DISSOLUTION AND PLANT-AVAILABILITY OF PHOSPHATE ROCKS IN SELECTED NEW ZEALAND AND INDONESIAN SOILS

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ABSTRACT

Use of phosphate rocks (PRs) as direct-application fertilizers has received considerable attention in countries that have large areas of acidic soils. Properties of acidic soils generally favour dissolution of PRs and increase their effectiveness as direct-application fertilizers. In this study, the dissolution and effectiveness of several PRs, North Carolina (NCPR), Moroccan (MPR) and Pati (PPR) phosphate rocks, was investigated in a range of New Zealand and Indonesian soils. The main objective of the thesis was to provide information that could assist in improving recommendations on their use in field situations.

Laboratory studies showed that the extent of PR dissolution could be estimated using sequential P fractionation techniques to measure amounts of residual (undissolved) PR in soils. In New Zealand soils, residual PR was accurately estimated from the increase in HCl-extractable P (ΔHCl-P) between NCPR-fertilized and unfertilized soils following sequential extraction of soil and soil/NCPR mixtures with 0.5 M NaCl/TEA (30 min), 1 M NaOH (16 h) and 1 M HCl (16 h). The ΔHCl-P method, however, was not suitable for use on strongly weathered Indonesian soils because of low recovery P in the HCl extractant following NaOH extraction. Tri-acid (HNO_3:HCl:$HClO_4$) digestion or H_2SO_4 (0.5-1 M) extraction overcame this problem. A ΔH_2SO_4-P method involving 0.5 M NaCl/TEA, 1 M NaOH and 0.5 M H_2SO_4 extractions was subsequently tested and shown to be suitable for measuring residual PR in acidic New Zealand and Indonesian soils. Measurement of ^{32}P-labelled synthetic francolite dissolution in these soils confirmed the accuracy of the new ΔH_2SO_4-P method.

Considerable evidence exists from this study to indicate that the capacity of soil to supply acid and remove Ca from the site of PR dissolution are most important in determining the extent of PR dissolution. The extent of NCPR dissolution in New Zealand soils was found to decrease with increasing additions of $CaCO_3$ or $NaHCO_3$ due to increases in soil pH (for $NaHCO_3$ and $CaCO_3$-amended soils) and exchangeable Ca (for $CaCO_3$-amended soils). The maximum extent of PR dissolution occurring in the range of acidic New Zealand and Indonesian soils incubated with NCPR and MPR was found to be negatively correlated with initial amounts of exchangeable soil Ca (r=0.83-

0.92) and the percentage Ca saturation of the cation exchange capacity (r=0.78-0.92). Also, increases in soil pH, and possibly solution concentration of Ca, were the main reasons for decreases in synthetic francolite dissolution in soils amended with increasing rates of plant residue. And finally, field trials conducted in Indonesia showed that the extent of PR (NCPR, MPR and PPR) dissolution was greater in the more acidic Ultisol (pH_{H2O}=4.8) than in the Entisol (pH_{H2O}=5.3).

Laboratory incubation studies showed that the key factors determining the chemical-availability (i.e. extractable with Olsen, Bray 1 and resin tests) of P derived from soluble P fertilizer or PRs in New Zealand and Indonesian soils were rate of addition, soil pH and P sorption characteristics and the nature of soil test. A short-term (30 days) glasshouse study using a range of New Zealand soils showed that the plant-P uptake from soil fertilized with NCPR was low, relative to monocalcium phosphate (MCP), indicating the low extent of NCPR dissolution. The plant-availability of soluble P and dissolved P from PR, however, was more dependent on soil P adsorption characteristics than on other soil properties.

Field trials in Indonesia showed that PRs were more effective agronomically than triple superphosphate (TSP) for maize in a P deficient Ultisol only when the PRs were applied to *Calopogonium caeruleum* cover crop 6 to 18 months prior to sowing maize. In an Entisol, PRs were less effective than TSP irrespective of application time. In the Ultisol, PR effectiveness was not affected by liming, provided that the PRs were applied 6 to 18 months prior to the addition of lime.

Results of the Indonesian field trials showed that Bray 1 test was a better predictor of plant growth responses than either Olsen or resin tests in PR-fertilized Ultisol, where high effectiveness of PRs was observed.

Three PR dissolution models of increasing complexity (Mitscherlich, Cubic, Kirk and Nye) were tested using NCPR and MPR dissolution data generated from a laboratory incubation study. Only Mitscherlich and Kirk and Nye models adequately described PR dissolution in the soils studied. A sensitivity analysis showed that any differences between observed and simulated PR dissolution by the Kirk and Nye model could be

attributed to problems in obtaining a representative measure of soil solution pH.

The Kirk and Nye model was modified to simulate PR dissolution in the field and tested using data from the Ultisol field site. The model adequately predicted NCPR and MPR dissolution over 545 days. In this case the accuracy of predictions was found to be dependent on the value of the initial soil pH and the accuracy of simulating daily soil water contents. The model showed potential for use in a wider range of soil-plant-climate conditions in order to assist with the selection of soils suitable for the use of direct-application PR fertilizers.

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This is to state the research carried out for the Ph.D. thesis entitled "Dissolution and Plant-availability of Phosphate Rocks in Selected New Zealand and Indonesian Soils" was done by D Tambunan in the Soil Science Department, Massey University, Palmerston North, New Zealand. The thesis material has not been used for any other degree.

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18th November 1992
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Date

CHAPTER 1
INTRODUCTION

Phosphorus (P) remains a key nutrient limiting food and fibre crop production in many regions of the world (Desai and Gandhi, 1990). In most soils, native and added fertilizer P is strongly immobilized so that regular fertilizer applications are required to maintain adequate supplies of plant-available P.

Water-soluble P fertilizers, such as single superphosphate (SSP), triple superphosphate (TSP) and diammonium phosphate (DAP), have been the major fertilizers used in the past to correct P deficiency in many countries. In New Zealand, for example, SSP has been applied to legume-based pastures as the sole P fertilizer. However, because of the escalation in costs of manufacture and distribution of soluble P fertilizers, cheaper P materials such as unacidulated reactive phosphate rocks (PRs) or partially acidulated phosphate rocks (PAPR) have become important as alternative P sources. Use of PRs, in particular, has received attention because of the availability of major deposits of high analysis PR, the occurrence of large areas of soils potentially suitable for their direct application as P fertilizers and the occurence of indigenous deposits.

Directly applied PRs can however be highly variable in agronomic effectiveness (Hammond., *et al*, 1986; Bolan *et al.*, 1990). The effectiveness of PR as a direct-application fertilizer depends mainly on whether its rate of dissolution in soil is fast enough to supply P for meeting plant growth requirements. The actual availability of PR-P to plants is affected by properties of PR, soil and plants and climate factors. Optimum conditions for PR use are most likely to be found in environments where the soil is acidic and constantly moist for most of the growing period.

In countries such as New Zealand and Indonesia, there are situations in which the use of PR as a direct-application fertilizer can be more cost effective than a water-soluble P source. However, more studies are required to provide information on the various mechanisms affecting the effectiveness of PR as a direct-application fertilizer.

Recently, studies have shown that mathematichal models can be used to describe the dissolution processes in soil (Kirk and Nye, 1986c; Rajan and Watkinson, 1988) and the subsequent plant-availability of the dissolved P (Kirk and Nye, 1986d). These models have yet to be applied to field situations where they could prove useful in assisting with the selection of soils and crops suited to PR use.

The objective of this study was to measure dissolution of PRs and their subsequent plant-availability in a range of New Zealand and Indonesian soils in order to provide information that can be used to formulate and improve recommendations for PR use.

This thesis comprises 10 chapters. Following this introduction is a review of literature on the properties, rates of dissolution and plant-availability of P dissolved from PR materials and the potential use of PR as direct application fertilizers in agriculture.

A method for measuring amounts of residual (undissolved) PR, and hence the extent of PR dissolution, was developed and then used to measure the dissolution of North Carolina phosphate rock (NCPR) and monocalcium phosphate (MCP) in pairs of PR-treated and untreated New Zealand soils of varying pH and exchangeable Ca contents (Chapter 3). The method was then evaluated using a range of New Zealand and Indonesian acidic soils (Chapter 4). From this evaluation, a modified method suitable for measuring PR dissolution under a wide range of soil conditions was developed and used to study various factors affecting PR dissolution in soils under laboratory (Chapters 5 and 7) and field (Chapter 8) conditions.

Use of models to simulate PR dissolution in soil, under laboratory conditions, is evaluated in Chapter 5. The residual effectiveness of various P fertilizers was evaluated using field trials on two contrasting Indonesian soils (Chapter 8). Measurements of PR dissolution in the field trials were used to evaluate a mechanistic model for predicting the dissolution of PRs in field situations (Chapter 9). Summary and suggestions for future research are presented in Chapter 10.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION

Of the three main nutrient elements: nitrogen (N), phosphorus (P) and potassium (K), P is the most limiting agricultural production in many highly weathered tropical soils.

Water-soluble fertilizers, such as single superphosphate (SSP) and triple superphosphate (TSP), have been traditionally used to overcome P deficiency in many countries. Recently, due to the high cost involved in the manufacturing these fertilizers, use of PRs for direct application has received considerable attention, particularly in countries that have large areas of acid soils and local deposits of PR.

Since the work presented in this thesis aims at evaluating the potential of PRs as direct-application fertilizers, it is important to review various aspects relating to the use of PR as a fertilizer for direct application. These include: sources and reactivity of PR materials, and dissolution and availability of the dissolved P in soil. The agronomic effectiveness of PR materials in New Zealand and Indonesia is reviewed.

2.2 WORLD PHOSPHATE ROCK RESERVES AND RESOURCES

The U.S. Geological Survey has proposed a general classification of ore resources and reserves (Cathcart, 1980; Slansky, 1986). "Reserves" have been defined as all rocks from which profitable industrial phosphate production can be envisaged now or in the foreseeable future, taking into account relevant economic and technological factors. "Resources", on the other hand, are defined as material for which there is geological information on the extent and thickness, but where drilling is limited or nonexistent, or, as deposits that are too low grade, contain too much deleterious elements, or can not be mined or processed profitably with existing technology.

1–5 U.S.A.: 1 Alaska; 2 Idaho, Wyoming, Montana; 3 Tennessee; 4 North Carolina; 5 Florida. *6–7 Mexico*: 6 Baja California; 7 Nuevo Leon, Queretaro, etc. *8 Venezuela*: Falcon (Riecito). *9 Colombia*: Norte de Santander, Santander, Boyaca, Huila. *10 Peru*: Sechura (Boyovar). *11–15 Brazil:* 11 Pernambuco (Olinda); 12 Minas Gerais (Patos de Minas); 13 Goias (Catalao); 14 Minas Gerais (Tapira, Araxa, etc.); 15 Sao Paulo (Jacupiranga). *16–17 Morocco;* 16 Oulad Abdoun, Ganntour; 17 Bou Craa. *18 Algeria*: Djebel Onk. *19 Tunisia*: Gafsa Basin, Sra Ouartane. *20 Egypt*: Red Sea, Nile Valley, Abu Tartur. *21 Mauritania*: Bofal. *22–23 Senegal*: 22 Matam; 23 Taïba. *24 Guinea Bissau*: Farim. *25 Mali*: Tilemsi. *26 Niger, Bukina Faso (Upper Volta), Benin*: Tapoa, Kodjari, Mekrou. *27 Togo*: Hahotoe. *28 Uganda*: Sukulu. *29 Angola*: Cabinda, Zaire. *30 Zimbabwe. 31–32 South Africa*: 31 Palabora; 32 Glenover. *33 Israel – Jordan*: Negev Desert — Ruseifa, Al Hasa. *34 Syria*: Khneifiss, Eastern. *35 Saudi Arabia*: Thaniyat, Turayf. *36 Iraq*: Akashat. *37 Turkey*: Mazidagi. *38–39 Finland*: 38 Sokli; 39 Siilinjärvi. *40–50 U.S.S.R.*: 40 Khibiny, Kovdor; 41 Maardu; 42 Moscow Basin; 43 Rudnichny; 44 Byelorussia, Ukraine; 45 Aktyubinsk; 46 Karatau; 47 Abakan; 48 Oshurkov; 49 Synnyr; 50 Seligdar. *51 Mongolia*: Hobsogol. *52 North Korea. 53–57 China*: Fanskan, Chingshan, Kaiyang, Omei, Kunming–Kunyang; *58 Vietnam*: Lao Kai. *59 India*: Udaipur. *60 Sri Lanka*: Eppawella. *61 Nauru. 62–63 Australia*: 62 Christmas Island; 63 Queensland (Duchess).

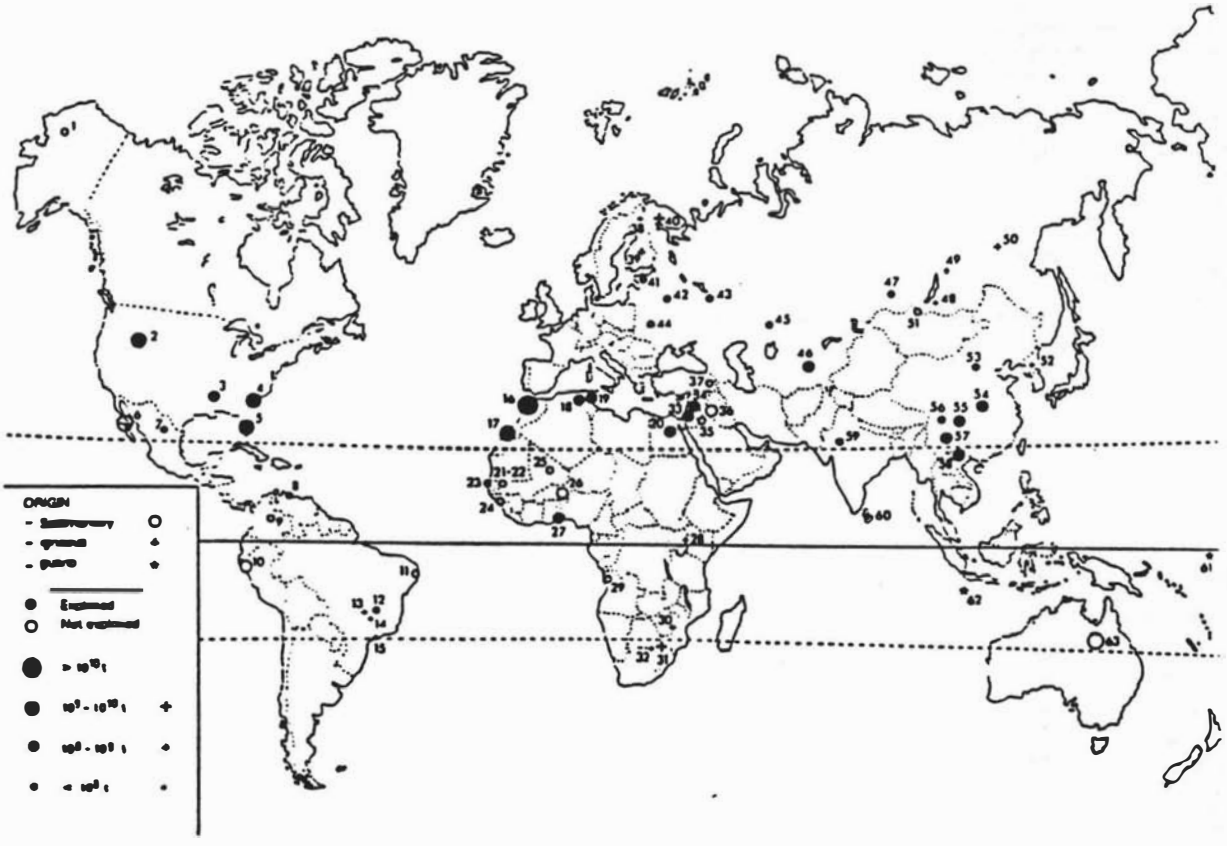

Figure 2.1 World distribution of identified phosphate resources, expressed in terms of commercial product (Slansky, 1986).

Phosphate rocks are distributed widely throughout the world, both geographically and geologically, and there are very large resources capable of meeting anticipated demand for many years. The world distribution of identified phosphate resources, expressed in terms of commercial product in the main deposits or groups of deposits around the world, is shown in Figure 2.1. Estimates of world resources vary considerably. According to Notholt *et al.* (1989) the total world resources are of the order of at least 163 x 10^3 million tonnes of all grades and types of phosphate rock. About 41% of them in Africa, 21% in USA, 13% in CIS (formerly known as USSR), and 10% in the Middle East. A total of 8 and 3% of the resources are distributed in Asia and South America, respectively. New Zealand and Australia together have 1%. Resources in Western Europe, a big phosphate consumer, account for <1%.

2.3 MINERALOGICAL COMPOSITION OF PHOSPHATE ROCK

Based on their mineralogical compositions, three types of phosphate rock are identified (McClellan and Gremillion, 1980). In the order of increasing economic importance they are categorized as follows.

2.3.1 Fe-Al phosphates

Lateritic alteration of pre-existing deposits of calcium phosphate leads primarily to aluminium phosphate minerals. Deposits of this type of PR occur in Senegal, Brazil, Venezuela and Liberia. Examples of phosphate minerals belonging to this group are wavelilite: $Al_3(PO_4)_4(OH)_3.5H_2O$), augelite: $Al_2PO_4(OH)_3$, and strengite: $FePO_4.2H_2O$.

2.3.2 Ca-Fe-Al-phosphates

The most common mineral groups in this type are crandallite: $Ca_2Al_6(PO_4)_4(OH)_{10}.2H_2O$, millisite:$(Na\text{-}K)CaAl_6(PO_4)_4(OH)_3.2H_2O$, and pallite, iron bearing varieties of millisite with low sodium content. Deposits of these minerals occur in Florida and Christmas Island.

