2004). Submergence in acid sulfate soils for rice cultivation also raises soil pH, if kept submerged until the pH increase sufficiently, Al toxicity is eliminated and Fe toxicity minimized. The management of acid sulfate soils by maintaining them in flooded conditions and under reducing conditions is fundamental. Liming and the application of P fertilizer are also important in their management. Because soluble phosphate is converted to insoluble phosphates with Al and Fe, the application of costly soluble P fertilizers alone offers very little benefit in acid sulfate soils. Therefore, it would be better if the soil P level is raised with the use of limestone or low cost P fertilizers such as rock phosphate.

2. Rock phosphate

Rock phosphates can be defined as rocks composed largely of phosphate minerals, especially apatite, that can be used as fertilizer and which are a source of the nutrient P. The World RP production for 1999 and the reserves are shown in Table 3. In 1999, the main four producers of RP (the United States of America, China, Morocco and Western Sahara and Russian Federation) produced about 72.0 percent of the world total. However, the largest reserves of RP in the world are located in Morocco and Western Sahara, which may possess over half of the world's RP reserves.

Table 3 World rock phosphate production in 1999 and reserves.

	Production in 1999	Reserves
	1 000 tones	
United States of America	40 867	4 000 000
China	30 754	1 200 000
Israel	4 128	180 000
Jordan	6 014	1 700 000
Morocco and Western Sahara	21 986	21 000 000
Senegal	1 879	1 000 000
South Africa	2 941	2 500 000
Togo	1 715	60 000
Tunisia	8 006	600 000
Russian Federation	11 219	1 000 000
Other countries	15 963	4 000 000
World total	145 472	37 000 000

Source: US Bureau of Mines (2001)

There are five types of rock phosphate deposits that are being mined in the world i.e. marine sedimentary, igneous, metamorphic, biogenic and rock phosphate deposits resulting from weathering. Approximately 75% of world's rock phosphate resources are sedimentary rock phosphate deposits, 15-20% are igneous and weathered deposits, and only 1-2% are from biogenic resources, largely bird and bat guano accumulations (Van Straaten, 2002). The different types of rock phosphates have widely differing mineralogical, chemical and textural characteristics. The major mineral group in rock phosphate is the apatite group. Apatite includes 10 mineral species and has the general formula $X_5Y(PO_4)_3$, where X is usually Ca^{2+} and Y is F^- , Cl^- , or OH^- . Calcium-phosphates of apatite are found mainly in sedimentary, metamorphic and igneous rocks and also found in weathering environments (Van Straaten, 2002). Other phosphates include minerals of the crandallite group as well as variscite and strengite which are Fe- and Al-containing phosphates found in highly weathered environments. Fluorapatite ($Ca_{10}(PO_4)_6F_2$) and hydroxyl apatite ($Ca_{10}(PO_4)_6(OH)_2$) are the major minerals in rock phosphate deposits of

igneous and metamorphic origin. Carbonate hydroxyl apatite ($\text{Ca}_{10}(\text{PO}_4\text{CO}_3)_6(\text{OH})_2$) is a mineral which was found in biogenic phosphate. Francolite ($\text{Ca}_{10-x-y}\text{Na}_x\text{Mg}_y(\text{PO}_4)_{6-z}(\text{CO}_3)_z\text{F}_{0.4z}\text{F}_2$), a carbonate substituted apatite, is a mineral which is commonly found in rock phosphate from marine sedimentary and weathered rocks (Van Straaten, 2002).

Rock phosphate deposits were approximately 0.3 million tones with a total amount of 5.6-15.7% in Thailand (Warinthornnuwat, 1999). Rock phosphates are found in the West, North, Northeast and the Southern parts of Thailand. The five important rock phosphates deposits in Thailand are shown in Table 4. There are four types of phosphates found in Thailand i.e. biogenic phosphate, sedimentary phosphate, Al containing phosphate, and nodule phosphate (Sapattavanija and Ratanajarurak, n.d.). There are few rock phosphate mines in Thailand, most rock phosphate production is a by-product from other mines. The biogenic rock phosphate deposit is the largest deposit in Thailand. Kanchanaburi rock phosphate, derived from bat guano from Western part of Thailand, is located close to the Central Plain where acid sulfate soils are found (Warinthornnuwat, 1999). Because of the low content of total P in some Kanchanaburi rock phosphate, the fertilizer manufacturers often add soluble phosphate fertilizer to increase total P in the rock.

Table 4 The important rock phosphate reserves in Thailand.

Province	Part of Thailand	Type of rock phosphate	Total P (%P)	Reserve (1 000 tones)
Kanchanaburi	Western	Guano	5.6-14.8	100-150
Roi-et	Northeast	Al containing phosphate	7.8-11.8	74
Lamphoon	Northern	Guano	15.7	57
Phetchaboon	Central	Guano	8.7-15.2	27
Phatthalung	Southern	Guano	10.9-15.7	20

Source: Sapattavanija and Ratanajarurak (n.d.)

2.1 Direct application of rock phosphate in acid sulfate soils

Rock phosphate is a primary raw material for producing P fertilizer. The mineralogical, chemical and textural characteristics of rock phosphate are used to determine its suitability for direct application. The most important factors in the assessment for direct application are: grade, suitability for beneficiation, and the reactivity of apatite.

Acid sulfate soils have low productivity potential and deficiencies of nitrogen (N) and P result in poor crop growth. Rock phosphate is a low cost P fertilizer, which may be suitable for direct application to the acid sulfate soils. Rock phosphate can be applied directly to rice and the residual effect from the first application can provide adequate available P for the next crop of rice (Sassanarakkit, 1982). The extreme acidity of acid sulfate soils, in which soil pH can be less than 3 to 4, make the use of RP a logical choice since acidity is a key factor to the dissolution of rock phosphate. In flooded acid sulfate soils, soil pH during submergence can increase to around 4.5-5 (Kyuma, 2004), which is still sufficiently acid to dissolve most RPs. Factors that influence the agronomic effectiveness of RP are: the reactivity of RP, soil properties, climatic conditions, crop species and management practices. High carbonate substitution for phosphate in the apatite crystal structure, low content of calcium carbonate as an accessory mineral and fine particle size (less than 0.15 mm) enhance the reactivity of RPs and increase their agronomic effectiveness.

2.2 Rate of rock phosphate application

Land Development Department of Thailand (n.d.) has recommended the rate of RP application for rice cultivation in acid sulfate soils varies from 1250 to 1875 kg RP ha⁻¹. This recommendation is based on empirical results and is not the result of an analysis of soil P, the rock phosphate, or soil acidity. The rate assumes an average P solubility in RP of Thailand of approximately 1.31-1.74 %P of rock, which is extracted by neutral ammonium citrate. This recommendation amount of RP is the same for all acid sulfate soils. The properties of RP materials and extent of P deficiency in acid sulfate soils are, however, widely different. In addition, crop management and cropping systems may

change the properties of soils and thus change the amount of RP needed. The decision on the rate of rock phosphate application needs to be based on soil P tests (Perrott and Wise, 2000), the rate of dissolution of RP, and its availability to plant (Sidibé-Diarra *et al.*, 2004).

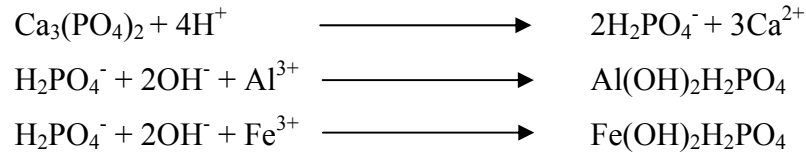
2.3 Rock phosphate dissolution

The dissolution of rock phosphate in soils is a reaction fundamental to the effectiveness of direct application of RP and it depends on both the RP and soil properties. The dissolution of RP can be measured by incubating RP with the selected soils with different properties. In addition, some RP materials have significant quantities of free carbonates and other minerals and have potential to change the characteristics of soil when the RP dissolves.

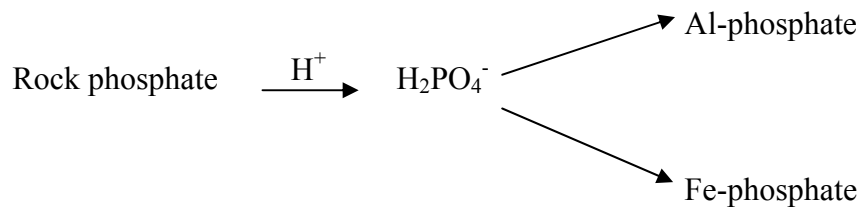
2.3.1 Effect of soil properties on the dissolution of rock phosphate.

The chemical and physical properties of both the rock phosphate and soil characteristics control the dissolution of the rock phosphate (Wright *et al.*, 1992). Wright *et al.* (1992) suggested that no single soil property controls the dissolution of rock phosphate in the soils. Dissolution of rock phosphates is enhanced by low soil pH, low exchangeable Ca, and low P concentration in the soil solution (Hammond *et al.*, 1986). MacKay *et al.* (1986) found that the percentage of Ca-saturation, P-sorption capacity, and Ca-exchange capacity were the most important soil properties controlling dissolution of rock phosphate in the soil at pH ranging from 5.0-6.5. Exchangeable Al, P-sorption capacity, soil pH, pH-buffering capacity and soil moisture are strongly correlated to the extent of rock phosphate dissolution (Babare *et al.*, 1997). Kanabo and Gilkes (1987) and Bolan and Hedley (1990) found that increased soil pH decreases the dissolution of rock phosphate. There is general agreement that soil acidity influences the dissolution of P from rock phosphate: the dissolution increases with decreasing soil pH (Chu *et al.*, 1962; Hammond *et al.*, 1986; Kanabo and Gilkes, 1987; Bolan and Hedley, 1990). This could be explained by the composition of rock phosphate, which is mostly fluoroapatite. Fluoroapatite is dissolved in acid conditions to form monocalcium phosphate and other

soluble compounds (Chu *et al.*, 1962), it can be represented by tricalcium phosphate reaction and also explain the reaction of H_2PO_4^- ion in acid soils by the following equations.



The above equations describe reactions occurring in soil containing high Al^{3+} and Fe^{3+} content as H_2PO_4^- may be adsorbed by Al and Fe oxides or hydroxides. Then, general mechanisms for rock phosphate dissolution in acid soil can be illustrated as follows:



Chu *et al.* (1962) reported that rock phosphate dissolved well in soils at low pH and low free iron content. Chien *et al.* (1980) found that the dissolution of rock phosphate increases with increasing P-sorption capacity in soil. High P sorption capacity enhanced the dissolution of RP by reducing the P concentration in soil solution (Smyth and Sanchez, 1982; Syers and MacKay, 1986). The P-sorption capacity was highly correlated with the amount of reactive aluminum in the soils. The soils having high clay and free Fe_2O_3 contents have high P-sorption capacity (Smyth and Sanchez, 1982). In flooded acid sulfate soils, increases in the active Fe and Al led to increased P-sorption (Jugsujinda *et al.*, 1995).

2.3.2 Effect of rock phosphate properties on dissolution of RP.

Rock phosphate solubility or reactivity, fineness and porosity were the important factors controlling RP dissolution (Yost *et al.*, 2003). The solubility of RP can be measured by 2-percent citric, 2-percent formic acid and neutral ammonium citrate (McClellan and Gremillion, 1980; Chien, 2005, personal communication). The P solubility

is usually expressed as a percentage of total P (Van Kauwenbergh and McClellan, 2004). Diamond (1979) proposed a threefold RP reactivity classification system (low, medium and high reactivity) according to 2-percent citric, 2-percent formic acid and neutral ammonium citrate (Table 5). The system was based on International Fertilizer Development Center (IFDC) data for the relative effectiveness of extraction media and the results of a wide variety of laboratory and field trials. The example of RP materials and their reactivity was shown in Table 6.

Table 5 Classification of RP for direct application by solubility.

Rock reactivity	Solubility (%P of rock)		
	Neutral ammonium citrate	Citric acid	Formic acid
High	>2.35	>4.10	>5.67
Medium	1.39-1.96	2.92-3.66	3.05-4.71
Low	<1.17	<2.61	<2.53

Source: Diamond (1979)

Table 6 Rock phosphates and their reactivity.

Name	Country of origin	Reactivity
Araxa	Brazil	Low
Gafsa	Tunisia	High
Jordan	Jordan	Low
Kodjari	Burkina Faso	Medium
Maroccan	Morocco	High
North Carolina	North Carolina	High
Tahua	Niger	Medium
Taiba	Senegal	Low
Tilemsi	Mali	Medium

Source: Yost *et al.* (2003)

In New Zealand and Australia, the recommended extractability level for RP for permanent pasture is 30 percent of total P soluble in 2-percent citric acid, whereas in European Community it is 55 percent soluble in 2-percent formic acid for crop. The P solubility as extracted by 2-percent citric acid is presented as percentage of rock in order to represent content of soluble P and the percentage of total P is represent the quality of soluble P. The extractable P values should always be considered together with the total P of rock phosphate. Generally, increasing RP solubility, as measured by chemical extractions, increased the RP dissolution in the soils, many soil factors and their interactions have been shown to affect the agronomic effectiveness of RP (Truong, 2004). However, the RP solubility as measured by neutral ammonium citrate correlated very well with grain yield of flooded rice in Thailand (Engelsted *et al.*, 1974).

The reactivity of rock phosphates is a measure of the rate of dissolution of RP under standard laboratory conditions or in given soil and under given field conditions (Rajan *et al.*, 1996). The chemical properties that influence the reactivity of RP are phosphate crystal (apatite) structure and the presence of accessory materials, especially calcium carbonate. Increasing the substitution of carbonate for phosphate in crystal structure generally increases the reactivity of RP. This substitution results in decreased a cell dimensions and also in a weakening of apatite crystal structure (Chien *et al.*, 1977). The most reactive RP are those with a molar $\text{PO}_4\text{:CO}_3$ ratio of 3.5-5. The particle size of rock phosphate and associated minerals in rock phosphate can influence the solubility test. Rock phosphates containing free carbonates (calcite and dolomite) have been shown to increase soil pH and hence decreasing aluminum toxicity to plant. Grinding provides fresh particle surfaces, increases geometric surface area, and increases solubility measurements. However, increases in RP solubility rarely justify grinding to a size less than 100 mesh for agronomic use (Rogers *et al.*, 1953).

2.3.3 Methods of measuring the dissolution of rock phosphate.

The methods for measuring the dissolution of rock phosphate in soils were adapted from the fractionation procedures of inorganic P. Increasing Fe-P and Al-P fractions in the soils, where the rock phosphate is applied, can provide an estimate of P dissolved from rock phosphate, whereas the increases in Ca-P are considered as a measure

of unreacted RP (MacKay *et al.*, 1986). MacKay *et al.* (1986) measured the dissolution of rock phosphate using a dilute NaOH method. The dilute NaOH can remove non-occluded Al-P and Fe-P from a soil (Syers *et al.*, 1972) whereas other minerals in rock phosphate do not dissolve in this solution (MacKay *et al.*, 1986). Another indirect method to measure the dissolution of RP is measuring changes of extractable calcium after the RP has dissolved (Hughes and Gilkes, 1984). The change in extractable calcium can be determined by shaking soil amended with RP and the unamended soil for 1 hour in 2M barium chloride buffered at pH 8.1. The difference in extractable calcium between fertilized and unfertilized soil is a measure of the dissolution of RP.

2.3.4 A Model to describe the dissolution of rock phosphate.

The dissolution of rock phosphate increased with increasing time, subsequently, the rock phosphate dissolved in soils could be estimated using a mathematical model. MacKay *et al.* (1986) described the dissolution of rock phosphate by a modified Mitscherlich's equation

$$Y = A(1 - e^{-CX})$$

in which Y = amount of rock phosphate dissolved at time x,

A = asymptote,

C = curvature coefficient.

X = time

MacKay *et al.* (1986) proposed a stepwise regression between the A coefficient in a modified Mitscherlich's equation and soil properties, which was independent of soil type.

$$A = 176 - 156 \text{calcium saturation} + 0.97P \text{ sorption capacity} - 0.033 \text{calcium exchange capacity} + 6.67 \text{ organic carbon}.$$

The dissolution of rock phosphate could be predicted by estimating the A coefficient from soil properties and substitution of the A and C coefficients into a modified Mitscherlich's equation. The intercept from the prediction of rock phosphate dissolution in all soils using a modified Mitscherlich's equation started at the same origin. Sidibé-Diarra *et al.* (2004) have modified Mitscherlich's equation which was proposed by MacKay *et al.* (1986) to describe the dissolution of Tilemsi RP in West Africa soils. Using

this equation a non-zero intercept of RP dissolution was necessary. The equation was as follows:

$$Y = A - Be^{-c \cdot \text{time}}$$

where Y = amount of Tilemsi RP dissolved, measured by NaOH extraction at time; A = asymptote; B = difference between the asymptote and the intercept; and c = curvature coefficient. The A and B coefficients can be estimated as follows:

$$A = 78.16 + 30.61 \text{soil acidity} - 0.63 \text{ soil calcium saturation}$$

$$B = -16.58 - 21.74 \text{soil acidity} + 4.07 \text{ Effective cation exchange capacity of the soil}$$

The dissolution of Tilemsi RP can be predicted by substitution of soil properties into algorithms for the estimating the A and B coefficients. However, both Mitscherlich equations proposed by MacKay *et al.* (1986) and Sidibé-Diarra *et al.* (2004) were used to estimate a particular RP dissolution in soils. It would be more useful if the equations can be generalized to predict various RP materials in various soils.

2.4 Sorption of dissolved rock phosphate

Generally the P availability increases in flooded soil due to the chemical reduction of insoluble ferric iron to the more soluble ferrous iron and the concomitant release of occluded phosphate by reduction of hydrated ferric oxide coatings, and the hydrolysis of Al and Fe phosphate (Kyuma, 2004 and Ponnampereuma, 1972). Moreover, high levels of total carbon, extractable P, soil solution P, and soil pH tend to reduce P sorption under reduced conditions (Khalid *et al.*, 1979 and Sah *et al.*, 1989). Shahandeh *et al.* (1994) observed that soils with higher levels of oxalate-extractable Fe sorbed more P under reduced conditions. In some cases, however, P sorption in acid sulfate soils under reduced conditions was higher than under oxidized conditions due to increased soil pH (Jugsujinda *et al.*, 1995). The removal of exchangeable, amorphous and crystalline forms of Fe, Al and Mn reduced the P-sorption in an acid sulfate soil of Thailand (Jugsujinda *et al.*, 1995). Patrick and Khalid (1974) and Khalid *et al.* (1977) suggested that anaerobic soils release P into the soil solution when solution P is low and sorb P from soil solution when soils have high solution P. The greater surface area of the reduced ferrous

compounds in anaerobic soils results in more soil P being solubilized where solution P is low. However, more solution phosphate is sorbed where solution phosphate was high (Patrick and Khalid, 1974). Krairapanond *et al.* (1993) also found that the P sorption capacity in acid sulfate soil of Thailand increased with increasing soil pH and decreasing Eh. Iron oxide was the primary factor increasing P sorption and Al oxide seemed to play a secondary role on flooded acid sulfate soils (Jugsujinda *et al.*, 1995).

Bray 1 and Bray 2-extractable P are used for estimating the available P in acid soils. Bray 2 extractable P is widely used to estimate P availability in Thailand. Aquino and Hanson (1984) and Reddy *et al.* (1991) found that extractable P from Bray 1 and Bray 2 significantly correlated with the cumulative P of plant uptake after a long period of the rock phosphate application. However, these two soil tests in soils fertilized with RP can underestimate (Bray 1) or overestimate (Bray 2) P availability. There are two promising soil tests that show suitable results in soils fertilized with soluble P fertilizer as well as RP fertilizer (Fageria *et al.*, 1997). These are the iron-oxide impregnated paper strip test (Pi strip test) and the mixed anion and cation exchange resins. In both cases, the strip and resins act as a sink for P mobilized in a soil solution, and depend on the concentration of P mobilized in solution. Both tests simulate sorption of P by plant roots without disturbing the chemical equilibrium (Fageria *et al.*, 1997). The P in soils fertilized with RP measured by these two tests showed a good correlation with plant response (Menon and Chien, 1995). The preparation of Pi strips is sufficiently simple and inexpensive as to enable almost all laboratories to produce them as opposed to purchasing expensive anion and cation resin (Menon *et al.*, 1989).

3. Model and algorithms for predicting rock phosphate requirement for crops

Phosphorus fertilizer recommendation software has been developed to estimate the P fertilizer requirement for crop. The Phosphorus Decision Support System (PDSS) is designed to assist in the diagnosis and correction of P deficiencies in soil and crop, with emphasis on tropical conditions as developed by University of Hawaii. The P prediction model implemented in PDSS was the following frequently used equation for predicting P requirement (Chen *et al.*, 1997):

$$\text{Preq} = \frac{b_c - b_0}{10 \times a_2} \times a_1 \times d \times \text{appvalue} \quad (\text{eq. 1})$$

where Preq = the fertilizer P requirement

b_0 = the initial extractable P level in soil

b_c = the P critical level for certain crop

a_1 = the long term retention rate of extractable P

a_2 = the buffering coefficient (the increase in extractable P per unit added fertilizer P)

d = the incorporation depth of P fertilizer

appvalue = a coefficient dependent on application method

The Phosphorus Decision Support System uses the P buffer coefficient, the soil critical level of extractable P, and the current extractable P level to estimate crop P requirement (Yost *et al.*, 1992). However, PDSS was developed for water-soluble P fertilizer and primarily estimates P requirement based on P sorption by soils. Phosphorus critical level, extractable P in soil, and the P buffer coefficient must be developed from the same extractant.

3.1 Phosphorus critical level

Phosphorus critical level is the minimum P level that plant needs for optimum yield. The critical level for a crop differs with different soil and for a particular extractant. The P critical level varies with soil properties. Lins and Cox (1989) proposed using clay percentage to estimate P critical level for soybean. Bray 2-extractable P at 131-218 and 65-87 mg P kg⁻¹ appears to be necessary to secure a sufficient number of rice tillers in the cool and warm climate region, respectively (Kyuma, 2004). However, Dobermann and Fairhurst (2000) proposed P critical level for lowland rice in acid soils which was extracted by Bray 2, Bray 1 and Olsen extraction as 12-20, 7 and 5 mg P kg⁻¹, respectively.

3.2 Phosphorus buffer coefficient

Phosphorus buffer coefficient is an indicator of change in soil P concentration per unit of P applied (Lin *et al.*, 1985). Wright *et al.* (1992) estimated P buffering coefficients by relating the P buffering coefficient to soil pH and P retention as estimated by Saunder's method (1965). Hughes and Gilkes (1994) and Cox (1994) predicted P buffering coefficient by clay content in the soil.

3.3 Revised structure of Phosphorus Decision Support System for estimating RP for crops

Yost *et al.* (2003) developed the algorithms for predicting the rock phosphate requirement for crops in West African soils and linked the algorithm into the PDSS software. This algorithm can, however, only predict the amount of Tilemsi RP that is needed for upland crop in West African soils (Sidibé-Diarra *et al.*, 2004). Rock phosphate deposits in West Africa and in the rest of the World differ widely in their properties and the cropping systems are diverse. Software for predicting the rock phosphate requirement for crops will be very useful if the user can select the type of rock phosphate suited for their areas and crops. One of our untested hypotheses is that because of many factors involved in making a determination amount of RP to apply in the soils, RP has been slow to be adopted and fully utilized. The RP prediction is therefore, important to be studied.

Sidibé-Diarra *et al.* (2004) used the P critical level, equation for predicting RP dissolution (modified MacKay's equation) and the ratio between RP dissolution and extractable P of dissolved RP to estimate amount of Tilemsi RP added for crops. The effect of P sorption as represented by the P buffer coefficient was not included in PDSS which was revised by Sidibé-Diarra *et al.* (2004). In order to do so, the structure of the PDSS software (equation 1) was revised to estimate the RP requirement for rice by adding algorithms for predicting RP dissolution and sorption. The relationship between dissolution and extractability were proposed to estimate the amount of RP that should be added to supply nutrient P from the following equation:

$$\text{RP added} = \frac{P_c - P_{\text{extractant}}}{\text{PBC}_{\text{extractant}}} \times \frac{\Delta P_{\text{NaOH}}}{\Delta P_{\text{extractant}}} \times \frac{500}{A - B e^{-cx}} \times \frac{\text{Depth}}{10} \times D_b \quad (\text{eq. 2})$$

Where: RP added	= the amount of RP the should be added (kg P ha^{-1})
P_c	= critical P level for the soil, (mg P kg^{-1})
$P_{\text{extractant}}$	= extractable P in soils, (mg P kg^{-1})
$PBC_{\text{extractant}}$	= P buffering coefficient
$A\text{-Be}^{-cx}$	= amount of $\Delta P\text{-NaOH}$ in soil at time x for the specific soil, (mg P kg^{-1})
Depth	= soil depth (cm)
D_b	= bulk density (g cm^{-3})

The procedure for estimating RP for rice in acid sulfate soils using equation 2 can be explained as follows:

(i.) Diagnosis of P deficiency and estimate the P requirement: The P deficiency can be diagnosed by the difference between the extractable P in soil and P critical level. A positive value for extractable P in soil subtracted from the P critical level indicates that P for the crops is inadequate and a P application is needed. The size of this difference is an estimate of the amount of P that should be applied. The availability of P fertilizer after application to the soil usually decreases due to the effect of P sorption by soil properties- the P buffer coefficient is developed to estimate this effect. Then, the P buffer coefficient which reflects the availability of P fertilizer after application to the soils will be added to estimate the P requirement for rice. This P requirement estimate is, therefore, based on extractable P, P critical level, and P buffer coefficient using the same method as the original PDSS. In this study, two methods of extractable P were used; Bray 2-extractable P and iron oxide impregnated paper strips.

(ii.) Converting the extractable P requirement into a NaOH-extractable P requirement. The dissolution of RP in soils is a critical factor to control the effectiveness of direct application of RP. The prediction of crop RP requirement must consider the RP dissolution that will occur when the RP is added to the soil. The dissolution of RP in acid sulfate soils was determined using dilute NaOH. Then, the extractable P requirement (assuming soluble P) for the crop was converted to the NaOH-extractable P requirement

using the ratio between RP dissolution and extractable P of RP dissolved ($\frac{\Delta P_{\text{NaOH}}}{\Delta P_{\text{extractant}}}$).

This ratio is proposed to represent the effect of P sorption by the soil after RP is added and dissolved in the soil.

(iii.) Estimating RP for crop based on RP dissolution. The amounts of rock phosphate for crops are therefore based on the predicted dissolution of RP in the specific soil. The amount of dissolved RP in soils estimated by modified Mitscherlich equation ($Y = A - Be^{-cx}$). The coefficient A, B and C in modified Mitscherlich equation are estimated using the specific soil properties and RP properties that affect the RP dissolution. The algorithm thus estimates the A, B and C coefficients based on the solubility of RP materials incubated with acid sulfate soils at the rate of 500 kg ha⁻¹. Then, the RP requirements for crops can be estimated based on the rock phosphate dissolution model and a coefficient dependent on the application method.

MATERIALS AND METHODS

This study consists of six experiments:

1. Experiment 1 A study of P buffer coefficients, which are used in PDSS to estimate RP requirement for rice cultivation in acid sulfate soils.

2. Experiment 2 A study of P critical levels, which are used in PDSS to estimate RP requirements for rice cultivation in acid sulfate soils.

3. Experiment 3 Predicting the individual dissolution of rock phosphates in flooded acid sulfate soils.

4. Experiment 4 The incubation of various rock phosphates with representative acid sulfate soils of Thailand. This study aimed to quantify the dissolution and to develop a model for predicting rock phosphate dissolution in flooded acid sulfate soils. This work is an effort to generalize the model of dissolution to other rock phosphates in other acid sulfate soils.

5. Experiment 5 The incubation and evaluation of the availability of dissolved rock phosphates in flooded acid sulfate soils of Thailand.

6. Experiment 6 Field testing of rock phosphate predictions for rice cultivation in two acid sulfate soils.

1. Experiment 1 A study of phosphorus buffer coefficients which are used in PDSS to estimate RP requirement for rice cultivation in acid sulfate soils.

1.1 Soil and analytical methods

Six acid sulfate soils, representing the most important acid sulfate soils in Thailand, were selected for these experiments (Table 7). The six acid sulfate soils namely, Rangsit very acid (Rsa); Ongkharak (Ok); Rangsit (Rs); and Sena (Se), are the soil series in Sulfaqueptic Dystraquerts great group while the Mahaphot (Ma) and Chachoengsao (Cc) are the soil series in the Ustic Dystraquerts great group. The Sena soil collected for this experiment was, however, more acidic than the typical Se soil series (Attanandana, 2003).