2.3.3 Ca-phosphates

This mostly consists of apatite groups of minerals. Apatite is one of the most abundant minerals in earth's crust and it occasionally occurs in massive concentrations of economic importance. Inspite of their crystal structure similarity, the chemical compositions of apatite vary. The mineral fluor apatite, for example, has the chemical formula of $Ca_{10}(PO_4)_6F_2$. Other apatite, exhibit various compositions due to isomorphous substitutions in the apatitic crystal lattice. Apatite deposits are mainly sedimentary in origin. Examples of these groups include the deposits found in North Africa (Morocco, Senegal, Algeria and Tunisia), Middle East (Jordan, Israel and Egypt), South America (Peru and Brazil), Australia (Queensland) and US (Florida, North Carolina and Idaho).

2.4 GEOLOGICAL FORMATION OF PHOSPHATE ROCK

The three main types of phosphate rock mined at present (McClellan and Gremillion, 1980; Slansky, 1986) are:

Sedimentary rocks, which are the most important, both in number and in volume, provide about 82% of the total world production. *In situ* concentration of P in sedimentary rocks often exceeds 9 or even 13%. In the Bou Craa deposit (Morocco) the concentration of P in the ore often exceeds 14 or even 15%. Sedimentary rocks have a wide variety of textures depending on the geologic origins and histories. They are generally formed by precipitation processes in marine detritus. Depending upon age, they may contain significant amounts of fossil apatite.

The general environment for the formation of sedimentary rocks deposits is thought to be in basins on ocean shelves and platforms, in which there is intermittent turbulence. This provides a stable environment with periodic influxes of nutrient rich waters and may initiate an explosion of organic activity, which is commonly diatomaceous.

According to Burnett (1977), the conditions necessary for precipitation of sedimentary rocks are:

(1) A relatively high pH (above neutral).

(2) high concentrations of phosphate in solution, enough to control the solubility of calcium ion so that calcium phosphate is formed rather than calcium carbonate.

(3) A high calcium to magnesium ratio in solution, to prevent the magnesium ion from competing with the calcium ion and inhibiting precipitation.

(4) The presence of nucleus grain, e.g. quartz, feldspar, glauconite, calcite, siliceous skeletal material.

(5) A relatively high temperature.

Igneous rocks are associated with intrusive alkaline complexes. The most abundant rocks are nepheline syenites, carbonatites, ijolites and pyroxenites. These deposits are less common, often less rich and smaller than sedimentary deposits. Some of the these deposits are, however, very important, such as those at Khibini (Russia) associated with a ring complex of nepheline syenites, containing 1600 million tonnes of ore with an average of 6% P. The Phalabowra deposits (South Africa), of a lower grade, contain equally large reserves of apatite, associated with an intrusion composed of carbonatite and pyroxenite.

Metamorphic rocks are transitional between the igneous and sedimentary rocks in their geologic history, texture and mineral assemblages. Metamorphic deposits are generally low grade, the rocks are hard and the minerals are more intimately mixed, but the basic sedimentary structures usually persist although massive beds of phosphate also can results. Deposits of metamorphic rocks occur in Brazil (Patos de Minas), India (Udaipur), Pakistan (Hazara), and Finland (Siilinjarvi).

Both igneous and metamorphic rocks are known to have less accessory or "gangue" materials than sedimentary rocks. Sedimentary rocks are microcrystalline in nature, and consist of fairly open loosely consolidated aggregates of microcrystals with relative large specific surface area. They are usually carbonate substituted apatite (McClellan and Lehr, 1969) with various degrees of isomorphously substituted CO_3^- replacing phosphate ions. They are also referred to as francolites and are often associated with 5 to 20%

gaunge material. The common gangue materials are quartz, alkaline earth carbonates, layer silicates, Fe and Al oxides and hydroxides, evaporites (chlorites and sulphates) and a number of accessory minerals, such as titanium, iron sulfides and fluorite.

2.5 CHEMICAL REACTIVITY OF PHOSPHATE ROCK

Reactivity of PR can be defined as the rate at which P in the apatite is released (Equation 2.1) under favourable chemical conditions (McClellan and Gremillion, 1980). The empirical equation for the P release from fluorapatie in soil solution can be written as follows (Khasawneh and Doll, 1978; Kirk and Nye, 1986b):

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- \quad (2.1)$$

Because reactivity of a PR determines its potential as a direct-application fertilizer (see Section 2.8), characterization of a PR in terms of its reactivity and its assessment is very important.

2.5.1 Compositional differences

Chemical characterization of a large number of PRs has shown that apatite minerals vary widely in physical, chemical and crystallographic properties (McClellan and Lehr, 1969; McClellan and Gremillion, 1980). Partial substitution of nearly all the ionic components in the fluorapatite structure was reported, in particular isomorphic substitution of carbonate for phosphate. Substitutions in the apatite structure of fluorapatite are given in Table 2.1.

Table 2.1 Substitutions in the apatite structure of fluorapatite (McClellan and Gremilion, 1980).

Constituent ion	Substituting ion
Ca^{2+}	Na^+, Sr^{2+}, Mn^{2+}, K^+, U^{4+}, Mg^{2+}, $RE^{2+,3+}$
P^{5+}	C^{4+}, S^{6+}, Si^{4+}, As^{5+}, V^{5+}, Cr^{6+}, Al^{3+}
F^+	OH^-, Cl^-
O^{2-}	F^-, OH^-

These substitutions do not occur simultaneously, neither are they equally permissible and often particular substitutions are coupled. The degree of substitution and ion involved determines the extent of structural change and the classification of the mineral

McClellan and Lehr (1969) have shown that the degree of isomorphic substitution o carbonate for phosphate profoundly influences the crystal structure, the physical anc chemical stability of apatite. Substitution of carbonate for phosphate also decreases crystalline size and increases the specific surface area. Thus, in general, phosphate rocks with considerable substitution are more reactive than those without substitution (Chien and Black, 1976; Chien, 1977b; Khasawneh and Doll, 1978; Anderson *et al.* 1985). The increased chemical reactivity of PR with increasing degree of carbonate substitution for phosphate results from an associated increase in free energy of formation of apatite (Chien and Black, 1976).

As only partial substitution occurs in the apatite structure, the empirical formula of francolite may be presented as follows (McClellan and Lehr, 1969):

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-\beta}(CO_3)_\beta F_{2+y}$$

with the average value for $\beta = 0$ to 1.5; $y = 0.4\beta$, $b = 0.4a$. Apatites with these compositions are called carbonate apatites or francolites.

Using X-ray diffraction, McClellan and Lehr (1969) demonstrated that substitution of carbonate for phosphate influenced the **a** dimensions of the apatite crystal structure. It was found that while the **a** dimension ranged from 9.322 to 9.376 Å, the **c** dimension ranged from 6.877 to 6.900 Å. Length of unit-cell **a** dimension and empirical formula of selected phosphate rocks are presented in Table 2.2.

The unit-cell **a** dimension and the a, b and β parameters of the empirical formula of francolite are strongly related by the following equation (McClellan and Lehr, 1969):

$$\text{a dimension} = 9.374-[0.024\beta/(6-\beta)]$$

$$a = 1.327[\beta/(6-\beta)]$$

$$b = 0.515[\beta/6-\beta)]$$

Table 2.2 Unit-cell a dimension and empirical formulas of apatites in selected PRs (Hammond *et al.*,1986).

Rock sample	Origin	Length of a dimension (Å)	Empirical formula
El-Hassa	Jordan	9.339	$Ca_{9.68}Na_{0.23}Mg_{0.09}(PO_4)_{5.12}(CO_3)_{0.88}F_{2.35}$
Mussoorie	India	9.352	$Ca_{9.80}Na_{0.14}Mg_{0.06}(PO_4)_{5.42}(CO_3)_{0.58}F_{2.23}$
Gafsa	Tunisia	9.328	$Ca_{9.59}Na_{0.30}Mg_{0.12}(PO_4)_{4.90}(CO_3)_{1.10}F_{2.44}$
Hahotoe	Togo	9.351	$Ca_{9.79}Na_{0.15}Mg_{0.06}(PO_4)_{5.39}(CO_3)_{0.61}F2.24$
Boyovar	Peru	9.337	$Ca_{9.03}Na_{0.74}Mg_{0.13}(PO_4)_{4.88}(CO_3)_{1.12}F_{2.29}(OH)_{0.72}$
Pesca	Colombia	9.346	$Ca_{9.76}Na_{0.18}Mg_{0.07}(PO_4)_{5.28}(CO_3)_{0.72}F_{2.29}$
Patos de Minas	Brazil	9.370	$Ca_{9.96}Na_{0.03}Mg_{0.01}(PO_4)_{5.88}(CO_3)_{0.12}F_{2.05}$
North Carolina	USA	9.322	$Ca_{9.53}Na_{0.34}Mg_{0.13}(PO_4)_{4.77}(CO_3)_{1.23}F_{2.49}$
Central Florida	USA	9.345	$Ca_{9.74}Na_{0.19}Mg_{0.07}(PO_4)_{5.26}(CO_3)_{0.74}F_{2.30}$
Tennesee	USA	9.357	$Ca_{9.85}Na_{0.11}Mg_{0.04}(PO_4)_{5.54}(CO_3)_{0.46}F_{2.16}$

Since the unit-cell **a** dimension can be measured by X-ray diffraction, the empirical formula and chemical composition of unknown apatite can be estimated from the relationships developed by McClellan and Lehr (1969).

The unit-cell **a** dimension of a PR decreases with increasing degree of carbonate substitution. This is indicated by a negative linear relationship between unit-cell a dimension and mol ratio CO_3/PO_4 in the apatite (Smith and Lehr, 1966).

2.5.2 Assessment of phosphate rock reactivity

Since the unit-cell **a** dimension of an apatite can be used as an indicator of the degree of carbonate substitution for phosphate, its measurement provides an accurate assessment of the reactivity of PRs. This procedure, however, is not practical because it requires an X-ray diffractometer (XRD), which is not readily available to all laboratories. Instead, assessments of PR reactivity using various chemical extraction tests were preferred. These assessments are quick, cheap and can easily be performed in a laboratory.

Chemical extractants used to assess PR reactivity are solutions of 2% citric and formic acid (e.g. Caro and Hill, 1956; Chien and Hammond, 1978; MacKay *et al.*, 1984c), and ammonium citrate solutions of acid (pH 3) (e.g. Chien and Hammond, 1978), neutral (e.g. Chien and Hammond, 1978; Mackay *et al.*, 1984c) and alkaline (pH 9.4) (e.g. Mackay *et al.*, 1984c) ammonium citrate. The selection of chemical extractants for assessing PR reactivity varies between countries: the neutral ammonium citrate is used in USA (McClellan and Gremillion, 1980; Chien and Hammond, 1978); the 2% citric acid is used in countries such as Brazil (Chien and Hammond, 1978), Malaysia (Wahab, 1978) and Indonesia (Martoyo and Suwandi, 1988) and New Zealand (White *et al.*, 1989); and the 2% formic acid is commonly used in EEC countries (Amberger, 1978).

Because of the differences in the extractant used in different countries, criteria used to rank the reactivity of PR are also different. According to EEC regulations (*Official Journal of the European Communities*, 1977), PRs (95%<63µm) which have 55% or more of their P soluble in 2% formic acid are identified as "soft" or reactive phosphate

rocks (RPRs) suitable for direct application to agricultural soils. In New Zealand, PRs are ranked as reactive if they have 30% or more of their P soluble in 2% citric acid (White *et al*, 1989). There are no particle size criteria. Based on this criterion, Syers *et al.* (1986) ranked Sechura (from Peru), North Carolina (from USA), Gafsa (from Tunisia) and Arad (from Israel) PR as the most reactive rocks, whereas Nauru, Christmas Island and Duchess (from Australia) PR are among the least reactive. Based on the formic acid solubility, Quin *et al.* (1987) grouped PRs into three categories as "reactive", "medium reactive" and "unreactive". The criteria used by Quin *et al.* (1987) are presented in Table 2.3.

The extractants used to assess the reactivity of PR are different in their properties. For example, solutions of 2% citric acid (0.29 moles H^+) is less acidic than 2% formic acid (0.43 mole H^+). Thus it extracts less amount of P from PR. However, citric acid has an additional chelation property which is more effective than formic acid to remove Al- and Fe-bound P in an apatite. Consequently, the amount of P extracted by these extractants may differ. To avoid confusion and misinterpretation in comparative evaluations of PR, McClellan and Gremillion (1980) derived some equations to correlate between the solubilities of P (%) of 36 PRs in neutral ammonium citrate, 2% citric acid and 2% formic acid. Selected regression equations relating the solubility of P in different extractants are presented in Table 2.4.

The regression equations presented in Table 2.4, however, can not be applied to all PRs. The presence of appreciable amounts of accessory minerals such as free carbonates (calcite and dolomite) and Fe and Al compounds in some PRs have been reported to affect the accuracy of the assessment of PR reactivity (Chien and Hammond, 1978; Khasawneh and Doll, 1978; Mackay *et al.*, 1984c) by influencing the solubility of apatite-P in the extracts through mechanisms such as common-ion effects, complexation, acid- base reactions and reduction (Braithwaite *et al.*, 1989). The presence of up to 20% of $CaCO_3$ in Chatham Rise phosphorite considerably depresses the solubility of its P in 2% formic and citric acids (Mackay *et al.*, 1984c). The neutralizing effect of free calcium carbonate in the extractants results in low extraction of P and consequently underestimates the chemical reactivity of the PR (Mackay *et al.*, 1984c). To overcome the neutralising effect of accessary compounds, such as $CaCO_3$, sequential extractions

Table 2.3 Reactivity of PRs based on their solubility in 2% formic acid (Quin *et al.*, 1987).

P Solubility (% of total P)	Reactivity
>55	Reactive
30 - 55	Medium reactive
<30	Unreactive

Table 2.4 Regression equations[1] relating P solubility of 36 PRs in neutral ammonium citrate (NAC), 2% citric acid and 2% formic acid based on ASI[2] values (adapted from McClellan and Gremillion, 1980).

Extractant	NAC	2% Citric acid	2% Formic acid
NAC	1	$1.259n+7.29$	$2.416n$
2% Citric acid	$0.79c-5.79$	1	$1.919c-13.99$
2% Formic acid	$0.4138f$	$0.521f+7.29$	1

[1] n = % P_2O_5, soluble in NAC; c = % P_2O_5, soluble in 2% citric acid; f = % P_2O_5, soluble in 2% formic acid.

[2] ASI (Absolute Solubility Index) is defined as:
ASI = extractant-soluble P_2O_5 (%)/theoretical P_2O_5 concentration of apatite (%).

with citric or formic acid (two or three extractions) have been recommended (Mackay *et al.*, 1984c; Syers *et al.*, 1986). Alternatively, a sequential extraction with neutral ammonium citrate can be employed (Chien and Hammond, 1978).

Comparisons of various chemical extractants to rank the chemical reactivity of PRs have been made by several workers (Chien and Hammond, 1978; Mackay *et al.*, 1984c; Syers *et al.*, 1986). For example, Syers *et al.* (1986) ranked 10 PR materials based on their solubility in 2% formic acid, 2% citric acid and neutral ammonium citrate. The results presented in Figure 2.2 show that the three extractants ranked North Carolina, Gafsa and Sechura as the most reactive PRs. Further sequential extractions with 2% citric acid also ranked Chatham Rise phosphorite, which contains up to 20% of calcium carbonate and was ranked as unreactive by single extractions, as one of the reactive materials. These results suggest that use of a single figure of 30% citric acid or 55% formic acid P solubility as the cut off between reactive and unreactive PRs can not be adopted for all PRs. For example, agronomic trials (Mackay et al., 1984b) have ranked Chatham Rise phosphorite (total P content=9%) as a reactive fertilizer, but it would not meet the formic acid solubility criteria or the criterion pertaining to the minimum total P content of PR for direct application as that stipulated by EEC regulations.

2.5.3 Chemical reactivity indices vs. agronomic effectiveness

A number of empirical studies have been conducted to assess the suitability of chemical extraction procedures for predicting the agronomic effectiveness of various PRs. The results, of mostly glasshouse trials, often show that the extraction procedures for estimating PR reactivity vary widely in their ability to predict agronomic effectiveness. Early glasshouse work by Caro and Hill (1956) showed that 2% citric acid extractable P was a good indicator of dry matter yield for PRs that ranged in % citric soluble P. Other workers (Terman *et al.*, 1970) found the % P extracted by neutral ammonium citrate to be useful. Recent glasshouse and field trials by Amberger (1978), Chien and Hammond (1978), Mackay *et al.* (1984c) and Hardjono (1987) showed that 2% citric acid-extractable P was best correlated with dry matter yield. Leon *et al.* (1986) showed that acid and neutral ammonium citrate, 2% citric acid and 2% formic acid had the same predictive ability in ranking the effectiveness of PRs as P sources for guinea grass in

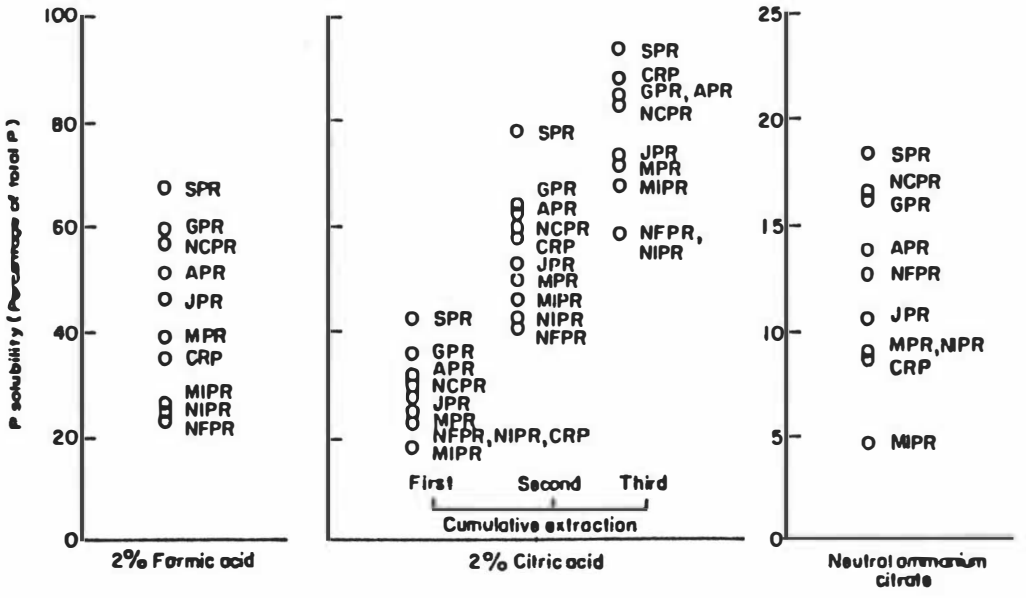

Figure 2.2 Solubility of phosphate rock materials in 2% formic acid, 2% citric acid and neutral ammonium citrate (Syers *et al.*, 1986).

pots of an acidic soil (Haplustox) from Colombia.