All the surface (0-10 cm) soils were collected from fields where rice was recently grown, air-dried, sieved (<2 mm) and thoroughly mixed. Chemical characteristics of the soils are summarized in Table 7. Soil pH was determined by glass electrode (soil: water ratio of 1:1), organic matter was determined by the method of Walkley and Black (Nelson and Sommers, 1996). Exchangeable cations were extracted with ammonium acetate (pH 7) and the contents were determined by atomic absorption spectrophotometer. Extractable aluminum was analyzed by three methods, i.e. 1) ammonium oxalate, pH 3 (Jackson *et al.*, 1986) 2) 1 M KCl extractions (Barnhisal and Bertsch, 1982) and 3) dithionite extraction (Asami and Kumada, 1959). Extractable Fe was measured by two methods: ammonium oxalate, pH 3 (Jackson *et al.*, 1986), and dithionite (Asami and Kumada, 1959). Phosphorus was extracted by Bray 1, Bray 2 (Bray and Kurtz, 1945), and ammonium oxalate, pH 3 (Guo and Yost, 1999). Effective cation exchange capacity (ECEC) was the summation of exchangeable bases and KCl-extractable Al (USDA, 1995). Cation exchange capacity (CEC) was measured by the ammonium acetate pH 7 method (Chapman, 1965). Phosphorus retention was measured by shaking five grams of air-dry soils with 25 ml of sodium acetate-acetic acid buffer at pH 4.6 and 0.032 M KH_2PO_4 for 24 hours and then determining the remaining P by the vanado-molybdo-phosphoric yellow color (Saunders, 1965). The percentage of P retention was calculated by subtracting the amount of P remaining from the amount of P added and then dividing by the amount of P added.

Table 7 Chemical properties of the selected acid sulfate soils from central Thailand.

Soil properties	Soil series					
	Rangsit very acid (Rsa)	Ongkharak (Ok)	Rangsit (Rs)	Sena (Se)	Mahaphot (Ma)	Chachoengsao (Cc)
pH _{water} (1:1)	3.76	3.69	4.04	3.38	4.45	4.16
Organic matter (g kg ⁻¹)	45.3	29.9	12.5	19.6	51.7	33.9
Extractable P (mg kg ⁻¹)†	1.90	0.43	1.03	1.38	0.48	0.71
Extractable P (mg kg ⁻¹)‡	7.64	3.67	12.1	9.67	5.85	12.4
Extractable P (mg kg ⁻¹)‡‡	2.00	1.38	3.27	1.69	2.95	2.31
Extractable P (mg kg ⁻¹)§	57.4	25.3	65.1	43.0	61.1	134
Extractable Al (g kg ⁻¹)§	4.10	2.78	1.24	1.80	2.42	1.17
Extractable Al (g kg ⁻¹)¶	1.03	0.92	0.22	0.91	0.21	0.14
Extractable Al (g kg ⁻¹)#	2.83	2.20	0.94	1.69	1.03	0.52
Al saturation (%)	72.9	70.1	17.2	50.3	20.2	12.2
Extractable Fe (g kg ⁻¹)§	3.69	7.20	7.10	8.31	10.8	11.4
Extractable Fe (g kg ⁻¹) #	4.48	11.3	8.95	13.7	15.1	13.3
Extractable Ca (g kg ⁻¹)††	0.20	0.15	0.72	0.86	0.97	0.70
ECEC (cmol _c kg ⁻¹)	15.6	14.5	14.0	20.2	11.2	12.8
CEC (cmol _c kg ⁻¹)	34.5	30.3	29.9	30.7	38.8	43.3
P retention (%)	56.7	75.0	62.0	60.3	50.0	68.0

Note: †Bray 1 extraction ‡Bray 2 extraction ‡‡modified Pi strip test
 §Ammonium oxalate extraction ¶1M KCl extraction
 #Dithionite extraction ††1M Ammonium acetate pH 7

1.2 Incubation study

Ten gram samples of six acid sulfate soils (Table 7) were amended with potassium hydrogen phosphate (KH₂PO₄) at the rate of 0, 25, 50, 100, 200, and 400 mg P kg⁻¹, respectively. The soil mixtures were flooded with 25 ml of distilled water and incubated at 30°C for 2 weeks. The soil mixtures were extracted with Bray 1 and Bray 2 extracting solutions. The concentration of Bray 1 was 0.025M HCl and 0.03M NH₄F but the soil in this study was flooded with water so solutions were prepared such that the final

Bray 1 concentration matched that of the Bray 1 method. Bray 2-extractable P was prepared in the same way as the Bray 1 extraction.

A new method for testing available P in soil, modified iron oxide impregnated strip test (modified Pi strip test), was also employed for the PBC study. The iron oxide impregnated strip test was suited to measure available P in soils fertilized with both soluble P fertilizer and RP. It simulates sorption of P by plant roots without disturbing the chemical equilibrium (Fageria *et al.*, 1997). The Pi strip test provides a rigorous quantification of short-term desorbable P (Van der Zee *et al.*, 1987). One gram samples of six acid sulfate soils (Table 7) were amended with potassium hydrogen phosphate (KH_2PO_4) at the rate of 0, 25, 50, 100, 200, and 400 mg P kg⁻¹, respectively. The soil mixtures were flooded with 30 ml of distilled water and incubated at 30°C for 2 weeks. The method for determining extractable P by modified Pi strip test can be explained as follows:

Preparation of Pi strip. Hardened, ash-free, 7-cm-diam. filter paper circles (Whatman no. 542) were used to prepare Pi strips. The filter papers were immersed in 0.65 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ containing 50 ml of conc. HCl overnight (Meyer *et al.*, 1997). The wet papers were allowed to drip dry at room temperature for a few hours. The dry papers were placed above ammonia solution (1:1v/v) (Menon *et al.*, 1989). The ammonia vapor reacted with Fe chloride, converting it into iron oxide and color of paper changed from yellow to brown. The intensity of the color depended on the amount of iron chloride.

Extraction and analysis. At 2 weeks after incubation, one gram of soil mixtures and water in screw cap tubes was added to 100 ml wide-mouthed plastic bottom. One filter paper coated with iron oxide was cut to two semicircles. A semicircle was placed between two mesh polyethylene screens, held by plastic clip and melting the screen edges with a flame. One of the paper-polyethylene screens was inserted into a wide-mouthed plastic bottom beaker (Meyer *et al.*, 1997). Normally the soil sample and modified Pi strip was shaken in 40 ml. of 0.02 M KCl solution for 16 h. But the soil in this study was flooded with water so solutions were prepared such that the final KCl

concentration was 0.02 M KCl. The Pi strip was taken out and washed free of soil and P sorbed was dissolved in 40 ml of 0.1M H₂SO₄ (Habib *et al.*, 1998).

The P content in all extracted solutions was determined using the method of Murphy and Riley (1962).

1.3 Statistical analysis.

Phosphorus buffer coefficients were estimated from the slope of the linear regression of extractable soil P regressed against added P. Stepwise regression procedure in Statistical Analysis System (SAS) was used to regress the P buffering coefficient on soil properties in order to determine which soil properties affected the P buffering coefficient.

2. Experiment 2 A study of phosphorus critical levels which are used in PDSS to estimate RP requirements for rice cultivation in acid sulfate soils.

2.1 Soil and phosphorus fertilizer

An Ongkharak soil (Sulfaqueptic Dystraquert) which was collected at Ongkharak district, Nakhonnayok province was used for this study. The P critical level in this study was developed with a field study using two types of P fertilizer i.e. soluble P fertilizer (triple superphosphate: TSP (0-46-0)) and RP (Kanchanaburi and Gafsa RP).

2.1.1 Soil analyses

The chemical characteristics of the Ongkharak soil are summarized in Table 8. Soil pH was determined by glass electrode (soil: water ratio of 1:1). Phosphorus was extracted by Bray 2 (Bray and Kurtz, 1945) and modified Pi strip test (Menon *et al.*, 1989; Meyer *et al.*, 1997 and Habib *et al.*, 1998). The method of modified Pi strip test was explained in Materials and Methods of experiment 2. Extractable aluminum was analyzed by 1 M KCl extractions (Barnhisal and Bertsch, 1982) and the ammonium oxalate extraction, pH 3 (Jackson *et al.*, 1986). Extractable Fe was measured by ammonium

oxalate extraction, pH 3 (Jackson *et al.*, 1986). Phosphorus retention was measured by shaking five grams of air-dry soils with 25 ml of sodium acetate-acetic acid buffer pH 4.6 and 0.032 M KH_2PO_4 for 24 hours and then the P remaining was determined by the vanado-molybdo-phosphoric yellow color (Saunders, 1965). Extractable potassium was extracted by 1M ammonium acetate pH 7.

Table 8 Chemical properties of the Ongkharak soil.

Properties	Ongkharak soil
pH _{water(1:1)}	3.90
Extractable P (mg kg ⁻¹) [†]	5.80
Extractable P (mg kg ⁻¹) [‡]	2.30
Extractable Al (g kg ⁻¹) [#]	0.65
Extractable Al (g kg ⁻¹) [§]	3.50
Extractable Fe (mg kg ⁻¹) [§]	5.50
Phosphorus retention (%)	76.0
Extractable potassium (mg kg ⁻¹) [¶]	180

Note: [†] Bray 2 extraction

[‡]Modified Pi strip test

[#] 1M KCl extraction

[§]Ammonium oxalate extraction

[¶]1M Ammonium acetate pH 7

2.1.2 Rock phosphate and analytical method

Two RP materials were used in this study; Kanchanaburi RP and Gafsa RP. A local rock phosphate from Kanchanaburi province and Gafsa rock phosphate from Tunisia were high reactivity rock phosphates (Table 9). These two RP materials were different samples from the KRP and Gafsa RPs used in experiments 3, 4 and 5. Total P of the rock phosphate was measured by the method of AOAC (1984). Phosphorus solubility of the two RP materials was measured by two methods: two extractions with 2-percent citric acid and two extractions with neutral ammonium citrate (AOAC, 1984). The calcium carbonate equivalent (CCE) was measured by digesting rock phosphates with 0.50 M HCl and

back titrating with 0.25 M NaOH to pH 5 (Sikora, 2002). The particle size distribution analysis was carried out using a 0.15 mm sieve.

2.2 Field study

The field experiment was performed to determine the P critical level of Ongkharak soil. Two types of phosphate fertilizer were used in this study. Phosphorus fertilizer was applied as triple superphosphates (0-46-0) 20 days after rice seeding, at the rates of 0, 8.2, 16.4, 24.6, 32.8 and 40.9 kg P ha⁻¹ in randomized complete block design with four replications. The individual plot size was 4 by 6 m. Suphanburi 1 rice seed was broadcast at the rate of 156 kg seeds ha⁻¹. Nitrogen fertilizer (urea, 46-0-0) was applied at the rate of 62.5 kg N ha⁻¹ as basal dressing and 62.5 kg N ha⁻¹ as top dressing at panicle initiation (PI) (55 days after broadcasting). The rice plant was harvested at maturity (116 days after broadcasting), from a harvest area of 3 by 5 m.

Kanchanaburi RP and Gafsa RP were applied and incorporated at the rates of 0, 1270, 2541, 5083 kg KRP ha⁻¹ and 518, 1037, 2075 kg Gafsa RP ha⁻¹, respectively at the same time of soil preparation. The individual plot size was 8 by 6 m. The design of the experiment was randomized complete block with four replications. Suphanburi 1 rice variety and nitrogen fertilizer were applied at the same rate and time as applied in plot where TSP was applied. The rice plant was harvested at maturity, same time as harvested in plot where TSP was applied, the harvesting area of 5 by 5 m.

Table 9 Chemical characteristics of Kanchanaburi and Gafsa rock phosphates.

Properties	Rock phosphates	
	Kanchanaburi	Gafsa
Total P (%)	7.67	11.97
2-percent citric acid (%P of rock), second extraction	3.78	4.55
Neutral ammonium citrate (%P), second extraction	1.58	2.34
Calcium carbonate equivalent (%)	62.0	52.0
Particle size passed through 100 meshes (%)	84.2	21.3
2-percent citric acid (% of total P), second extraction	49.3	38.0

2.2.1 Plant and soil data collection.

Grain and straw weights were recorded including the number of grains per panicle, percentage of unfilled grains and 1000-grain weight. The soil in each plot which received TSP was collected after harvest and extracted with Bray 2-extractable P and the modified Pi strip test. The soil in each plot which received two RP materials was collected at 4 weeks after RP application because at 4 weeks after RP application is the predicted maximum dissolution of RP. The P content in the extracted solutions was determined using the method of Murphy and Riley (1962).

2.2.2 Statistical analysis.

The effect of both types of P fertilizer application on grain yield and yield components was analyzed using analysis of variance (ANOVA). Means were compared using the Duncan's Multiple Range Test (DMRT) method in the SAS. The curves between rice yield and initial extractable P after TSP was applied indicated the minimum P level in acid sulfate soils that rice needed. The initial extractable P was estimated from Cox's model by the following equation (Cox *et al.*, 1981):

$$X = X_{eq} + (X_{init} - X_{eq})e^{(-kT)} \quad (\text{eq. 3})$$

Where X = extractable nutrient level after harvest, kg ha⁻¹

X_{eq} = equilibrium level of X, kg ha^{-1} . X_{eq} is a minimum value for soil test P and can be estimated if the soil test level is reduced to point where yields are nil (Cox, 1994).

X_{init} = initial level of X, kg ha^{-1}

k = loss constant, year^{-1}

T = time, years

The X_{eq} of Ok soil as extracted by Bray 2-extraction and modified Pi strip test was estimated using the extractable P in unfertilized plots after the 2nd rice crop harvest. The k value of Ok soil as extracted by Bray 2-extraction and modified Pi strip test was estimated using the SAS program (PROC NLIN). The initial extractable P in Ok soil, plots which TSP was applied, as extracted by Bray 2-extraction and modified Pi strip test were predicted. The grain yield was then regressed on predicted initial extractable P by the two methods using the Linear Response Plateau method (LRP) (Anderson and Nelson, 1975) according to the following equation:

$$Y = a + b \cdot \min(x, \text{node}) \quad (\text{eq. 4})$$

Where

Y = crop yield

a = the intercept

b = the slope of the linear portion

node = the intersection

x = extractable nutrient in soil

The node value in equation 4 indicated the minimum initial extractable-P level necessary for maximum crop yield (critical level) in Ok soil fertilized with TSP.

The P critical level in Ok soil fertilized with RP was also estimated. The grain yield was also regressed on extractable P, Bray 2-extraction and modified Pi strip test, in Ok at 4 weeks after applied RP using the LRP method (Anderson and Nelson, 1975).

3. Experiment 3: Predicting the individual dissolution of rock phosphate in flooded acid sulfate soils

3.1 Soil and analytical methods.

Acid sulfate soils in this experiment were the same as those used in experiment 1 (Table 7).

3.2 Rock phosphates and analytical methods

There were three rock phosphates used in this study namely, Kanchanaburi RP; Gafsa RP; and Kanchanaburi RP mixed with soluble phosphate fertilizer (KRPS). Kanchanaburi RP from Thailand and Gafsa RP from Tunisia were the high reactivity rock phosphates. Kanchanaburi RP mixed with soluble phosphate fertilizer is a mixture of Kanchanaburi RP and mono ammonium phosphate fertilizer (MAP) (16-20-0) at the ratio of 2:1 by weight. Kanchanaburi rock phosphate was mixed with mono ammonium phosphate fertilizer by fertilizer manufacturers to increase total P.

Total P, total Ca and water soluble P of the rock phosphate were measured by the method of AOAC (1984) and Official Methods of Analysis of Fertilizer (The National Institute of Agricultural Sciences Ministry of Agriculture, Forestry, and Fisheries, Japan, 1982) (Table 10). Phosphorus solubility of the four RP materials was measured by three methods: two extractions with 2-percent citric acid, an extraction with 2-percent formic and two extractions with neutral ammonium citrate. The analyses of solubility of rock phosphates in Table 10 were performed by IFDC (courtesy U. Singh). The calcium carbonate equivalent (CCE) was measured by digesting rock phosphates with 0.50 M HCl and back titrating with 0.25 M NaOH to pH 5 (Sikora, 2002). Titration to pH 5.0 was an adaptation suggested by Sikora (2002), to improve the accuracy of estimating the CCE of rock phosphates. The particle size distribution analysis was carried out using a 0.15 mm sieve (100 mesh).

Table 10 Selected chemical and physical characteristics of Kanchanaburi and Gafsa rock phosphates.

Properties	Rock phosphates		
	Kanchanaburi	Kanchanaburi containing soluble phosphate	Gafsa
Total P (% of rock)	4.45	10.1	12.5
Water soluble P (%)	0.01	0.71	0.006
Neutral ammonium citrate, second extraction (%P of rock) †	1.48	2.07	2.26
Citric acid, second extraction (%P of rock) †	2.05	3.75	4.36
Formic acid, first extraction (%P of rock) †	1.92	5.19	7.97
NaOH-Extractable P (% of rock)	0.006	1.40	0.002
Total Ca (%)	25.6	19.5	33.4
CaCO ₃ (%)	34.5	23.0	2.10
Particle size (%) (<100 mesh)	64.0	82.2	19.2
Calcium Carbonate Equivalent (%)	62.5	42.0	52.0

Note: † Analyzed by International Fertilizer Development Center (courtesy U. Singh).

3.3 Incubation study of rock phosphate dissolution

The unground rock phosphate materials were added to the six acid sulfate soils at the rate of 0 and 500 mg total P kg⁻¹ with 3 replications. Screw cap tubes containing one gram of the soil-RP mixture were flooded with 30 ml distilled water and incubated at 30 °C for 56 days. The soil mixtures were sampled after 0, 3, 5, 7, 14, 28, 42, and 56 days of incubation for determining the dissolution of RP materials. The dissolution of the RP materials was estimated by extracting the soil with 0.5M NaOH at a soil to solution ratio of 1: 100 for 16 hours after an hour of pre-washing with 1M NaCl (MacKay *et al.*, 1986).

The prewashing with 1M NaCl was done by adding ten milliliters of 4M NaCl to the soil mixture which was flooded with 30 ml of distilled water (NaCl concentration was 1M NaCl and soil/water ratio was 1:40). The differences in P levels (ΔP) from the dilute NaOH extraction between RP-treated and RP-untreated samples were used as an estimate of RP dissolution (ΔP_{NaOH}). The P content in the extracted solutions was determined using the method of Murphy and Riley (1962). Ten grams of soil from the treatments were flooded with 25 ml distilled water and incubated at 30 °C for 56 days. The soil-rock phosphate mixtures were sampled at 0, 3, 5, 7, 14, 28, 42, and 56 days of incubation for measuring the soil pH during those incubation periods (soil: water ratio of 1:2.5).

3.4 Incubation study of rock phosphate sorption

Screw cap tubes containing ten grams of the soil mixtures for each sampling time were flooded with 25 ml distilled water. The soil mixtures were incubated and sampled under the same conditions and times as in the dissolution study. The soils were extracted with Bray 1 and 2 solutions to estimate the sorption of dissolved rock phosphates (Bray and Kurtz, 1945). The concentration of Bray 1 is 0.025M HCl and 0.03 M HN_4F but the soil in this study was flooded with water so solutions were prepared such that the final Bray 1 concentration matched that of the Bray 1 method. Bray 2-extractable P was prepared in the same way as the Bray 1 extraction so that the final concentration was that specified by the Bray 2 procedure. The soil mixtures were extracted with Bray 2 at soil and solution ratio 1:10 for one minute. The P content in the extracted solutions was determined using the method of Murphy and Riley (1962).

The differences in P level from the Bray 1 or 2 from soil mixtures with and without RP were used as an estimate of RP sorption. The pH (soil and water ratio 1:2.5) was measured during the incubation period. Bray 2-extractions are used widely in Thailand because they give highly significant correlations with crop response. However, the high acidity in this extractant can dissolve RP giving an overestimate.

3.5 Statistical analysis and model development

The changes in $\Delta\text{NaOH-P}$ over time were analyzed for significant differences from previous points in time using repeated measures in SAS. The differences between of least square means were computed using Tukey-Kramer adjustment method.

Changes in NaOH-P over time were modeled using a Mitscherlich equation (Sidibé-Diarra *et al.*, 2004) as follows:

$$Y (\Delta\text{NaOH-P}) = A - Be^{-cx} \quad (\text{eq. 5})$$

Where $Y (\Delta\text{NaOH-P}) = (\text{amount of NaOH-P in the soils} + \text{rock phosphate}) - \text{NaOH-P}$
in soil alone, mg P kg^{-1}

$A =$ maximum dissolution of the added phosphate, mg P kg^{-1}

$B =$ the difference between asymptote and intercept, mg P kg^{-1} , if $B=A$
then the Y intercept $= 0$

$C =$ curvature coefficient

$X =$ time (days)

The changes in $\Delta\text{P_NaOH}$ in KRP, Gafsa RP and KRPS over time in acid sulfate soils were used to fit the Mitscherlich equation (eq.5) for each soil using the SAS program (PROC NLIN) (SAS, 1985). The residual mean square was computed to indicate the goodness of fit. The estimated coefficient A from the Mitscherlich fit represents the maximum rock phosphate dissolution and was correlated with properties of six acid sulfate soils to explain the relationship between rock phosphate dissolution and soil properties.

The coefficients A , B and C resulting from fitting the Mitscherlich equation (5) to the of six acid sulfate soils were then regressed on soil properties to determine which soil properties affected the coefficients, using a stepwise regression procedure in SAS. Finally, the dissolution of KRP, Gafsa and KRPS in soil was estimated by substituting the predicted coefficients A , B and C into equation (5) for each of the six soils. The residual mean square was computed to indicate the goodness of fit.

4. Experiment 4 Incubation of various rock phosphates with representative acid sulfate soils of Thailand.

4.1 Soil and rock phosphate.

Acid sulfate soils in this experiment were the same as those used in experiment 1 (Table 7).

4.2 Rock phosphates and analytical method

There were four rock phosphates used in this study namely, Kanchanaburi RP; Gafsa RP; Tilemsi RP; and Taiba RP (Table 11). Kanchanaburi RP from Thailand and Gafsa RP from Tunisia were the high reactivity rock phosphates. Tilemsi and Taiba RP from Mali and Senegal were medium and low reactivity rock phosphates, respectively.

Total P, total Ca and water soluble P contents of the rock phosphate were measured by the method of AOAC (1984) and Official Methods of Analysis of Fertilizer (The National Institute of Agricultural Sciences Ministry of Agriculture, Forestry, and Fisheries, Japan, 1982) (Table 11). The solubility of P in the four RP materials was measured by three methods: two extractions with 2-percent citric acid, an extraction with 2-percent formic and two extractions with neutral ammonium citrate. The analyses of solubility of rock phosphates in Table 11 were performed by IFDC (courtesy U. Singh). The P solubility as determined by 2-percent citric acid is presented as percentage of rock in order to represent content of soluble P based on the percentage of total P in order to represent the quality of the P in the RP. The calcium carbonate equivalent (CCE) was measured by digesting rock phosphates with 0.50 M HCl and back titrating with 0.25 M NaOH to pH 5 (Sikora, 2002). Titration to pH 5.0 was an adaptation suggested by Sikora (2002), to improve the accuracy of estimating the CCE of rock phosphates. The particle size distribution analysis was carried out using a 0.15 mm sieve (100 mesh).

Table 11 Selected chemical and physical characteristics of rock phosphates.

Properties	Rock phosphates			
	Kanchanaburi	Gafsa	Tilemsi	Taiba
Total P (% of rock)	4.45	12.5	12.1	15.9
Neutral ammonium citrate, second extraction (%P of rock)†	1.48	2.26	1.87	2.23
2-percent citric acid, second extraction (%P of rock) †	2.05	4.36	4.88	4.23
2-percent formic acid, first extraction (%P of rock) †	1.92	7.97	5.19	6.72
Water soluble P (%P)	0.01	0.006	0.005	0.001
Calcium Carbonate Equivalent (%)	62.5	52.0	41.7	46.3
Total Ca (%)	25.6	33.4	30.5	35.0
Particle size (%) (<100 mesh)	64.0	19.2	96.7	48.5
2-percent citric acid, second extraction (%P of total P)	46.0	34.8	40.3	26.6

Note: †Analyzed by International Fertilizer Development Center (courtesy U. Singh).

4.3 Incubation study of rock phosphate dissolution

The unground rock phosphate materials were added to the six acid sulfate soils at the rate of 0 and 500 mg total P kg⁻¹ with 3 replications. Screw cap tubes containing one gram of the soil-RP mixture were flooded with 30 ml distilled water and incubated at 30 °C for 56 days. The soil mixtures were sampled after 0, 3, 5, 7, 14, 28, 42, and 56 days of incubation for determining the dissolution of RP materials. The dissolution of the RP materials was estimated by extracting the soil with 0.5M NaOH at a soil to solution ratio of 1: 100 for 16 hours after an hour of pre-washing with 1M NaCl (MacKay *et al.*, 1986). The prewashing with 1M NaCl was done by adding ten milliliters of 4M NaCl to the soil mixture which was flooded with 30 ml distilled water (NaCl concentration was 1M NaCl and soil/water ratio was 1:40). The differences in P levels (Δ P) from the dilute NaOH extraction between RP-treated and RP-untreated samples were used as an estimate of RP

dissolution (ΔP_{NaOH}). The P content in the extracted solutions was determined using the method of Murphy and Riley (1962). Ten grams of soil from the treatments were flooded with 25 ml distilled water and incubated at 30 °C for 56 days. The soil-rock phosphate mixtures were sampled at 0, 3, 5, 7, 14, 28, 42, and 56 days of incubation for measuring the soil pH during those incubation periods (soil: water ratio of 1:2.5).

4.4 Statistical Analysis and model development

The changes in NaOH-P over time were modelled to describe the dissolution of RPs in flooded acid sulfate soils using a Mitscherlich equation which was described in experiment 3 (equation 5).

The Statistical Analysis System program (PROC NLIN) was used to estimate the coefficients A, B and C of the Mitscherlich equations describing the dissolution of the four RPs in six acid sulfate soils (SAS, 1985). Coefficients A, B and C were correlated with soil and RP properties to determine the correlation between RP dissolution with soil and RP properties, using SAS program (PROC CORR). Coefficients A, B and C were then regressed on soil and RP properties to determine which property affected the coefficient, using stepwise regression procedure in SAS (PROC STEPWISE). All soil and RP properties which were highly correlated with A, B and C coefficients, were candidate variables in the stepwise regression procedure. Variables with the highest correlation between soil or RP properties and three coefficients, evaluated by adj. R^2 , were first selected and added to the model step by step (i.e. forward selection based on correlation).

5. Experiment 5: Incubation evaluation of the availability of dissolved rock phosphate in flooded acid sulfate soils.

5.1 Acid sulfate soils and rock phosphates

Acid sulfate soils and rock phosphates in this experiment were the same as those used in experiments 1 and 4, respectively (Table 7 and 11).

5.2 Incubation study

The unground rock phosphate materials were added to the six acid sulfate soils at the rate of 0 and 500 mg total P kg⁻¹ with 3 replications. Screw cap tubes containing ten grams of the soil mixtures for each sampling time were flooded with 25 ml distilled water. The soil mixtures were incubated and sampled under the same conditions and times as in the dissolution study. The soils were extracted with Bray 1 and Bray 2 solutions to estimate the availability of dissolved rock phosphates (Bray and Kurtz, 1945). The method of P extraction by Bray 1 and Bray 2 were similar to the method which used in study of P buffering coefficient. The differences in P level from the Bray 1 or Bray 2 from soil mixtures with and without RP were used to estimate availability of dissolved RP ($\Delta P_{\text{extractant}}$). Bray 2-extractions are used widely in Thailand because of the highly significant correlations of extractable P with crop response. However, the high acidity in this extracting solution can dissolve unavailable RP and likely resulting in the overestimation.

5.3 Sorption of dissolved rock phosphate

The ratio between portion of dissolved RP (ΔP_{NaOH}) and extractable Bray 1 or Bray 2 ($\Delta P_{\text{extractant}}$) which is a variable in PDSS as calculated. The ratio of $\frac{\Delta P_{\text{NaOH}}}{\Delta P_{\text{extractant}}}$ was plotted with time of incubation.

6. Experiment 6: Field testing of rock phosphate predictions for rice cultivation in two acid sulfate soils.

6.1 Acid sulfate soils and rock phosphates materials

The experiment was conducted on the actual acid sulfate soils namely; Rangsit (Sulfaqueptic Dystraquerts), and Ongkharak (Sulfaqueptic Dystraquerts) at Ongkharak district, Nakhonnayok province. This experiment was conducted on Ongkharak soil at the same site as in experiment 2. The chemical properties of Ongkharak and Rangsit soils were

shown in Table 8 and 12, respectively. The analytical methods of chemical properties of Rangsit soil were similar to the methods as used for Ongkharak soil.

Two high reactivity RP materials, KRP and Gafsa RP, were used in this experiment. Two rock phosphates were the samples from the KRP and Gafsa RPs used in experiments 2 (Table 9).

6.2 Field experiments

Two field experiments were conducted to test the RP prediction rate for Rangsit and Ongkharak soils. The prediction rates of two RP materials were calculated using the revised structure of PDSS for RP (equation 2). The parameters required in the PDSS structure such as P critical level, P buffering coefficient, algorithms for predicting RP dissolution and ratio between dissolution and availability of RP were based on results from experiments 1-5. The RP materials were applied at the rates of 0, $\frac{1}{2}$, 1 and 2 times of the predicted rate. The design of the experiment was randomized complete block with four replications. The individual plot size was 6 by 6 m for the Rs soil and 8 by 6 m for the Ok soil. Nitrogen fertilizer (urea, 46-0-0) was applied at the rate of 62.5 kg N ha⁻¹ as basal dressing and 62.5 kg N ha⁻¹ as topdressing at panicle initiation stage of rice. Rock phosphates were broadcast and incorporated into the soils during land preparation. Suphanburi 1, a non photoperiod sensitive rice variety with 120-125 days duration was planted as broadcast at the rate of 156 kg ha⁻¹ after RP application. The rice plant was harvested at maturity from a harvest area of 5 by 5 m.

The third experiment was conducted on an Ongkharak soil to examine the residual effect of RP applications. The 8 by 6 m plots of the previous experiment were divided into 2 individual plot sizes of 4 by 6 m for residual effect of RP in this experiment. The RP materials were re-applied at the same rate as the first crop in the first individual plots while there was no RP applied in the second individual plots. Nitrogen fertilizer applications and the rice variety were the same as in the first crop. The rice plant was harvested at maturity with the harvesting area of 3 by 5 m.

Table 12 Chemical properties of the Rangsit soil.

Properties	Rangsit soil
pH _{water(1:1)}	4.07
Extractable P (mg kg ⁻¹) [†]	14.0
Extractable P (mg kg ⁻¹) [‡]	4.90
Extractable Al (g kg ⁻¹) [#]	0.18
Extractable Al (g kg ⁻¹) [§]	1.78
Extractable Fe (mg kg ⁻¹) [§]	6.40
Phosphorus retention (%)	68.0
Extractable potassium (mg kg ⁻¹) [¶]	230

Note: [†] Bray 2 extraction[‡]Modified Pi strip test[#] 1M KCl extraction[§]Ammonium oxalate extraction[¶]1M Ammonium acetate pH 7

6.3 Plant and soil data collection.

Grain and straw weight were recorded including the number of grains per panicle, percentage of unfilled grains and 1000-grain weight. Grain and straw were oven-dried at 70 °C for 48 h to determine the dry weight. Samples of grain and straw were digested in a mixture of 1:1 (v/v) conc. HNO₃ and conc. HClO₄ (Jones, 2001). Phosphorus content in grain and straw were determined by the vanado-molybdate colorimetric method (Jones, 2001).

Soil in each plot was collected every 2 weeks during the cropping season. The soil samples in both Rangsit and Ongkharak soils were extracted with dilute NaOH to determine dissolved RP during cropping season. The differences in P levels (ΔP) from the dilute NaOH extraction between RP-treated and RP-untreated plots were used as an estimate of dissolved RP (ΔP_{NaOH}). However, dissolved RP which was measured during the cropping season may not be the actual RP dissolved because dissolved RP may have been absorbed by the rice. The soil pH in each plot also was measured.

The soil samples which were collected from the Ongkharak soil in the first crop, at 4 weeks after RP application, were extracted with the modified Pi strip test. The modified Pi strip test-extractable P at 4 weeks after RP application was used to estimate $\Delta P_{NaOH}/\Delta P_{modified\ Pi\ strip\ test}$. The P content in the extracted solutions was determined using the method of Murphy and Riley (1962).

6.4 Statistical analysis.

The effects of RP application on grain yield and yield component were analyzed using the LRP method (Anderson and Nelson, 1975) and analysis of variance. The mean comparison was computed using DMRT in SAS.

RESULTS AND DISCUSSION

1. Experiment 1: A study of phosphorus buffer coefficients which are used in PDSS to estimate RP requirement for rice cultivation in acid sulfate soils.

Phosphorus buffer coefficient is an indicator of change in soil P concentration per unit of P applied. The P buffer coefficient can be predicted by soil properties. Wright *et al.* (1992) estimated P buffering coefficient by relating the P buffering coefficient to soil pH and P retention as estimated by Saunder's method (1965). Hughes and Gilkes (1994) and Cox (1994) predicted P buffering coefficients from the clay content in the soil. Using the following equation, P requirements can be estimated if the following variables are known: the soil P level, the P critical level of the crop, and the P buffer coefficient.

$$P_{\text{req.}} = (P_c - P_0)/\text{PBC} \quad (\text{Eq. 6})$$

Where: $P_{\text{req.}}$ = the P requirement

P_c = the P critical level of the crop using the same extractant as was used to estimate P_0 and PBC

P_0 = the extractable P level of the soil for $P_{\text{req.}}$ prediction.

PBC = the P buffer coefficient (the ratio of extractable P to added P), dimensionless.

This equation forms the fundamental equation in the Phosphorus Decision Support System software (Yost *et al.*, 1992).

A hypothesis of this study is that P buffer coefficients may be a useful indicator of the change in soil P concentration per unit of P added. Soil properties usually control the P buffer coefficient in aerobic soils (Cox, 1994). Thus, measuring P buffer coefficients in flooded acid sulfate soils may provide a useful model that can estimate P fertilizer for rice cultivation in the acid sulfate soils. The objectives of this study were (1) to measure P buffer coefficient of flooded acid sulfate soils and (2) to develop an algorithm to estimate P buffer coefficient in flooded acid sulfate soils.

Phosphorus buffering coefficients were estimated from the slope of the linear regression of extractable P versus applied P. The linear regression between P added and

extractable P was estimated for three soil test methods (Bray 1, Bray 2 and modified Pi strip test) in Ok and Rs soils and is shown in Figure 1. The P buffer coefficients as calculated for three soil test methods in six acid sulfate soils are shown in Table 13. The P buffering coefficient which was estimated by Bray 2-extraction, was higher than the PBC that was estimated by the other two methods. This was an expected result and was probably due to the high acidity of Bray 2 which permits the extraction of more phosphate. The high value of P buffering coefficient indicates a large proportion of the applied P remains extractable. The higher P buffering coefficient indicates less P sorption of the soil.

Stepwise regression analysis between PBC which measured by three soil test methods and soil properties (Table 7) indicated that ECEC, P retention, oxalate-extractable Fe and Al were the main factors affecting PBC as follows:

$$PBC_{\text{Bray 1}} = 0.58365 - 0.00931\text{ECEC} \quad \text{adj. } R^2 = 0.36 \quad (\text{eq. 7})$$

$$PBC_{\text{Bray 2}} = 1.0661 - 0.00580P_{\text{retention}} - 0.0111\text{Fe}_{\text{ox}} - 0.0234\text{Al}_{\text{ox}} \quad \text{adj. } R^2 = 0.90^{**} \quad (\text{eq. 8})$$

$$PBC_{\text{modified Pi strip test}} = 0.5917 - 0.0129\text{CEC} \quad \text{adj. } R^2 = 0.64^* \quad (\text{eq. 9})$$

The P buffering coefficients as determined by Bray 1 and modified Pi strip extractions increased with decreasing ECEC and CEC. High ECEC and CEC indicate high exchange site for cations in the soils and most of cations in acid sulfate soils should be iron and aluminum. Decreasing ECEC or CEC may indicate less binding ability of iron and aluminum, which can bind with P in the soil (Han *et al.*, 2005). Therefore, P sorption in low ECEC or CEC soil may be less than that of other soils. The decreases in P retention and oxalate extractable iron and aluminum increased PBC as estimated by Bray 2. The soil properties which affect P sorption in flooded soil such as oxalate-extractable Fe and Al, dithionite-extractable Fe and Al, P retention, and organic matter may have an effect on P buffering coefficient (Sah and Mikkelsen, 1989, Jugsujinda *et al.*, 1995 and Sahandeh *et al.*, 1994).

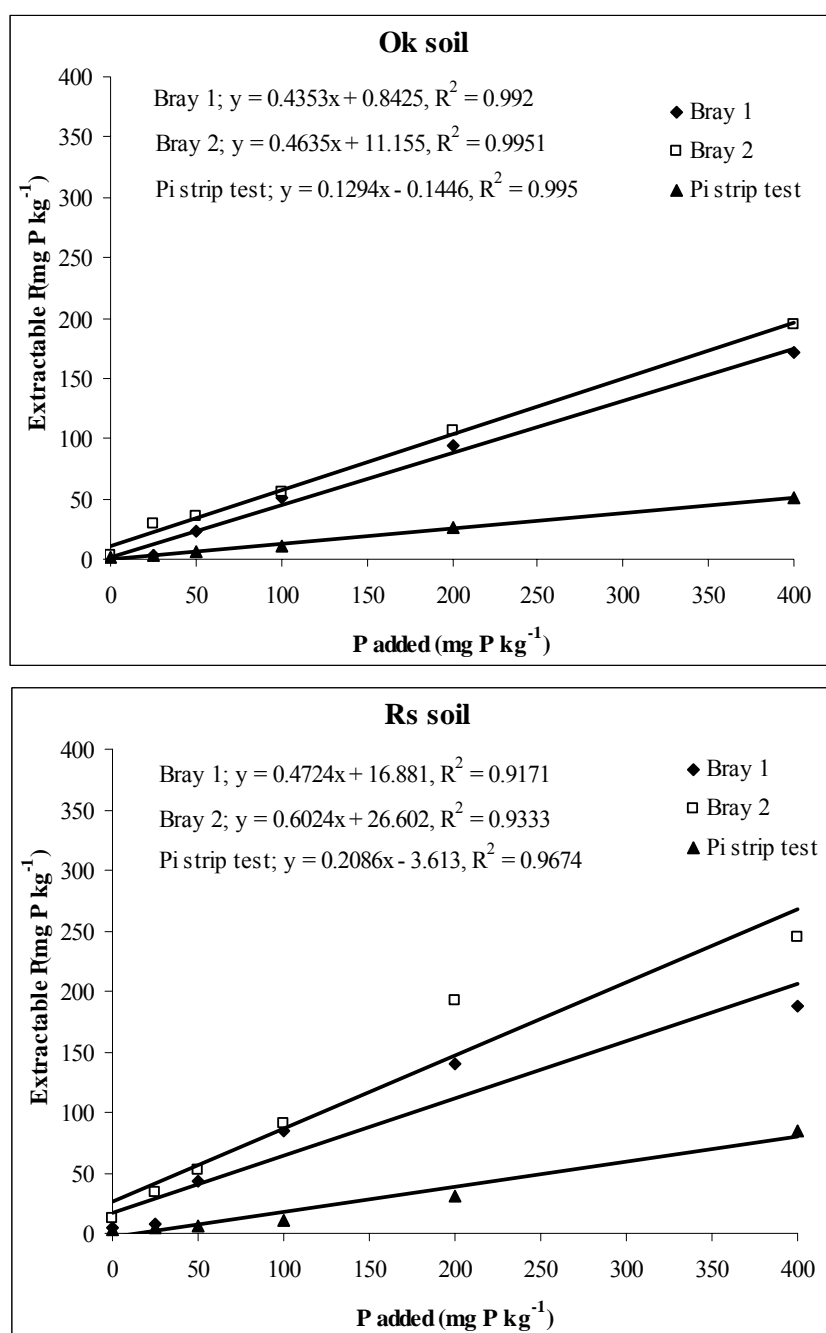


Figure 1 The relationship between extractable P by three soil test methods (Bray 1, Bray 2 and modified Pi strip test) and P applied to Ongkharak (Ok) and Rangsit (Rs) soils.

Table 13 The P buffering coefficient of six acid sulfate soils as measured by three soil test methods.

Soil series	Phosphorus buffer coefficient (PBC)		
	Bray 1	Bray 2	Modified Pi strip test
Rangsit very acid (Rsa)	0.4611	0.5897	0.2047
Ongkharak (Ok)	0.4353	0.4635	0.1294
Rangsit (Rs)	0.4724	0.6024	0.2086
Sena (Se)	0.3776	0.5712	0.2309
Mahaphot (Ma)	0.4359	0.5493	0.0760
Chachoengsao (Cc)	0.4976	0.5159	0.0236

Soil properties (Table 7) were substituted into equation (7), (8) and (9) to predict the PBC in six acid sulfate soils which were measured by Bray 1, Bray 2-extractions and modified Pi strip test, respectively. The predicted PBCs in six acid sulfate soils were plotted with observed PBC (Figure 2). The predicted PBC, measured by three soil test methods, was close to the observed PBC, especially the predicted PBC as measured by Bray 2-extracting solution. This might be due to high correlation between the P buffering coefficient as measured by Bray 2 and soil properties. Nevertheless, it seems that the P buffering coefficient which was measured by three soil test methods can be satisfactorily predicted by soil properties.

Phosphorus requirements of six acid sulfate soils were calculated by substitution of soil P, P critical level and predicted PBC into equation 6. The soil P levels of six acid sulfate soils which was determined by three soil test methods are shown in Table 14. The P critical level in acid soils for rice cultivation which was extracted by the Bray 1 extracting solution was 7 mg P kg⁻¹ (Dobermann and Fairhurst, 2000). The P critical level for rice cultivation in Ongkharak soil which was measured by Bray 2 extraction and modified Pi strip test were 12.0 and 5.1 mg P kg⁻¹, respectively (results from experiment 2). The predicted PBC in six acid sulfate soils, measured by three soil test methods, which was satisfactorily predicted by soil properties were used to calculate P requirement.

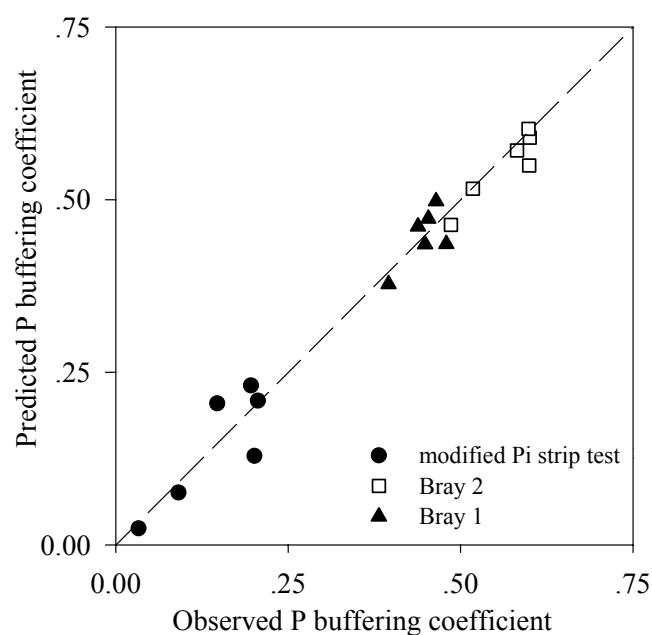


Figure 2 The P buffering coefficient in six acid sulfate soils which was predicted by soil properties. The dashed line indicates a 1:1 relationship.

Table 14 Predicted phosphorus requirement which was predicted by the fundamental equation in the Phosphorus Decision Support System software (equation 6).

soil	Soil P level (P ₀), mg P kg ⁻¹			Predicted P requirement (P req.), kg P ha ⁻¹ †		
	Bray 1	Bray 2	modified Pi strip test	Bray 1	Bray 2	modified Pi strip test
Rangsit very acid (Rsa)	1.9	7.64	2.01	13.96	8.66	25.46
Ongkharak (Ok)	0.43	3.67	1.38	17.57	20.49	22.35
Rangsit (Rs)	1.03	12.1	3.27	15.80	0.00	10.78
Sena (Se)	1.38	9.67	1.69	17.05	4.74	21.04
Mahaphot (Ma)	0.48	5.85	2.95	16.32	12.25	28.56
Chachoengsao (Cc)	0.71	12.4	2.31	16.25	0.00	101.78

Note: † calculation based on soil depth = 10 cm. and bulk density = 1.2 g cm⁻³

The predicted P requirement in the same soil which was calculated by different soil test methods was different (Table 14). The differences in predicted P requirement may depend on the ability of soil test methods to measure available P and PBC. The predicted P requirement which was calculated using modified Pi strip test was higher than using other soil test methods except in the Rs soil. This might be due to the predicted PBC measured by modified Pi strip test being lower than that measured by other soil tests methods which was indicated high P sorption in six acid sulfate soils. High P sorption in the soils indicated high P fertilizer application to meet the crop requirement. The predicted P requirement in Rs and Cc soils which was calculated by Bray 2-extraction were zero indicated that P in the soils is adequate for rice cultivation. Then, P fertilizer may not need to be applied in these two soils. However, the prediction of P requirement in these two soils using Bray 1 and modified Pi strip test indicated that P fertilizer was needed. Therefore, a field test was needed to be conducted to test the predictions of P requirement for rice cultivation in the two acid sulfate soils. The response of rice yield with P fertilizer application rate could then be used as an indicator to evaluate the precision of predicted P requirement.

2. Experiment 2: A study of phosphorus critical levels which are used in PDSS to estimate RP requirement for rice cultivation in acid sulfate soils.

The P critical level is the minimum P level that a plant needs for optimum yield. It is an important index to diagnose the P deficiency, therefore this factor is always included in software for predicting P requirement such as PDSS software. The P critical level varies with soil properties. The critical level for a crop differs with different soils and the particular extractant. The type of P fertilizer materials gave different values of P critical level (Chien, 2005). Using the fundamental equation in the PDSS software (equation 6), the P deficiency can be diagnosed by the difference between the extractable P in soil and P critical level. A positive value for extractable P in soil subtracted from the P critical level indicates that P for the crops is inadequate and a P application is needed.

A hypothesis of this study was that the P critical level in the soil which developed by soluble P fertilizer and RP might be different (Chien, 2005). The high acidity of some soil test methods such as Bray 2 and Mehlich 1-extracting solution can be remove

unreactive RP. Under these conditions, response of crop yield with available P in soil fertilized with soluble P fertilizer and RP were different. A promising soil test method as Pi strip test might be a good method to study the response of crop yield with available P in soil fertilized with both soluble P fertilizer and RP (Chien, 2004). The Pi strip test method uses iron oxide as a sink to sorb and retain P mobilized in soil solution. It simulates sorption of P by plant roots without disturbing the chemical equilibrium (Fageria *et al.*, 1997). The objectives of this study were (i) estimate P critical level in Ongkharak soil using Bray 2-extractable P and modified Pi strip test and (ii) to compare the value of P critical level which developed by triple superphosphate and rock phosphates. The experiment was conducted in Ongkharak soil and two types of P fertilizer, triple superphosphate and RP, were used in this study. The available P in soils after the application of two types of P fertilizer, initial P, were regressed with rice yield to indicate P critical level.

2.1 Response of grain yield to the application of P fertilizer.

This experiment was conducted in an Ongkharak soil during December, 2003-April, 2004 (dry season) in Thailand. About 70 days after planting the rice plants were affected with water stress. Irrigated water which was contaminated with sea water was inadvertently pumped into the field. The electrical conductivity of water in the field experiment was about 3.20 dS m^{-1} . The water stress during reproductive stages reduced grain yield (Fageria *et al.*, 1997). Salinity is an important limiting factor on rice growth and yield, especially grain yield (Fageria *et al.*, 1997). The average grain yield of Suphanburi 1 rice variety was approximately 5037 kg ha^{-1} (Department of Agriculture, n.d.) but the maximum grain yield in Ok soil applied with TSP and RP were only 2028 and 2256 kg ha^{-1} , respectively (Table 15 and 16). This might be due to the water stress and salinity from sea water which decreased the grain yield of rice.

The application of TSP in the Ongkharak soil significantly increased rice yield at the rate of $16.4 \text{ kg P ha}^{-1}$ (Table 15) while a significant increase in straw weight was obtained at the $24.6 \text{ kg P ha}^{-1}$ application rate. Percent of unfilled rice grains in the no TSP application plot was higher than the other treatments. The application of TSP resulted in

higher 1000-grain weight, however, the 1000-grain weight in the experiment was lower than the average 1000-grain weight (Department of Agriculture, n.d.).

The experiment to estimate P critical levels where RPs are applied was the same experiment used to test predictions of RP quantity. The application of KRP and Gafsa RP in the Ongkharak soil significantly increased rice yield at the rate of 1,270 and 518 kg RP ha⁻¹, respectively (Table 16). The application of KRP and Gafsa RP in the Ok soil, however, did not increase straw weight and 1000-grain weight. The percent of unfilled rice grains in the no RP application plot and the KRP applied at the rate of 1,270 kg RP ha⁻¹ were higher than the other treatments.

Table 15 Rice grain yield, straw dry weight, number of grains per panicle, percent of unfilled grains and 1000 grain weight from the soluble P critical level study in Ok soil.

Rate of TSP application (kg P ha ⁻¹)	grain yield (kg ha ⁻¹)	straw dry weight (kg ha ⁻¹)	grains/panicle	unfilled grains (%)	1000-grain weight (g)
0.00	1468b	6380b	57.85b	40.41	20.47b
8.20	1593b	7348ab	66.63b	35.05	22.31a
16.40	2022a	7256ab	66.80b	32.58	22.17a
24.60	2028a	7813a	63.33b	32.96	22.19a
32.80	1906a	7450ab	69.95ab	31.57	22.01a
40.90	1912a	7783a	73.43a	34.72	22.59a
F-test					
Block	ns	ns	ns	ns	ns
Treatment	**	*	**	ns	*
C.V.	8.31	11.21	11.78	19.28	4.97

Note: Means within a column followed by the same letter do not differ significantly at $\alpha = 0.05$ by DMRT

** Significant at $\alpha = 0.01$ * Significant at $\alpha = 0.05$

ns = not significant

Table 16 Rice grain yield, straw dry weight, number of grains per panicle, percent of unfilled grains and 1000 grain weight in P critical level study in Ok soil with applied RP.

Treatment	Application rate (kg RP ha ⁻¹)	grain yield (kg ha ⁻¹)	straw dry weight (kg ha ⁻¹)	grains/panicle	unfilled grains (%)	1000-grain weight (g)
No RP	0	1450e	7104	76.85ab	32.5	19.9
KRP1/2	1270	1853dc	7577	76.35ab	33.0	21.2
KRP1	2542	2108abc	8123	79.80ab	20.9	21.2
KRP2	5083	2256a	7997	90.53a	22.5	21.5
Gafsa 1/2	518	1809d	7985	62.70b	24.8	21.5
Gafsa 1	1038	1966bcd	7561	75.48ab	25.7	20.8
Gafsa 2	2075	2147ab	8485	70.30ab	22.5	21.6
F-test						
Block		ns	ns	ns	ns	ns
Treatment		**	ns	*	ns	ns
C.V.		8.79	12.13	12.28	13.67	7.61

Note: Means within a column followed by the same letter do not differ significantly at $\alpha = 0.05$ by DMRT

** Significant at $\alpha = 0.01$ * Significant at $\alpha = 0.05$

ns = not significant

2.2 Predicting phosphorus critical level.

2.2.1 Triple superphosphate application

The P critical level in the Ongkharak soil that received TSP was estimated by plotting the extractable initial P with grain yield. The extractable initial P in each plot was calculated using Cox's equation (Cox *et al.*, 1981) as follow:

$$P = P_{eq} + (P_{init} - P_{eq})e^{(-kT)} \quad (\text{eq. 10})$$

The P after harvest was extracted by Bray 2-extraction and modified Pi strip test (Table 17). The P_{init} of Bray 2-extractable P and modified Pi strip test were 6.95 and 2.76 kg P ha⁻¹, respectively, (extractable P before planting rice; Table 8). Because the experiment for testing prediction of RP in experiment 6 was conducted in the same site, then the extractable P measurements after the 2nd rice crop in the unfertilized plots were used to estimate the P_{eq} and k parameter in this experiment. The P_{eq} for Bray 2-extractable P and modified Pi strip test were 6.65 and 1.97 kg P ha⁻¹, respectively. The k constant of Ok soil as extracted by Bray 2-extraction and modified Pi strip test was estimated by procedure nonlinear regression in SAS. The predicted k constants of Ok soil as extracted by Bray 2-extraction and modified Pi strip test were 1.068 and 1.372, respectively. The initial Bray 2-extractable P and modified Pi strip test-extractable P in other plots where TSP was applied were calculated by substituting P_{eq} , the predicted k constant and P (P after harvesting) into equation 10. The time used for calculation was 0.3 (4 months for rice planting). The predicted initial P (P_{init}) which was extracted by Bray 2-extraction and modified Pi strip test is shown in Table 17. The predicted initial extractable P which was extracted by two soil test methods increased with increasing TSP application rates at 24.6 kg P ha⁻¹. The predicted initial extractable P of TSP application at the rate of 32.8 and 40.9 kg P ha⁻¹ which was measured by two soil test methods were lower than the predicted initial extractable P at 24.6 kg P ha⁻¹. It may due to the extractable P after harvest of TSP application at the rate of 32.8 and 40.9 kg P ha⁻¹ was lower than the extractable P after harvest of TSP application at the rate of 24.6 kg P ha⁻¹.

Table 17 Soil P as extracted by Bray 2 and the modified Pi strip test after harvest and the predicted initial extractable P by Cox's model.

Rate of TSP application (kg P ha ⁻¹)	Extractable P after harvest (kg P ha ^{-1†})		Predicted initial extractable P (kg P ha ^{-1†})	
	Bray 2	Modified Pi strip	Bray 2	Modified Pi strip
0	6.87	2.49	6.95	2.76
8.2	10.44	3.65	11.87	4.50
16.4	12.25	4.75	14.37	6.16
24.6	13.63	6.57	16.27	8.91
32.8	12.64	5.62	14.90	7.48
40.9	13.76	5.61	16.44	7.47

Note: † calculation based on soil depth = 10 cm. and bulk density = 1.2 g cm⁻³

The predicted initial Bray 2 and Pi strip test-extractable P were regressed with grain yield using the LRP method (Figure 3). Linear response plateau analysis indicated that the minimum P level in Ongkharak soil that rice needed were 11.97 and 5.12 mg P kg⁻¹ which were extracted by Bray 2 and modified Pi strip test, respectively. The predicted initial extractable P as measured by modified Pi strip test (adj R² = 0.83) seems to be better correlated with grain yield than predicted by Bray 2-extractable P (adj R² = 0.78).

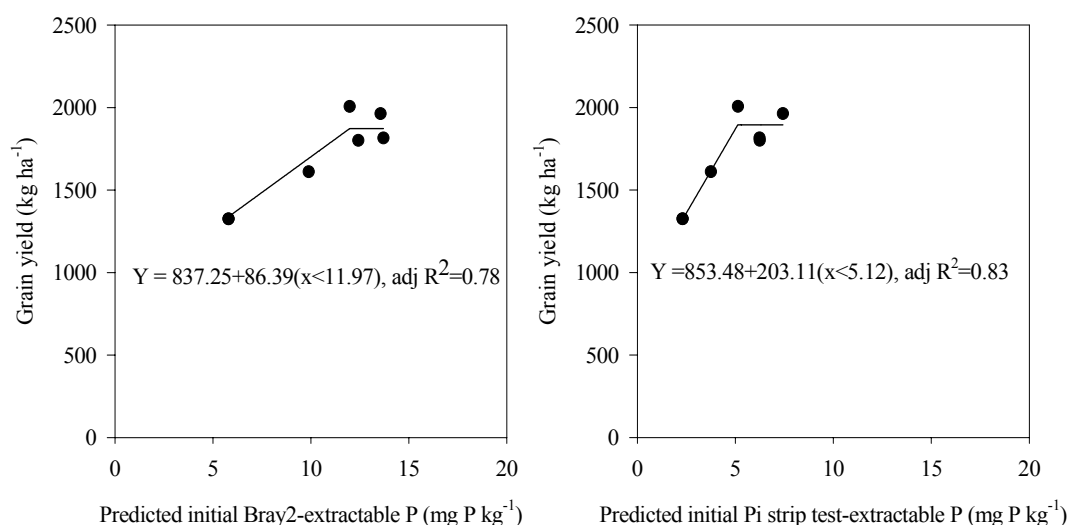


Figure 3 The response of grain yield with predicted initial extractable Bray 2 and modified Pi strip test in Ongkharak soil which applied TSP. Symbol- experiment data: line-predicted by Linear Response Plateau method (LRP).

2.2.2 Rock phosphate application

Grain yield was regressed on the extractable P, Bray 2-extraction and modified Pi strip test, at 4 weeks after the application of KRP and Gafsa RP using the LRP method. The LRP analysis indicated that the P critical level in Ok soil where RPs were applied which was measured the Bray 2 method and the modified Pi strip test were 13.09 and 5.40 mg P kg⁻¹, respectively (Figure 4).

The predicted P critical level in the Ok soil where RPs were applied seem to be close to the predicted P critical level in Ok soil where TSP was applied, especially P critical level which was measured by modified Pi strip test. Chien (2004) reported that the response curve of Bray 2-extractable P in the soil where RPs were applied gave a different curve than with soil fertilized with soluble P fertilizer. In this experiment, the predicted P critical level in Ok soil fertilized with TSP and RPs which was extracted by Bray 2 were 11.97 and 13.09 mg P kg⁻¹. The predicted P critical level in Ok soil fertilized with RP was high rather than predicted P critical level in Ok soil fertilized with TSP. It might be due to higher dissolution of RP in highly acidic soil such as Ok soil. The initial

extractable P was estimated from the soil sample at 4 weeks after application then, RP dissolution may reach equilibrium. However, the predicted P critical level in Ok soil where RPs were applied, which was measured by modified Pi strip test was close to the predicted P critical level in Ok soil where TSP was applied. The modified Pi strip test reacts more like a plant root and without disturbing the chemical equilibrium, consequently both P critical levels in Ok soil fertilized with RP and TSP were similar.