From a glasshouse trial using less acidic New Zealand soils, Mackay *et al.* (1984c) found that the percentage of P dissolved by sequential extraction with 2% formic acid, 2% citric acid and neutral ammonium citrate were equally good predictors for agronomic effectiveness of a range of PRs.

Out of controlled glasshouse or narrow environmental boundaries, the usefulness of PR reactivity as an agronomic index alone should be interpreted with caution. Providing soil-plant growth system conditions remain equal, PR reactivity may be a useful index of agronomic effectiveness. A measure of PR reactivity may be less useful across a range of soil types or environmental conditions, since soil acid supply and dissolution product's fate are highly dependent upon the prevailing soil chemistry, plant cover and climate (see later discussion).

2.6 DISSOLUTION OF PHOSPHATE ROCK IN SOIL

In addition to the chemical nature and particle size of PR fertilizer added to soil, PR dissolution in soil is influenced by several soil and plant processes. Bolan *et al.* (1990) have presented a diagrammatic representation of factors affecting PR dissolution in soil (Figure 2.3). By considering the simplistic equation describing PR dissolution (Equation 2.1) it is apparent that any soil process increasing the supply of acid to PR surface or removing dissolution products will enhance PR dissolution. The availability of the dissolved P to plants will depend on the rate of dissolution in relation to the rate of P fixation or immobilisation by soil process.

2.6.1 Factors affecting phosphate rock dissolution

2.6.1.1 Phosphate rock factors

As discussed earlier carbonate substitution for phosphate in the apatite determines the chemical reactivity and thereby effects the solubility of apatite in water (Kirk and Nye,

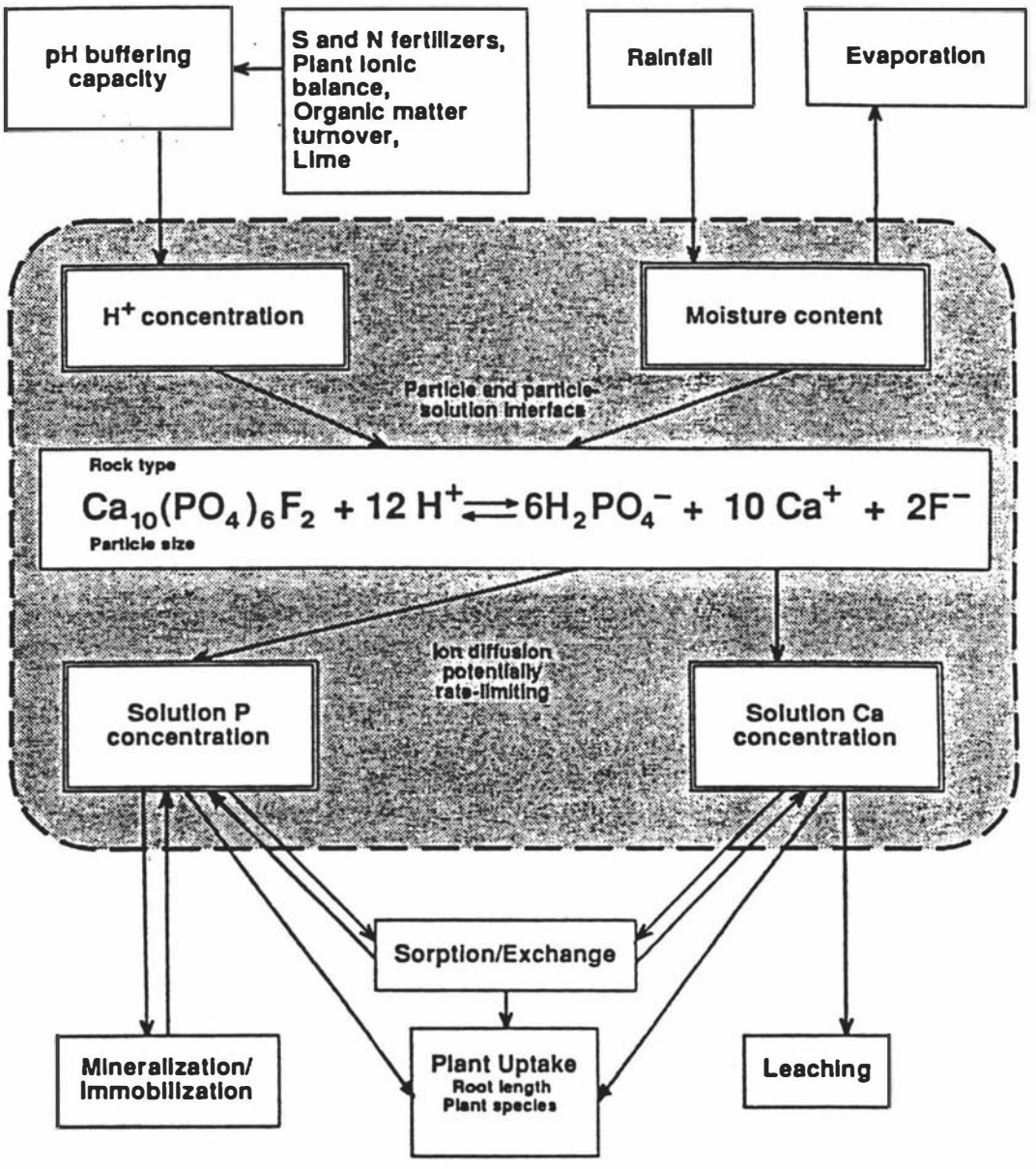

Figure 2.3 Schematic diagram showing the rate-limiting factors (boxes in stippled area) for phosphate rock dissolution in soils and the variables (boxes outside stippled area) which determine the magnitude and degree of interaction of the rate-limiting factors (Bolan *et al.*, 1990).

1986b; 1986c). Generally there has been a consensus among early workers (Caro and Hill, 1956; Armiger and Fried, 1957; Smith and Lehr, 1966) that the rate and extent of PR dissolution increase with increases carbonate substitution. More recent research has confirmed this general relationship and demonstrated increased plant availability of P (Anderson, 1985) and increased dissolution of PR in field soils (Chien *et al.*, 1987) with either increased carbonate substitution or citrate solubility.

Hughes and Gilkes (1986b) found the CaO/P_2O_5 ratio of 18 PRs was a slightly better predictor of the extent of PR dissolution in a range of temperate and tropical soils than the apatite unit cell a dimension although neither explained more than 60% of the variation in PR dissolution data. Further demonstrations of the importance of PR reactivity in affecting PR dissolution have been reported by several other workers (e.g. Kumar and Mishra, 1986; Bolan and Hedley 1989; 1990).

In addition to the chemical reactivity of the apatite mineral, particle size to which a PR is ground (milled) affects its rate of dissolution in a chemical extractant and the soil environment. Extraction time and PR:solution ratios will be important in determining the influence of particle size on PR dissolution. In short-term extractions with weak acid, the rate of PR dissolution will be related to the extent of PR surface exposed to the reagent. In longer-term extractions, dissolution may reach equilibrium hence little influence of particle size may be evidence from the final amount of P extracted unless milling exposes a fresh less weathered P surface to the extractants, which may raise equilibrium P concentration.

The dissolution of PR in a chemical extractant such 2% formic acid increases with decreasing particle size. White *et al.* (1989) have shown that the P solubility of Sechura PR in 2% formic acid (30 min extraction time) increased from 55 to 70% with decreasing mean particle size from 185μm to 63μm. Syers *et al.* (1986), however, suggested that surface area of a PR plays a secondary role to chemical reactivity in controlling the solubility of a PR in chemical extractant.

In soil, Kanabo and Gilkes (1988a) observed that the extent of NCPR dissolution (applied at 400 mg P kg^{-1}) after 35 days increased by 6% when the particle size of the

PR decreased from 150-250 to 45-53μm. The increase in the extent of PR dissolution with decreasing particle size is generally associated with increasing specific surface area of PR, which in turn increases the degree of contact between PR particle and soil. The increased contact between PR and soil provides greater exposure for the apatite to react with soil acids. Additionally, it also increases contact between the dissolution products, Ca and P, and surfaces of soil minerals capable of anion and cation exchange or sorption, thereby reducing the concentration of Ca and P in the zone of influence of PR particle. Application rate to soils will also influence dissolution rate because higher rates of application will reduce the mean distance between particles and reduce the length of time before the diffusion zones of products away from particles overlap (Kirk and Nye, 1986b). Other studies (e.g. Kanabo and Gilkes, 1988b; Bolland and Barrow, 1988) provide evidence for these effects. Kirk and Nye (1986c) have derived a mathematical model required to describe the influence of particle size and rate of application of insoluble P fertilizer, as yet the precise nature of these relationships has been tested only for dicalcium phosphate dihydrate (DCPD) in laboratory incubated soils (Kirk and Nye, 1986c). The model predictions of DCPD dissolution were sufficiently accurate that it offers promise for modelling RPR dissolution in field soils.

2.6.1.2 Soil factors

Kirk and Nye (1986b; 1986c) provided a mechanistic description of the influence of soil on PR dissolution. The important processes are:

(1) Dissolution-reaction at the PR-solution interface.

(2) Diffusion of base, phosphate and calcium into the soil around a PR particle.

As discussed earlier, dissolution of PR is initiated by the supply of H^+ (Equation 2.1). As PR dissolves, the rate of PR dissolution is then controlled by the diffusive fluxes of the reaction products, such as base, phosphate and Ca, away from PR particle surface (Kirk and Nye, 1986c). The fluxes of these ions are controlled by their concentrations in soil solution. For base, its concentration in solution is controlled by pH and pH buffer capacity of the soil. Phosphate concentrations in soil solution are controlled by phosphate buffer capacity and various sinks for phosphate. For calcium, its concentration in soil solution is balanced against total anion concentration, and strongly

related to exchangeable Ca^{2+} and other sinks such as plant uptake.

Experimental evidence for the importance of soil pH and H^+ for PR dissolution is provided by studies conducted by Ellis *et al.*, 1955; Pauw, 1965; Kanabo and Gilkes, 1987a; Peaslee *et al.*, 1962; Bolan and Hedley, 1990; Robinson and Syers, 1990; Rajan *et al.*, 1991b; Wright *et al.*, 1992. The extent of PR dissolution increases with increased proton supply resulting from decreased soil pH. For example, Bolan and Hedley (1990) observed that dissolution of PRs in a volcanic soil from New Zealand increased from 18 to 79% as soil pH decreased from 6.5 to 3.9. Kanabo and Gilkes (1987a) and Wright *et al.* (1992) showed that PR dissolution also increased with increasing pH buffer capacity of soil.

Khasawneh and Doll (1978) and Wilson and Ellis (1984) provided evidence for the influence of Ca activity in soil solution on PR dissolution. At a constant pH, increases in Ca concentration in soil solution decreases PR dissolution. Robinson and Syers (1990) found a negative exponential relationship between the extent of PR dissolution and Ca concentration in soil solution. These workers also found that additional Ca sinks increased PR dissolution. Other soil properties, such as percent Ca saturation and exchangeable Ca are also correlated with PR dissolution (Mackay *et al.*, 1986) because they are related to Ca^{2+} concentrations in soil solution. Kirk and Nye (1986c), show how the diffusion rate of dissolved Ca away from a PR particle decreases with increasing concentration of Ca in the soil solution. As a result, PR dissolution decreases.

The effect of phosphate concentration in soil solution on PR dissolution was found to be less pronounced than other soil properties, such as Ca concentration in soil solution (Mackay *et al.*, 1986). This is probably because the concentration of Ca in soil solution is generally a lot higher than that of the phosphate. In most soils, P concentrations in solution are low because of the removal of phosphate from soil solution through adsorption or immobilization. Thus, P retention capacity of soil can also be important for PR dissolution. Increases in PR dissolution with increased P retention capacity have been shown by Chien *et al.*, 1980; Smyth and Sanchez, 1982; Hammond *et al.*, 1986; Syers and Mackay , 1986; Kanabo and Gilkes, 1987b; Wright *et al.*, 1992). Several

measures of soil Al, including exchangeable Al, active Al, and reactive Al, are related to P sorption capacity (Ballard and Fiskel, 1974; Chien *et al.*, 1980) and therefore can be related to PR dissolution (Wright *et al.*, 1982).

2.6.1.3 Plant factors

Plants can increase PR dissolution by several mechanisms. Firstly, plant roots act as sinks for Ca^{2+} and $H_2PO_4^-$. Thus continuous removal of these ions from soil solution decreases their concentrations and induces PR dissolution to continue (van Ray and van Diest, 1979; Bekele *et al.*, 1983). Secondly, plants have the ability to acidify rhizosphere soil (Nye, 1981; Hedley *et al.*, 1982b; Haynes, 1990). This, in turn, increases the dissolution of PR through increasing the supply of H^+ (Nye, 1986d). Legumes can acidify their rhizosphere when they are actively fixing nitrogen (Bolan *et al.*, 1989). Utilization of symbiotically fixed N_2 by legume causes a strongly alkaline uptake pattern (an excess of cations over anions absorbed) resulting in soil acidification (Aguilar and Van Diest, 1981; Bekele *et al.*, 1983) as H^+ is released from roots to maintain a charge balance at the soil-root interface (Haynes, 1990).

For non-legumes, the ability of their roots to acidify the rhizosphere mainly depends on the form in which N is being taken up (Haynes, 1990). Absorption of N mainly as NH_4^+ results in H^+ release (Haynes, 1990). Some plants such as buckwheat have alkaline uptake patterns regardless of the form of N absorbed (Aguilar and Van Diest, 1981).

The role of particular plants as tools in improving the efficiency of PR as a direct-application fertilizer requires further investigation.

2.6.1.4 Climatic conditions

The dissolution of PR occurs under moist conditions. Soil volumetric water content (θ) influences the cross sectional area of the pathway available for diffusion of ions in soils and the path length (Kirk and Nye, 1986a). Thus soil moisture controls the rate of PR dissolution through its effect on the diffusion of H^+ and dissolution products away from PR particles (Kirk and Nye, 1986c). In the presence of plants, soil moisture also affects

the uptake of Ca and P. Kanabo and Gilkes (1988c) have demonstrated increased PR dissolution with increasing soil moisture content. Dissolution of PR is generally enhanced by soil remaining sufficiently wet (Reinhorn and Hagin, 1978; Kanabo and Gilkes, 1988c), but drying and wetting decrease PR dissolution. Provided that soil acidity is not limiting, Hanafi *et al.* (1992a) have observed that dissolution of PR is higher under open-leaching than under closed incubation system. The increased PR dissolution under open conditions is associated with increased leaching of Ca from soil increasing the Ca sink size for the dissolved Ca. Such climatic conditions can be used as indices for selecting soils for direct application of PR. Such soils commonly have vigourous biological cycles and depending upon temperature may have high organic matter content; factors which will also enhance PR dissolution, through removing products of dissolution (see later section).

2.6.1.5 Soil amendments

Soil amendments such as lime, N and S fertilizers and organic matter also affect PR dissolution. Applications of lime, which aim to alleviate aluminum toxicity, generally decrease PR dissolution due to increases in soil pH and exchangeable Ca (Mackay and Syers, 1986; Rajan *et al.*, 1991b; Thibaud *et al.*, 1992).

Dissolution of PR may be enhanced by mixing it with other fertilizer materials. Apthorp *et al.* (1987) found that the application of N fertilizers increased PR dissolution in the following order: ammonium sulphate>urea>potassium nitrate. The extent of increased PR dissolution was related to the amount of soil acidity generated by the fertilizers by nitrification. Mixing PR with superphosphate causes some initial increases in dissolution because of the acidity produced by the hydrolysis of MCP in the superphosphate. The presence of high concentrations of calcium and phosphate in solution ultimately inhibits further dissolution of PR (Le Mare, 1991). Additions of elemental sulphur to soil, either applied directly or through granulation with PR, also increase PR dissolution (Rajan, 1982; Lee *et al.*, 1987; Pathiratna, 1989). Oxidation of the S° to sulphuric acid by bacteria *Thiobacillus* sp (Swaby, 1975) produces H^{+} which subsequently reacts with the PR.

Positive effects of organic matter on PR dissolution are related to the bonding of Ca, thus providing an effective sink for Ca (Khasawneh and Doll, 1978) and supply of protons due to oxidation of organic materials. Incorporation of Mussoori PR into compost enhanced its dissolution, indicating similar reactions to those in organic soils (Bungar *et al.*, 1985). However, there has been no reported studies on the effect of plant residues on the dissolution of PRs.