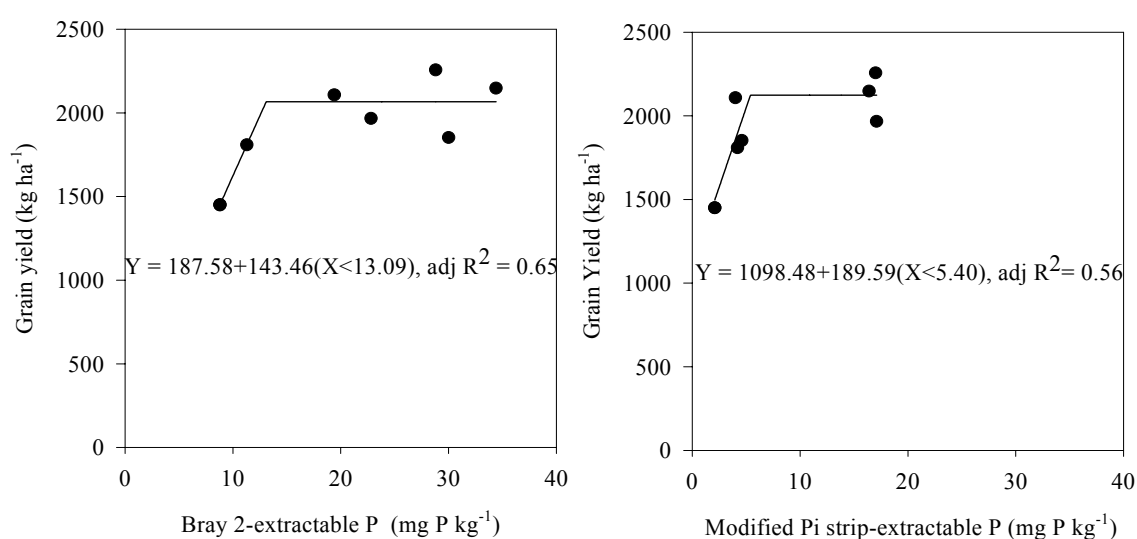


Figure 4 Response of rice yield in Ok soil with extractable P which was extracted by the Bray 2-extraction and modified Pi strip test at 4 weeks after RP application. Symbol- experiment data: line-predicted by Linear Response Plateau method (LRP).

The relationship between P uptake by rice (straw+grain) and Bray 2-extractable P in Ok soil applied with TSP seem to be slightly higher than the curve in Ok soil applied with RPs (Figure 5A). The result indicated that Bray 2-extracting solution gave a different curve in the Ok soil that had received the different type of P fertilizer. Bray 2-extractable P in Ok soil fertilized with RPs was higher than Bray 2-extractable P in the soil fertilized with TSP at the same point of P uptake by rice (Figure 5A). The result indicated that Bray 2-extracting solution may overestimate available P from RPs as compared with TSP.

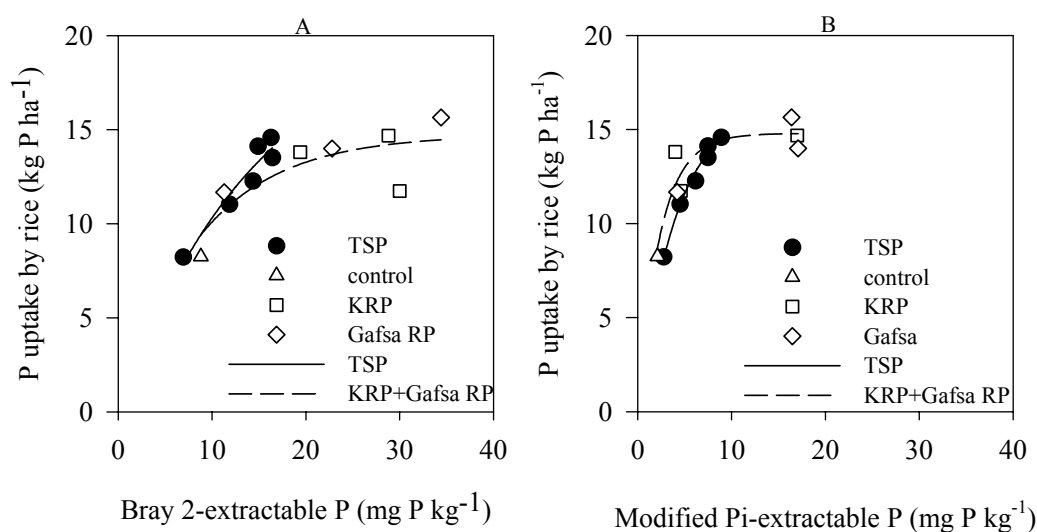


Figure 5 The relationship between P uptake by rice and extractable P as extracted by two soil test methods, Bray 2 (5A) and modified Pi strip test (5B), in Ok soil treated with KRP, Gafsa RP and TSP.

The relationship between P uptake by rice (straw+grain) and modified Pi strip test-extractable P in Ok soil applied with TSP and RPs seem to be similar (Figure 5B). This result suggests that the modified Pi-strip test can be used to evaluate available P in soil which is fertilized with both RP and TSP which was the case of Ok soil. Consequently, it appears that the modified Pi strip test may better suited to evaluate available P than Bray 2-extracting solution, especially where rock phosphate has been added.

3. Experiment 3: Predicting the individual dissolution of rock phosphates in acid sulfate soils

A hypothesis of this study was that the dual processes of dissolution and sorption determine the plant availability of RP and provide a useful structure for an algorithm to estimate the amount of RP that should be added to the soil to correct P deficiencies. The objectives of this study were, for each of three rock phosphates, (1) determine which properties of acid sulfate soils influence RP dissolution (2) determine which factors affect P sorption and (3) develop a tentative model that brings these factors together for a

quantitative estimate of the requirements of each rock phosphate for rice cultivation in acid sulfate soils of Thailand. Later field testing, adjustment, and validation are sure to be needed.

3.1 Rock phosphate dissolution

3.1.1 Kanchanaburi rock phosphate (KRP)

The Kanchanaburi rock phosphate, a local RP from Western Thailand, was selected for the study. The Gafsa rock phosphate was selected as a reference rock phosphate to provide a standard to assist in evaluating the transferability of the results. Small amounts of P (0.006%) in KRP were extracted by 0.5M NaOH. The increase in NaOH-extractable P (P_{NaOH}) in the KRP-treated soils relative to the KRP-untreated soils was used to estimate the amount of P dissolved from the KRP (Δ P_{NaOH}). The KRP dissolution in six acid sulfate soils immediately after addition was approximately 100-150 mg P kg⁻¹ with more dissolved in Rsa, Ok and Se soils (Figure 6). The rate of dissolution after 56 days of incubation increased to 47-54 % of the total P added. The KRP dissolved only to a small extent in Rs, Ma and Cc soils. It appears that the increasing soil pH strongly limited KRP dissolution in these soils. The soil pH in Rsa, Ok and Se soils amended with KRP (0 days of incubation) increased only about 0.5 pH unit to 4.5, after phosphate addition. The Rs Ma and Cc soils, in contrast, when amended with KRP (0 day after incubation), increased to pH 5.5. This substantial increase in soil pH seems to be a result of the high calcium carbonate content of KRP (Table 10) and the reduction of soil after flooding. The KRP dissolution in six acid sulfate soils, therefore, appears to have been limited by reduced soil acidity in soil system after adding KRP. Attanandana and Vacharothayan (1984) observed that the simultaneous application of RP and lime in paddy soils increased soil pH to 5.5 and reduced the availability of the added rock phosphate. The KRP dissolution in Rsa, Rs and Se soils was not significantly different after 14 days of incubation (Table 18), it appears that KRP dissolution in Rsa, Rs and Se soil reached a plateau after 14 days of incubation. KRP dissolution in Ok soil was not significantly different after 28 days of incubation; it might suggest that KRP dissolution reached a plateau after 28 days of incubation. The KRP dissolution in Ma and Cc soils shows a significant difference by the end of incubation.

The change in ΔP_{NaOH} over time where KRP was applied to six acid sulfate soils was fitted with a Mitscherlich equation (equation 5) to describe the dissolution. The resulting prediction from the Mitscherlich equation for each soil is plotted with the experimental data (Figure 6). The residual mean square of KRP dissolution in six acid sulfate soils as fitted by a Mitscherlich equation (eq. 5) was below 16.1 except for KRP dissolution in the Rsa soil (Table 19).

Table 18 A test of change in NaOH-P contents between times of incubation with rock phosphate. Results of a repeated measures analysis using PROC MIXED of SAS.

Soils	Rock phosphates								
	KRP			Gafsa			KRPS		
	Difference of least square means between times (days)			Difference of least square means between times (days)			Difference of least square means between times (days)		
	14-28	28-42	42-56	14-28	28-42	42-56	14-28	28-42	42-56
Rsa	ns	ns	ns	**	ns	ns	ns	**	**
Ok	**	ns	ns	**	ns	ns	**	ns	ns
Rs	ns	ns	ns	ns	**	ns	**	**	**
Se	ns	ns	ns	**	ns	ns	**	**	**
Ma	**	**	**	ns	**	ns	ns	ns	*
Cc	ns	ns	**	ns	**	ns	ns	ns	**

Note: ns= not significant * significant at $\alpha = 0.05$ ** significant at $\alpha = 0.01$

Table 19 Comparisons among the equations to predict RP dissolution in six acid sulfate soils as fitted by a Mitscherlich equation and the model developed from soil properties.

Rock	Soil	Mitscherlich fit		Model fit	
Phosphates		Equation	RMS [§]	Equation	RMS
KRP					
	Rsa	Y= 239.2-105.7e ^{-0.1027x}	30.5	Y= 270.3-118.9e ^{-0.0922x}	38.8
	Ok	Y= 262.8-98.52e ^{-0.0945x}	15.0	Y= 230.5-102.2e ^{-0.1095x}	40.1
	Rs	Y= 127.5-17.96e ^{-0.2515x}	2.40	Y= 130.7-23.41e ^{-0.2047x}	3.04
	Se	Y= 238.1-112.1e ^{-0.1197x}	9.71	Y= 239.1-94.78e ^{-0.1128x}	13.2
	Ma	Y= 124.2-19.88e ^{-0.2391x}	16.1	Y= 130.0-20.93e ^{-0.2113x}	14.9
	Cc	Y= 120.2-15.46e ^{-0.1856x}	6.65	Y= 115.2-10.99e ^{-0.2578x}	9.08
Gafsa RP					
	Rsa	Y= 324.1-251.2e ^{-0.1175x}	26.0	Y= 330.0-269.3e ^{-0.1105x}	27.3
	Ok	Y= 363.7-287.8e ^{-0.1266x}	23.3	Y= 340.7-276.8e ^{-0.1296x}	30.6
	Rs	Y= 287.9-228.7e ^{-0.0815x}	24.3	Y= 283.1-218.5e ^{-0.2318x}	89.5
	Se	Y= 387.3-336.5e ^{-0.1323x}	14.2	Y= 393.6-333.8e ^{-0.1284x}	15.3
	Ma	Y= 234.2-170.7e ^{-0.2015x}	16.2	Y= 181.6-112.1e ^{-0.2584x}	46.1
	Cc	Y= 231.2-172.5e ^{-0.2726x}	11.0	Y= 277.5-209.8e ^{-0.2087x}	37.4
KRPS					
	Rsa	Y= 373.8-144.3e ^{-0.1103x}	15.4	Y= 397.6-186.5e ^{-0.1425x}	28.0
	Ok	Y= 390.7-166.4e ^{-0.0962x}	14.7	Y= 370.3-150.8e ^{-0.1323x}	18.3
	Rs	Y= 294.8-107.9e ^{-0.1929x}	19.5	Y= 306.8-48.9e ^{-0.1914x}	41.7
	Se	Y= 376.7-170.5e ^{-0.1051x}	16.3	Y= 374.8-147.5e ^{-0.0178x}	62.0
	Ma	Y= 319.9-40.06e ^{-0.2813x}	10.7	Y= 293.9-77.38e ^{-0.2435x}	42.3
	Cc	Y= 284.1-39.60e ^{-0.2150x}	8.35	Y= 301.3-67.21e ^{-0.2104x}	16.6

Note: [§]Residual mean square

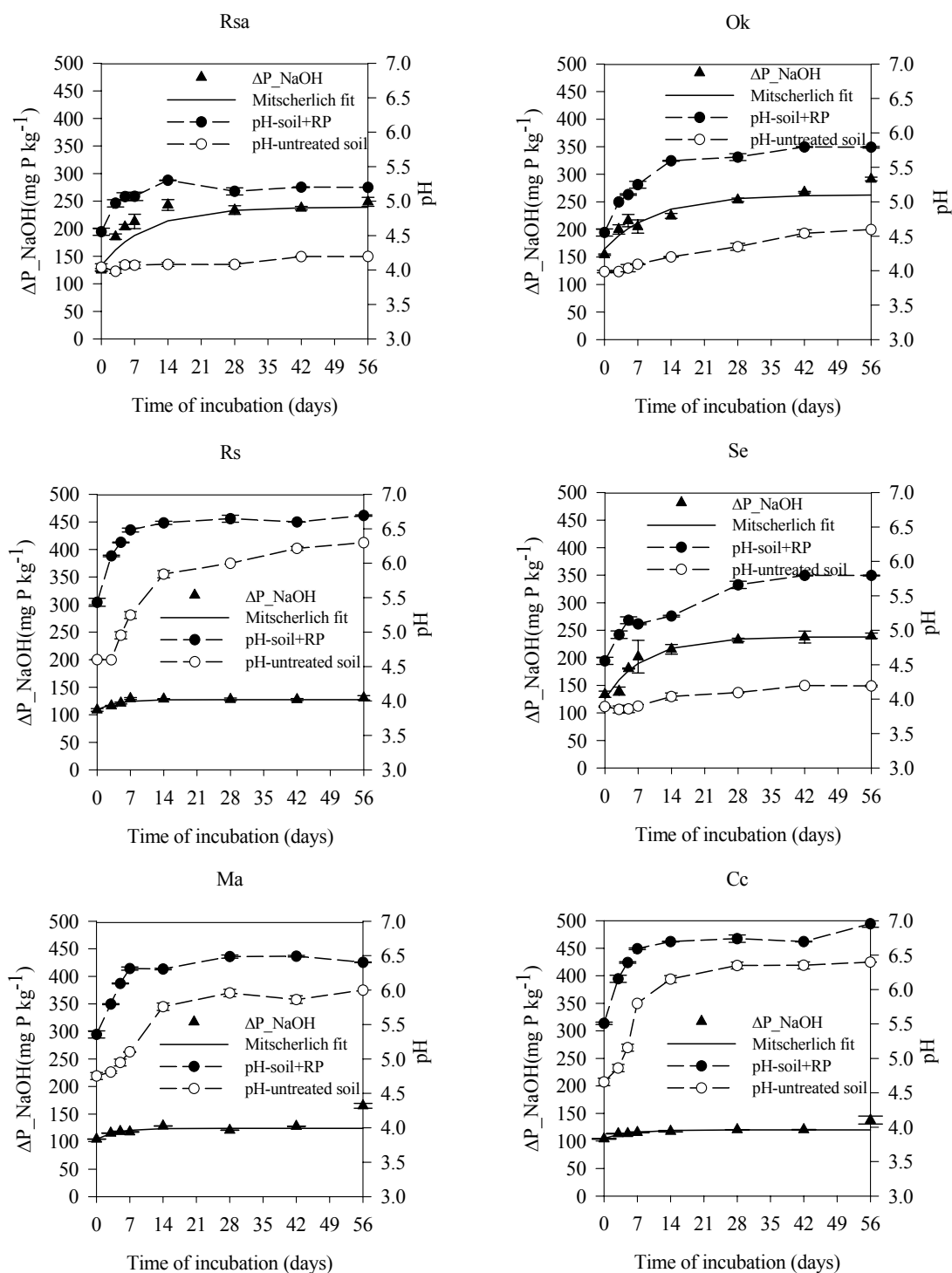


Figure 6 The dissolution of Kanchanaburi rock phosphate (KRP) as represented by the differences in NaOH-extractable-P, Mitscherlich curve fits, and changes of soil pH between KRP-amended (KRP 500 mg P kg⁻¹) and unamended acid sulfate soils.

3.1.2 Gafsa rock phosphate

The initial change in NaOH-P where Gafsa RP was applied to six acid sulfate soils was less than that with KRP or approximately 50-100 mg P kg⁻¹ (Figure 7). The dissolution at initial time was less than the KRP dissolution because 64% of the KRP has a particle size less than 0.15 mm while only 19% of the Gafsa RP was smaller than 0.15 mm (Table 10). The KRP and Gafsa RP were not ground before incubating. The dissolution of highly reactive unground rock phosphate may be initially different but after reaching equilibrium they were not different (Chien, 1998).

More Gafsa rock phosphate dissolved during the flooding than KRP probably because of the pH of Gafsa amended six acid sulfate soils remained lower than the pH of soils amended with KRP (Figure 7). The small increase in pH of six acid sulfate soils after Gafsa RP addition (0 day after incubation) was less than the increase in soil pH after flooding. Increasing pH was an expected effect of reduction and likely a limiting factor to the dissolution of Gafsa RP for some soils. Gafsa RP dissolved in Rs, Ma and Cc soils did not significantly increase after 42 days (Table 18), then Gafsa RP dissolution in Rs, Ma and Cc soils reached a plateau at 42 days. The Gafsa RP dissolution in the more acid Rsa Ok and Se soils did not significantly increase after 28 days of incubation (Table 18) while the soil pH remained at pH 5.0 or lower, even with flooding. The high solubility of Gafsa RP may be a factor that permitted the greater dissolution of Gafsa RP than KRP. A second neutral ammonium citrate extraction in Gafsa RP also indicated Gafsa RP had higher solubility than KRP (Table 10).

The changes in ΔP_{NaOH} of Gafsa RP over time in six acid sulfate soils were also fitted with a Mitscherlich equation and plotted with experimental data (Figure 7). The residual mean square of Gafsa RP dissolution in Rsa, Ok and Rs soils as fitted by Mitscherlich equation was somewhat higher than that of other soils indicating a high deviation of the observed value with the equation (Table 19).

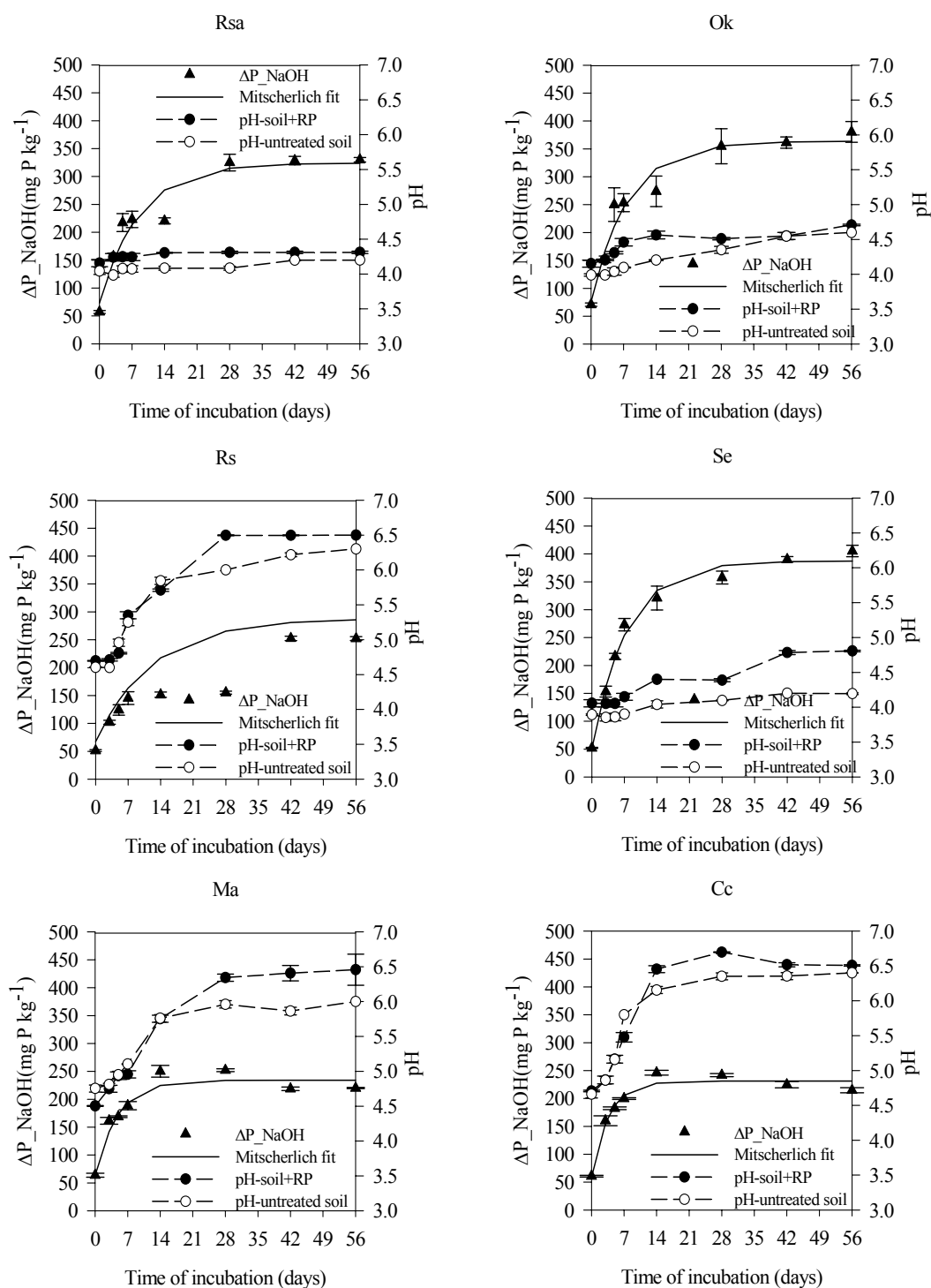


Figure 7 The dissolution of Gafsa rock phosphate (RP) as represented by the differences in NaOH-extractable-P, Mitscherlich curve fits, and changes of soil pH between Gafsa RP-amended (Gafsa RP 500 mg P kg⁻¹) and unamended soils.

3.1.3 Kanchanaburi rock phosphate with soluble P (KRPS)

The KRPS contained around 1.4 % soluble P when extracted by NaOH or 0.71% P when extracted with water (Table 10). This means that about 70 mg of soluble P kg⁻¹, as extracted by NaOH, should have been detected where KRPS was applied at the rate 500 mg P kg⁻¹. This amount of NaOH-P may reflect the possibility that the monoammonium phosphate (MAP) mixed with KRP may have soluble P. Since, the KRPS contained KRP and MAP in a ratio of 2:1 by weight, the KRPS should contain around 140 mg P kg⁻¹ soluble P when KRPS was applied at a rate of 500 mg P kg⁻¹. It might be suggested that the loss of 70 mg P kg⁻¹ of MAP was due to precipitation with the Ca from MAP and the free CaCO₃ of KRP when KRP was mixing with MAP.

The dissolution of KRPS in six acid sulfate soils at time 0 of incubation was high (Figure 8). The pH of six acid sulfate soils after the addition of KRPS increased only slightly in some soils. When KRPS dissolved in Ok soil, ΔP_{NaOH} was nearly constant after 28 days of incubation (Table 18). The KRPS dissolution in Rsa, Se, Rs and Cc soils continuously increased until the end of incubation while KRPS dissolution in Ma soil was not significantly different after 14 days of incubation (Table 18). The KRPS dissolution thus could be described relatively better by a Mitscherlich function than in the case for KRP and Gafsa RP dissolution (Table 19).

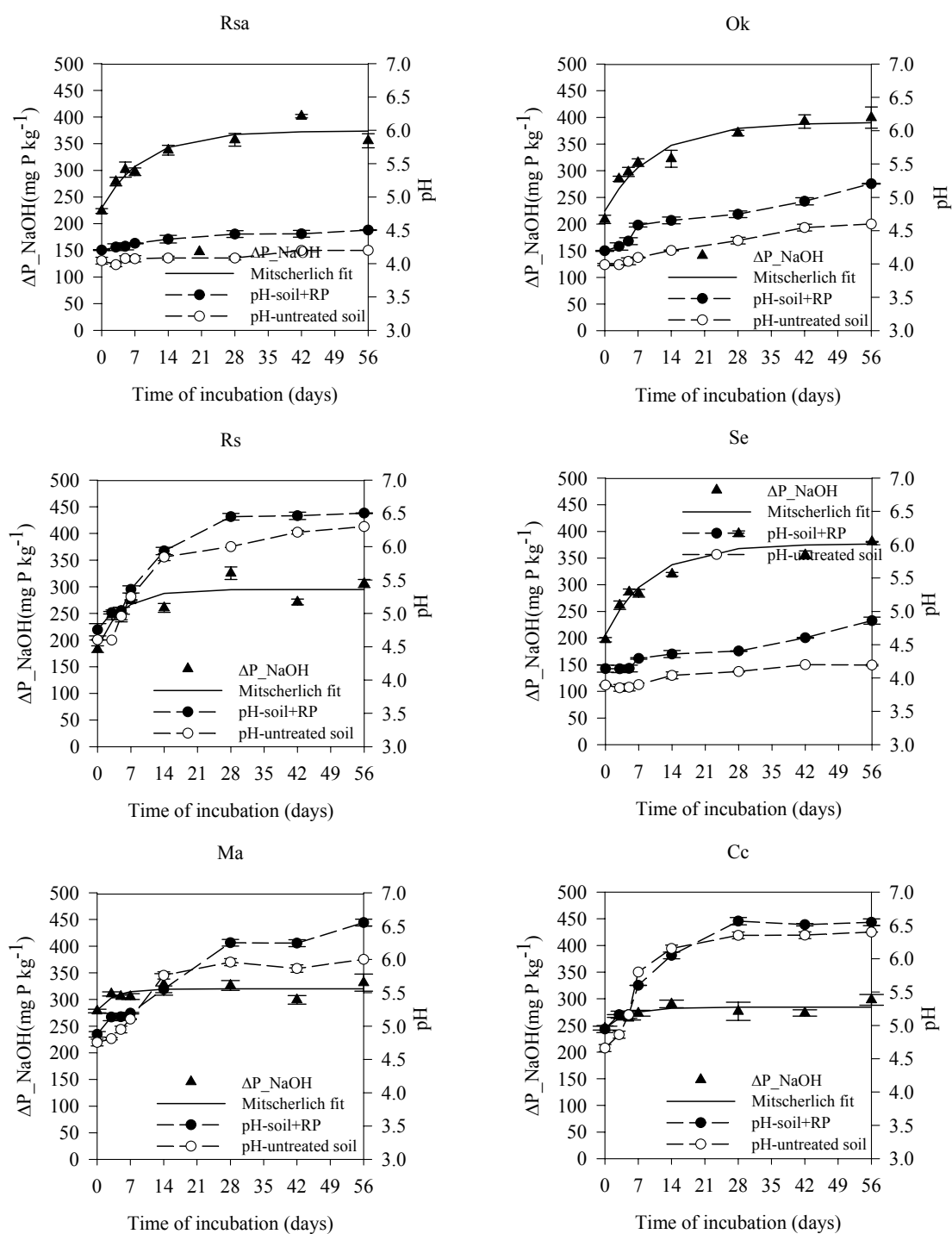


Figure 8 The dissolution of KRPS as represented by the differences in NaOH-extractable-P, Mitscherlich curve fits, and changes of soil pH between KRPS-amended (KRPS 500 mg P kg⁻¹) and unamended soils.

3.2 Predicting rock phosphate dissolution

The A coefficient, resulting from Mitscherlich fit, which indicates the maximum dissolution of KRP in six acid sulfate soils, was highly correlated with soil properties (Table 20). The soil acidity before incubation as represented by soil pH, KCl-extractable Al, and Al saturation percentage, was significantly related to the maximum dissolution (coefficient A) of KRP, Gafsa and KRPS. The maximum dissolved KRP, Gafsa and KRPS increased with increasing soil acidity which has also been suggested by many others (Chu *et al.*, 1962; Bolan and Hedley, 1990; Wright *et al.*, 1992; Kanabo and Gilkes, 1987). Soil acidity increased rock phosphate dissolution in all six acid sulfate soils. The extractable aluminum increased with decreasing soil pH. The dissolution of rock phosphate appears to increase when the soil pH decreases because of the protons become available for dissolution of rock phosphates (Bolan and Hedley, 1990). The soil properties that were highly correlated with maximum dissolution of KRP, Gafsa and KRPS were used in a multiple regression equation to predict the A, B and C coefficients of each soil.

3.2.1 Predicting dissolution of KRP

The regression of coefficients A, B and C and soil properties indicated that the dissolution of KRP increased with increasing extractable aluminum. The B value, the difference between the asymptote and intercept, increased with increased extractable aluminum. A high B value represents less dissolution of KRP at time 0 of the incubation. Decreasing extractable aluminum led to an increased C value. The examples of regression between A, B and C coefficient of KRP dissolution in Rs soil were given the following equation:

$$A = 95.30 + 156.69Al_KCl \quad \text{adj. } R^2 = 0.93 \text{ (eq. 11)}$$

$$B = -1.05 + 111.19Al_KCl \quad \text{adj. } R^2 = 0.96 \text{ (eq. 12)}$$

$$C = 0.2337 - 0.1331Al_KCl \quad \text{adj. } R^2 = 0.79 \text{ (eq. 13)}$$

The coefficients for testing the KRP dissolution in each soil were substituted into eq. 5 to predict KRP dissolution. The predictions of KRP dissolution in six acid sulfate soils from model as based on soil properties were calculated and the residual mean squares were compared to estimate the goodness of fit with Mitscherlich equation (Table 19). The residual mean square of model prediction of KRP dissolution in Rsa and Ok soils was slightly higher than the residual mean square of Mitscherlich while for other soils there was not much difference, which indicates that, in general, the prediction of dissolution based on soil properties was quite accurate.

Table 20 The correlation between maximum dissolution of KRP, Gafsa and KRPS (the Mitscherlich coefficient A, $Y = A - Be^{-cx}$) and properties of six acid sulfate soils.

Soil properties	Rock phosphates		
	KRP (<i>r</i>)	Gafsa(<i>r</i>)	KRPS(<i>r</i>)
pH _{water} (1:1)	-0.85*	-0.95**	-0.75
Extractable P (mg kg ⁻¹)†	0.48	0.55	0.34
Extractable P (mg kg ⁻¹)‡	-0.46	-0.54	-0.58
Extractable P (mg kg ⁻¹)§	-0.70	-0.75	-0.80
Extractable Al (g kg ⁻¹)§	0.62	0.31	-0.68
Extractable Al (g kg ⁻¹)¶	0.98**	0.87*	0.95**
Extractable Al (g kg ⁻¹)#	0.88*	0.69	0.88*
Al saturation (%)	0.96**	0.79	0.94**
Extractable Fe (g kg ⁻¹)§	-0.64	-0.64	-0.51
Extractable Fe (g kg ⁻¹) #	-0.37	-0.03	-0.20
Extractable Ca (g kg ⁻¹)††	-0.67	-0.42	-0.57
ECEC (cmol _c kg ⁻¹)	0.67	0.84	0.60
P retention (%)‡‡	0.32	0.32	0.16

Note: †Bray 1 ‡Bray 2 §Ammonium oxalate ¶1M KCl
 #Dithionite ††1M Ammonium acetate pH 7 ‡‡Saunders (1965)

3.2.2 Predicting dissolution of Gafsa RP

The regression between A, B and C coefficients and soil properties indicated that soil acidity in acid sulfate soils was the important effect on Gafsa RP dissolution. The Gafsa RP dissolution increased with decreased soil pH. Decreasing extractable aluminum led to an increased C value. The amount of soil acidity in acid sulfate soils was important in predicting both Gafsa RP dissolution and KRP dissolution. The example of the regression between A, B and C coefficients on soil properties for predicting A, B and C coefficient of Gafsa RP dissolution in Rs soil is given by the following equations:

$$A = 947.77 - 164.52\text{pH} \quad \text{adj. } R^2 = 0.87 \text{ (eq. 14)}$$

$$B = 891.62 - 166.63\text{pH} \quad \text{adj. } R^2 = 0.88 \text{ (eq. 15)}$$

$$C = 0.2637 - 1458\text{Al_KCl} \quad \text{adj. } R^2 = 0.81 \text{ (eq. 16)}$$

The predicted values of A, B, and C coefficients were also substituted into eq. 5 to predict Gafsa RP dissolution in the six acid sulfate soils. The prediction of Gafsa RP dissolution in Ok, Rs, Ma and Cc soil was not close to the experimental data according to the high residual mean square in those soils (Table 19). The residual mean square of predicting Gafsa RP dissolution in Rsa and Se soils by model fit was not different with the residual mean square of Mitscherlich fit, which again indicates that predictions of dissolution based on soil properties was quite accurate.

3.2.3 Predicting dissolution of KRPS

Dissolution of KRPS was also estimated by fitting equation 5 to the dissolution and then determining which soil properties affected the fitted A, B and C values. Stepwise multiple linear regressions between the fitted A, B, C coefficients and soil properties were also obtained from the incubation of the acid sulfate soils with KRPS. The dissolution of KRPS increased with increasing extractable aluminum. The B value increased with increased KCl-extractable Al of the soils. Increasing soil pH led to an increased C value. A high C value indicates that the dissolution of KRPS reached

equilibrium rapidly. The example of regression between the A, B and C coefficients of KRPS dissolution in Rs soil were given the following equations:

$$A = 284.87 + 99.97Al_KCl \quad \text{adj. } R^2 = 0.86 \text{ (eq. 17)}$$

$$B = 15.86 + 150.02Al_KCl \quad \text{adj. } R^2 = 0.90 \text{ (eq. 18)}$$

$$C = -0.5569 + 0.1848pH \quad \text{adj. } R^2 = 0.84 \text{ (eq. 19)}$$

The prediction of KRPS dissolution in Ok soil by model fit revealed residual mean square close to the Mitscherlich equation fit while the residual mean square of the prediction of KRPS dissolution in the other soils was higher than the Mitscherlich fit (Table 19).

3.3 Phosphorus sorption

3.3.1 Kanchanaburi rock phosphate (KRP)

The P extractability from KRP, Gafsa RP and KRPS was estimated by both Bray 1 and Bray 2 (Figures 9 and 10). The P extractability from KRP in Rsa, Ok, and Se soils with Bray 1 at 0-7 days increased and was relatively stable after 14 days of incubation (Figure 9). The P extractability in Rs, Ma and Cc soils, however, continued to slightly increase. The P extractability by Bray 2 in six acid sulfate soils increased from 0-7 days and decreased little after 14 days of incubation (Figure 10).

The decrease in Bray 1 extractable P after a few days of incubation may be due to several factors including re-adsorption on newly formed Fe^{2+} and residual hydrous oxide phases as well as by P precipitation by Fe^{2+} and Ca^{2+} (Holford and Patrick, 1979). The higher acid concentration of the Bray 2 extractant seems to have reduced subsequent decreases. The P sorption capacity increased in reduced soil at the final soil pH increased to around 6.4 (Holford and Patrick, 1979) and with a high level of added P (Khalid *et al.*, 1977). The pH of Rs, Ma and Cc soils increased to 6.5-7 and the extractability by Bray 1 in those soils was reduced.

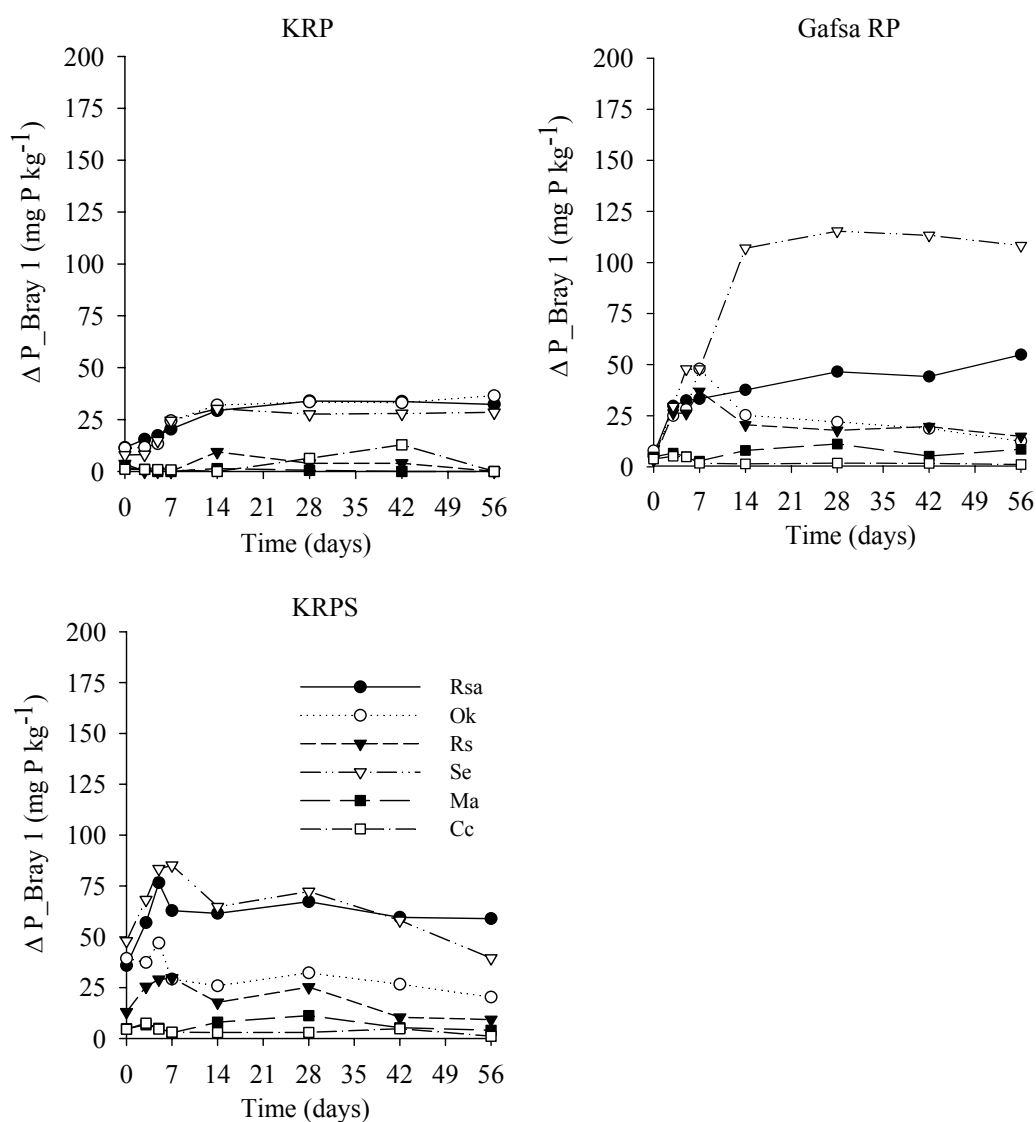


Figure 9 Extractable phosphorus from acid sulfate soils as represented by the differences in Bray 1 extractable P between RP-amended ($\text{RP } 500 \text{ mg P kg}^{-1}$) and unamended soils.

3.3.2 Gafsa rock phosphate

The P extractable by Bray 1 where Gafsa RP had been applied to six acid sulfate soils was similar to KRP extractability except in the Ok and Rs soils (Figure 9). The Bray 1-extractable P in Ok and Rs soils increased from 0-7 days and then decreased after 14 days of incubation. In contrast, the P extractability by Bray 2, with the higher acid

concentration, increased with time in most soils except in Ok soils where the extractability decreased after 14 days of incubation.

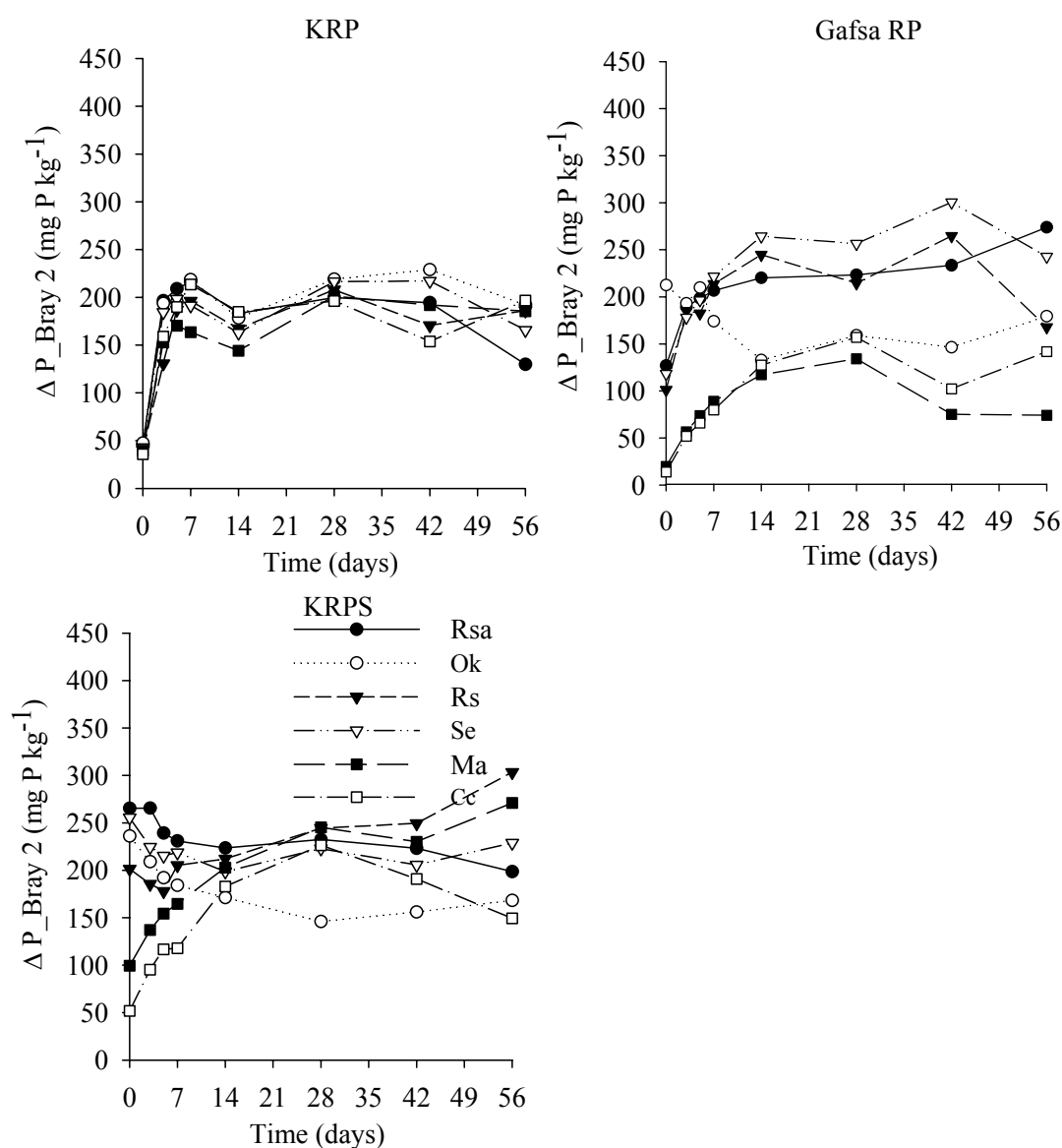


Figure 10 Extractable phosphorus from acid sulfate soils as represented by the differences in Bray 2 extractable P between RP-amended ($\text{RP } 500 \text{ mg P kg}^{-1}$) and unamended soils.

3.3.3 Kanchanaburi rock phosphate with soluble P (KRPS)

The extractability of P by Bray 1 where KRPS had been applied in six acid sulfate soils reached the maximum after 3-7 days of incubation. After that the extractable P decreased (Figure 9). Perhaps the decrease in Bray 1 extractable P after 7

days of incubation occurred because of high P content in soil solution from the soluble P in KRPS led to re-adsorption.

The extractability of P from KRPS in Rsa, Ok, Se, and Rs soils by Bray 2 also decreased with increasing time (Figure 10). In the Ma and Cc soil, the P extractability initially increased as the incubation time increased and then became constant after 28 days of incubation.

3.4 An algorithm to estimate the amount of RP to be added

When RP is added to the soil, P can be released from the RP but not all of the dissolved phosphate will be available to the plant. Several researchers have tried to correlate the relationship between dissolution of RP with crop yield and P uptake by plant but the correlation was poor (Syers and MacKay, 1986; Bolan and Hedley, 1990). Sorption of the dissolved P from rock phosphate apparently plays an important role in P availability to the plant.

The ratio between $\Delta P_{NaOH}/\Delta P_{Bray\ 2}$, is proposed to represent the effect of P sorption by the soil after RP is added and dissolved in the soil. The ratio between ΔP_{NaOH} and $\Delta P_{Bray\ 2}$ in KRP, Gafsa RP and KRPS in six acid sulfate soils was different at the initial time of incubation but reached an approximate steady state at 28 days of incubation (Figure 11). A similar ratio between ΔP_{NaOH} and Bray 1 or Olsen P appeared to reach a steady state value for aerobic soils in West Africa (Sidibé et.al, 2004). The relationship between dissolution and P extractability (Bray_P2) can be used to convert a Bray 2 extractable P requirement to a NaOH-extractable P requirement. Then, the RP requirement can be estimated based on the rock phosphate dissolution model.

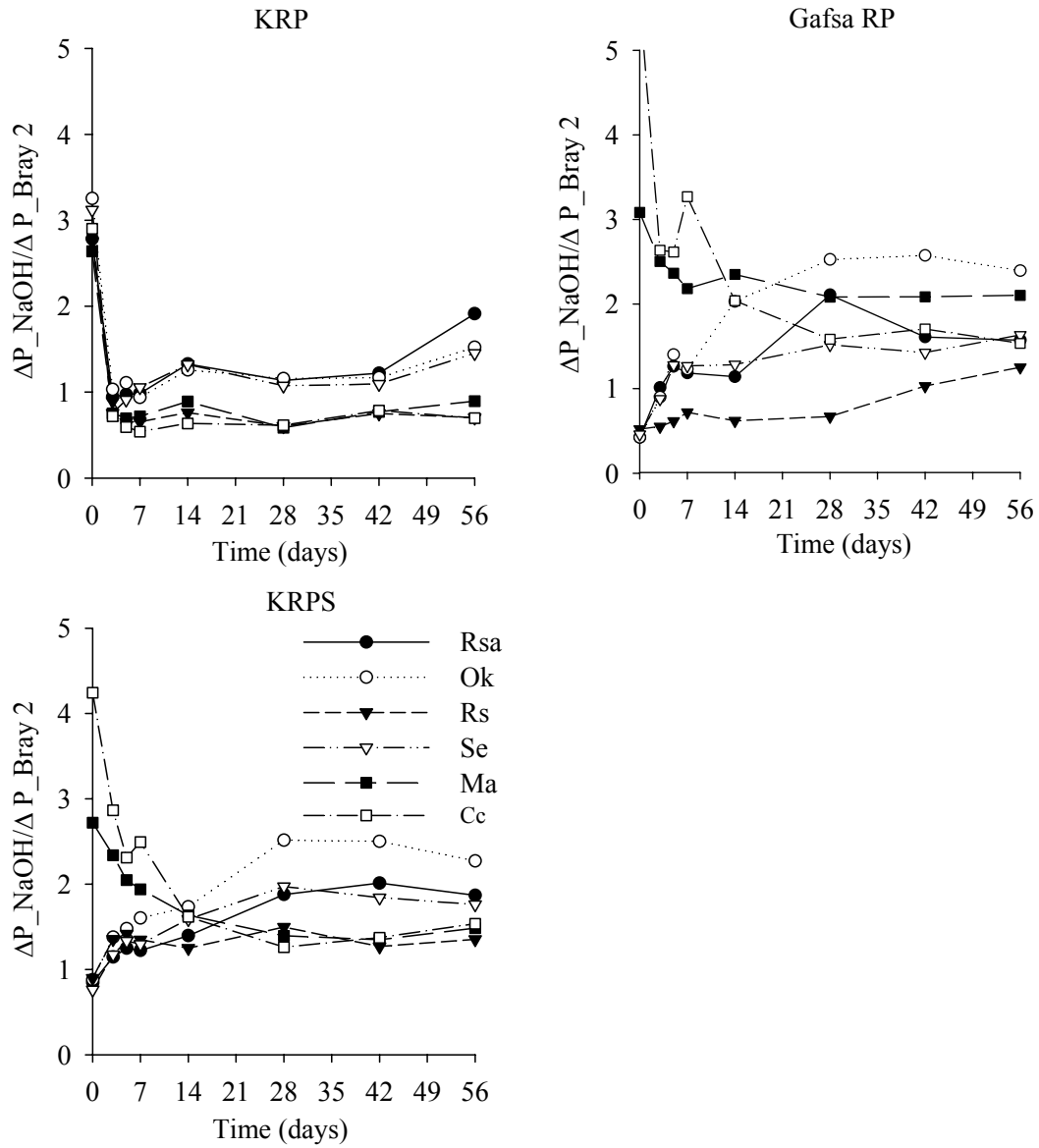


Figure 11 The $\Delta P_{NaOH}/\Delta P_{Bray 2}$ ratios from acid sulfate soils that have received rock phosphates while submerged

From the relationship between dissolution (NaOH-P) and extractability (Bray_P2) we propose estimating the amount of RP that should be added to supply nutrient P from the following equation:

$$RP_{added} = \frac{P_c - P_{Bray2}}{PBC_{Bray2}} \times \frac{\Delta P_{NaOH}}{\Delta P_{Bray2}} \times \frac{500}{A - Be^{-cx}} \times \frac{Depth}{10} \times D_b \quad (\text{eq. 20})$$

Where:

RP added = the amount of RP the should be added (kg P ha^{-1})

P_c = critical Bray 2 P level for the soil, (mg P kg^{-1})

P_{Bray2} = P in soils extracted by Bray 2, (mg P kg^{-1})

$\text{PBC}_{\text{Bray2}}$ = P buffering coefficient as measured by Bray 2

$A - Be^{-cx}$ = amount of ΔP_{NaOH} in soil at time x for the specific soil, (mg P kg^{-1})

Depth = soil depth (cm)

D_b = bulk density (g cm^{-3})

The stepwise regression analysis between PBC as extracted by Bray 2 and soil properties, resulting from experiment 1, indicated that decreases in P retention, iron and aluminum as extracted by oxalate increased the P buffering coefficient (equation 8). Then, the PBC of flooded acid sulfate soils can be estimated by substituting values for the soil properties in equation 8.

Several cautions in the use of equation 20 are noted:

- The effect of P uptake by the plant in increasing the P requirement is not considered in eq. 20. This suggests eq. 20 may under-estimate RP requirement. At the same time absorption of P from soil solution is expected to enhance dissolution. This would suggest eq. 20 would over-estimate P requirement.

- The amount of rock phosphate added to assess dissolution (500 mg P kg^{-1} total P) may be too high in some soils. The estimates of the dissolution of RP are based on laboratory incubations in which there is no leaching or removal of reaction products. In a field situation, there will be leaching of reaction products and thus dissolution is expected to be more rapid than that predicted from the laboratory incubations. However, in paddy rice conditions, certainly leaching is reduced or prevented and thus the estimates from closed laboratory incubations may approximate field conditions. This will not be the case in aerobic soils. Field tests are planned to evaluate these predictions using paddy rice growing in acid sulfate soils where leaching are minimal, but which occurs, and where flooded conditions are roughly analogous to the reduced conditions of the incubations.

4. Experiment 4: Incubation of various RPs with representative soils of the acid sulfate region of Thailand.

The dissolution of RP in soils is a reaction fundamental to the effectiveness of direct application of RP and it depends on both the RP and soil properties. A hypothesis of this study is that the dissolution of RP can be measured by incubating various RPs with the various selected soils with representative properties (Sidibé-Diarra et al., 2004). A generalized model for predicting RP dissolution should be developed using both soil and RP properties. Then the various RPs dissolution in various soils can be predicted. The objectives of this study were (1) to determine which properties of acid sulfate soils and RP materials exert the major influences on RP dissolution and (2) to develop the algorithm and model using those properties in an attempt to estimate the dissolution of a range in RP materials in six representatives acid sulfate soils of Thailand.

4.1 Effect of soil properties on RP dissolution

The change of $\Delta\text{NaOH-P}$ in six acid sulfate soils when incubated with four RP materials was used to describe the dissolution of four RP materials (MacKay et al., 1986). The four RP materials dissolved differently in different soils (Figure 12). The four RP materials dissolved more readily in Rsa, Ok and Se soils than in Rs, Ma and Cc soils. The greater dissolution that occurred in the highly acidic soils such as Rsa, Ok and Se was related to the high acidity of the soils as measured by KCl-extractable Al, Al saturation and soil pH (Table 7). The challenge in this study was to quantitative predict the effects of greater acidity on RP dissolution. Changes in soil pH after the soils were flooded and mixed with four RP materials in flooded condition are likely important in controlling RP dissolution and thus will be measured and considered in the algorithm.

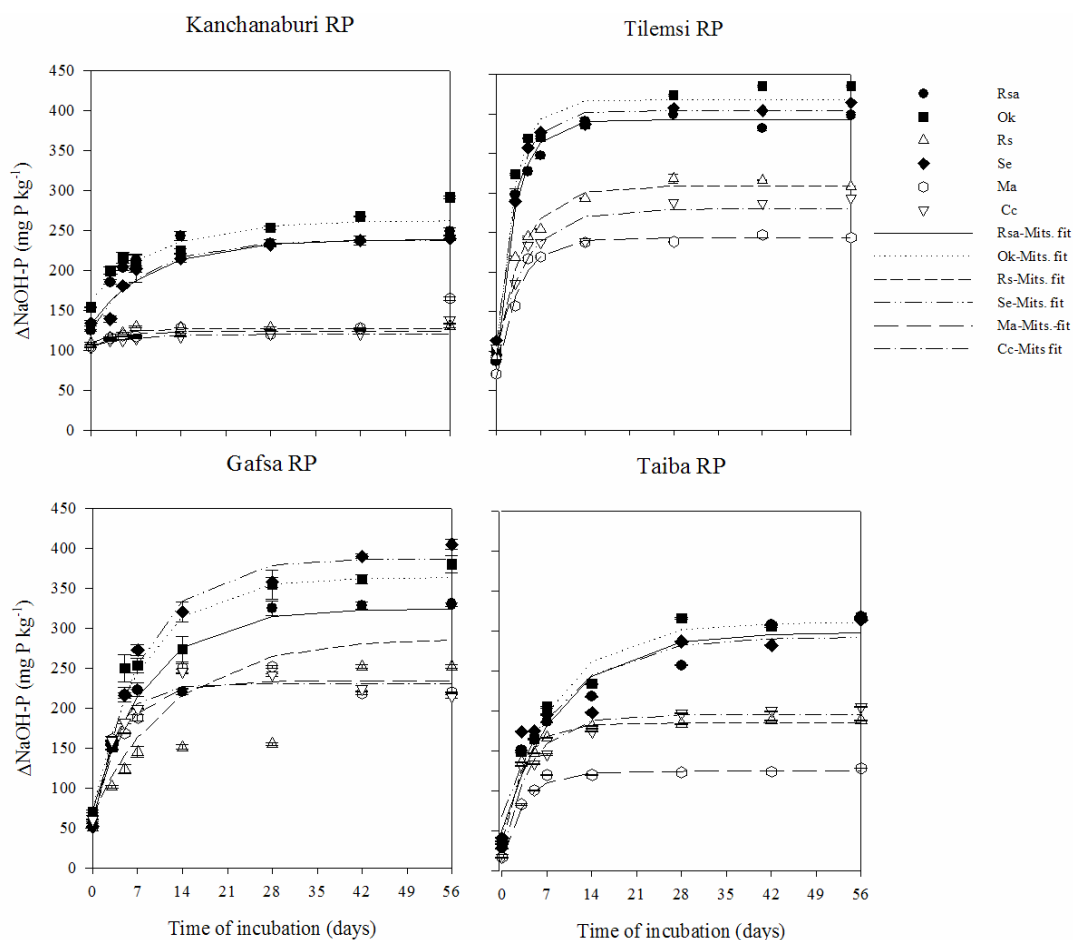


Figure 12 The dissolution of KRP, Gafsa RP, Tilemsi RP and Taiba RP in six acid sulfate soils as represented by the differences in NaOH-extractable-P.

Normally, the pH of flooded acid soils increases to near neutral after submergence due to the reduction of ferric oxide (Ponnamperuma, 1972). In acid sulfate soils, however, soil pH during submergence can remain around 4.5-5.0 depending on soil chemical properties (Kyuma, 2004). Soil pH of untreated Rsa, Ok and Se soils after flooding for 56 days increased from 4.0, 3.9, and 3.8 to 4.2, 4.5 and 4.2, respectively (Table 21). Soil pH of untreated Rs, Ma and Cc soils after flooding for 56 days, however, increased from 4.5, 4.8 and 4.6 to 6.3, 6.2 and 6.4, respectively. The changes in soil pH in the six acid sulfate soils when mixed with four RP materials at the end of incubation were not much different from the untreated soils except for Rsa, Ok and Se soils when mixed with KRP (Table 21). Thus, the significant difference between pH increase in Rsa, Ok and Se soils and Rs, Ma and Cc soils during submergence might be one of the limiting factors

affecting dissolution of the four RP materials. The dissolution of four RP materials in Rsa, Ok and Se soils was higher than the dissolution of four RP materials in Rs, Ma and Cc soil.

Table 21 Soil pH of six acid sulfate soils after incubation with four RP materials at 0 days and the end of incubation (56 days).

Rock phosphates	Time of incubation (days)	pH after mixed with RP material (soil:water ratio of 1:2.5)					
		Rsa	Ok	Se	Rs	Ma	Cc
No RP							
	0 days	4.0	3.9	3.8	4.5	4.8	4.6
	56 days	4.2	4.5	4.2	6.3	6.2	6.4
KRP							
	0 days	4.6	4.5	4.6	5.3	5.4	5.3
	56 days	5.2	5.8	5.8	6.7	6.4	6.7
Gafsa RP							
	0 days	4.1	4.0	4.0	4.6	4.8	4.7
	56 days	4.3	4.7	4.8	6.5	6.5	6.5
Tilemsi RP							
	0 days	4.0	3.9	3.8	4.5	4.8	4.7
	56 days	4.5	4.6	4.7	6.5	6.5	6.5
Taiba RP							
	0 days	4.0	3.9	3.8	4.5	4.8	4.6
	56 days	4.5	4.6	4.5	6.5	6.5	6.5

The low initial pH and high acidity of Rsa, Ok and Se soils probably delayed the gradual increase in soil pH due to flooding, although organic matter in Rsa soil was high and iron content in the Se and Ok soils was high. These results also suggest that soil pH is a result and not a predictor of acidity that will remain after flooding. A similar result on study of soil pH changes in acid sulfate soils of Thailand during submergence has been reported (Chareonchamratcheep et al., 1987).