2.6.2 Availability of dissolved P

Several workers (e.g. Chien *et al.*, 1980; Bolan and Hedley, 1990) have observed that, in short-term experiments, the amount of dissolved P becoming plant-available, whether measured by either chemical extractants or plant uptake, was always smaller than the amount of P dissolved. Adsorption by soil components appears to be the main process affecting decreasing P availability (Sample *et al.*, 1980). Chien *et al.* (1987) hypothesized that the low solution concentration of P maintained due to the slow dissolution of PR favours surface adsorption of P by oxides of Al and Fe.

As discussed in Section 2.6.1.2, the dissolution of PR may increase with increasing soil P retention capacity. However, the amount of available P decreases with increasing soil P retention capacity (Smyth and Sanchez, 1982; Syers and Mackay, 1986). Working with a variable charged New Zealand soil adjusted to a range of soil pHs, Bolan and Hedley (1990) observed that although the dissolution of PRs increased with decreasing soil pH, the proportion of the dissolved P becoming plant-available decreased. These workers concluded that the decrease in amount of plant-available P with decreasing soil pH resulted mainly from an increase in phosphate adsorption at lower soil pHs.

The mechanistic basis for such observations is that increased P sorption decreases the effective diffusive flux of P to plant roots (Nye and Tinker, 1977; Barber, 1984). Thus across a range of soils, although availability of P from PR is controlled by the rate of dissolution of the PR (Hammond *et al.*, 1986), PR dissolution does not necessarily increase the availability of dissolved P to plants (Hammond *et al.*, 1986; Syers and Mackay, 1986; Bolan and Hedley, 1991). Often low pH is associated with higher P sorption capacity simply because acidic highly weathered soils usually contain greater

quantities of short range order of Fe and Al oxides. Sorption of P is principall; controlled by these soil components (Parfit, 1978; White, 1980).

2.7 METHODS OF ASSESSING PHOSPHATE ROCK DISSOLUTIOI IN SOIL

Dissolution of PR in soil is a necessary prerequisite to plant uptake. Thus an accurat measurement of the extent of PR dissolution and the availability of the dissolved P is useful for making recommendations for PR use. This section discusses various methods used to measure the extent of PR dissolution in soil and its availability to plants.

2.7.1 Measurement of phosphate rock dissolution

Several methods have been proposed to measure the extent of dissolution of PR added to a soil. In most methods dissolution of PR has been estimated directly by measuring amounts of dissolved P or Ca, or indirectly, by measuring amounts of residual rock P or PR-Ca remaining in the soil. The proposed methods are as follow.

2.7.1.1 Δ extractable Ca (ΔCa) method

This method measures the increase in soil exchangeable Ca (ΔCa) following the addition of PR. The Ca released from PR accumulates and becomes an exchangeable cation (Khasawneh and Doll, 1978). The increase in exchangeable Ca in PR treated over control (PR untreated) soil is assumed to have resulted from the dissolved Ca. This method employs neutral 1 M NH_4OAc solution to extract Ca in pairs of PR treated and untreated soils.

Smyth and Sanchez (1982) modified the ΔCa method by replacing neutral 1 M NH_4OAc with 1 M KCl to estimate the dissolution of North Carolina and Patos de Minas PRs in an acid Brazilian soil. Hughes and Gilkes (1984) used 0.5 M $BaCl_2$/TEA (pH 8.1) instead of 1 M KCl or neutral 1 M NH_4OAc to remove exchangeable Ca^{2+} from soils. The ΔCa method of Hughes and Gilkes (1984) has often been used by several workers

to estimate the dissolution of PRs (e.g. Kanabo and Gilkes, 1987a, 1987b; Bolan and Hedley, 1989; Wright *et al.*, 1992).

The estimation of PR dissolution by ΔCa method, however, is limited to soils that have low amounts of native exchangeable Ca. For example, Hughes and Gilkes (1984, 1986a; 1986b) reported that the increase in exchangeable Ca, as measured by the $BaCl_2$/TEA method, (Δ$BaCl_2$/TEA-Ca) adequately estimated PR dissolution in many acidic soils which contained relatively low amounts of exchangeable Ca (generally in the range 0-12 mmol kg^{-1}). Their method, however, has not been evaluated in soils containing large amounts of exchangeable Ca or in limed soils. In such soils, this method may not give an accurate estimate of PR dissolution because the amount of Ca derived from the PR at a normal application rate (around 30 kg P ha^{-1}) will be low relative to the amounts of native soil exchangeable Ca.

The ΔCa method may underestimate PR dissolution in soil in the presence of plants, or in soils where leaching occurs, unless the dissolved Ca taken up by plant or leached is taken into account.

2.7.1.2 Fractionation of inorganic P.

Chang and Jackson (1957) developed a sequential extraction procedure for measuring amounts of inorganic P fractions in soil. These procedures arbitrarily fractionate soil P into Al-P, Fe-P and Ca-P fractions. While the increases in Fe-P and Al-P fractions in PR treated over control (PR untreated) soil provides an estimate of the dissolved PR, decreases over time in Ca-P fraction over its control provides an estimate of amounts of undissolved PR. This method has been used by Chu *et al.* (1962) and Juo and Kang (1978) to measure PR dissolution in Virginian and Nigerian soils, respectively.

More recently, the inorganic P fractionation procedures have been further modified for measuring PR dissolution in soil. The new proposed methods are as follow:

Δ NaOH-extractable Pi (ΔNaOH Pi) method

According to this method, the increase in 0.5 M NaOH-extractable inorganic P (Pi) in

a soil treated with PR over its control (untreated) should provide a good estimate of the amount of PR dissolved. In soils that have a high exchangeable Ca, a pre-extraction with 1 M NaCl is necessary to prevent $CaCO_3$ precipitation during NaOH extraction. The use of this method to measure PR dissolution in soils has been reported by several workers (Mackay and Syers, 1986; Bolan and Hedley, 1989; 1990; Robinson and Syers, 1990, 1991; Wright *et al.*, 1992). As in the case of the ΔCa method, the use of the ΔNaOH-Pi method to measure PR dissolution in soil in the presence of plants requires the amounts of P dissolved from PR taken up by plant to be taken into account. Another limitation of this method is that over longer periods of time dissolved P is incorporated into soil organic matter and would not be determined by this method.

The ΔNaOH-Pi has been successfully used to provide an acceptable estimate of PR dissolution in soils that contain up to 98 mmol kg^{-1} of exchangeable Ca (Mackay *et al.*, 1986; Syers and Mackay, 1986).

Δ acid-extractable P (Δacid-P) method

Estimation of PR dissolution by this method is based on measuring the amount of acid soluble apatite remaining in soil following extraction with NaOH. The acid used is either 1 M HCl (Apthorp *et al.*, 1987) or 0.5 M H_2SO_4 (Rajan, 1983). This method has an advantage over the ΔCa and ΔPi methods that it can be used to measure PR dissolution under field condition more accurately provided that the undissolved PR remain in the sampling zone.

It is important to note, however, that in both ΔNaOH-Pi and Δacid-P methods pre-extraction with 1 M NaCl is required prior to NaOH extraction in order to remove any soluble or exchangeable Ca. Pre-extraction prevents precipitation of $Ca(OH)_2$, or $CaCO_3$ during NaOH extraction (Syers *et al.*, 1972) and subsequent adsorption (or co-precipitation) of P dissolved from PR material by these precipitates. In acid soils, however, the presence of NaCl may result in the exchange of solution Na^+ for soil surface H^+ thereby lowering solution pH and inducing the dissolution of PR during pre-extraction. Thus, the existing methods for measuring PR dissolution may need further evaluation for use in a range of acid soils.

All the three methods described above are based on the assumption that dissolved P or Ca derived from PR dissolution remains extractable. However, under field conditions, where dissolved P and Ca can be removed by plant uptake or leaching (for Ca), both ΔCa and ΔNaOH-Pi methods could underestimate the extent of the dissolution process (Bolan and Hedley, 1990). It is reasonable to suggest that the amount of residual PR measured by the Δacid-P might provide a more accurate estimate of the extent of PR dissolution, provided the undissolved PR remains in zone of soil sampled.

2.7.2 Measurement of plant-availability of dissolved P

Amounts of plant-available P in soil have been measured by various soil P tests. The suitability of a soil test for assessing P availability is generally evaluated by correlating soil P as measured by various extractants with plant parameters such as yield, P uptake or plant P concentration. The suitability of a soil test is influenced by soil properties (Kamprath and Watson, 1980; Sparling *et al.*, 1985). With increasing use of less soluble P fertilizers such as PR and partially acidulated phosphate rock (PAPR), the type of P fertilizer applied has now been considered as another factor that also influences the suitability of a soil test (Saggar *et al.*, 1991a). It is evident that relationships between soil test values and crop yield (or plant P uptake) in soils fertilized with water-soluble P and PR sources are different (Hammond, 1979; Rajan *et al.*, 1991a; 1991b; Saggar *et al.*, 1991a) indicating that fertilizer P recommendation based on soil tests developed for water-soluble P sources may not be applicable to PR (Hammond *et al.*, 1986; Saggar *et al.*, 1991a).

Various soil P tests have been recommended for measuring P availability in soil (see reviews by Kamprath and Watson, 1980 and Sibessen, 1983). A limited number of studies show that only a few of these soil P tests are suitable for use in soil fertilized with PR. Among the chemical extraction soil tests, Bray 1 P (Bray and Kurtz, 1945) has been shown to be a good predictor of available P in various temperate and tropical soils (Peaslee *et al.*,1958, Barnes and Kamprath, 1975; Chien, 1978; Mackay *et al.*.1984d; Syers and Mackay, 1986; Fageria *et al.*, 1991). The results obtained by any acid extraction test, such as Bray 1, however, should be interpreted with caution because they tend to dissolve some of the undecomposed PR during the extraction process

(Chien, 1978; Syers and Mackay, 1986). Although it is unclear whether this dissolved P represents a useful unit for predicting agronomically effective P.

Other workers (Peaslee *et al.*, 1962; Bolan and Hedley, 1989; Rajan *et al.*, 1991b) have obtained a good relationship between soil P extracted by Olsen P (Olsen *et al.*, 1954) and P uptake in temperate soils. Similarly, the Colwell test (Colwell, 1963), which is a modification of the Olsen test, is commonly used to measure plant available P in soils fertilized with either water-soluble P fertilizer or PR (e.g. Bolland, 1985, 1986).

Soil P extracted by anion exchange resin (AER) has been shown to be a better index for plant response than Bray 1 in soil fertilized with PR (Peaslee *et al.*, 1962; Reinhorn and Hagin, 1978). Similarly, Saggar *et al.* (1991b) have shown that soil P extracted from several PR treated New Zealand soils by the combined AER and cation exchange resin (CER) was a better index of plant response to various PRs than either the Olsen, Colwell, Bray 1 or Truog test.

The iron hydroxide-impregnated filter paper (Pi) test which was recently developed by Menon *et al.* (1989c) has been shown to be a better soil test in soils fertilized with fertilizer P of different solubility (Menon *et al.*, 1989a; 1989b). Adherence of soil particles to the filter paper surface appears to be a major limitation of this method (Perrot and Wise, 1992).

Use of isotope dilution techniques to measure the relative availability of several PRs was proposed by Kucey and Bole (1984). Isotope dilution principles assume that all radioisotopic P added to an incubated mixture of soil and PR remains in isotopic equilibrium with P dissolved from the PR and the final specific activity is uniform in the equilibrated exchange system. This method measures the amount of exchangeable soil P, commonly referred as the E value (White, 1976). Kucey and Bole (1984) found that this method was more reliable in predicting plant P uptake than the conventional soil P extraction tests. Use of this technique is, however, not recommended in high P fixing soils (Wolf *et al.*, 1986). Another disadvantage of the isotope dilution technique, of course, is the requirement for expensive equipment such as a scintillation counter. This makes the technique less attractive as a routine technique.

Current information on the suitability of various soil P tests for measuring plant available P in soil fertilized with PRs remains restricted to certain ranges of soil groups, climatic regions and plant types. Given the important influences of soil properties, climate and crop on PR dissolution and uptake of dissolved P, further investigations under conditions applicable to Indonesian soils and climate are necessary.

2.8 USE OF PHOSPHATE ROCK FOR DIRECT APPLICATION IN NEW ZEALAND AND INDONESIAN AGRICULTURE

As discussed earlier (Section 2.6.1), factors affecting PR dissolution in soil include properties of the PR and soil, type of crop and climatic conditions. Numerous glasshouse and field trials have demonstrated that these factors also determine the effectiveness of PR as a fertilizer (For reviews, see Khasawneh and Doll,1978; Hammond *et al.*, 1986; Bolland *et al.*, 1988; Bolan *et al.*, 1990).

This section briefly discusses results of some studies on the effectiveness of PR for direct application in New Zealand and Indonesian agriculture. Agronomically, PR is considered suitable for direct application if its cost effectiveness as a P fertilizer is comparable or better than a standard water-soluble P fertilizer such as single superphosphate (SSP) or triple superphosphate (TSP). In glasshouse trials monocalcium phosphate (MCP) is often chosen as a standard soluble P fertilizer.

2.8.1 New Zealand

In New Zealand, the use of PRs as alternatives to water-soluble P fertilizers has been evaluated mainly for pastures. Following an extensive review of research on the use of PR for direct application, Bolan *et al.* (1990) proposed the following criteria for a PR to be effective fertilizer:

- The PR must be classed as reactive
- The soil has a pH (in water) of 6.0 or less
- The site has a mean annual rainfall >800 mm

These criteria were derived mainly based on information from pasture field trials. The following discussion summarizes the evidence to support the adoption of the above criteria.

With respect to chemical properties of PR, it has been shown that reactive PRs (RPRs) such as Sechura, North Carolina, Gafsa and Arad PRs generally perform better in New Zealand's acidic pasture soils than unreactive PRs such as Nauru, Christmas Island and Florida (Figure 2.4). Chatham rise PR has also been identified as a reactive PR (Mackay *et al.*, 1984a, 1984b; Syers *et al.*, 1986). Results of a glasshouse trial by Mackay *et al.* (1984a), for example, demonstrated that Sechura reactive PR was 4 to 20 times more effective than unreactive Tennessee PR for ryegrass grown on six New Zealand soils. Several long-term field studies have shown that RPRs were equally or more effective than water-soluble P fertilizers (e.g. Gregg *et al.*, 1988; Mackay *et al.*, 1984b; Rajan and Gillingham, 1986, Mackay and Wewala, 1990; Rajan *et al.*, 1991a). Provided soil pH and climatic conditions are met, the effectiveness of RPRs generally increased with time and, after a lag period of 1 to 2 years RPRs, were as effective or slightly more effective than soluble P fertilizers (Sinclair and Dyson, 1988).

Although fine PRs (<150 μm) have higher dissolution rates than the coarser materials, a number of field studies (e.g. Mackay and Wewala, 1990; Rajan *et al.*, 1991a), have shown that the unground "as received" PRs are still suitable for direct application. Under field conditions, granulated RPRs are also equally effective as the finely ground materials (Mackay *et al.*, 1984b, Officer, 1989). It appears that under New Zealand pasture conditions chemical reactivity of PR may be more important than the particle size.

High effectiveness of RPRs in New Zealand pasture soils is generally obtained in soils with pHs (in water) less than 6.0. It has been discussed in Section 2.6.1 that soil acidity plays an important role in controlling PR dissolution. In most New Zealand soils with pH <6.0, the amount of soil acidity, as measured by titration, is not likely to be limiting PR dissolution (Bolan *et al.*, 1990). These workers estimated that the amount of acid in these soils is sufficient to dissolve between 294 to 998 kg PR-P ha^{-1} provided that moisture (i.e. transport of H^+ to PR) is not limiting. The size of Ca sinks, which also

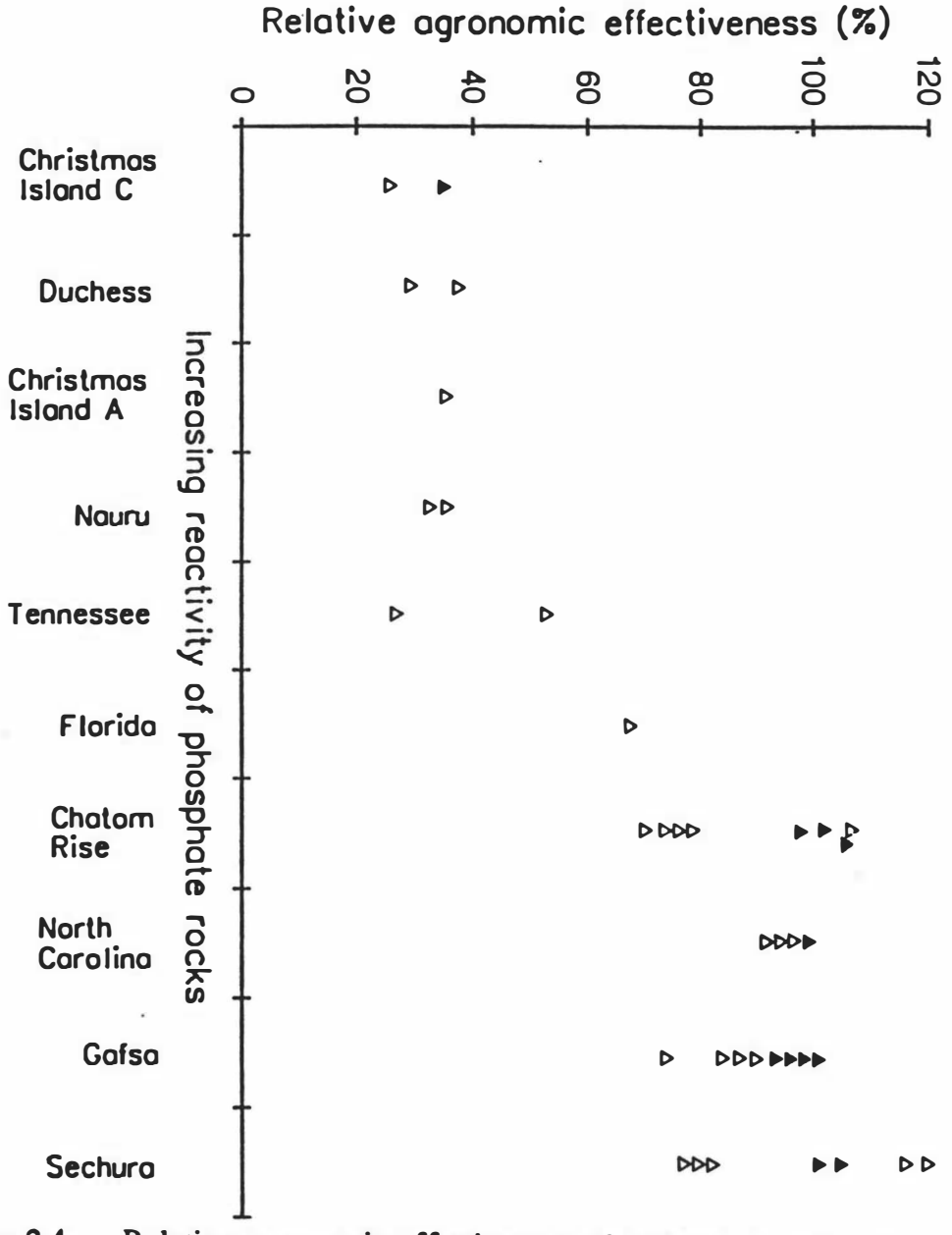

Figure 2.4 Relative agronomic effectiveness of various phosphate rocks for pastures in New Zealand soils under glasshouse (▷) and field (▶) conditions (Compiled from Bolan *et al.*, 1990).

controls PR dissolution, is relatively large in most New Zealand acid soils (Bolan *et al.*, 1990) thereby not limiting PR dissolution under field conditions.

Because of the low concentration of phosphate maintained by PR in soil solution, perennial crops and others with permanent extensive root systems are most likely to use PR-P most effectively. In New Zealand agriculture, PR is considered an effective direct-application fertilizer for perennial crops such as grass-clover pastures but not suitable for annual crops such as cereals (wheat, barley, maize) that require high P uptake over a short season with limited P cycling during the season. For this reason, RPRs are mainly used on grass-white clover based pasture. The presence of perennial legume (white clover) in pasture has a beneficial effect on the effectiveness of RPR due to its acidifying effect in the clover rhizosphere which can increase PR dissolution (Section 6.2.1) and the availability of P to the plant. The accumulation of high quality organic matter in permanent pasture soils due to plant (and animal) residues may also supply extra acid during decomposition (Williams, 1980) which can be important for PR dissolution.

Provided that soil acidity is not limiting, the dissolution of PR is controlled by moisture since it controls the diffusion of base and dissolution products (Section 2.6.1). Additionally, it also affects the rate of nutrient uptake by plants. Most field trials showing high effectiveness of RPR have been conducted in areas with evenly distributed annual rainfall of at least 800 mm. In areas with soil pH of 6.2 and a mean annual rainfall of 1000 mm, RPR was as effective as water-soluble P fertilizer (Mackay *et al.*, 1984b). On the other hand, in areas with annual rainfall intensity less than 800 mm, the effectiveness of RPRs is low even if the soil is acidic. It is apparent that the sink size for Ca in soil is likely to increase with increasing rainfall intensity due to increased Ca leaching, increased plant growth and higher soil organic matter contents.

Based on the tentative criteria listed above, Bolan *et al.* (1989) estimated that there are about 8 million ha of land in New Zealand which is potentially suitable for direct application of RPRs to pasture. It should be pointed out, however, that the high effectiveness of RPRs for pasture can only be achieved if other nutrient deficiencies are overcome.

2.8.2 Indonesia

Phosphate rocks were the main P fertilizer in Indonesia for many years until triple superphosphate (TSP) was introduced in the 1960's (I.G.P Widjaya-Adhi, pers. comm.). Phosphate rock is still used as a direct-application fertilizer particularly for perennial crops such as rubber, oil palm and some legumes grown among young rubber or oil palm trees. There is interest in increasing the use of low cost PRs for both perennial and annual crops.

The number of studies examining the potential of PRs as direct-application fertilizers for different crops has increased in the past six years. Despite the limited information available, this section attempts to discuss the suitability of PR for direct application to perennial and annual crops on Indonesian soils, which are dominated by Ultisols and Oxisols.

The Indonesian fertilizer regulations (Martoyo and Suwandi, 1989) stipulate the following criteria for a PR to be used as a fertilizer: the total P content of the PR must be at least 11.5%, 60% of the PR particle size should be below 190μm (80 mesh) and the 2% citric acid solubility of the PR must be at least 30% of total P content. The citric acid solubility criterion is similar to that used in New Zealand to distinguish "reactive" and "unreactive" PR. Using these criteria, PRs which qualify for direct application include Sechura, North Carolina and ground Gafsa and Arad PRs. Whereas PRs of lower reactivity such as Jordan, Khouribga, Tennessee, Christmas Island PRs do not qualify for direct application.

2.8.2.1 Perennial crops

Results of both glasshouse and field trials have shown that PRs of different reactivity are suitable as direct-application fertilizers for many perennial crops, provided that the soils are acidic. Glasshouse trials (e.g. Hardjono, 1988a; 1988b) showed that the medium reactive PRs (<190 μm) such as Jordan, Moroccan, Florida and Togo were as

effective as or more effective than TSP for perennial legumes, such as *Calopogonium caeruleum* and seedlings of cocoa and oilpalm grown on two Oxisols (pH 4.4 - 4.9). Nasution *et al.* (1986), however, demonstrated that Christmas Island PR (CIPR) was consistently less effective than TSP for different species of perennial legumes (*Pueraria phaseoloides, Centrocema pubescens, Calopogonium muconoides and Calopogonium caeruleum*) grown on a podsolic soil under glasshouse conditions. The low effectiveness of PR reported in this experiment can be attributed to the low chemical reactivity of CIPR and the relatively high soil pH, which was 6.3.

The effectiveness of PR for many perennial crops is generally high under field conditions, and also less dependent on its chemical reactivity. Hardjono (1981), for example, reported that ground Christmas Island (grade A) PR was as effective as TSP for rubber seedlings grown on an acidic Ultisol (pH 4.6). High effectiveness of CIPR was also reported for rubber (Pek, 1966) and oilpalm (Martoyo and Suwandi, 1989) grown on soils with pH less than 4.9. In addition to soil and climatic conditions, the high effectiveness of PR for many perennial crops grown on very acid soils is probably attributed to their slow P uptake, low P requirements and P recycling within the system.

2.8.2.2 Annual crops

The effectiveness of PRs of varying chemical reactivity relative to TSP has been tested for annual upland crops such as rice, maize and soybean. Following is a brief discussion of results from a limited number of studies.

The effectiveness of PRs as direct-application fertilizers for annual crops generally increases with time indicating increased residual effectiveness. Long-term field trials showed that PRs with a range of reactivities, applied at a single application rate (80 to 180 kg P ha^{-1}), were generally less effective than TSP in the first growing season, but became as effective as or more effective than TSP after the first season (Moersidi *et al.*, 1982; Hartatik and Adiningsih, 1987). Harris *et al.* (1985), however, observed that PRs were as effective as TSP or SSP in maize-soybean-maize rotations from the first growing season in an Ultisol (pH 4.8).

As in the case of perennial crops, the effectiveness of PR for annual crops observed under field conditions is less affected by its chemical reactivity than glasshouse observations. Phosphate rocks such as North Carolina, Tunisia, North Florida and Christmas Island (Grade A) PRs generally had equal effectiveness in most Indonesian Ultisols and Oxisols (Hakim and Moersidi, 1982; Moersidi *et al.*, 1982; Harris *et al.*, 1985). This is likely to be attributed to the low soil pH and high annual rainfall (>2250 mm) (see Section 2.6.2.4). The intense leaching of Ca^{2+} in acid soils due to high rainfall also provides large sinks for Ca^{2+} thereby inducing rapid PR dissolution.

The effect of particle size on the effectiveness of PRs varied between soils. Harris *et al.* (1985), for example, did not observe any difference in the effectiveness between TSP, SSP, finely ground (<60 μm) North Carolina and Jordan PRs, and their granulated forms in maize-soybean-maize rotations on an Ultisol (pH 4.8). Contrasting results were reported by Moersidi and Adiningsih (1988) in similarly low pH soils. They observed that grinding increased the effectiveness of Tunisia PR in a soybean-rice rotation in acid Oxisols (pH 4.5 to 4.7) with high aluminum saturation (52 to 57%), but granulation decreased the effectiveness of the PR in these soils. Such results, where mechanistic explanations of contrasting PR effectiveness are absent, reduce the confidence in PR use.

In a rice-soybean-rice rotation experiment on a previously limed Ultisol (pH=5.3, aluminum saturation=1%), Moersidi and Adiningsih (1988) observed that Tunisia PR of different particle sizes ("as received", finely ground and granulated materials) were more effective than TSP for rice in the first and third seasons, but was less effective than TSP for soybean in the second season. Low effectiveness for PR during the second season was associated with the occurrence of drought.

The effectiveness of PRs for annual crops is also affected by rate and frequency of PR application (Hakim and Moersidi, 1982; Hartatik and Adiningsih, 1987). Phosphate rocks were generally as effective as or more effective than TSP in crop rotation when they were applied at high rates (80 to 140 kg P ha^{-1}) at the beginning of the first growing season. Reapplication of PR at low rates before each crop, on the other hand, decreased the effectiveness of PRs. This is probably because of the low rates of application did not supply sufficient P for the short-term requirements of each crop.

Despite agronomic evidence showing the potential of PR use as a direct-application fertilizer in many acid soils of Indonesia, further studies on the mechanistic reasons why soil, soil management and crop influence the effectiveness of PR use are still required. Such studies might be very useful in assisting the selection of potential sites where economic risks involved in PR use are acceptable.

2.9 SUMMARY OF LITERATURE REVIEW AND RESEARCH OBJECTIVES

Phosphate rocks differ in mineralogy and chemical composition which influences their chemical reactivity. These properties, plus PR particle size along with soil, climatic conditions and type of crops are important in determining PR dissolution in soil and their agronomic effectiveness as direct-application fertilizers.

Numerous field and glasshouse trials have tested the effectiveness of PR fertilizers against soluble P fertilizers for a number of crop species. In general the effectiveness of PR as fertilizers is high when soils are acidic and have low Ca saturation and are consistently moist. For example, a review of field and glasshouse trial information in New Zealand led to the following suggestions for criteria used to select sites suitable for direct application of PR. Reactive PRs can be used as direct-application fertilizers in New Zealand permanent pastures provided that the soil pH <6.0 (in water) and the mean annual rainfall exceeds 800 mm. In Indonesia, limited field trial information is available concerning the suitability of PR as a direct-fertilizer and has not been synthesised into fertilizer recommendations. However, there are indications that PRs of different reactivity can be as effective as TSP on very acid soils, predominantly Ultisols and Oxisols, for both perennial crops, such as rubber, oil palm and creeping legumes, and annual upland crops such as rice, maize and soybean.

In New Zealand and Indonesia there are clear agronomic opportunities where agricultural costs can be reduced by using PR instead of soluble P fertilizers. These situations need more clearly identifying by investigating the mechanism of PR dissolution in representative soils. Information on PR dissolution can be used to test whether currently

available mechanistic computer models are capable of simulating PR dissolution in these soils. Successful simulation by these or modified models could be used to select suitable sites for PR use.

The objectives of this thesis are:

(a) to develop improved methods to study dissolution of PRs and availability of the dissolved P in a range of temperate (New Zealand) and tropical (Indonesian) soils;

(b) to investigate suitable procedures for describing dissolution of PR in soils, including field soils;

(c) to test those procedures using measured rates of PR dissolution in soils, including field soils; and

(d) to compare the residual effectiveness of a range of PRs and TSP under field conditions.

CHAPTER 3
PHOSPHATE ROCK DISSOLUTION IN SOILS OF VARYING pH AND EXCHANGEABLE Ca CONTENTS

3.1 INTRODUCTION

Significant amounts of residual (undissolved) phosphate rock (PR) are likely to remain in some soils several years after application (Rajan *et al.*, 1991b). Thus for the purpose of fertilizer recommendation it is very important to measure the dissolution rate of PR in soils fertilized with PR based fertilizer (see Section 2.6.1, Chapter 2). The amount and frequency of PR to be applied largely depend on the rate of PR dissolution in soils.

Current methods proposed for estimating the extent of PR dissolution include:

(1) Δ exchangeable Ca (ΔCa) method, which estimates PR dissolution in soil/PR mixtures from increases in the amounts of exchangeable Ca (e.g. Hughes and Gilkes, 1984);

(2) ΔNaOH-extractable inorganic Pi (ΔNaOH-Pi) method, which estimates PR dissolution in soil/PR mixtures from increases in the amounts of NaOH extractable inorganic P (Pi) (e.g. Mackay *et al.*, 1986); and

(3) Δ acid-extractable P (Δ Acid-P; ΔHCl-P or ΔH_2SO_4-P) method, which estimates PR dissolution in soil/PR mixtures from changes in amounts of residual PR-P (1 M HCl- or 0.5 M H_2SO_4-P) (e.g. Rajan, 1983; Apthorp *et al.*, 1987).

The limitation of the ΔCa method for measuring PR dissolution in laboratory incubations is that it may not adequately estimate PR dissolution in soils with large amounts of native exchangeable Ca or in limed soils. The ΔNaOH-Pi method, on the other hand, has been successfully used to provide an acceptable estimate of PR dissolution in soils that contain up to 98 mmol kg^{-1} of exchangeable Ca. This method, however, requires pre-extraction of the soil with 1 M NaCl in order to avoid high Ca concentrations in the subsequent NaOH extract which may result in the formation of insoluble Ca-P (Mackay *et al.*, 1986). In acid soils, however, pre-extraction with NaCl is likely to lower solution pH which may induce dissolution of PR during pre-extraction.

In field soils, dissolved P and Ca can be removed by plant uptake or leaching of Ca under field conditions. Thus both ΔCa and ΔNaOH-Pi methods could underestimate the extent of the PR dissolution. In the presence of plant roots the amounts of residual PR measured by the Δacid-P methods might provide a more accurate estimate of the extent of PR dissolution. To date these methods have not been fully evaluated for use in New Zealand soils.

3.2 OBJECTIVES

The main objective of this study was to develop accurate methods for measuring residual (undissolved) PR in a range of New Zealand soils contrasting in pH and exchangeable Ca (Section 3.3.1). The resultant method was then used to study the extent of dissolution of North Carolina phosphate rock (NCPR) in a laboratory incubation study (Section 3.3.2).

3.3 MATERIALS AND METHODS

3.3.1 Experiment 1. Development of a sequential extraction method for measuring residual phosphate rock in soil

3.3.1.1 Soils and soil pretreatment

Dannevirke silt loam (Typic Eutrochrept) soil, obtained from a sheep farm, was used in this study. Some properties of this soil are shown in Table 3.1. The soil samples were air-dried and sieved to pass a 2 mm sieve. Samples were preincubated with different amounts (ranging from 0 to 0.097 g $CaCO_3$ per 100 g soil) of analytical grade $CaCO_3$. After 9 weeks incubation soil pHs were measured and two samples with pHs of 5.4 and 6.7 (representing soils which had received 0.004 and 0.048 g $CaCO_3$ per 100 g soil) were chosen for further study.

Table 3.1 Some properties of the soil used in Experiment 1.

Soil	Soil Taxonomy	pH (H_2O)	Org.C (%)	Olsen-P (mg kg^{-1})	CEC (cmol (+) kg^{-1})	Ca sat*. (%)	P retention (%)
Dannevirke silt loam	Typic Eutrochrept	5.5	10.2	4.7	38.1	14.0	71

* Ca sat.=Ca saturation.

3.3.1.2 Phosphorus source characteristics

The P source used in this study was North Carolina phosphate rock (NCPR). Selected chemical and physical characteristics of the NCPR are shown in Table 3.2.

Table 3.2 Some chemical and physical characteristics of North Carolina phosphate rock (NCPR).

Particle diameter (μm)	Proportion of total weight (% w/w)	Total P (%)	2% Citric acid-soluble P (% of total P)
		As received	
<106	1.84	14.21	33.6
106 - 150	18.72	13.15	41.1
150 - 250	56.25	13.60	40.6
250 - 500	23.19	11.59	46.9
Whole sample	100	13.0	38.1

3.3.1.3 Recovery of NCPR-P and NCPR-Ca from soil

Works-ground NCPR was added to 20 g of each soil sample at a rate of 400 mg P kg^{-1} soil. A control soil, to which no NCPR was added, was also prepared. Three samples of each treatment were taken for immediate P chemical fractionation.

3.3.1.4 Sequential extraction of P and Ca from soil/NCPR mixtures

Soils were pre-extracted with either 1 M NaCl (Mackay *et al.*, 1986) or 0.5 M NaCl buffered with TEA (0.5 M NaCl/TEA, pH7), and then extracted sequentially with 1 M NaOH and 1 M HCl. The 1 M NaOH extractant removes inorganic P (Pi) and organic P (Po) associated with amorphous hydrous oxides of Al and Fe (Hedley *et al.*, 1982). Any difference in the NaOH extractable-Pi between NCPR-treated and untreated soil is mainly due to the PR dissolution in the pre-extractions. Because 1 M HCl removes mainly apatite-bound P, any increase in HCl-extractable P (ΔHCl-P) between NCPR-fertilized and unfertilized soils is taken to indicate the amount of residual NCPR.