4.2 Effect of RP properties on RP dissolution

The changes in $\Delta\text{NaOH-P}$ where four RP materials were applied in six acid sulfate soils were clearly different with different RP materials. The order of dissolution of four RP materials at 0 day of incubation was KRP>Tilemsi RP>Gafsa RP>Taiba RP (Table 22). The order of dissolution can be related to P solubility (% of the RP total P that is soluble) as measured by the second extraction with 2-percent citric acid expressed as a percentage of total P which was 46.0, 40.3, 34.8, and 26.6 in KRP, Tilemsi RP, Gafsa RP and Taiba RP, respectively (Table 11). The solubility of KRP in 2-percent citric acid as the percentage of total P was higher than the other RP materials. However, the order of dissolution of four RP materials at the end of incubation was Tilemsi RP>Gafsa RP>Taiba RP> KRP (Table 23) which is related to P solubility measured by 2-percent citric acid extraction as the percentage of rock (Table 11). The second extractions with 2-percent citric acid as the percentage of rock were 4.88, 4.36, 4.23, and 2.05 in Tilemsi RP, Gafsa RP, Taiba RP and KRP, respectively (Table 11).

The lower dissolution of KRP at the end of incubation is probably due to the high calcium carbonate equivalent of KRP (Table 11) in which the carbonate content of KRP neutralized the soil acidity and reduced rock phosphate dissolution. The four RP materials were added to the soils at the rate of 500 mg P kg⁻¹. The total P in KRP was 4.45 %P while total P in Gafsa, Tilemsi and Taiba RP were 12.5, 12.1 and 15.9 %P, respectively. The amount of KRP added to the soils was 11.24 g kg⁻¹soil while Gafsa RP, Tilemsi RP and Taiba RP were added to the soils at the rate of only 4, 4.1 and 3.1 g RP kg⁻¹ soil, respectively. The calcium carbonate equivalent of KRP was higher than all other RP materials which was about 7.02 g of lime from KRP per kilogram of soil. On a field scale this is approximately equivalent to the extremely high application of 14,000 kg of lime per hectare. Thus, the soil pH at the end of incubation of six acid sulfate soils receiving KRP was higher than the pH of the soils receiving the other RP materials (Table 21). The pH of Rsa, Ok, and Se soils incubated with KRP increased to 5.2, 5.2 and 5.8, respectively, while the pH of these soils mixed with the Gafsa RP increased only to 4.3, 4.7 and 4.7, respectively. The pH of Rsa, Ok, and Se soils receiving KRP was, therefore, higher than the pH of these soils receiving Gafsa RP by about 0.9, 0.5 and 1.1 units, respectively.

Table 22 Dissolution of Kanchanaburi RP, Gafsa RP, Tilemsi RP and Taiba RP in six acid sulfate soils at time 0 as represented by the differences in NaOH-extractable-P. Application rate 500 mg P kg⁻¹.

Soil series	Dissolution of rock phosphates (mg P kg ⁻¹)			
	Kanchanaburi	Gafsa	Tilemsi	Taiba
Rangsit very acid (Rsa)	125.01	56.31	86.25	27.55
Ongkharak (Ok)	154.07	70.54	99.36	33.82
Rangsit (Rs)	110.47	51.03	93.38	37.52
Sena (Se)	133.84	52.02	112.18	40.92
Mahaphot (Ma)	104.49	63.65	70.29	16.15
Chachoengsao (Cc)	103.92	60.58	102.63	17.29

Table 23 Dissolution of Kanchanaburi RP, Gafsa RP, Tilemsi RP and Taiba RP in six acid sulfate soils at the end of incubation (56 days) as represented by the differences in NaOH-extractable-P. Application rate 500 mg P kg⁻¹.

Soil series	Dissolution of rock phosphates (mg P kg ⁻¹)			
	Kanchanaburi	Gafsa	Tilemsi	Taiba
Rangsit very acid (Rsa)	248.33	330.25	408.68	317.52
Ongkharak (Ok)	292.26	380.37	435.04	316.43
Rangsit (Rs)	130.82	252.68	307.64	187.93
Sena (Se)	240.65	405.08	413.01	315.33
Mahaphot (Ma)	165.97	219.98	242.84	128.63
Chachoengsao (Cc)	137.41	214.72	291.17	205.5

4.3 Developing rock phosphate dissolution model

4.3.1 Developing a RP dissolution model based on the Mitscherlich equation

The change in $\Delta\text{NaOH-P}$ in six acid sulfate soils incubated with four RP materials was modeled using a Mitscherlich equation (eq. 5) for describing the RP dissolution. A high A value indicates that a large amount of RP was dissolved. A high B value represents a greater difference in RP dissolution between time 0 and the end of incubation. Soils with high C values tend to reach an equilibrium in RP dissolution more quickly than those with small values. The equations describing KRP, Gafsa RP, Tilemsi RP and Taiba RP dissolution in six acid sulfate soils are shown in Table 24. In general, the dissolution of Tilemsi RP in the six acid sulfate soils was well described by the Mitscherlich equation as indicated by the low residual mean squares. The residual mean square of fit of the Mitscherlich model to the dissolution of four rock phosphates in Rsa, Ok and Se soils was higher than the residual mean square of Rs, Ma and Cc soil (Table 24). Thus the Mitscherlich equation better described dissolution of the four RP dissolutions in the Rs, Ma and Cc soils than in the Rsa, Ok and Se soils. The A, B and C coefficients of the four RP materials in six acid sulfate soils were clearly different with different RP materials and soils (Table 24).

Table 24 Equations describing the dissolution of diverse RP in six acid sulfate soils as fitted by Mitscherlich equation ($Y = A - Be^{-cx}$) and the resulting residual mean square.

Soils	Rock phosphates			
	Kanchanaburi RP		Gafsa RP	
	equation	RMS [†]	equation	RMS
Rsa	$Y = 239.2 - 105.7e^{-0.1027x}$	30.5	$Y = 324.1 - 251.2e^{-0.1175x}$	26.0
Ok	$Y = 262.8 - 98.52e^{-0.0945x}$	15.0	$Y = 363.7 - 287.8e^{-0.1266x}$	23.3
Rs	$Y = 127.5 - 17.96e^{-0.2515x}$	2.40	$Y = 287.9 - 228.7e^{-0.0815x}$	24.3
Se	$Y = 238.1 - 112.1e^{-0.1197x}$	9.71	$Y = 387.3 - 336.5e^{-0.1323x}$	14.2
Ma	$Y = 124.2 - 19.88e^{-0.2391x}$	16.1	$Y = 234.2 - 170.7e^{-0.2015x}$	16.2
Cc	$Y = 120.2 - 15.46e^{-0.1856x}$	6.65	$Y = 231.2 - 172.5e^{-0.2726x}$	11.0

Table 24 (cont'd)

Soils	Rock phosphates			
	Tilemsi RP		Taiba RP	
	equation	RMS	equation	RMS
Rsa	$Y = 392.7 - 308.4e^{-0.3381x}$	12.5	$Y = 298.0 - 247.0e^{-0.1078x}$	23.1
Ok	$Y = 418.0 - 321.9e^{-0.3664x}$	17.5	$Y = 310.9 - 265.7e^{-0.1211x}$	15.9
Rs	$Y = 309.0 - 213.6e^{-0.2515x}$	8.82	$Y = 185.2 - 148.5e^{-0.3088x}$	4.40
Se	$Y = 404.4 - 298.0e^{-0.3353x}$	8.21	$Y = 292.5 - 223.9e^{-0.1105x}$	28.1
Ma	$Y = 242.9 - 177.0e^{-0.2901x}$	7.65	$Y = 124.6 - 110.6e^{-0.2901x}$	4.68
Cc	$Y = 279.8 - 172.9e^{-0.2050x}$	15.3	$Y = 195.6 - 173.3e^{-0.2239x}$	12.2

Note: [†]Residual mean square

The A, B and C coefficients were then regressed on soil and RP properties to determine whether they could be adequately predicted from measured soil properties. Increasing soil acidity as measured by pH, KCl-extractable Al and Al saturation gave high correlations with increasing values of coefficient A (Table 25). An

increase in coefficient A of Gafsa RP also occurred with increasing effective cation exchange capacity. The P solubility of RP materials as measured by 2-percent citric acid (second extraction) gave a high positive correlation with coefficient A for the six acid sulfate soils (Table 26). Calcium carbonate equivalent was negatively correlated with the A coefficient of five acid sulfate soils. In the Mahaphot soil there was no significant correlation. The high soil pH, iron content and organic matter in Mahaphot soil may have enhanced the reduction of iron after flooding, therefore pH of this soil increased quickly. The pH of Mahaphot soil without RP and incubated with KRP at 56 days was 6.2 and 6.4, respectively while pH of this soil incubated with other RP materials was 6.5. The calcium carbonate in RP may not have been neutralized in this soil.

Table 25 The correlation between maximum dissolution of KRP, Gafsa, Tilemsi RP and Taiba RP (the Mitscherlich coefficient A, $Y = A - Be^{-cx}$) and selected chemical properties of six acid sulfate soils.

Soil properties	Rock phosphates (r)			
	KRP	Gafsa RP	TilemsiRP	Taiba RP
pH _{water} (1:1)	-0.85*	-0.95**	-0.93**	-0.92**
Extractable P (mg kg ⁻¹) [†]	-0.46	-0.54	-0.40	-0.23
Extractable Al (g kg ⁻¹) [‡]	0.98**	0.87*	0.93**	0.92**
Al saturation (%)	0.96**	0.80**	0.89*	0.89*
Extractable Fe (g kg ⁻¹) [#]	-0.37	-0.03	-0.44	-0.16
Extractable Fe (g kg ⁻¹) ^{††}	-0.64	-0.75	-0.69	-0.78
Extractable Ca (g kg ⁻¹) ^{‡‡}	-0.67	-0.42	-0.67	-0.72
Effective cation exchange capacity (cmol _c kg ⁻¹)	0.67	0.85*	0.75	0.72
P retention (%) ^{##}	0.32	0.32	0.44	0.49

Note: [†]Bray 2 [‡]1M KCl [#]Ammonium oxalate ^{††}Dithionite

^{‡‡} 1M Ammonium acetate pH 7

^{##}Saunders (1965)

*significant at α 0.05

**significant at α 0.01

Table 26 The correlation between maximum dissolution (the Mitscherlich coefficient A, $Y = A - Be^{-cx}$) of KRP, Gafsa, Tilemsi RP and Taiba RP in six acid sulfate soils with some properties of four RP materials.

RP properties	Soils (<i>r</i>)					
	Rsa	Ok	Rs	Se	Ma	Cc
Total P (% of rock)	0.55	0.05	0.49	0.49	0.30	0.64*
Neutral ammonium citrate, second extraction (%P of rock)	0.39	0.40	0.49	0.50	0.23	0.52
2-percent citric acid, second extraction (%P of rock)	0.89**	0.87**	0.86**	0.86**	0.68*	0.94**
2-percent formic acid, first extraction (%P of rock)	0.34	0.50	0.50	0.51	0.34	0.48
Calcium Carbonate Equivalent (%)	-0.88**	-0.81**	-0.71**	-0.70**	-0.50	-0.88**
Total Ca (%)	0.42	0.39	0.44	0.45	0.21	0.53
Particle size (%) (<100 mesh)	0.36	0.28	0.07	0.05	0.08	0.21
2-percent citric acid, second extraction (%P of total P)	-0.17	-0.12	-0.14	-0.15	0.10	-0.28

Note: *significant at α 0.05 **significant at α 0.01

4.3.2 Developing a model for generalization of rock phosphate dissolution in acid sulfate soils.

So far, Mitscherlich equations (eq. 5) have been fitted to the dissolution of a single rock phosphate in numerous soils (Sidibé-Diarra *et al.*, 2004). In this study Mitscherlich equations have adequately described the dissolution of several individual rock phosphates in numerous acid sulfate soils. So far, no study has predicted the dissolution of many rock phosphates in many acid sulfate soils. The utility of the algorithm it would be

much greater if the dissolution of nearly any rock phosphate could be predicted in nearly any acid sulfate soil. The work in this section seeks to determine if such a generalization is possible, and if so, what the general equation would include.

From the previous studies in experiment 3 have shown that individual dissolution of RPs in acid sulfate soils can be predicted from the soil properties. The objective of this study was to generalize the prediction of RP dissolution to include various RP materials and various soils. Both soil and RP properties gave a high correlation with the A coefficient of four RP materials' dissolution in six acid sulfate soils. This provided the basis for generalizing the model that was successful in predicting the dissolution of a single RP but in multiple soils (Sidibé-Diarra *et al.*, 2004) to include variety of rock phosphates. A model for predicting the dissolution of four RP materials in six acid sulfate soils was developed using both soil and RP properties. This model can generalize the dissolution of various RP materials in acid sulfate soils. The precision of predicting RP dissolution from the RP dissolution model which was developed from both soil and RP properties was evaluated by residual mean squares of the prediction equation.

The model coefficients of RP dissolution in flooded acid sulfate soils were then estimated from the effects of both soil and RP properties on the RP dissolution using regression methods. The A, B and C coefficients of four RP materials dissolution in six acid sulfate soils were related to both the soil and RP properties using stepwise regression analysis. The regression between A, B and C coefficients and soil and RP properties provided the following equations:

$$A = -245.9 + 155.9 \text{KCl-extractable Al} + 66.82 \text{citric acid content of the RP (\%P of rock)} + 4.69 \text{citric acid content of the RP (\% P of Total P in the RP)}$$

$$\text{adj. } R^2 = 0.91^{**} \quad (\text{eq. 21})$$

$$B = -149.0 + 132.79 \text{KCl-extractable Al} + 67.15 \text{citric acid content of the RP (\%P of rock)}$$

$$\text{adj. } R^2 = 0.91^{**} \quad (\text{eq. 22})$$

$$C = -0.2864 + 0.084 \text{soil pH} + 0.019 \text{citric acid content of the RP (\%P of rock)} + 0.0016 \text{size of the RP (\% less than 100 mesh)}$$

$$\text{adj. } R^2 = 0.41^{**} \quad (\text{eq. 23})$$

Increasing soil acidity as measured by KCl-extractable Al increased coefficients A and B of RP dissolution reflecting greater dissolution. The A coefficient increased with both increasing content and quality of soluble P in rock phosphate as extracted by 2-percent citric acid. The content and quality of soluble P in RP was represented by both the P solubility percentage of the rock and the total P in the rock, respectively. The importance of both of these factors indicates that both the amount of P in the rock phosphate as well as its solubility are crucial. Soil pH, RP solubility measured by the second extraction with 2-percent citric acid and the particle size of RP were the factors controlling the C coefficient. The substitution of soil and RP properties into equation (21), (22) and (23) was then used to estimate coefficients A, B and C. The A, B and C coefficients were substituted into equation 5 in order to estimate the dissolution of each rock in each of the flooded acid sulfate soils.

The predicted coefficients A, B and C of KRP, Gafsa RP, Tilemsi RP and Taiba RP dissolution in six flooded acid sulfate soils by the RP model and their residual mean square are shown in Table 27. This residual mean square was slightly higher than the residual mean square of predicted four RP materials dissolution by Mitscherlich fit (Table 24). This indicated that the predicted dissolution based on the general model was slightly less accurate than predicting RP dissolution by individual RP models. However, the RP dissolution model was used to predict KRP, Gafsa RP, Tilemsi RP and Taiba RP dissolution in flooded six acid sulfate soils at 56 days as a maximum dissolution of four RP materials during incubation period. The predicted dissolution of KRP, Gafsa RP, Tilemsi RP and Taiba RP in six acid sulfate soils at 56 days was plotted with the observed RP dissolution in order to evaluate the developed model (Figure 13). The predicted RP dissolution at 56 days was close to the observed RP dissolution, suggesting that the generalized model could satisfactorily predict dissolution for combinations of rock phosphates of solubility varying from highly soluble to low solubility and in a range of acid sulfate soils.

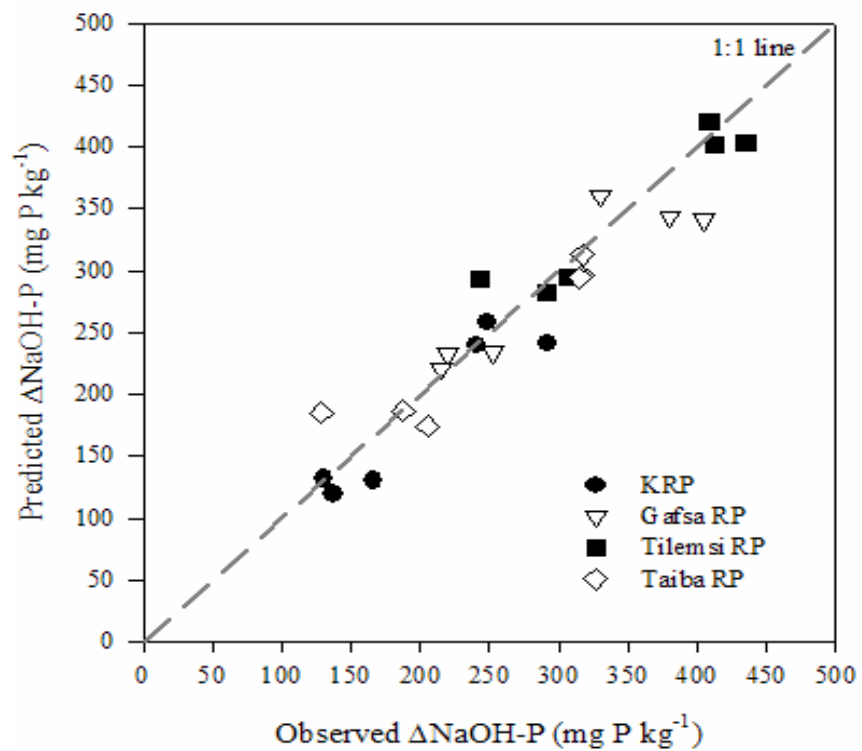


Figure 13 The dissolution of KRP, Gafsa RP, Tilemsi RP and Taiba RP dissolution in six acid sulfate soils at 56 days as predicted by a model developed from both soil and RP properties. The dashed line indicates a 1:1 relationship.

Table 27 Equations describing RP dissolution in six acid sulfate soils as fitted by RP model ($Y = A - Be^{-cx}$) which were developed using soil and RP properties.

Soils	Rock phosphates			
	Kanchanaburi RP		Gafsa RP	
	equation	RMS [†]	equation	RMS
Rsa	$Y = 258.3 - 125.4e^{-0.1729x}$	39.8	$Y = 360.1 - 280.5e^{-0.1467x}$	47.9
Ok	$Y = 241.2 - 110.7e^{-0.1670x}$	27.4	$Y = 343.0 - 265.8e^{-0.1408x}$	26.7
Rs	$Y = 132.1 - 17.82e^{-0.1964x}$	4.50	$Y = 233.9 - 172.9e^{-0.1702x}$	45.8
Se	$Y = 239.6 - 109.4e^{-0.1409x}$	11.8	$Y = 341.4 - 264.5e^{-0.1147x}$	41.7
Ma	$Y = 130.5 - 16.49e^{-0.2309x}$	16.1	$Y = 232.3 - 171.6e^{-0.2048x}$	16.9
Cc	$Y = 119.6 - 7.20e^{-0.2065x}$	7.80	$Y = 221.4 - 162.3e^{-0.1804x}$	24.8

Table 27 (cont'd)

Soils	Rock phosphates			
	Tilemsi RP		Taiba RP	
	Equation	RMS	equation	RMS
Rsa	$Y = 420.7 - 315.3e^{-0.2809x}$	25.1	$Y = 313.0 - 271.7e^{-0.1910x}$	45.3
Ok	$Y = 403.5 - 300.7e^{-0.2750x}$	31.9	$Y = 295.9 - 257.1e^{-0.1851x}$	24.3
Rs	$Y = 294.4 - 207.8e^{-0.3045x}$	14.1	$Y = 186.7 - 164.2e^{-0.2146x}$	16.4
Se	$Y = 402.0 - 299.4e^{-0.2489x}$	22.7	$Y = 294.3 - 255.8e^{-0.1590x}$	31.9
Ma	$Y = 292.8 - 206.5e^{-0.3390x}$	52.1	$Y = 185.2 - 162.8e^{-0.2491x}$	50.6
Cc	$Y = 281.9 - 197.2e^{-0.3146x}$	22.0	$Y = 174.2 - 153.5e^{-0.2247x}$	22.2

Note: [†]Residual mean square

5. Experiment 5: Incubation evaluation of the availability of dissolved rock phosphate in flooded acid sulfate soils.

This experiment was conducted to review the second of the two key processes that determine the plant availability of rock phosphates added to soils in direct application. The two processes are 1) dissolution of the rock phosphate and 2) The sorption of the dissolution products and their plant availability. The sorption of the dissolved RP can be expressed by the proportion of dissolved RP that remains available to plant. These important reactions depend on soil and RP properties. The ratio of dissolved RP that remains available to plants may provide a useful algorithm to estimate the sorption of dissolved RP, which, when coupled with the estimation of rock phosphate dissolution, may provide the quantitative estimation of the amount of RP needed to supply a P deficit identified by a soil test. In this section we describe the sorption of the dissolved P as a measure of its plant availability.

The objectives of this study were (1) to measure the availability of dissolved RPs in six flooded acid sulfate soils and (2) to develop an algorithm to estimate sorption of the dissolved RP and thus estimate the amount available to plants. The derived algorithm should be amenable to inclusion in the PDSS software.

5.1 Determination of RP availability by Bray 1 and 2 method

5.1.1 Bray 1-extractable dissolved rock phosphates.

The plant availability of the P dissolved from rock phosphate where KRP, Gafsa RP, Tilemsi RP and Taiba RP were applied was estimated by Bray 1 (Figure 14). The Bray 1 extractable P from KRP in Rsa, Ok and Se soils at 0-7 days increased and became relatively stable after 14 days of incubation. The extractable P in Rs, Ma and Cc soils decreased after 21 days of incubation, and thereafter, however, continued to slightly increase. The decrease in Bray 1 extractable P after a few days of incubation may be due to several factors including re-adsorption on newly formed Fe^{2+} and residual hydrous oxide phases as well as by P precipitation by Fe^{2+} and Ca^{2+} (Holford and Patrick, 1979). The P

sorption capacity increased in reduced soil at the final soil pH around 6.4 (Holford and Patrick, 1979) with a high level of added P (Khalid *et al.*, 1977). The pH of Rs, Ma and Cc soils increased to 6.5-7 and the extractability of P Bray 1 was reduced.

The P extracted by Bray 1 where Gafsa RP was applied to six acid sulfate soils was similar to the extractable P in soils where KRP was applied except in the Ok and Rs soils (Figure 14). The Bray 1-extractable P in Ok and Rs soils increased from 0-7 days and then decreased after 14 days of incubation. Bray 1-extractable P at 0-7 days of incubation increased where Tilemsi RP was applied and became stable after 14 days of incubation. The Bray 1-extractable P with RP incubation in Rsa, Ok and Se soils where Taiba RP was applied increased and became stable after 14 days of incubation. Bray 1-extractable P at 0-14 days of incubation in Rs, Ma and Cc soils where Taiba RP was applied continuously increased and became stable after 14 days of incubation.

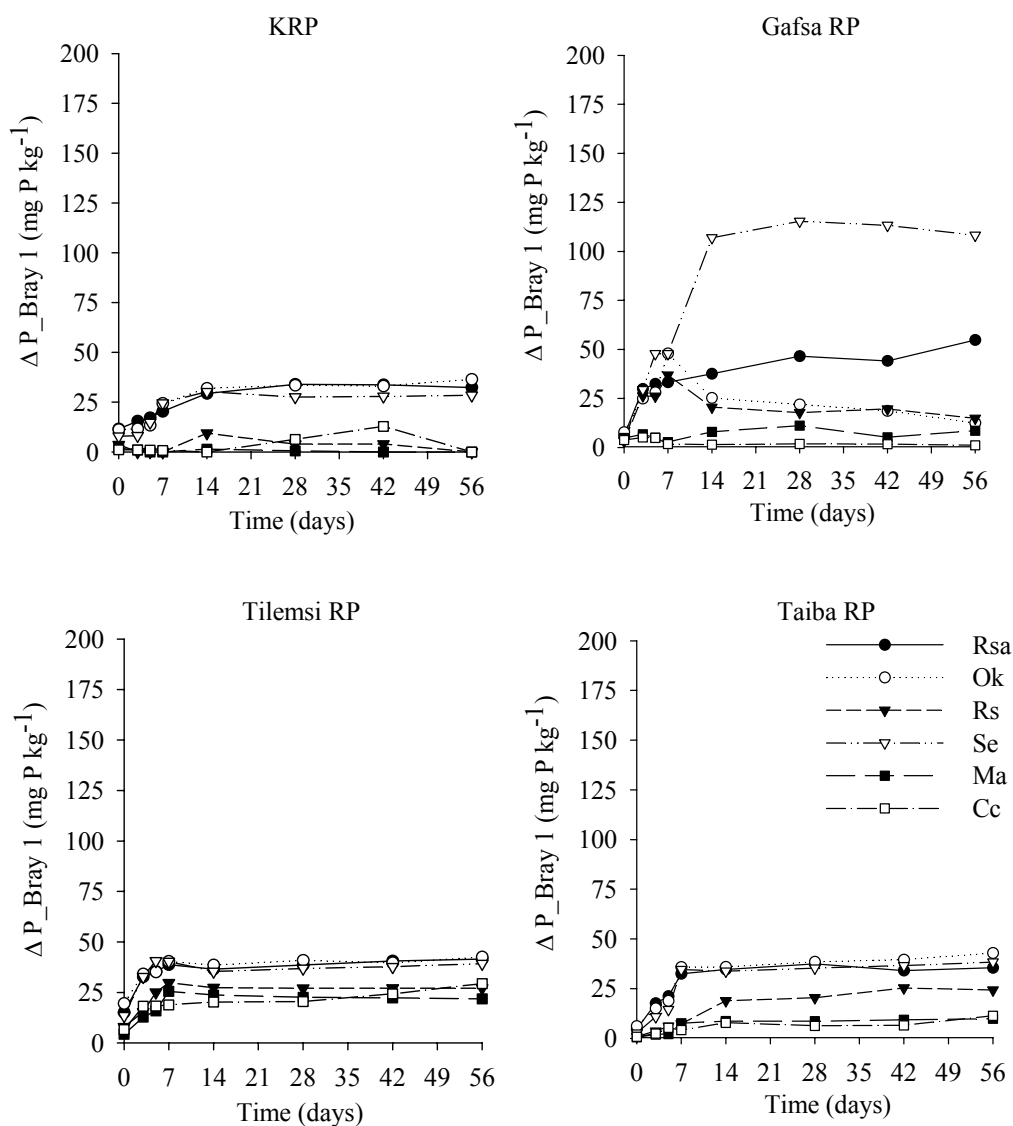


Figure 14 Extractable P from acid sulfate soils as represented by the differences in Bray 1 extractable P between RP-amended ($\text{RP } 500 \text{ mg P kg}^{-1}$) and unamended soils.

5.1.2 Bray 2-extractable dissolved rock phosphate.

The availability of P in six acid sulfate soils where KRP, Gafsa RP, Tilemsi RP and Taiba RP were applied was estimated by Bray 2 extraction (Figure 15). The Bray 2-extractable P in six acid sulfate soils where four RP materials were applied increased from 0-7 days. After 14 days of incubation Bray 2-extractable P in six acid sulfate soils slightly decreased and become stable except in Ok soils where Gafsa RP was applied. However, the strong acidity of Bray 2 extraction can dissolve a substantial

amount of undissolved rock phosphate during extraction (Chien, 2004). Then, the RP availability which was determined by Bray 2-extraction can be overestimated (Yost *et al.*, 1992).