The 0.5 M $BaCl_2$/TEA (pH 8.1) extractant can be used to remove soluble and exchangeable soil Ca (Bascomb, 1964). However, this extractant is not suitable for a combined Ca and P extraction procedure because barium sulphate precipitation is likely to occur when the inorganic P in the $BaCl_2$/TEA extract is measured using the Murphy and Riley (1962) colorimetric procedure. Use of the 0.5 M NaCl/TEA extractant would be expected to extract smaller amounts of Ca than 1 M NaCl or 0.5 M $BaCl_2$/TEA or other pre-extractions, however, both Ca and P can be readily determined in the resultant extract. The buffering of this extractant at pH 7 prevents any dissolution of PR during this extraction. The 0.5 M NaCl/TEA extract used in this study was prepared in a similar manner to that for $BaCl_2$/TEA (Bascomb, 1964), except that the buffer was adjusted to pH 7 by addition of 2 M HCl. The titration curve of 0.5 M NaCl/TEA (Appendix 3.1) shows that sufficient buffer power still remains below pH 7 for the buffer to maintain a soil suspension pH in the region of pH 6-7 to suppress PR dissolution.

Inorganic P (Pi) was measured in the extracts using the Murphy and Riley (1962) procedure after centrifugation (3000 rpm for 10 min) and filtration (Whatman paper no 42). Recovery of Pi from soil by various extractants was checked using the method of standard additions. A correction was made to account for the contribution of P in the entrapped solution to the subsequent extract.

In all experiments extractions were carried out at a soil:solution ratio of 1:40 with an extraction time of either 30 minutes (for pre-extraction with NaCl or NaCl/TEA) or 16 h (for both NaOH and HCl extractions).

Concentrations of Ca in prewash solutions and HCl extracts were measured using standard atomic absorption spectrophotometry (AAS) as described in Section 3.3.3.1. As with Pi, any difference in the amount of HCl-Ca extracted from NCPR-treated and untreated (control) soils is assumed to be derived from residual NCPR.

Recovery of P (or Ca) from the NCPR was calculated as the difference between extractable P or Ca from NCPR-treated and untreated soils expressed as a percentage of the amount of P (or Ca) added using the following equation:

$$\text{NCPR-P or NCPR-Ca recovery}(\%) = \frac{\Delta\text{NCPR-P (or Ca)}}{\text{added NCPR-P (or Ca)}} \times 100 \qquad (3.1)$$

3.3.2 Experiment 2. Measurement of the extent of phosphate rock dissolution in soil

3.3.2.1 Soils

Tokomaru silt loam, Dannevirke silt loam and Tihoi sand with different P retention capacities were used in this study (Table 3.3). All three soils were sampled from sheep farms to a depth of 75 mm, air dried, and passed through a 2 mm sieve. The pH of the soils was adjusted by incubating the air-dried soils at 80% of their respective "field moisture capacities" with different amounts of analytical grade $CaCO_3$. In the case of Dannevirke soil a second pH adjustment was made separately by incubating the soil with a dilute $NaHCO_3$ solution for two weeks. These pH adjustments produced soils with different exchangeable Ca and Na levels. Four soil samples with different pH levels were selected from the pH amended range of each soil (Table 3.4) for subsequent incubation with NCPR and monocalcium phosphate (MCP). Dannevirke soils amended with $CaCO_3$ and $NaHCO_3$ were subsequently denoted as Dannevirke 1 and Dannevirke 2, respectively.

3.3.2.2 Phosphorus sources

The P sources used were "as received" NCPR (13% P) and analytical grade monocalcium phosphate (24.6% P). The particle size distribution, solubility in 2% citric acid and total P content of the NCPR are presented in Table 3.2.

3.3.2.3 Incubation study

Soil samples (100-200 g) were mixed with either NCPR or MCP at the rate of 400 mg P kg^{-1} (soil oven-dry basis) in 500 ml polythene plastic bags. Deionized water was added to bring the soils to 80% "field moisture capacity", which had previously been determined for each soil using a Haynes apparatus. The soil/fertilizer mixtures were

Table 3.3 Some original chemical properties of the soils used in Experiment 2.

Soil	pH_{1120}	Org.C (%)	CEC (cmol (+) kg^{-1})	P retention (%)
Tokomaru silt loam/ Typic Fragiaqualf	5.5	1.9	11.1	18
Dannevirke silt loam/ Typic Euthrochrept	5.6	8.9	32.3	84
Tihoi sand/ Typic Udivitrand	5.2	8.4	33.4	60

Table 3.4 The range of adjusted pH values and exchangeable Ca contents.

Soil	Amendments	pH	Exchangeable Ca (cmol (+) kg^{-1})
Tokomaru	$CaCO_3$	5.2-6.8	4.6-9.4
Dannevirke 1	$CaCO_3$	5.2-6.8	5.5-21.9
Dannevirke 2	$NaHCO_3$	5.7-6.4	4.5-4.8
Tihoi	$CaCO_3$	4.5-6.4	4.3-19.5

then stored in a dark room at 16±2°C. Control soils were prepared as above but without addition of phosphate. At weekly intervals the soils were mixed and water was added as required. After 30 days incubation subsamples were taken for chemical analyses and a pot experiment (Chapter 6). The incubation of the remaining soils continued for another 50 days. All subsamples withdrawn were immediately oven-dried at 40°C for 16 h in preparation for chemical analyses or for the pot experiment.

3.3.3 Soil analysis

3.3.3.1 General soil chemical analysis

The following chemical properties of the soil were measured:

a. *Soil pH*

Soil pH was measured in distilled water at a soil-solution ratio of 1:2.5 after a 16 h equilibrium period.

b. *P retention capacity*

P retention capacity was determined by the method of Saunders (1965) after shaking 5 g of soil for 16 h in a 25 ml of 0.2 M sodium acetate solution containing 1000 mg P l^{-1} as KH_2PO_4 and adjusted to pH 4.65 with glacial acetic acid. The P retention capacity was calculated from the amount of P removed from the soil solution by the soil, expressed as a percentage of the amount added.

c. *Organic C content*

Organic C was measured using the wet oxidation and titration procedure of Bremner and Jenkinson (1960).

d. *$NaHCO_3$-extractable P*

Plant-available P in soil was determined using Olsen method (Olsen *et al.*, 1954) in which soil was shaken for 30 minutes with 0.5 M $NaHCO_3$ (pH 8.5) at a solution:soil ratio of 20:1 on an end-over-end shaker. The suspension was then centrifuged at 5000 rpm before filtering. Inorganic P in the extract was determined colorimetrically at 712

nm using the method of Murphy and Riley (1962) on a Pye Unicam SP 1800 B spectrophotometer.

e. *Cation exchange capacity (CEC) and exchangeable Ca*

The CEC and exchangeable Ca were measured after leaching the soil with neutral 1 M ammonium acetate (Blakemore *et al.*, 1987). After washing with ethanol, soil was leached with 100 ml of 1 M NaCl. Concentration of Ca in the ammonium acetate extract was measured using a standard AAS procedure in the presence of 2000 mg $Sr(NO_3)_2$ l^{-1}, as an ionisation suppressant. The CEC of the soil was determined as the amount of NH_4-N in the NaCl extract using an autoanalyzer (Technicon, 1976).

3.3.3.2 Sequential extraction of soil/P fertilizer mixtures

Various methods of sequential extraction were used in Experiment 1 (Section 3.3.1.4). In Experiment 2, the soil/PR mixtures were sequentially extracted with 0.5 M NaCl/TEA, 1 M NaOH and 1 M HCl (Section 3.3.1.4). Concentrations of Pi in the extracts were measured as described previously (Section 3.3.1.4). The extent of dissolution was calculated using Equation 3.1.

3.3.4 Fertilizer analysis

Physical and chemical characteristics of fertilizer was carried using the following procedures:

3.3.4.1 Particle size

Subsamples of dry NCPR (20 g) were placed on a sieve stack. The stack which consisted of a set of sieves of different sizes was shaken for approximately 15 minutes. Any oversized material remaining on each sieve was gently brushed until the weight changed by <1% after which material remaining on each sieved was weighed.

3.3.4.2 Total P content

Total P content was determined using a tri-acid [concentrated HNO_3, HCl and $HClO_4$ (5:5:7)] digestion method (Johnson and Ulrich, 1959). A known weight (1 g) of fertilizer was digested with 25 ml of acid mixture in a 250 ml Erlenmeyer flask at 260°C until white fumes appeared. The digest was then filtered (Whatman No. 41 filter paper) and made up to 100 ml with deionized water. After dilution, P concentration was measured using the vanadomolybdate method (AOAC, 1975).

3.3.4.3 Solubility

Solubility of the NCPR was assessed using the 2% (w/w) citric acid (Fertilizer Regulations, 1969) method which is usually regarded as the standard measure of "reactivity" of PR materials, at least in New Zealand.

A sample of fertilizer (0.4 g) was extracted with 40 ml of 2% citric acid for 30 min then centrifuged at 8000 rpm for 10 min and filtered (Whatman's No. 41 filter paper). Solution P was determined using the metavanadate method (AOAC, 1975).

3.4 RESULTS AND DISCUSSION

3.4.1 Experiment 1. Development of a sequential extraction method for measuring residual phosphate rock in soil

3.4.1.1 Recovery of NCPR-P and NCPR-Ca in different extractants

The concentrations of Pi extracted from Dannevirke soil and the recoveries of added NCPR-P by different extractants with and without NaCl or NaCl-TEA pre-extraction are presented in Table 3.5. Percentage recovery of NCPR-P in NaOH and HCl extracts ranged from 0 to 21% and 84 to 101%, respectively. Very small amounts of Pi were recovered by NaCl and NaCl/TEA extracts. Virtually all (96 to 105%) the NCPR-P

Table 3.5 PR-P recovered from soil by sequential extraction with and without pre-extraction following an immediate addition of 400 mg P kg^{-1} soil of NCPR.

Soil pH	Method	Pre-extraction	Extract sequence	Extractable P (mg kg^{-1})*		PR-P recove: (%)
				Soil	Soil+PR	
5.4	1	NaCl	NaCl	0.6a	1.3a	0.4
			NaOH	1098.5a	1180.6b	20.5
			HCl	328.8a	666.0b	84.3
			Total	1431.9	1847.9	105.1
	2	NaCl/TEA	NaCl/TEA	1.8a	1.5a	0.0
			NaOH	1116.9a	1130.8a	3.5
			HCl	377.4a	758.2b	95.2
			Total	1496.1	1890.3	98.7
	3	None	NaOH	1063.4a	1063.4a	0.0
			HCl	356.3a	740.8b	96.1
			Total	1419.7	1804.3	96.1
6.7	1	NaCl	NaCl	0.6a	0.8a	0.0
			NaOH	1056.8a	1074.0b	4.4
			HCl	387.0a	776.5b	97.4
			Total	1444.4	1851.3	101.9
	2	NaCl/TEA	NaCl/TEA	1.7a	2.2a	0.0
			NaOH	1092.1a	1091.6a	0.0
			HCl	374.3a	769.9b	98.9
			Total	1468.1	1861.5	98.9
	3	None	NaOH	974.6a	975.8a	0.2
			HCl	479.8a	882.0a	100.6
			Total	1454.4	1857.8	100.8

*Mean treatments followed by the same letter in a row are not significantly different at $P<0.05$.

added was recovered by sequential extraction. Apart from the low recovery of Ca when NaCl pre-extraction was used on soil with pH 5.4, recoveries of NCPR-Ca were similar (Table 3.6) to those of NCPR-P.

Pre-extraction with NaCl, particularly at low pH resulted in an increase in P recovery in NaOH, and a decrease in HCl, extracts. Recoveries of P in NaOH and HCl extracts from soil with pH 5.4 were 21% and 84%, respectively, indicating a relatively high NCPR dissolution induced by NaCl pre-extraction. The corresponding values for soil with pH 6.7 were 4 and 97%, respectively. Compared to NaCl (method 1), pre-extraction with NaCl/TEA (method 2) caused only relatively small amounts of NCPR-P and NCPR-Ca to dissolve. At both soil pHs, P recovery in NaOH and HCl extracts ranged from 0 to 4% and 95 to 99%, respectively.

The omission either a NaCl or NaCl/TEA pre-extraction (method 3) in the sequential extraction procedure had no effect on Pi (Table 3.5) or Ca (Table 3.6) recovery in HCl. Following NaOH extraction only, almost total (96 to 101% for P and 108% for Ca) recovery of added NCPR-P and NCPR-Ca was recovered in HCl extracts regardless of soil pH. In the case of soil with pH 6.7, the concentration of P in the NaOH extract was less without pre-extraction with either NaCl or NaCl/TEA, than was the case with pre-extraction. The most likely cause of this difference recovery is due to adsorption by, or co-precipitation of P with $Ca(OH)_2$ or $CaCO_3$ formed during NaOH extraction (Mackay *et al.*, 1986). Although most of the added Pi was recovered by HCl extraction, the apparent redistribution of soil P during NaOH extraction at high soil pH indicates the importance of a pre-extraction when the extent of NCPR dissolution is measured in soil with a significant exchangeable Ca content.

Any increase in NCPR dissolution during NaCl pre-extraction (referred to as ΔHCl-P (16%, Table 3.5) and ΔHCl-Ca (35%, Table 3.6)) may be due to the weakly buffered nature of the NaCl extractant as measured by the measured depression of pH during NaCl extraction (Table 3.7). This comes about in strongly acidic soils by exchange of soil H^+ with Na^+ from NaCl resulting in increased H^+ concentration in the solution thereby decreases solution pH. In the acid soil (pH_{H2O} = 5.4), the pH of NaCl extracts ranged from 4.6 to 4.7 which were 1.8 to 1.9 units lower than that of the 1 M NaCl

Table 3.6 PR-Ca recovered from soil by sequential extraction with and without pre-extraction following an immediate addition of 1068 mg Ca kg^{-1} soil of NCPR.

Soil pH	Method	Pre-extraction	Extract sequence	Ca (mg kg^{-1})*		PR-Ca recovery (%))
				Soil	Soil+PR	
5.4	1	NaCl	NaCl	2455.0a	2611.7b	14.7
			NaOH	-	-	-
			HCl	1716.6a	2413.3b	65.2
	2	NaCl/TEA	NaCl/TEA	2006.7a	1983.3a	0.0
			NaOH	-	-	-
			HCl	2147.8a	3204.7b	99.5
	3	None	NaOH	-	-	-
			HCl	3775.0a	4933.4b	108.5
6.7	1	NaCl	NaCl	4150.0a	4315.3b	15.4
			NaOH	-	-	-
			HCl	2718.6a	3616.9b	85.0
	2	NaCl/TEA	NaCl/TEA	3383.3a	3364.7a	0.0
			NaOH	-	-	-
			HCl	3190.5a	4281.7b	102.2
	3	None	NaOH	-	-	-
			HCl	6566.8a	7729.4b	108.9

* Mean treatments followed by the same letter in a row are not significantly different at $P<0.05$. (-): not determined

extractant (i.e. 6.5). Any increase in H^+ concentration would lead to an increased rate of PR dissolution (Bolan and Hedley, 1990; Hughes and Gilkes, 1984; Robinson and Syers, 1990). On the other hand, NaCl/TEA extractant is slightly buffered against pH change even when the soil has a high titratable acidity. As shown in Table 3.7, the pH of the NaCl/TEA extracts decreased by 0.1 unit from that of the original solution. The amount of NCPR-P dissolved, as indicated by percent recovery in the NaOH plus NaCl/TEA extracts (Table 3.5), was only 4% in the acidic soil, and negligible in the less acidic soil (ΔCa results in Table 3.6 showed negligible dissolution). For these reasons, use of 0.5 M NaCl/TEA pre-extraction is preferred for both acidic and alkaline soils.

Table 3.7 Values of pH of the NaCl and NaCl/TEA extracts* of soil and soil+PR mixture.

Soil pH (H_2O)	NaCl extract		NaCl/TEA extract	
	Soil	Soil+PR	Soil	Soil+PR
5.4	4.6	4.7	6.9	6.9
6.7	6.0	6.0	6.9	6.9

*pH of the 1 M NaCl and 0.5 M NaCl/TEA extractants were 6.5 and 7.0, respectively.

In acidic soils containing low amounts of exchangeable Ca, pre-extraction with NaCl or NaCl/TEA may not necessary when NCPR dissolution is measured using sequential NaOH and HCl extraction. But in soils with higher amounts of exchangeable Ca, pre-extraction is required to overcome problems associated with $Ca(OH)_2$ precipitation during NaOH extraction.

Use of a ΔHCl-P method for measuring PR dissolution has several advantages over a ΔNaOH-P method. Firstly, in the presence of plants ΔHCl-P method seems to give a more accurate estimate of PR dissolution than the NaOH method because it measures undissolved PR. As suggested by Bolan and Hedley (1989), the ΔNaOH method tends to underestimate actual PR dissolution unless the amounts of Pi, either taken up by plants or immobilized in soil organic matter from the dissolved PR, are taken into account. Secondly, in soils with large amounts of native NaOH extractable P, as occurs in soil with high organic matter or allophane content, the ΔNaOH-P method may not be sensitive enough to detect a relatively small increase in the NaOH-extractable P due to

PR dissolution. In such soils organically bound-P or aluminium bound-P are hydrolysed during NaOH extraction resulting in relatively high background concentrations of P in the extracts. In contrast, use of ΔHCl-P method would overcome the difficulties encountered in the ΔNaOH-P method and would be suitable for use in all soils, except calcareous ones with high levels of Ca bound-P. However, in calcareous soils, reactive phosphate rock (RPR) use is unlikely to be an issue.

3.4.1.2 Comparison of ΔHCl-P vs. ΔHCl-Ca methods

The ability of ΔHCl-Pi (Table 3.5) and the ΔHCl-Ca (Table 3.6) methods to measure amounts of residual NCPR in soil of pH 5.4 and 6.7 was compared. Comparable recoveries of residual NCPR-P and NCPR-Ca were found only when the soils were sequentially extracted in the presence of NaCl/TEA. When soils were pre-extracted with NaCl prior to NaOH extraction, ΔHCl-Ca method tended to overestimate PR dissolution in soils at both pHs. On the other hand, in the absence of any pre-extraction ΔHCl-Ca method appeared to underestimate NCPR dissolution in limed soils. In soils containing high levels of background Ca, the estimates of NCPR dissolution using the ΔHCl-Ca are less reliable than the HCl-P. For example, ΔHCl-Ca needs to be 178 ug g^{-1} before a significant ($P<0.05$) amount of residual NCPR-Ca can be detected in soil of pH 6.7 soil using method 1 (Table 3.6). This would require an approximately additional of 503 kg NCPR ha^{-1} (100 mm soil depth at a bulk density of 1000 kg m^{-3}). The ΔHCl-P method, however, could detect residual NCPR at 28 kg NCPR ha^{-1} (equivalent to approximately 14% of normal RPR annual application rates to New Zealand pasture soils (Bolan *et al.*, 1990)).

In summary, the results show that for estimating residual PR in soils of differing pH and Ca contents, pre-extraction with 0.5 M NaCl/TEA prior to sequential 1 M NaOH and 1 M HCl extraction is advisable. This method has advantages over the 1 M NaCl pre-extraction, suggested by MacKay *et al.* (1986) by minimising PR dissolution during extraction of PR from acid soils and by preventing Pi resorption or precipitation (Syers *et al.*, 1972) in soils with high Ca saturation. One of the benefit of the NaCl/TEA-ΔHCl-P method is the greater sensitivity compared with either the ΔNaOH-Pi or NaCl/TEA-ΔHCl-Ca methods.

3.4.2 Experiment 2. Measurement of the extent of phosphate rock dissolution in soil

3.4.2.1 Amounts of residual NCPR and extent of NCPR dissolution

Amounts of P in residual (undissolved) NCPR as measured by the ΔHCl-P method at 30 and 80 days of incubation in soils are presented in Figure 3.1. Amounts of residual MCP were very small (<8 mg ΔHCl-P kg^{-1}) compared to those of NCPR and therefore are not presented. Amounts of residual NCPR generally decreased with time. After 80 days, amounts of residual NCPR decreased as soil pH decreased indicating an increase in extent of NCPR dissolution.

The percentage dissolution of NCPR and MCP at 30 and 80 days calculated using Equation (3.1) are presented in Figure 3.2. As expected, MCP dissolved very rapidly regardless of soil pH. After 30 days almost all (93-99%) of the P added as MCP had dissolved. In contrast, only small amounts of NCPR had dissolved (9-21%) depending on soil type and pH. The extent of dissolution of NCPR increased in all soils as soil pH decreased although the trend was more apparent after 80 days of incubation. The extent of NCPR dissolution after 30 days incubation for pH range 5.2-6.8 (Tokomaru), 5.2-6.3 (Dannevirke 1), 5.7-6.4 (Dannevirke 2) and 4.6-6.5 (Tihoi) were 8 to 9%, 13 to 22%, 11 to 14% and 11 to 18 %, respectively. At 80 days the corresponding ranges were 0 to 23%, 15 to 34%, 19 to 32% and 11 to 30%, respectively.

Greatest NCPR dissolution at 30 and 80 days appeared to occur at the two lowest pH levels and was higher in soil with greater P retention capacity (Dannevirke and Tihoi). As the contact period increased to 80 days, dissolution substantially increased, particularly at the lowest pH level, amounting to an increased NCPR dissolution of 13, 12, 18 and 12% for Tokomaru, Dannevirke 1, Dannevirke 2 and Tihoi soil, respectively for the intervening 50 day period. At the highest pH levels (6.4-6.7) prolonged contact period after 30 days did not increase the dissolution considerably. It is likely that at this stage there was insufficient H^+ in the soil solution or CEC sites to dissolve the residual apatite. Alternatively, the sinks for Ca dissolved from NCPR became limited and hence restricted further NCPR dissolution.

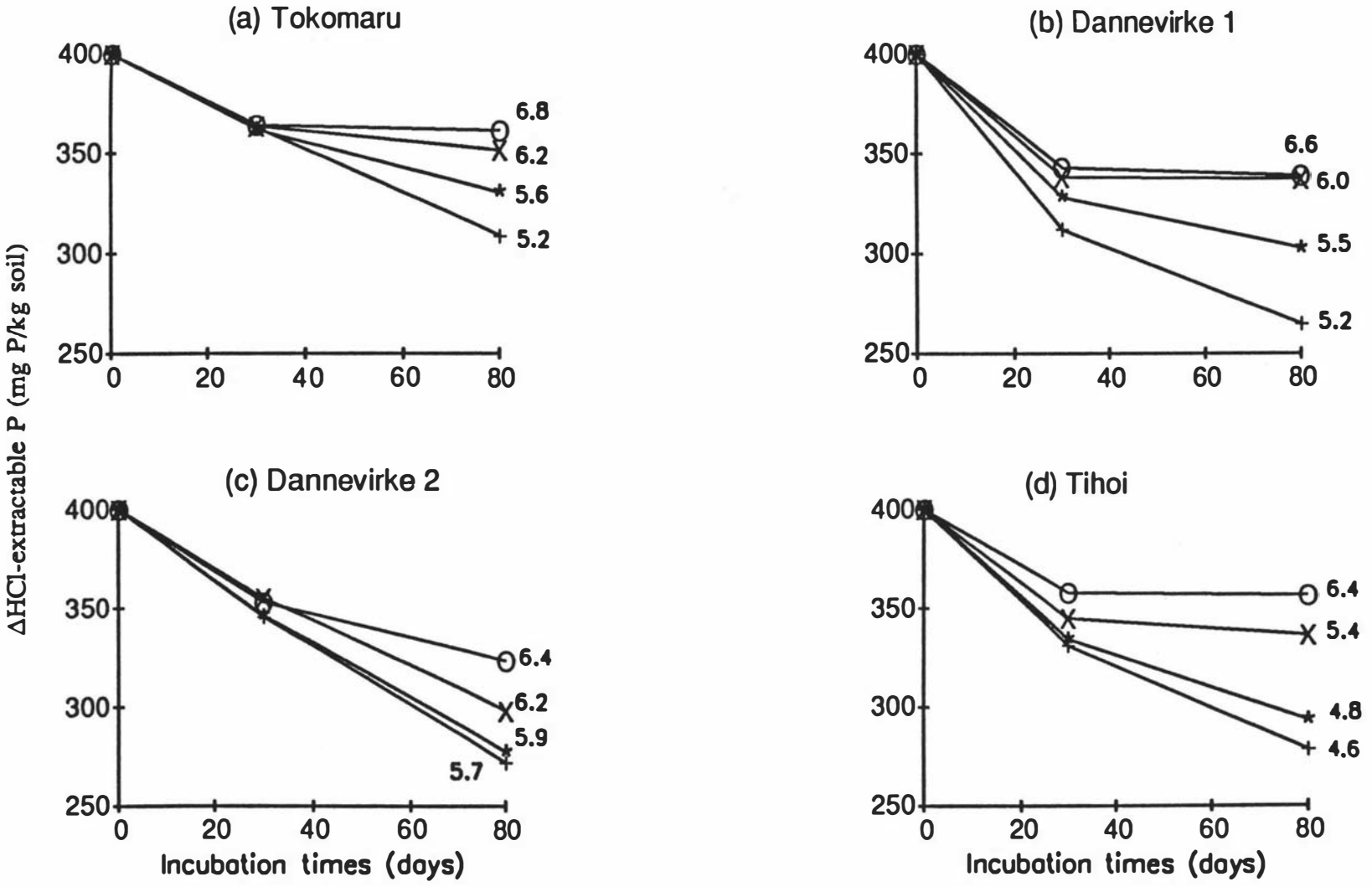

Figure 3.1 Effect of pH and incubation time on amounts of ΔHCl-extractable P in soils fertilized with NCPR.

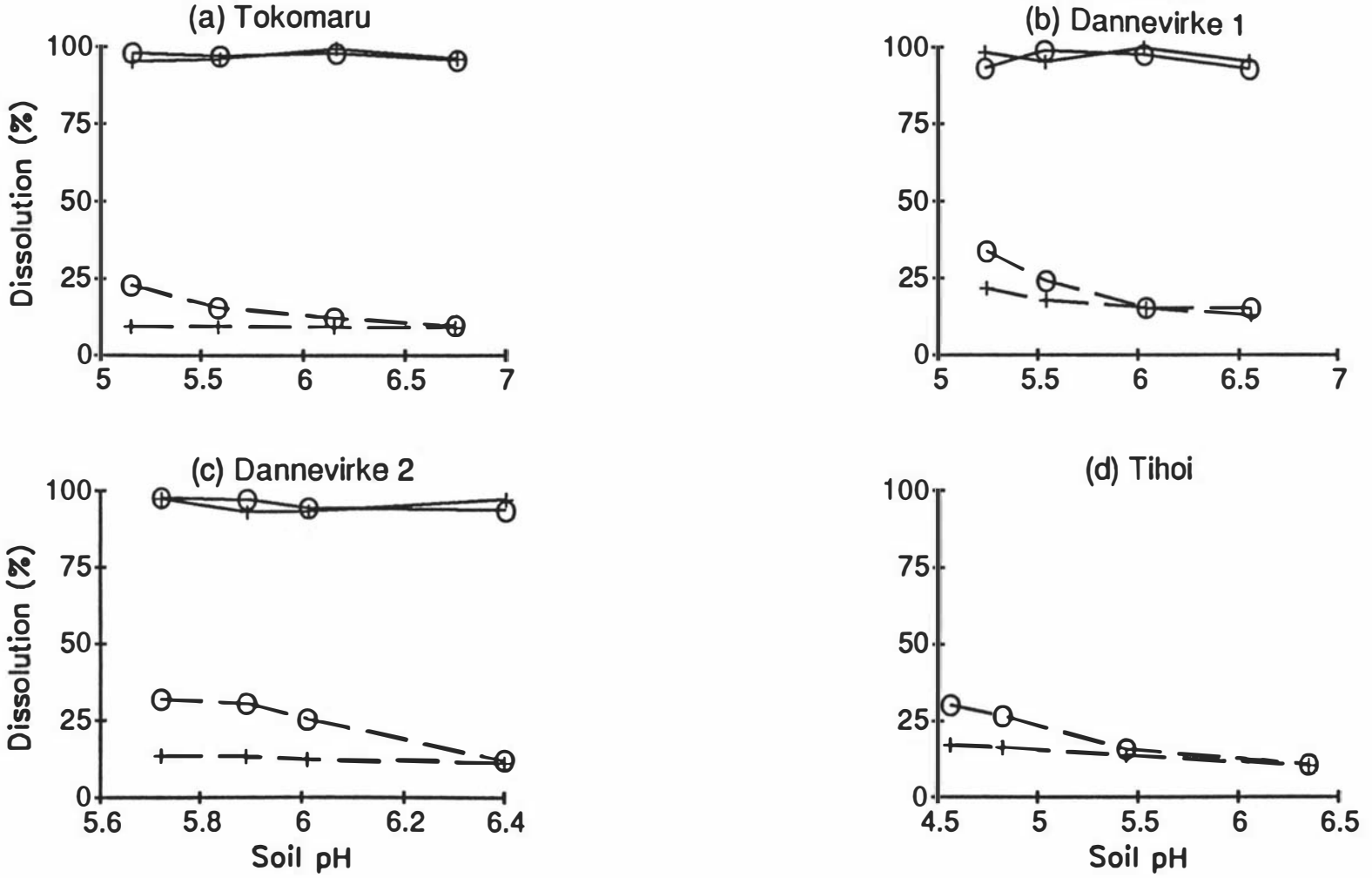

Figure 3.2 Effect of pH on the extent of MCP (–) and NCPR (--) dissolution in 30 (o) and 80 (+) day-incubated soils.

3.4.2.2 Relationships between soil pH and NCPR dissolution

It was not possible to use analysis of variance techniques to assess the effect of pH on the rate and extent of NCPR dissolution across all soil types from the data presented in Figure 3.2. This is because the pH values between soils were not closely grouped. However, because same amount of PR was added to soil and PR dissolution followed similar trends (Mackay *et al.*, 1986; Kanabo and Gilkes, 1987a), regression analysis was used to examine the effect of pH on dissolution. The curvilinear relationship between pH and extent dissolution was described using the following equation (Kanabo and Gilkes, 1987a):

$$\log(\%\text{dissolution}) = a - b(\text{pH}) \qquad (3.2)$$

The regression equations describing the dissolution of NCPR in each soil pH set for the 30 and 80 days period of contact are presented in Table 3.8.

The fitted linear regressions for the 80 day data describe NCPR dissolution well for each soil type, but the lower R^2 values for the regression equations across all soils indicate that soil characteristics other than pH also influencing dissolution and thereby contributing to variation in the data.

Results of a t-test between slopes in the regression equations describing the dissolution of NCPR for the 80 day-incubated soils showed non-significant differences indicating that the rate of decrease in NCPR dissolution due to an incremental increase in soil pH was the same for all soils. This suggests that the magnitude of NCPR dissolution in the soils at a selected pH increased with increasing values of the intercept in the linear regression equations. From these regression equations it can be predicted that the extent of NCPR dissolution in the soils at a selected pH value would be in the order of Dannevirke 2>Dannevirke 1>Tihoi>Tokomaru.

In general, the relationship between soil pH and extent of PR dissolution will be determined by the concentrations of Ca^{2+}, $H_2PO_4^-$ and H^- in soil solution at the surface of the dissolving NCPR particle. For maximally substituted carbonate apatite, such relationships can be described by the following equation (Kirk and Nye, 1986):

Table 3.8 Regression equations describing the effect of soil pH on dissolution of NCPR in 30 and 80 day-incubated soils.

Soil	Incubation time (days)	Regression equation	R^2
Tokomaru	30	Log(%diss)=1.071-0.020pH	0.63
	80	Log(%diss)=2.496-0.227pH	0.94
Dannevirke 1	30	Log(%diss)=2.190-0.165pH	0.96
	80	Log(%diss)=2.884-0.267pH	0.80
Dannevirke 2	30	Log(%diss)=1.670-0.093pH	0.89
	80	Log(%diss)=3.451-0.338pH	0.91
Tihoi	30	Log(%diss)=1.792-0.118pH	0.88
	80	Log(%diss)=2.646-0.257pH	0.96
All soils	30	Log(%diss)=1.668-0.099pH	0.22
	80	Log(%diss)=2.497-0.210pH	0.48

Values of R^2 greater than 0.76 and 0.23 are significant at $P<0.05$ for each soil type and across all soils, respectively.

$$8.7pCa+4.5pH_2PO_4-12pH=-18.96 \quad (3.3)$$

where pCa, pH_2PO_4 and pH are the negative logarithms of the activities of the respective ions. With respect to changes in solution pH, this equation clearly shows that any increase in solution pH at a constant activity of Ca would decrease the activity of H_2PO_4 ions in soil solution and decrease the extent of PR dissolution. On the other hand, a decrease in soil solution pH would increase the extent of PR dissolution.

With respect to soil pH, the important effect of liming on PR dissolution can be attributed to the neutralization of soil proton. In consequence, PR dissolution also decreases due to decreases in supply proton. The decreased amount of proton in soil solution also decreases the acidity diffusion coefficient (Ameloko and Nye, 1991) and the concentration gradient controlling the basic ions (Kirk and Nye, 1986c). As a result, PR dissolution decreases.

Effects of changes in exchangeable Ca

In soils amended with $CaCO_3$, the increase in soil pH is always accompanied by an increase in exchangeable Ca levels (Table 3.4). Strong correlations (r=0.93-0.99) between soil pH and exchangeable Ca were therefore found in Tokomaru, Dannevirke 1 and Tihoi soils. In Dannevirke 2 soil, which was amended with $NaHCO_3$, the correlation between soil pH and exchangeable Ca was poor (r=0.57).

Concentrations of Ca in soil solution would be expected to increase with increased exchangeable Ca. In a closed system where there is no removal of Ca, an increase in Ca concentration in soil solution caused by an external addition of Ca would decrease the concentration gradient of Ca away from the PR particle. As a result, the diffusion of dissolved Ca from the PR is affected (Kirk and Nye, 1986c). Equation (3.3) shows that an increase in the activity of Ca in soil solution at the surface of a dissolving PR at a constant soil solution pH would decrease the activity of H_2PO_4 ions and a lesser amount P would be dissolved from the PR.

Additions of $CaCO_3$ to variable charge soils may also increase soil CEC. However, because most of the exchange sites created are occupied by the added Ca (Hanafi *et al.*,

1992b), the sink for Ca becomes more limiting. Continuous release of Ca to soil solution from PR may exceed the solubility product of PR and thereby inhibiting PR dissolution (Wilson and Ellis, 1984; Robinson and Syers, 1990).

Effects of changes in P sorption

In addition to soil acidity factor, some of the variation in extent of NCPR dissolution between soils has been shown to be due to differences in their P retention capacities of each soil (Table 3.3). Similar finding has been reported by Smyth and Sanchez (1982), Kanabo and Gilkes (1987b; 1978c) and Bolan and Hedley (1990). Phosphate adsorption isotherms (Figure 3.3) show that the four soils used in these study have different P adsorption characteristics. It is clear Tokomaru soil adsorbs less phosphate the other three soils. The P adsorption characteristics of the soils studied is in the general order of Dannevirke 2$\geq$ Dannevirke 1> Tihoi> Tokomaru.