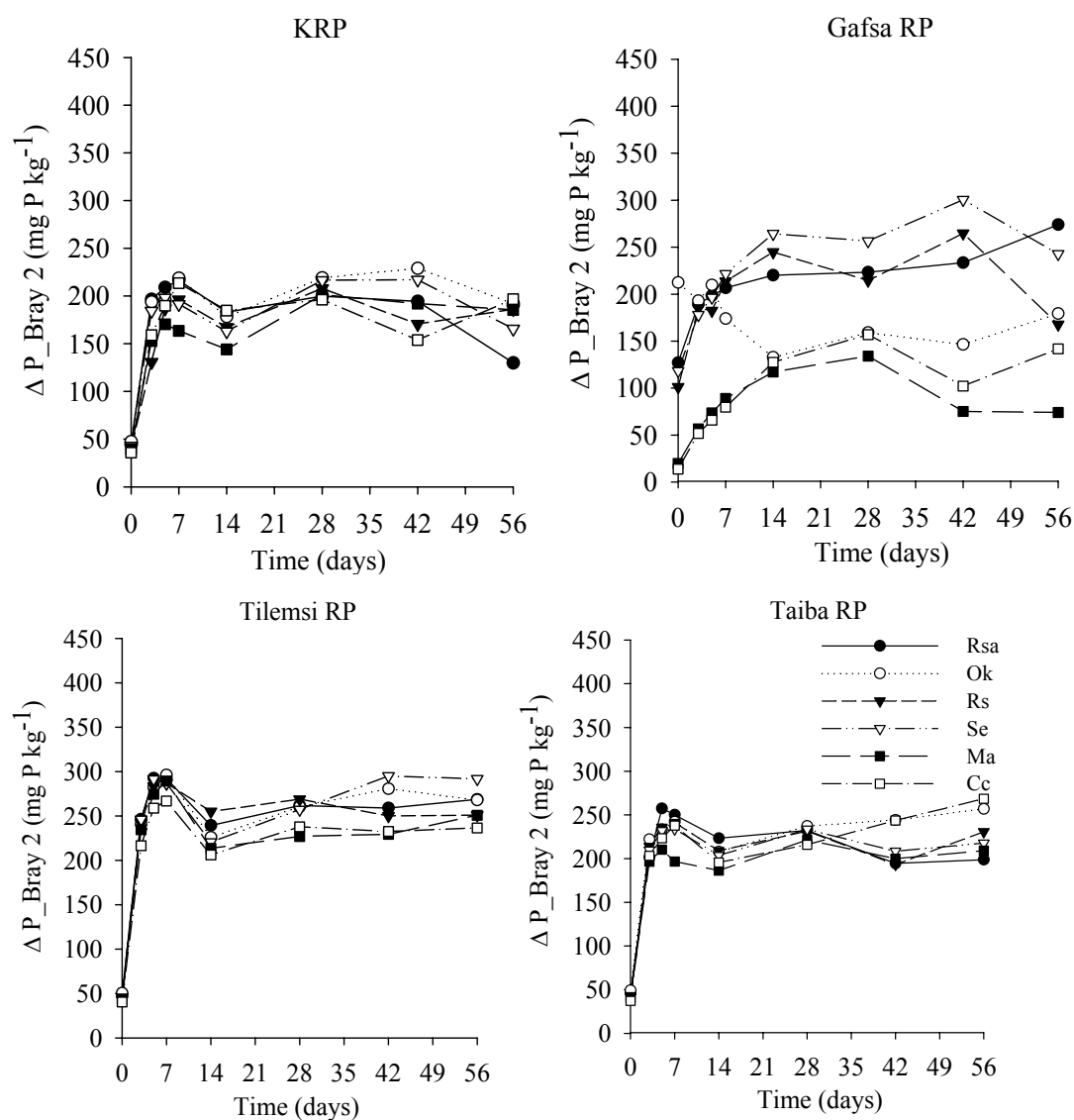


Figure 15 Extractable P from acid sulfate soils as represented by the differences in Bray 2 extractable P between RP-amended (RP 500 mg P kg⁻¹) and unamended soils.

5.2 Estimating the $\Delta P_{\text{NaOH}} / \Delta P_{\text{extractant}}$ ratio as the variable in PDSS

Returning to the basic concepts of rock phosphate availability, we have shown that the dissolution of RP is only one process affecting its availability. The second step is the sorption that occurs of the dissolved RP. Not all of the dissolved phosphate will be available to the plant. Several researchers have tried to correlate the relationship between dissolution of RP with crop yield and P uptake by plant but the correlation was poor (Syers and MacKay, 1986; Bolan and Hedley, 1990). Sorption of the dissolved P from rock phosphate apparently plays an important role in P availability to the plant. A ratio of the dissolved RP to a measure of the availability of the dissolved RP is proposed to represent the effect of P sorption by the soil after RP is added and dissolved in the soil. We tested this proposed measure by calculating the ratio of the change in NaOH-P (ΔP_{NaOH}) to the usual indexes of P availability Bray 1 or Bray-2. In other studies, the ratio of ΔP_{NaOH} to Bray 1 or Olsen P in West Africa soils could be predicted using percent clay (Sidibé-Diarra et.al, 2004).

The ΔP_{NaOH} of four RP materials in six acid sulfate soils of experiment 4 were used to calculate the ratio of $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ and Bray 2. The ratio of $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ was different in different soils and RPs. The $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ ratio of four RP materials in six acid sulfate soils was different at the initial time of incubation (Figure 16 and Appendix Table 1). The $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ ratios of four RP materials in Rsa and Se soils seemed to stabilize after 7 days of incubation while the ratio in other soils fluctuated and reached a high value (Appendix Table 1). The relationship between RP dissolution and Bray 1-extractable P can be explained by $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ ratio. For example, the $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ ratio of KRP in Rsa soil at 14 days after incubation was 8.3 (Appendix Table 1), which indicates that the RP dissolution to Bray 1-extractable P ratio was 8.3:1. If KRP dissolved in Rsa soil at 83 mg P kg⁻¹ then the Bray 1-extractable P was 10 mg P kg⁻¹. So, the P sorption of dissolved KRP in Rsa soil, extracted by Bray 1, was 73 mg P kg⁻¹. A high value of $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ ratio indicated that a large amount of RP must be dissolved to provide even small amounts of available P, or, in other words, the soil sorbed the dissolved P very strongly. As shown in Figure 16, the ratio tended to stabilize after 7 days for the high and medium solubility RP, but 14 days was required for the low solubility RP.

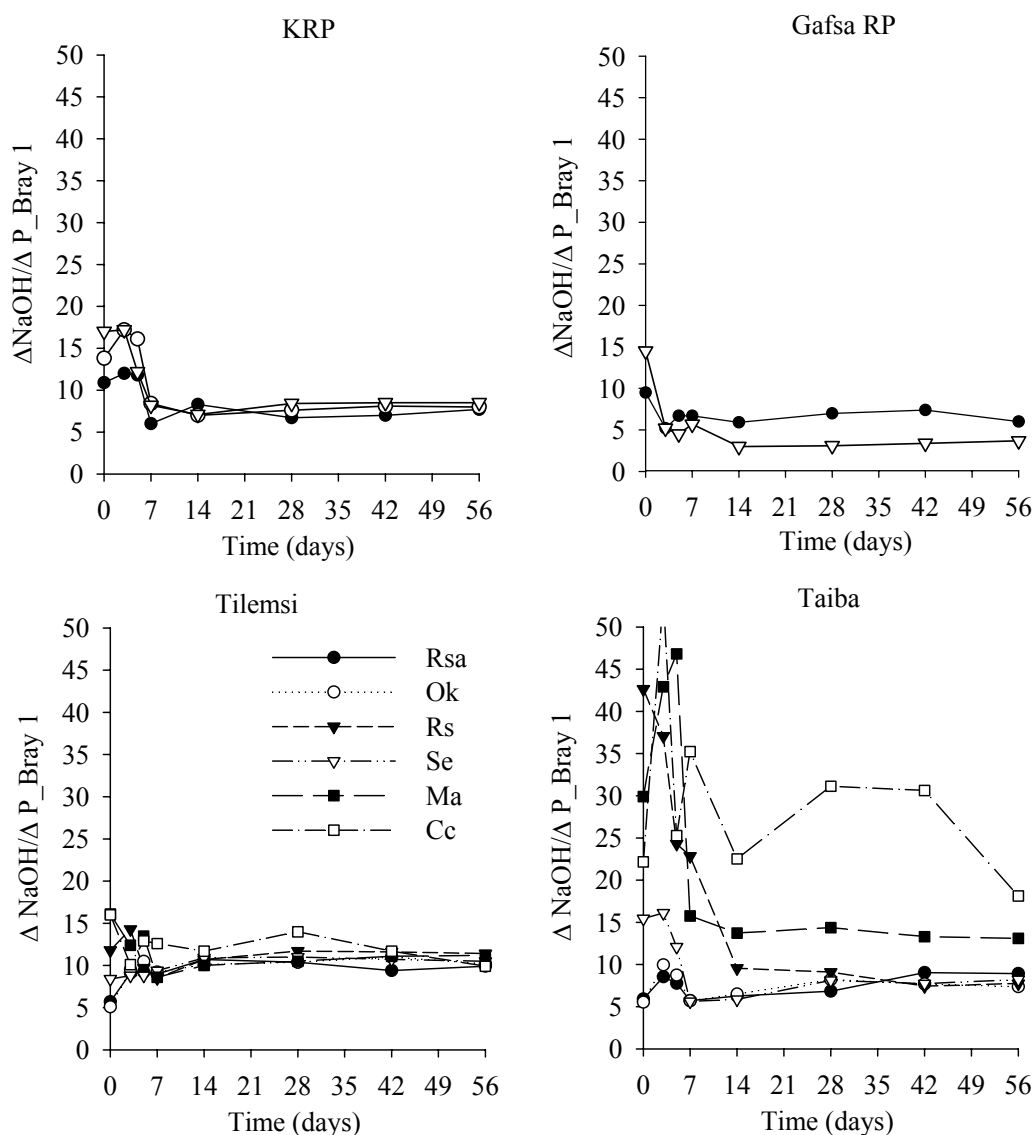


Figure 16 The $\Delta\text{P_NaOH}/\Delta\text{P_Bray 1}$ ratio of six acid sulfate soils in which four RP materials have been applied under submerged condition.

The $\Delta\text{P_NaOH}/\Delta\text{P_Bray 2}$ ratio of KRP, Tilemsi RP and Taiba RP in six acid sulfate soils was generally much lower than the ratio of $\Delta\text{P_NaOH}/\Delta\text{P_Bray 1}$ (Figure 16 and 17; Appendix Table 2). The $\Delta\text{P_NaOH}/\Delta\text{P_Bray 2}$ ratio of four RP materials in six acid sulfate soils seem to stable after 7 days of incubation (Figure 17). The $\Delta\text{P_NaOH}/\Delta\text{P_Bray 2}$ ratio of four RP materials in six acid sulfate soils after 7 days of incubation was approximately 0.54-2.97. Then RP dissolution: Bray 2-extractable P ratio was 0.54-2.97:1. The amount of dissolved RP which was extracted by Bray 2 was much

higher than that extracted by Bray 1 resulting in the lower ratio. This would be expected from the high acidity in the Bray 2-extracting solution, which extracts much more P than the Bray 1-extracting solution. Therefore, P sorption of dissolved RP which was evaluated by Bray 2 was lower than that estimated by Bray 1 extraction. The ratio of $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 2}}$ become relatively stable with time and thus can be used to make the conversion between the deficits in extractable P and the NaOH-extractable P for RP. It is a crucial conversion to enable the quantitative predictions of amounts of RP model to generate the ΔP_{NaOH} .

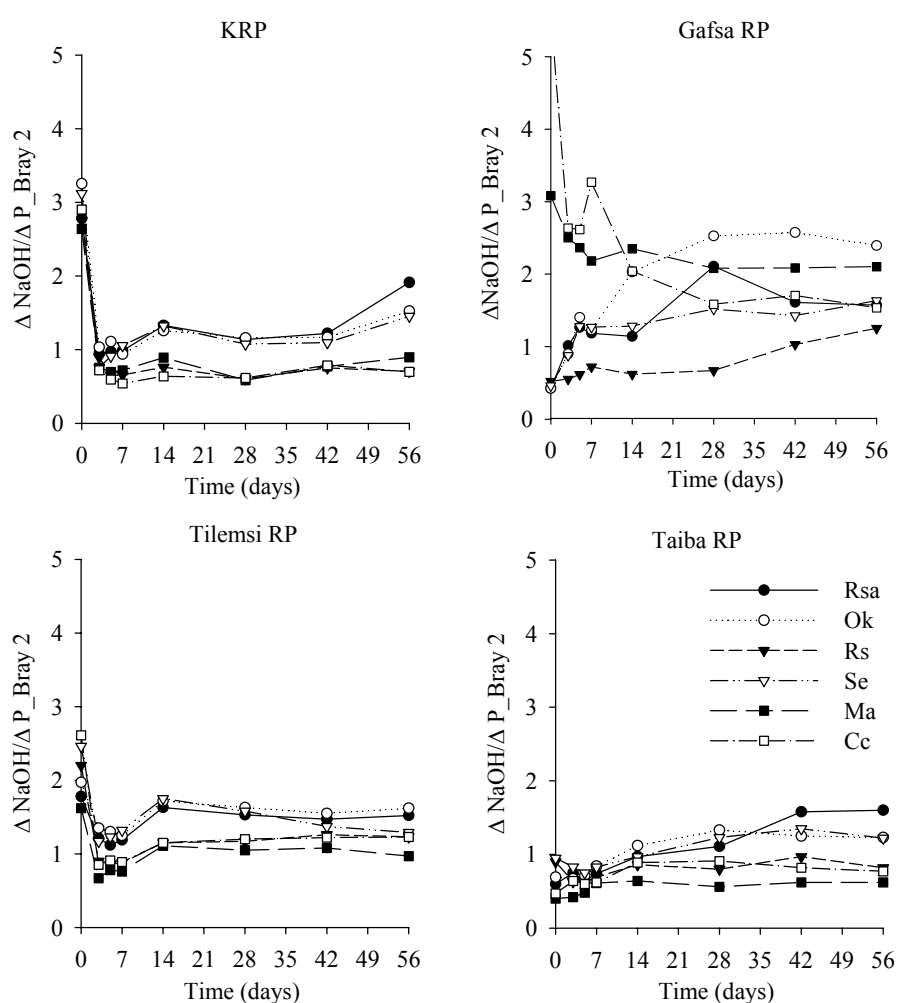


Figure 17 The $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 2}}$ ratio of six acid sulfate soils in which four RP materials have been applied under submerged condition.

6. Experiment 6: Field testing of rock phosphate predictions for rice cultivation in two acid sulfate soils.

The PDSS software which is a software for the diagnosis, correction, and economic evaluation of P nutrient limitations of crops in Tropical zone can be revised to predict RP for rice cultivation in flooded acid sulfate soils. Variables such as those represented in the RP dissolution model, ratio of RP dissolution and availability of dissolved RP and P buffer coefficient were developed in laboratory conditions. The objective of this experiment was to field test on paddy rice, the predictions of RP application rate from the revised PDSS that includes the newly proposed algorithm that considers both soil and RP properties.

6.1 Testing of rock phosphate prediction in Rangsit soil.

6.1.1 Prediction of rock phosphate application rates for the Rangsit soil.

The KRP and Gafsa RP recommendation rates for Rs soil were estimated using PDSS equation (equation 2). The algorithm which was used in PDSS equation was developed using the Bray 2 extracting solution. The first step of estimation RP recommendation rate was to diagnose P deficiency by comparing the soil P with the P critical level. If the soil P was higher than P critical level, it indicates that P in the soil was adequate for crop growth and it is not necessary to apply P fertilizer. Bray 2-extractable P in Rs soil was 14 mg P kg⁻¹ which was lower than P critical (20 mg P kg⁻¹) as proposed by Dobermann and Fairhurst (2000). The P critical level which was proposed by Dobermann and Fairhurst (2000) was used in this study. KRP and Gafsa RP application rates were calculated according to the RP algorithm. The RP application rates were estimated by substituting soil (Table 12) and RP properties (Table 9) into the following equations:

$$RP_{\text{ added}} = \frac{P_c - P_{\text{Bray2}}}{PBC_{\text{Bray2}}} \times \frac{\Delta P_{\text{NaOH}}}{\Delta P_{\text{Bray2}}} \times \frac{500}{A - B e^{-cx}} \times \frac{\text{Depth}}{10} \times D_b \quad (\text{eq. 24})$$

$$A = -245.9 + 155.9 \text{KCl-extractable Al} + 66.82 \text{citric acid content of the RP (\%P of rock)} + 4.69 \text{ citric acid content of the RP (\% P of Total P in the RP)} \quad (\text{eq. 25})$$

$$B = -149.0 + 132.79 \text{KCl-extractable Al} + 67.15 \text{citric acid content of the RP (\%P of rock)} \quad (\text{eq. 26})$$

$$C = -0.2864 + 0.084 \text{soil pH} + 0.019 \text{citric acid content of the RP (\%P of rock)} + 0.0016 \text{size of the RP (\% less than 100 mesh)} \quad (\text{eq. 27})$$

$$\text{PBC}_{\text{Bray 2}} = 1.0661 - 0.0058 \text{P}_{\text{retention}} - 0.0111 \text{Fe}_{\text{ox}} - 0.0234 \text{Al}_{\text{ox}} \quad (\text{eq. 28})$$

Depth = 10 cm

$$D_b = 1.2 \text{ g cm}^{-3}$$

The $\Delta\text{P}_{\text{NaOH}} / \Delta\text{P}_{\text{Bray 2}}$ ratios of KRP and Gafsa RP in the Rs soil at 14 days were 0.76 and 0.62, respectively (Appendix Table 2). The prediction of KRP and Gafsa RP application rates for Rs soil were 240 and 196 kg RP ha⁻¹, respectively (Table 28). The prediction of RP application rates for Rs soil were calculated only using algorithms which was developed by Bray 2 extraction because $\Delta\text{P}_{\text{NaOH}} / \Delta\text{P}_{\text{modified Pi}}$ strip test ratio in Rs soil had not been carried out.

Table 28 Prediction of KRP and Gafsa RP recommendations for Rangsit and Ongkharak soils based on algorithms using Bray 2-extraction and modified Pi strip test P extracting methods.

Soil	P critical level (P _c) (mg P kg ⁻¹)		P in soil (mg P kg ⁻¹)		Prediction of RP recommendation rate (kg RP ha ⁻¹)	
	Bray 2	Modified Pi	Bray 2	Modified Pi	Bray 2	Modified Pi
		strip test		strip test		strip test
Rangsit						
KRP	20.0 [‡]	-	14	-	240	-
Gafsa RP	20.0	-	14	-	196	-
Ongkharak						
	TSP experiment (P _c _TSP)					
KRP	11.97	5.12	5.8	2.3	284	2542
Gafsa RP	11.97	5.12	5.8	2.3	282	1038
	RP experiment (P _c _RP)					
KRP	13.09	5.40	5.8	2.3	335	2794
Gafsa RP	13.09	5.40	5.8	2.3	333	1141

Note: [‡] P critical level in acid soil (Dobermann and Fairhurst, 2000)

6.1.2 Changes of soil pH and amount of dissolved RP during the rice growth.

The pH of Rs soil before RP application was 4.07 (air-dry soil) and increased to be 4.6 after land preparation. The pH of Rs soil with KRP and Gafsa application increased from 4.6 to 6.3 and it was constant after 2 months of RP application (Figure 18 and 19). The pH of Rs soil with different RPs application was not different. The dissolved KRP and Gafsa RP increased until 1 month after application (Figure 18 and 19). Afterwards, the dissolved KRP and Gafsa RP decreased until the end of cropping season. The decrease in the dissolved RPs may be related to the increasing of soil pH. At 4 weeks after RP application the dissolved RPs decreased while the pH of soil increased from 5.0-6.0. This was similar to the dissolved RPs in incubation study in which the dissolution of RPs reached an equilibrium at a soil pH of 5.0-6.0. The amount of dissolved RPs decreased after the pH of Rs soil was higher than 5.5. The dissolved RPs in the different rates of KRP and Gafsa applications at 0-4 weeks after application were different and the dissolved RP increased with increasing RPs application rates. After 10 weeks of application, the dissolved RPs in Rs soil where RPs were applied at the rate of 1 time of the recommendation seemed to be higher than the dissolved RPs in Rs soil which RPs were applied at the rate of 2 times of recommendation. The amount of dissolved Gafsa RP throughout the cropping season was higher than the amount of dissolved KRP (Figure 18). This might be due to the higher reactivity of Gafsa RP which was indicated by a higher solubility of RP as measured by 2-percent citric acid and neutral ammonium citrate (Table 9). However, the dissolved RPs in the experiment were determined in soil samples which were collected during cropping season. Therefore, dissolved RPs may not be actual dissolved RP because some of the dissolved RP may have been absorbed by the rice. Consequently, the decrease in dissolved RPs after 1 month of RPs application may due to uptake of dissolved RPs by rice.

6.1.3 Application of predicted RP application rate on rice yield in Rs soil.

The effects of KRP and Gafsa RP applications on rice yield were not significantly different (Table 29). The application of KRP and Gafsa RP in the Rs soil significantly increased P content in rice straw at the rates of 480 and 392 kg RP ha⁻¹ application, respectively (Table 30). However, the P uptake by grain and straw was not

significantly different. It might be that there was no response of rice yield with application of RP due to the high soil P which was already adequate for rice growth.

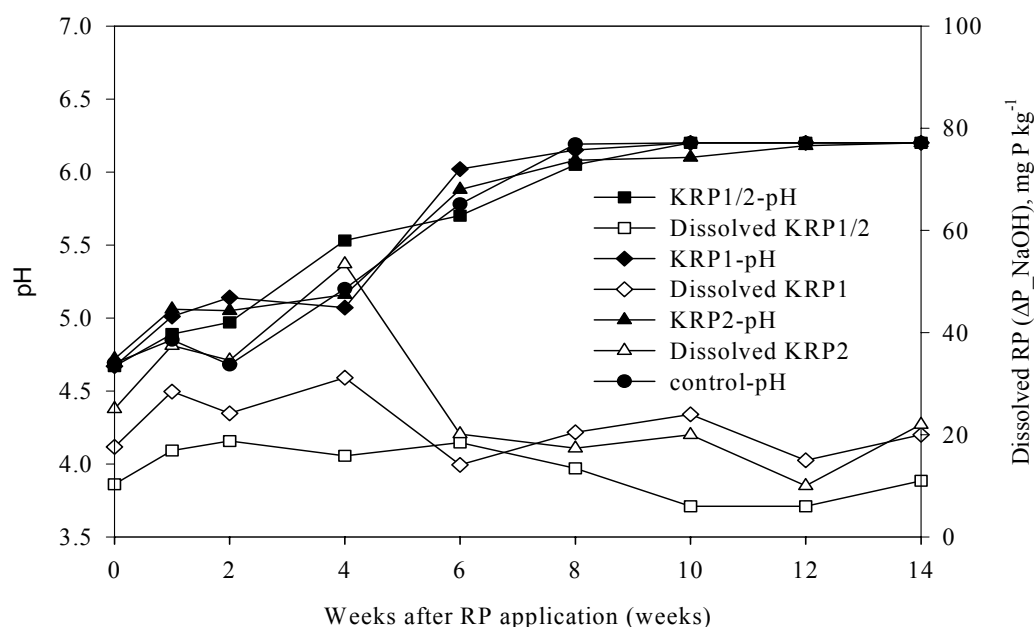


Figure 18 The dissolved KRP and changes of pH in Rs soil with KRP application.

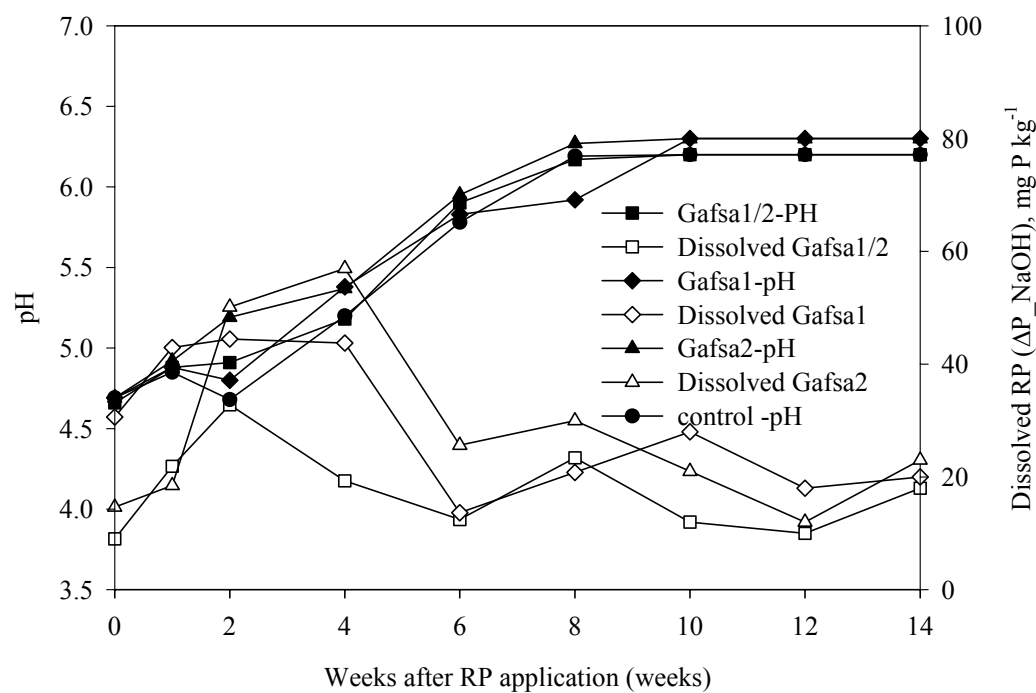


Figure 19 The dissolved Gafsa RP and changes of pH in Rs soil with Gafsa RP application.

Table 29 Rice grain yield, straw dry weight, number of grains per panicle, percent of unfilled grains and 1000 grain weight from the field comparison of actual and predicted RP application rate for the Rs soil.

Treatment	RP application rate (kg RP ha ⁻¹)	Grain yield (kg ha ⁻¹)	straw dry weight (kg ha ⁻¹)	grain/panicle	unfilled grain (%)	1000- grain weight (g)
No RP	0	4237	5694	70.03	18.43	26.75
KRP1/2	120	4418	5453	77.88	19.58	27.00
KRP1	240	4243	5947	64.90	20.45	27.14
KRP2	480	4487	5713	79.23	19.47	26.29
Gafsa 1/2	98	4531	6010	71.83	17.76	26.82
Gafsa 1	196	4387	5655	68.35	21.01	26.41
Gafsa 2	392	4468	6243	71.43	19.01	26.99
F-test						
	Block	ns	ns	ns	ns	ns
	Treatment	ns	ns	ns	ns	ns
	C.V.	5.61	14.29	13.21	18.72	3.35

Note: ns = not significant

Table 30 Phosphorus content in grain and straw and P uptake by grain and straw in the field test of the generalized RP algorithm for the Rs soil.

Treatment	Application rate (kg RP ha ⁻¹)	P content (%P)		P uptake (kg P ha ⁻¹)	
		grain	straw	grain	straw
No RP	0	0.24	0.08c	10.13	4.72
KRP1/2	120	0.23	0.09bc	10.25	5.23
KRP1	240	0.24	0.10abc	10.32	6.22
KRP2	480	0.24	0.12a	10.81	6.85
Gafsa 1/2	98	0.25	0.10abc	11.45	6.10
Gafsa 1	196	0.24	0.09bc	10.66	5.59
Gafsa 2	392	0.24	0.11ab	10.91	6.70
F-test					
Block		ns	ns	ns	ns
Treatment		ns	*	ns	ns
C.V.		7.05	14.67	10.11	23.58

Note: Means within a column followed by the same letter do not differ significantly at $\alpha = 0.05$ by DMRT

* Significant at $\alpha = 0.05$ ns = not significant

6.2 Field testing the generalized RP prediction algorithm in the Ongkharak soil.

6.2.1 Prediction of rock phosphate application rates for the Ongkharak soil.

The Bray 2-extractable P and modified Pi strip test in the Ok soil were 5.8 and 2.30 mg P kg⁻¹, respectively, which were lower than the P critical level as estimated in experiment 1 (Table 28), consequently, the Ok soil needed P fertilizer. The RP application rates were estimated by substitution of soil (Table 8) and RP properties (Table 10) in the equation 24-28.

There was no data for the $\Delta P_{\text{NaOH}} / \Delta P_{\text{modified Pi}}$ strip test ratio, so the $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ ratio of KRP and Gafsa RP in Ok soil after 7 days after incubation (Appendix Table 1) was considered a useful approximation and used to calculate RP application rates. The $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ ratios were used instead of the $\Delta P_{\text{NaOH}} / \Delta P_{\text{modified Pi}}$ strip test ratios because of Bray 1-extracting solution is a slightly acidic extracting solution. Then, Bray 1-extraction might extract available dissolved RP rather than undissolved RP (Chien, 2004). Therefore, the $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ ratios should approximate the $\Delta P_{\text{NaOH}} / \Delta P_{\text{modified Pi}}$ strip test ratios. However, use of the $\Delta P_{\text{NaOH}} / \Delta P_{\text{Bray 1}}$ ratio instead of the $\Delta P_{\text{NaOH}} / \Delta P_{\text{modified Pi}}$ strip test ratio might cause some error in the prediction of the RP requirement.

The predicted KRP and Gafsa RP application rates for Ok soil using P critical value from the TSP experiment were 284 and 282 kg RP ha⁻¹, respectively. The predicted KRP and Gafsa RP application rates for Ok soil using Pi strip test-extractable P and P critical value from TSP experiment were 2542 and 1038 kg RP ha⁻¹, respectively (Table 28). The prediction of KRP and Gafsa RP application rates which were calculated using P critical values from the RP experiment were relatively higher than using P critical value from TSP experiment (Table 28). The prediction of KRP and Gafsa RP application rates for Ok soil by two soil test methods also produced different values. However, KRP and Gafsa RP were applied to Ok soil based on the prediction of the algorithms using the modified Pi strip test method and P critical value from TSP experiment. The predicted RP application rates were applied at the rate of ½, 1 and 2 times of RP prediction in order to develop a response curve that could be used to determine the accuracy of the generalized RP prediction algorithm.

6.2.2 Changes of soil pH and amount of dissolved RP during the rice growth.

The amount of dissolved KRP and Gafsa RP at 2-4 weeks after application was at a maximum and decreased after that which might be due to the effect of pH increase (Figure 20). The pH increased with increasing RP application rate and time (Figure 20). The increase in soil pH might be due to the effect of flooding and the high calcium carbonate equivalent (CCE) of RP (especially of the KRP). The amount of

dissolved RPs in Ok soil where RPs were applied at the rate of 2 times predicted RPs rates was lower than the amount of dissolved RPs in Ok soil where RPs were applied at the rate of $\frac{1}{2}$ and 1 times of the predicted RPs rates. It might be due to the pH of KRP and Gafsa RP application, which, at 2 times of the predicted recommendation rates, was higher than the other RP application rates. Thus the CCE, thus appears to be crucial in RP application.

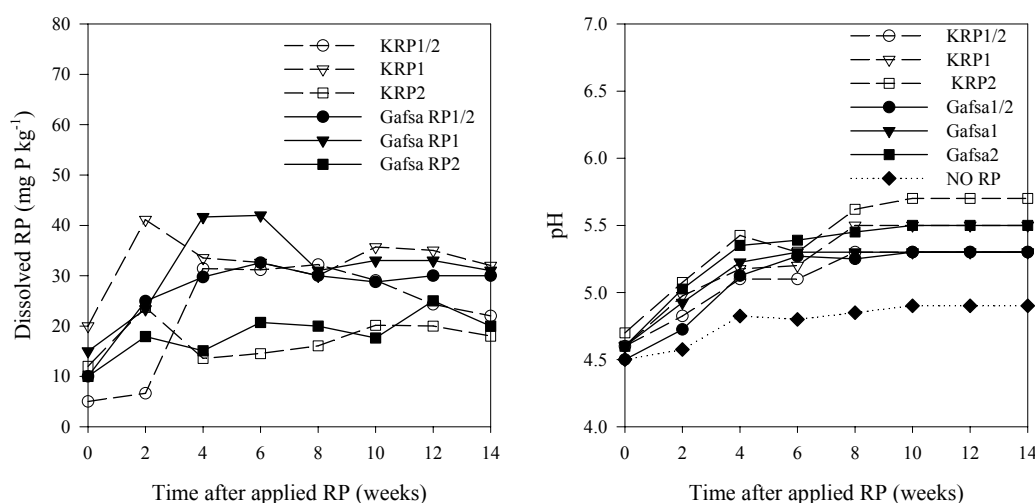


Figure 20 The amount of dissolved Kanchanaburi and Gafsa rock phosphate and change of pH during rice growth in Ok soil.

6.2.3 Response of rice to the application of RP predicted from the generalized prediction model for both various RPs and various acid sulfate soils.

The experiment was conducted at the same site and time with the study of P critical level, and unfortunately, the rice growth was also depressed by water stress and salinity from the sea water. The linear response plateau analysis between rice yield and RP application rate indicated that the maximum response of rice yield with KRP and Gafsa RP applications at the rates of 2215 and 1088 kg RP ha⁻¹, respectively. This amount of RP is close to the prediction of the generalized algorithm using modified Pi strip test method for initial P determination (Figure 21). The predicted KRP application rate which was calculated using the P critical level from RP experiment (2794 kg RP ha⁻¹) was higher than the observed KRP requirement for maximum yield. However, the predicted Gafsa RP

application rate which was calculated using P critical level from RP experiment (1141 kg RP ha⁻¹: Table 28) was close to the P requirement determined by field response.

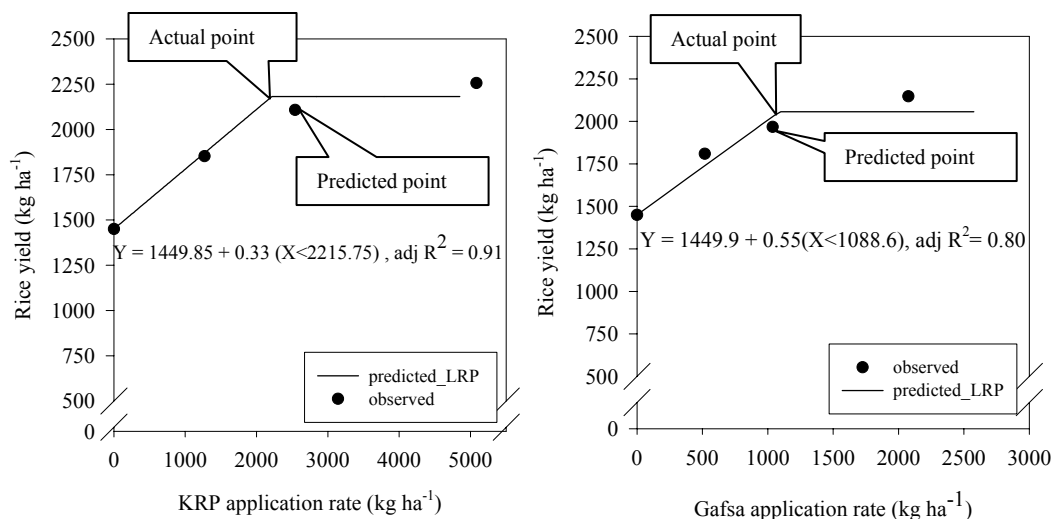


Figure 21 Field response of rice yield in Ok soil where KRP and Gafsa RP were applied according to generalized RP algorithm. Symbol- experiment data: line-predicted by Linear Response Plateau method (LRP).

Due to the fact that $\Delta P_NaOH/\Delta P_Bray$ 1 ratios were used to calculate RPs application rates instead of $\Delta P_NaOH/\Delta P_modified$ Pi strip test ratio and additional comparison was made. The $\Delta P_NaOH/\Delta P_modified$ Pi strip test ratios were studied. The soils at the highest rate of RPs application were collected at 4 weeks after RP application to determine ΔP_NaOH and $\Delta P_modified$ Pi strip test. The $\Delta P_NaOH/\Delta P_modified$ Pi strip test ratio of KRP and Gafsa RP were calculated. The $\Delta P_NaOH/\Delta P_modified$ Pi strip test ratio at the highest rate of KRP and Gafsa RP application were 7.75 and 4.89, respectively.

The $\Delta P_NaOH/\Delta P_modified$ Pi strip test ratios were used to calculate RP application rate for rice cultivation in Ok again to test the precision of algorithms which was developed by modified Pi strip test. The predicted KRP and Gafsa RP application rates which used $\Delta P_NaOH/\Delta P_modified$ Pi strip test ratios were 2578 and 1052 kg RP ha⁻¹, respectively. The predicted KRP and Gafsa RP application rates which was predicted by the $\Delta P_NaOH/\Delta P_modified$ Pi strip test ratios were lower than used the

$\Delta P_NaOH/\Delta P_Bray$ 1 ratios. However, the predicted KRP and Gafsa RP application rates which were predicted by the $\Delta P_NaOH/\Delta P_modified$ Pi strip test ratios were close to the RP requirement for maximum yield (2215 kg KRP ha⁻¹ and 1088 kg Gafsa RP ha⁻¹), especially for Gafsa RP. The minimum data which use to predict amount of RP application for rice cultivation in acid sulfate soils using modified Pi strip test is shown in appendix Table 3. Thus the error resulting from the use of $\Delta P_NaOH/\Delta P_Bray$ 1 ratios rather than $\Delta P_NaOH/\Delta P_modified$ Pi strip test ratios was small.

The analysis of variance and mean comparisons between rice grain yield and yield components is shown and explained in experiment 2 (Table 16). The RP application increased the P content in rice grain and straw (Table 31). The P content in rice grain yield was higher with KRP and Gafsa RP application at the rate of 1270 and 1038 kg RP ha⁻¹, respectively. The P content in rice straw was significantly increased with Gafsa RP applications at the rate of 2542 and 1038 kg RP ha⁻¹, respectively (Table 31). The application of KRP and Gafsa RP significantly increased P uptake in grain at the rate of 1270 and 518 kg RP ha⁻¹, respectively (Table 31). The application of KRP and Gafsa RP also significantly increased P uptake in rice straw at the rate of 5083 and 1037 kg RP ha⁻¹, respectively (Table 31).

Table 31 Phosphorus content in rice grain and straw and P uptake by rice grain and straw grown on Ongkharak soil.

Treatment	Application rate (kg RP ha ⁻¹)	P content (%P)		P uptake (kg P ha ⁻¹)	
		grain	straw	grain	straw
No RP	0	0.18b	0.08c	2.70c	5.55b
KRP1/2	1270	0.25a	0.09bc	4.67ab	7.07ab
KRP1	2542	0.24a	0.11ab	5.12ab	8.69ab
KRP2	5083	0.24a	0.12a	5.43a	9.25a
Gafsa 1/2	518	0.22ab	0.09bc	4.03b	7.65ab
Gafsa 1	1038	0.24a	0.12a	4.82ab	9.18a
Gafsa 2	2075	0.23a	0.12a	5.05ab	10.6a
F-test					
Block		ns	ns	ns	ns
Treatment		ns	*	**	*
C.V.		12.94	26.78	15.09	11.54

Note: Means within a column followed by the same letter do not differ significantly at $\alpha = 0.05$ by DMRT

** Significant at $\alpha = 0.01$ * Significant at $\alpha = 0.05$ ns = not significant

6.3 Residual effects of RP application in Ongkharak soil.

The residual effects of RP application on rice cultivation need to be evaluated because RP is also a slow release P fertilizer. The prediction of RP application rate should consider the length of time a RP application will remain effective. Consequently, the 8 by 6 m individual plot in the experiment from the RP prediction study in the Ongkharak soil was divided into two plots (plot size 4 by 6 m). The KRP and Gafsa RP were applied to the first plot at the same rate which was applied to the previous crop. There was no RP fertilizer applied in the second plot. The experiment was conducted in Ongkharak soil during August-November, 2005 (rainy season) in Thailand. The rice plants were affected

by excessive flooding about 30 days after planting until harvesting. The grain yield was lower than the average yield due to the flooding.

The maximum rice yield in this study was 1766 kg ha^{-1} , which was lower than the rice grain yield in the previous crop. The grain yield, yield components, P content and uptake in grain and straw were not different in the treated and untreated RP application plot (Table 32-35). The rice yield and straw dry weight responded with application of KRP and Gafsa RP at $\frac{1}{2}$ of the predicted RP application rate. The number of grains/panicle in this study was lower than number of grains/panicle in the previous crop. The number of grains/panicle increased with the application of KRP at the rate of 1 times the predicted rate of RP. The effects of residual RP application and predicted RP application rate on percent of unfilled grains and 1000-grain weight were not significantly different (Table 33).

The effect of RP application rate on P content in grain yield was not significantly different (Table 34). The P content of rice straw increased with the application of KRP and Gafsa RP at the rate of $\frac{1}{2}$ times the predicted recommendation rate (Table 34). The P uptake by rice grain significantly increased with the application of Gafsa RP at the rate of 2 times of predicted recommendation rate (Table 35). The P uptake by rice straw responded to the application of KRP and Gafsa at the rate of $\frac{1}{2}$ times the predicted recommendation rate (Table 35).

The freshly applied RP had no significant effect on rice yield or yield components i.e. number of grains per panicle, percent of unfilled grains and 1000-grain weight. Consequently, the residual effects of RP continued well into the second crop of rice. It remains to be seen how long such applications of RP will last and remain effective. The application of RP in Ok soil can be used by paddy rice for at least two crops.

Table 32 Rice grain yield, straw dry weight, number of grains per panicle for various rock phosphates as predicted by the generalized algorithm in Ongkharak soil for a second crop.

Treatment	Grain yield (kg ha ⁻¹)			Straw dry weight (kg ha ⁻¹)			Grain/panicle		
	applied	residual	Mean	applied	residual	Mean	applied	residual	Mean
No RP	1165	1241	1203b	2560	2586	2573b	50.91	52.82	51.87b
KRP1/2	1497	1550	1524a	3333	3323	3328a	62.00	55.80	58.90ab
KRP1	1773	1773	1773a	3930	3944	3937a	63.23	66.93	65.08a
KRP2	1668	1577	1623a	4083	3891	3987a	65.33	64.00	64.66a
Gafsa 1/2	1678	1565	1622a	3240	3382	3311a	58.15	61.15	59.65ab
Gafsa 1	1830	1701	1766a	3700	3743	3722a	59.91	57.38	58.65ab
Gafsa 2	1735	1716	1726a	3941	3769	3855a	57.77	58.63	58.20ab
Mean	1621	1589	1605	3541	3520	3531	62.10	60.21	61.00
	F-test			F-test			F-test		
Block			*			*			*
Treatment			*			**			*
Residual			ns			ns			ns
C.V.			19.91			19.85			13.87

Note: Means within a column followed by the same letter do not differ significantly at $\alpha = 0.05$ by DMRT

** Significant at $\alpha = 0.01$ * Significant at $\alpha = 0.05$ ns = not significant

Table 33 Percent of unfilled grains and 1000-grain weight on different RP application in Ongkharak soil at the second crop.

Treatment	unfilled grains (%)			1000-grain weight (g)		
	applied	residual	Mean	applied	residual	Mean
No RP	28.77	27.95	28.36	25.53	25.58	25.56
KRP1/2	25.65	24.17	24.91	25.42	24.94	25.18
KRP1	22.70	22.57	22.63	25.54	25.63	25.59
KRP2	24.84	21.08	22.96	25.63	25.38	25.51
Gafsa 1/2	25.15	22.53	23.84	25.68	25.23	25.46
Gafsa 1	24.83	20.95	22.89	25.05	25.55	25.30
Gafsa 2	24.86	22.90	23.88	24.99	25.18	25.09
Mean	25.26	23.16	24.21	25.41	25.36	25.39
			F-test			
Block	ns			ns		
Treatment	ns			ns		
Residual	ns			ns		
C.V.	22.63			3.84		

Note: ns = not significant

Table 35 Phosphorus uptake by rice grain and straw from RP applications to the Ongkharak soil for the second crop.

Treatment	P uptake (kg P ha ⁻¹)					
	grain			Straw		
	applied	residual	Mean	applied	residual	Mean
No RP	2.87	4.02	3.45b	1.58	1.78	1.68d
KRP1/2	3.75	3.42	3.59b	2.90	3.08	2.99bc
KRP1	4.00	4.45	4.23ab	3.52	3.43	3.48ab
KRP2	4.68	4.94	4.81ab	3.45	3.21	3.33ab
Gafsa 1/2	5.02	4.15	4.59ab	2.53	2.77	2.65c
Gafsa 1	5.51	5.23	5.37a	3.23	3.38	3.31ab
Gafsa 2	5.05	4.19	4.62ab	3.67	3.76	3.72a
Mean	4.41	4.34	4.38ab	2.98	3.06	3.02
			F-test			
Block			ns			
Treatment			*			
Residual			ns			
C.V.			23.38			

Note: Means within a column followed by the same letter do not differ significantly at $\alpha = 0.05$ by DMRT

** Significant at $\alpha = 0.01$ * Significant at $\alpha = 0.05$

ns = not significant

CONCLUSION

The direct application of rock phosphate to soils depends on two reactions: 1) dissolution of RP and 2) sorption of the dissolved RP. The structure of Phosphorus Decision Support System (PDSS) was revised to include the newly proposed RP algorithm and to estimate RP application rates for rice in some representative, flooded acid sulfate soils of Thailand. The parameters that were used in PDSS calculations such as P critical level, P buffer coefficient, algorithms for predicting RP dissolution and sorption of dissolved RP were developed and tested in the field. The field tests, in general, validated the predictions based on the algorithm.

Phosphorus buffer coefficients in flooded acid sulfate soils were determined using three soil test methods i.e. Bray 1, Bray 2 and modified Pi strip test. The P buffer coefficient which was estimated by Bray 2-extraction was higher than the other two soil test methods. Phosphorus buffer coefficients of those flooded acid sulfate soils were regressed with selected soil properties. The phosphorus buffer coefficients, which were extracted by Bray 1 and modified Pi strip test increased with decreasing ECEC and CEC. This might be due to ECEC and CEC in soil, reflecting the binding ability of iron and aluminum with P in soil. Decreasing P retention, oxalate extractable-iron and aluminum increased PBC which was estimated by the Bray 2-extraction. The PBC which was measured by the modified Pi strip test predicted higher P requirement than the other two methods. This may be due to the modified Pi strip test providing a more accurate measure of desorption of P to the soil solution. The property measured by the modified Pi strip test may, consequently, be better described as a desorption coefficient rather than a sorption coefficient.

A determination of the P critical level was conducted in the Ongkharak soil with triple superphosphate and two rock phosphates used as the phosphorus materials. The two P soil testing methods, Bray 2-extraction and modified Pi strip test, were used to evaluate available P. The P critical levels using TSP as extracted by Bray 2 and Pi strip test were 11.97 and 5.12 mg P kg⁻¹, respectively. The P critical levels using RP as extracted by Bray 2 and Pi strip test were 13.09 and 5.40 mg P kg⁻¹, respectively. The relationship between P uptake by rice and Bray 2-extractable P indicated that P critical level in soil fertilized with

TSP and RP were different values. However, in the case of using modified Pi strip test to measure extractable P, it gave the same value of P critical level in soil fertilized with both TSP and RP. This may suggest that where mixtures of RP and soluble P are used, the modified Pi strip test might be preferable to Bray 2 extraction.

In this study, the dissolution of several rock phosphates in several acid sulfate soils could be predicted using a generalized algorithm. Soil acidity and RP solubility were the key factors affecting the differential dissolution of four RP materials in six flooded acid sulfate soils as estimated by the difference in NaOH extractable P in soils incubated with rock phosphate. Soil acidity as measured by soil pH and KCl-extractable Al and rock phosphate solubility measured by a second extraction of 2-percent citric acid and particle size of RP were the key factors in the generalized RP dissolution model. However, the availability of RP also depends on the sorption of the dissolved RP by the soils.

The sorption of dissolved RP was quantified by Bray 1 and Bray 2 extraction. Bray 1-extraction appears to extract slightly dissolved RP. Then, the RP dissolution and availability of dissolved RP ratio was very high value. As expected the more acidic Bray 2 extracting solution extracted more P than Bray 1. The high acidity of Bray 2-extraction seems to dissolve unavailable RP because of Bray 2-extractable P at initial incubation was higher than dissolution of RP at the same time of incubation. Also because the P uptake was lower for the same value of Bray 2 for RP than for TSP. However, the RP dissolution and availability of dissolved RP ratio which was estimated by Bray 1 and Bray 2-extraction was calculated to explain sorption of dissolved RP.

Phosphorus critical level, P buffer coefficient, and algorithms for predicting RP dissolution and RP dissolution and dissolved RP ratio were used to calculate RP application rates for Rangsit and Ongkharak soils. The P critical level as extracted by Bray 2-extraction of Rs soil was 20 mg P kg^{-1} which was proposed by Dobermann and Fairhurst (2000). Bray 2-extractable P in the Rs soil was lower than the P critical level which indicated P in the soil was inadequate for rice growth. Then, KRP and Gafsa RP application rate were calculated for rice cultivation in Rs soil. The predicted KRP and Gafsa RP application rates for Rs soil were 240 and 196 kg RP ha⁻¹, respectively. However, there was no response of rice yield in Rs soil to KRP and Gafsa RP application rate.

The prediction of KRP and Gafsa RP application rates were estimated for Ongkharak soil using algorithms based on the modified Pi strip test method to extract soil P and for the critical P level. The predicted KRP and Gafsa RP application rates which were calculated from the P critical level using TSP were 2542 and 1038 kg RP ha⁻¹, respectively. The predicted KRP and Gafsa RP application rates which were calculated from the P critical level using RP were 2578 and 1052 kg RP ha⁻¹, respectively. The predicted KRP and Gafsa RP which was calculated from P critical level using TSP was designed in different levels and applied to Ok soil. The rice yield response indicated that the predicted amounts of KRP and Gafsa were, therefore, close to the field-determined RP rates necessary for maximum yield. The predicted KRP and Gafsa RP application rates which were calculated from algorithms using Bray 2-extraction were slightly underestimated. This underestimation might be due to a low value of $\Delta P_{NaOH}/\Delta P_{Bray\ 2}$ ratio, indicated low P sorption of dissolved RP, then the predicted RP application was too low.

The residual effect of RP application on Ok soil was evaluated. The residual and current RP applications did not differ in grain yields and yield components. This indicated a substantial residual effect of RP applied to Ok soil. This confirms suggestions in the literature that applications of RP to the acid sulfate soils remains available for several crops and at least for two crops as confirmed in this study.

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Appendix

Appendix1. Analytical method

1. Extracting P by the modified iron-oxide impregnated paper strip test (Pi strip test)

1.1 Preparation of Pi strip test

Hardened, ash-free, 7-cm-diam. filter paper circles (Whatman no. 542) were used to prepare Pi strips. The filter papers were immersed in 0.65 M FeCl₃.6H₂O containing 50 ml of conc. HCl overnight (Meyer *et al.*, 1997). The wet papers were allowed to drip dry at room temperature for a few hours. The dry papers were placed above an ammonia solution (1:1v/v) (Menon *et al.*, 1989). The ammonia vapor reacted with Fe chloride and converted the Fe into oxide and color of paper changed from yellow to brown. The intensity of the color depended on the amount of iron chloride.

1.2 Extraction and analysis

One filter paper coated with iron oxide was cut to two semicircles. One semicircle was placed between two mesh polyethylene screens, held by a plastic clip the screen edges were melted with flame. One gram of soil sample was added to 100 ml wide-mouthed plastic bottom. One of paper-polyethylene screen was inserted into plastic wide-mouthed beaker (Meyer *et al.*, 1997). The soil sample and modified Pi strip test was shaken in 40 ml. of 0.02 M KCl solution for 16 h. The modified Pi strip test was taken out and washed free of soil and P sorbed was dissolved in 40 ml of 0.1 M H₂SO₄ (Habib *et al.*, 1998). The amount of P in soil extracts was determined using the ammonium molybdate method, with ascorbic as the reducing agent (Murphy and Riley, 1962)

2. Extracting Al and Fe by dithionite (Asami and Kumada, 1959)

2.1 Reagent

- 0.02M EDTA solution
- 1% NaCl
- Sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$)

2.2 Procedure

Take 0.5-2.0 g of air dry soil into 200 ml Erlenmeyer flask. Three grams of sodium hydrosulfite and 100 ml of 0.02M EDTA solution were added into Erlenmeyer flask. Place it on a boiling water bath and maintain at 70 °C for 15 min. with occasional shaking. After the treatment, filter the supernatant solution into a 250 ml volumetric flask, then transfer the residual on the filter paper and wash it 3 time with 1% NaCl solution. Fill up to volume and mix well. The extractable Fe and Al were determined by atomic absorption spectrophotometer.

3. Extracting Al and Fe by oxalate (Jackson *et al.*, 1986)

3.1 Reagent

- 0.2M acid ammonium oxalate, The solution was prepared by dissolving 65.53 g oxalic acid and 96.65 g ammonium oxalate in 6 L deionized water. Solution pH was adjusted to 3.0 with dilute HCl or NH_4OH .

3.2 Procedure

One gram of soil samples and 60 ml of acid ammonium oxalate were added to screw-cap centrifuge tubes. The sealed centrifuge tubes were placed immediately inside a covered box to eliminate light and shaken for 2 h. After shaking, the tubes were centrifuged at 3500 rpm for 20 min, and supernatant from each tube was decanted into plastic tube. The extractable Fe and Al were determined by atomic absorption spectrophotometer.

Appendix Table 1 The $\Delta P_{NaOH} / \Delta P_{Bray 1}$ ratio of four RP materials incubated with six acid sulfate soils.

Rock phosphates	Days after incubation	$\Delta P_{NaOH} / \Delta P_{Bray 1}$					
		Soils					
		Rsa	Ok	Rs	Se	Ma	Cc
KRP	0	10.9	13.8	30.4	17.0	56.2	100.9
	3	12.0	17.2	1166.9	17.2	115.1	114.3
	5	11.8	16.1	1212.3	12.2	1186.7	123.8
	7	6.0	8.4	1284.2	8.2	1175.9	162.4
	14	8.3	7.0	13.5	7.1	96.5	1177.6
	28	6.7	7.6	32.8	8.4	245.7	19.1
	42	7.0	8.1	32.5	8.5	127.5	9.4
	56	7.7	8.0	1308.2	8.5	166.0	1374.1
Gafsa RP	0	9.5	9.1	16.5	14.5	13.3	15.9
	3	5.2	6.1	3.9	5.2	24.1	31.2
	5	6.7	8.9	4.8	4.5	34.0	37.2
	7	6.7	5.3	3.9	5.7	69.2	119.6
	14	5.9	10.9	7.4	3.0	31.3	179.5
	28	7.0	16.2	8.7	3.1	22.6	135.1
	42	7.4	19.4	12.8	3.4	41.9	141.3
	56	6.0	30.6	17.0	3.7	25.9	200.7
Tilemsi RP	0	5.7	5.1	11.8	8.4	16.1	16.0
	3	9.1	9.5	14.3	8.8	12.4	10.1
	5	9.2	10.5	9.7	8.8	13.5	12.9
	7	9.0	9.2	8.5	9.4	8.6	12.6
	14	10.7	10.1	10.7	10.9	10.0	11.7
	28	10.4	10.4	11.7	11.0	10.5	14.0
	42	9.4	11.0	11.6	10.7	11.1	11.7
	56	9.9	10.2	11.4	10.5	11.2	9.9
Taiba RP	0	5.9	5.5	42.6	15.4	29.9	22.2
	3	8.5	9.9	37.1	16.1	42.9	53.4
	5	7.8	8.7	24.3	12.1	46.8	25.3
	7	5.7	5.7	22.8	5.6	15.7	35.2
	14	6.3	6.5	9.5	5.8	13.7	22.5
	28	6.9	8.2	9.1	8.1	14.4	31.1
	42	9.0	7.7	7.4	7.7	13.3	30.6
	56	8.9	7.4	7.8	8.2	13.1	18.1

Appendix Table 2 The $\Delta P_{NaOH} / \Delta P_{Bray 2}$ ratio of four RP materials incubated with six acid sulfate soils.

Rock phosphates	Days after incubation	$\Delta P_{NaOH} / \Delta P_{Bray 2}$					
		Soils					
		Rsa	Ok	Rs	Se	Ma	Cc
KRP	0	2.78	3.25	2.75	3.12	2.64	2.90
	3	0.94	1.03	0.89	0.76	0.75	0.72
	5	0.97	1.11	0.65	0.91	0.70	0.59
	7	0.99	0.94	0.65	1.06	0.72	0.54
	14	1.33	1.26	0.76	1.32	0.89	0.64
	28	1.14	1.16	0.60	1.07	0.59	0.61
	42	1.22	1.17	0.75	1.09	0.77	0.79
	56	1.91	1.52	0.70	1.45	0.90	0.70
Gafsa RP	0	0.44	0.33	0.50	0.44	3.22	4.37
	3	0.83	0.79	0.55	0.86	2.85	3.09
	5	1.09	1.19	0.68	1.10	2.29	2.77
	7	1.08	1.46	0.68	1.23	2.12	2.51
	14	1.00	2.06	0.62	1.21	2.14	1.93
	28	1.46	2.23	0.72	1.39	1.88	1.54
	42	1.41	2.47	0.95	1.30	2.91	2.20
	56	1.21	2.12	1.51	1.67	2.97	1.52
Tilemsi RP	0	1.78	1.97	2.20	2.46	1.62	2.61
	3	1.21	1.35	0.90	1.17	0.67	0.85
	5	1.12	1.30	0.86	1.23	0.78	0.91
	7	1.19	1.25	0.88	1.32	0.76	0.89
	14	1.63	1.72	1.15	1.75	1.11	1.15
	28	1.53	1.63	1.17	1.58	1.05	1.20
	42	1.47	1.55	1.26	1.37	1.08	1.22
	56	1.52	1.62	1.23	1.29	0.97	1.23
Taiba RP	0	0.60	0.69	0.90	0.95	0.40	0.47
	3	0.75	0.67	0.63	0.83	0.42	0.64
	5	0.64	0.71	0.62	0.75	0.48	0.60
	7	0.74	0.84	0.69	0.83	0.61	0.62
	14	0.97	1.12	0.86	0.97	0.64	0.89
	28	1.11	1.33	0.80	1.23	0.56	0.91
	42	1.58	1.25	0.97	1.35	0.62	0.82
	56	1.60	1.23	0.82	1.22	0.62	0.77

Appendix Table 3 Minimum data which use to predict RP application rates using modified Pi strip test algorithms and their sensitivity.

Data	Unit	Sensitivity
Soil properties		
Phosphorus critical level [†]	mg kg ⁻¹	-
Phosphorus in the soil [†]	mg kg ⁻¹	-
KCl-extractable Al	g kg ⁻¹	0.1-1.2
pH	-	3-5
Cation exchange capacity	cmol _c kg ⁻¹	5-40
Bulk density	g cm ⁻³	-
Rock phosphate properties		
Total phosphorus	%P of rock	-
2-percent citric acid, second extraction	% of total P in RP	15-50
Size of rock phosphate	(%less than 100 mesh)	10-100

Note: [†]measure by modified Pi strip test

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1) Sukunya Yampracha, Tasnee Attanandana, Aminata Sidibe-Diarra, and Russell S. Yost. 2005. Predicting the Dissolution of Rock Phosphates in Flooded Acid Sulfate Soils. *Soil Science Society of America Journal*. 69: 2000-2011.

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