Data presented in Figure 3.3 show that, in each soil, changes in soil pH did not significantly effect the P adsorption characteristic of each soil. Small increases in P sorption with decreases in soil pH were observed on Tihoi and Tokomaru soils; but in the case of Dannevirke soils there was no effect. This may suggest that the variation in the extent of NCPR dissolution in each soil due to changes in soil pH can not be attributed to changes in the P adsorption.

The results reported here differ from the findings of Bolan and Hedley (1990) who worked with another variably charged soil (Patua silt loam). They reported a significant increase in P adsorption with decreasing soil pH and this had a significant enhancing effect on PR dissolution and availability of dissolved P. It is not clear why soil pH had a negligible effect on P adsorption by the Dannevirke soils which also produce pH dependent charge. However, it should be pointed out that Bolan and Hedley (1990) adjusted the soil pH by adding either dilute acid or alkaline solutions, and the P adsorption isotherms on these amended soils were constructed using varying amounts of P added as KH_2PO_4 in 0.1 M NaCl matrix. In the present study, soil pH adjustment was achieved by adding either $CaCO_3$ or $NaHCO_3$, and the matrix for constructing the P adsorption isotherm was 0.001 M $CaCl_2$ containing varying amounts of P added as

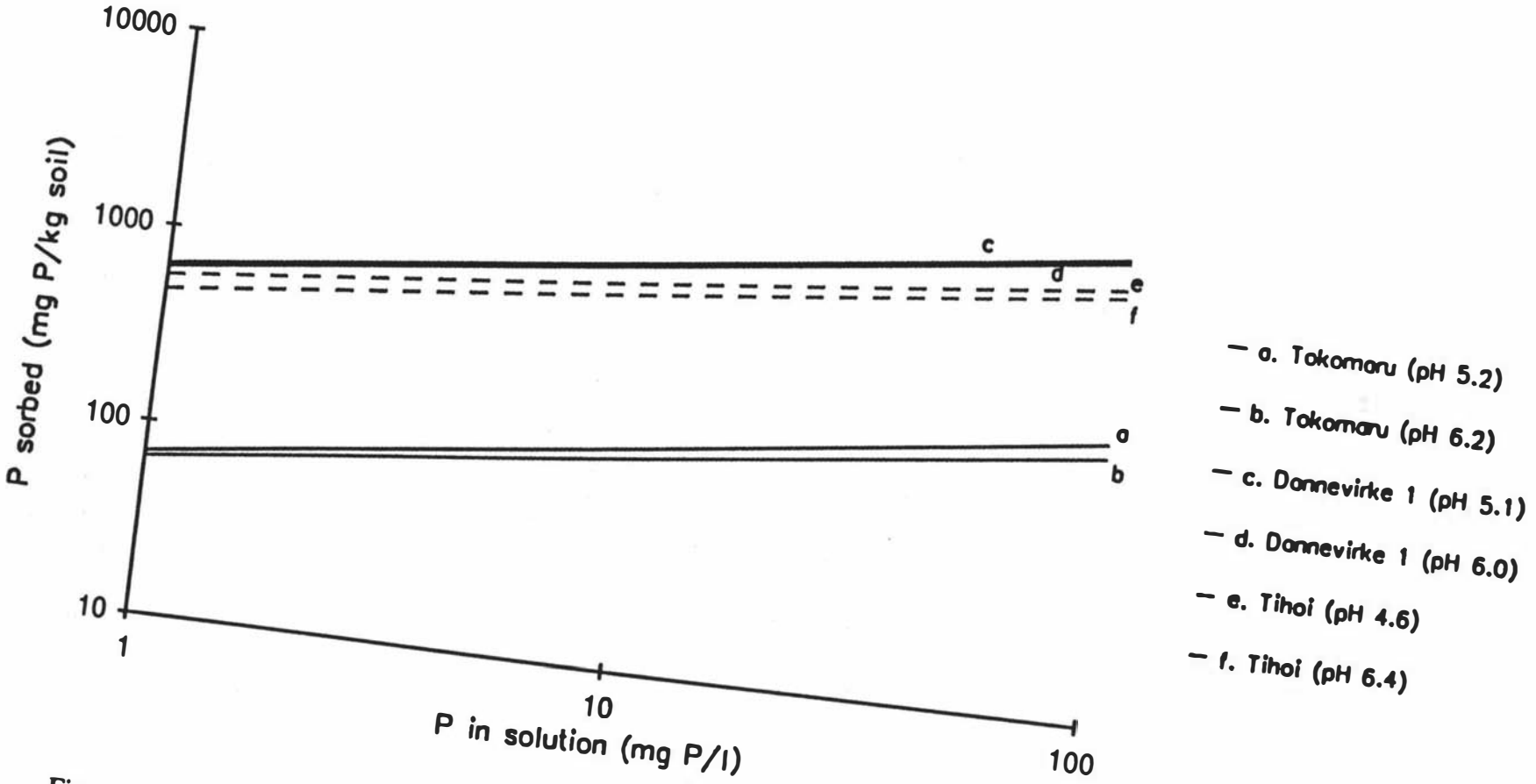

Figure 3.3 Phosphate adsorption isotherms of selected soils amended to two different pH values.

CaH_2PO_4. The use of relatively high Ca concentrations in the Ca-system for constructing the P adsorption isotherm in the present study may have increased the positive charge at the surface due to specific sorption of Ca by hydrous metal oxides (Kinniburgh *et al.*, 1975). This increase in positive charges would be expected to increase the P sorbed by the soil thereby masking the expected effect of pH on P adsorption. Overall, this may partly explain the small decreases in P adsorption noted when soil pH was increased.

3.5 CONCLUSIONS

A method of measuring residual PR in soils using a modified sequential extraction procedure is proposed in which amounts of residual PR is estimated from the difference in the amount of P extracted by 1 M HCl from PR-treated and untreated soils following pre-extraction with 0.5 M NaCl/TEA (pH 7.0) and 1 M NaOH. In soils varying in pH and exchangeable Ca levels, pre-extraction with 0.5 M NaCl/TEA improved the accuracy of the residual PR measurements.

Although the method for measuring amounts of residual PR in New Zealand soils can be used in various experimental situations including laboratory, glasshouse and field conditions (provided the PR remains in the sampling zone), further evaluation may still be needed before it is used for measuring amounts of residual PR in highly weathered tropical soils. These soils are normally very acidic and contain very low amounts of exchangeable Ca. An evaluation of the method in Indonesian soils is presented in Chapter 4.

Measurement of NCPR dissolution in a range of New Zealand soils showed that the extent of NCPR dissolution decreased with increasing soil pH. In soils amended with $CaCO_3$ the decrease was related to an increase in exchangeable Ca level and decrease in soil proton due to the neutralization of soil H^+. The former decreases the concentration gradient of Ca in soil solution by increasing Ca concentrations in soil solution. In soils amended with $NaHCO_3$, the decrease in the extent of NCPR dissolution was mainly due to a decrease in proton supply.

Across all soils, differences in the extent of NCPR dissolution across can be partly attributed to differences in the P adsorption characteristics. Since the soil P adsorption was less affected by changes in soil pH, the finding of a decrease in NCPR dissolution in the soils with increasing soil pH can not be attributed to the changes in P adsorption characteristics.

CHAPTER 4
A COMPARATIVE EVALUATION OF METHODS FOR MEASURING RESIDUAL PHOSPHATE ROCK IN A RANGE OF NEW ZEALAND AND INDONESIAN SOILS

4.1 INTRODUCTION

A sequential extraction method (ΔHCl-P method) for measuring residual (undissolved) phosphate rock (PR) in a range of New Zealand soils has been proposed (Chapter 3). This method involves the sequential extraction of the soil with 0.5 M NaCl/TEA, 1 M NaOH and 1 M HCl. The amount of residual PR as measured by the difference in the HCl-extractable P between PR-fertilized and unfertilized soils has been used to estimate the extent of PR dissolution in New Zealand soils of varying pH and exchangeable Ca contents (Chapter 3).

Although the ΔHCl-P method has been found to be useful for estimating residual PR in New Zealand soils, this method has not been proven for use in highly weathered tropical soils, such as those found in Indonesia. Many highly weathered tropical soils are very acidic and contain very low amounts of solid and solution phase P and Ca. The clay fraction of such soils is usually dominated by 1:1 layer silicates (kaolinite and/or halloysite) and hydrous oxides of iron, aluminum and silicon (Uehara, 1978). Some of these components may affect the recovery of P by the proposed method.

4.2 OBJECTIVE

The objective of this study was to evaluate the ΔHCl-P method for measuring amounts of residual (undissolved) PR in a range of acid soils from New Zealand and Indonesia. Although the method being evaluated was previously tested using a range of New Zealand soils only (Chapter 3), in this chapter its use is extended to cover the extent of PR dissolution in Indonesian soils both under laboratory and field conditions.

4.3 MATERIALS AND METHODS

4.3.1 Soils

Six surface (0-75 mm) soils, three from New Zealand and three from Indonesia were used in this study. The New Zealand soils were taken from sheep farms, whereas the Indonesian soils were taken from areas growing trees for rubber production. Some relevant properties of the soil used are given in Table 4.1. Prior to use, all samples had been air-dried and sieved to pass a 2 mm sieve.

4.3.2 Phosphate fertilizer characteristics

The main P fertilizer source used in this study was North Carolina phosphate rock (NCPR). The particle size distribution, total P content and P solubility in 2% citric acid of ground and unground NCPR are presented in Table 3.2 (Chapter 3). Monocalcium phosphate (MCP, analytical grade) was used as a contrasting water-soluble P source in some experiments. The NCPR was characterised by the procedure described in Section 3.3.4.

4.3.3 Recovery of NCPR-P from soil

Different particle size ranges of NCPR were used in this study. However, unless otherwise stated, the size range used was 150-250 m. NCPR, equivalent to a rate of 500 mg P kg^{-1} soil, was mixed thoroughly with 20 g of each air-dry soil.

4.3.4 Soil analysis

4.3.4.1 General soil analysis

The soils were analysed for pH, organic C, Olsen P, CEC, exchangeable Ca and P retention capacity as described in Section 3.3.3 (Chapter 3).

Titratable acidity was determined after shaking 5 g soil with 50 ml 0.5 M $BaCl_2$/TEA

Table 4.1 Selected properties of the soils used in the study.

Soil	pH (H_2O)	Org.C (%)	Olsen-P (mg kg^{-1})	CEC (cmol (+) kg^{-1})	Ca[1] sat.(%)	TA[2] (me %)	P retention (%)
Dannevirke silt loam/ Typic Eutrochrept (NZ)	5.6	9.0	7.9	32.3	14.0	15.7	84
Tokomaru silt loam/ Typic Fragiaqualf (NZ)	5.5	2.2	14.5	11.1	43.2	49.0	18
Ramiha silt loam/ Typic Dystrochrept (NZ)	5.3	8.8	16.6	34.0	18.9	52.1	74
Sembawa clay loam/Typic Paleudult (Indonesia)	4.8	2.8	4.5	9.0	5.0	13.3	32
Prabumulih loamy sand/Typic Paleudult (Indonesia)	5.0	7.8	1.5	11.7	2.6	52.2	74
Lubuk Linggau clay loam/ Typic Tropudult (Indonesia)	5.4	6.4	6.7	9.8	6.1	32.6	48

[1] Ca sat. : Ca saturation
[2] TA : titratable acidity

(pH 8.2) for 16 h (Blakemore *et al.*, 1987). A known volume (25 ml) of the extract was then titrated against 0.1 M HCl using an automatic titrator to an end point at pH 4.7. Titrations on blanks ($BaCl_2$/TEA extractants) were also carried out in a similar manner. The amount of titratable soil acidity (cmol (+) kg^{-1}) was calculated as the difference between the amount of acid required to titrate the $BaCl_2$/TEA extracts of the blank and that of the soil sample.

4.3.4.2 Sequential extraction of soil/NCPR mixtures

The amounts of residual NCPR in Indonesian soils were initially determined using the method developed for New Zealand soils (Chapter 3). In subsequent experiments the method was modified by varying the concentrations of HCl, substituting H_2SO_4 for HCl or using a tri-acid mixture of concentrated HCl, HNO_3 and $HClO_4$ (5:5:7). Recoveries were checked using additions of MCP (12.5 mg P l^{-1} extractant) to assess the degree of secondary adsorption of Pi during extraction.

After each extraction step tubes were centrifuged (3000 rpm for 10 minutes) and then filtered (Whatman no 42) and weighed and the concentration of the inorganic P (Pi) in the extracts was measured. A correction was made to account for the contribution of P in the entrapped solution to the subsequent extract.

Because NCPR was blended with dry soils in this study, no dissolution would be expected between addition and the start of the sequential extraction procedure. Sequential extraction methods were judged suitable if they recorded nil dissolution during the extraction of dry blended soil/NCPR mixtures.

Recoveries of NCPR-P and MCP-P from soil in different extracts were calculated using Equation 3.1 (Chapter 3).

4.4 RESULTS

4.4.1 Recovery of NCPR-P from New Zealand and Indonesian soils by sequential extraction involving NaCl/TEA, NaOH and HCl

Recovery of added NCPR-P using the sequential extraction with NaCl/TEA, NaOH and HCl on acidic New Zealand soils (Table 4.2) shows that a small amount of NCPR-P was recovered in the NaCl/TEA plus NaOH extracts (range 1-4%), whereas almost total recovery was achieved in the HCl extract (99-108). This is similar to results for the Dannevirke (1) soil reported in Table 3.5 (Chapter 3). In Indonesian soils, however, although slightly higher recoveries of NCPR-P were obtained in the NaCl/TEA extracts (4.9%), subsequent recoveries in HCl extracts were incomplete (62-86%). Overall total recoveries in Indonesian soils ranged from 71 to 90%.

4.4.2 Recovery of NCPR-P from soil by sequential extraction including either 1 M HCl extraction or tri-acid digestion

Two sets of Indonesian soils (Sembawa and Prabumulih) (a set comprising the soil alone and their soil/NCPR mixtures) were resampled and sequentially extracted. After NaOH extraction each soil set was either extracted with 1 M HCl or digested in a tri-acid mixture. Again low NCPR-P recoveries were obtained using the ΔHCl method (Table 4.3). Only 63 and 86% of the added NCPR was recovered in the HCl extract of Sembawa and Prabumulih soils, respectively, with total recovery (ΔHCl-P + ΔNaOH-P) ranging from 69 to 90%. These results were consistent with those reported earlier (Table 4.2). In contrast to the recovery of NCPR-P in 1 M HCl extract, tri-acid digestion recovered 93 to 99% and total recoveries ranged from 99 to 105%.

4.4.3 Recovery of NCPR-P from soil by sequential extraction following immediate additions of NCPR varying in particle size

Recovery of NCPR-P after 1 M HCl extraction of Sembawa soil for different particle sizes of NCPR ranged from 43 to 75% (Table 4.4). Total P recovery ranged from 48 to 83%. The results (Table 4.4) showed that low recovery of NCPR-P was not confined

Table 4.2 Recovery of added NCPR-P (500 mg kg^{-1} soil) from soils following 0.5 M NaCl/TEA, 1 M NaOH and 1 M HCl extractions.

Extract sequence	Extractable P (mg P kg^{-1})		Recovery[1] (%)	Extract sequence	Extractable P (mg P kg^{-1})		Recovery[1] (%)
	Soil	Soil+PR			Soil	Soil+PR	
	New Zealand soils				Indonesian soils		
Tokomaru				**Sembawa**			
NaCl/TEA	1.2	2.5	0.3	NaCl/TEA	1.1	1.2	0.0
NaOH	193.3	214.7	4.2	NaOH	83.7	111.2	5.5
HCl	75.9	602.5	105.3	HCl	0.0	317.4	63.4
Total	270.4	819.7	109.8	Total	84.8	429.9	68.9
Dannevirke				**Prabumulih**			
NaCl/TEA	1.3	1.3	0.0	NaCl/TEA	1.2	1.2	0.0
NaOH	565.2	433.3	0.8	NaOH	92.1	110.3	3.6
HCl	74.4	544.3	107.5	HCl	0.0	430.5	86.1
Total	640.9	979.0	108.3	Total	93.3	540.8	89.5
Ramiha				**Lubuk Linggau**			
NaCl/TEA	1.2	1.4	0.0	NaCl/TEA	1.2	1.2	0.0
NaOH	428.1	433.1	1.0	NaOH	161.6	204.7	8.6
HCl	48.6	544.3	99.1	HCl	0.0	308.1	61.6
Total	477.9	979.0	100.2	Total	162.2	514.0	70.2

[1]Means of three replicates, SED<5%.

Table 4.3 Recovery of added NCPR-P (500 mg kg^{-1} soil) from Sembawa and Prabumulih soils by sequential extraction including either 1 M HCl extraction or tri-acid digestion.

Extract sequence	Extractable P (mg P kg^{-1})		Recovery (%)[1]	Extract sequence	Extractable P (mg P kg^{-1})		Recovery (%)[1]
	Soil	Soil+PR			Soil	Soil+PR	
				Sembawa			
NaCl/TEA	3.2	3.2	0.0	NaCl/TEA	3.2	3.2	0.0
NaOH	88.1	115.5	5.5	NaOH	88.1	120.3	6.4
HCl	0.0	317.2	63.4	Tri-acid	76.4	568.7	98.5
Total	91.3	435.9	68.9	Total	167.7	692.2	104.9
				Prabumulih			
NaCl/TEA	3.2	3.2	0.0	NaCl/TEA	3.2	3.2	0.0
NaOH	101.3	119.2	3.6	NaOH	91.0	120.5	5.9
HCl	0.0	430.9	86.1	Tri-acid	54.6	519.5	93.0
Total	104.5	553.3	89.7	Total	148.8	643.2	98.9

[1]Means of three replicates, SED<5%

to any specific size fraction of NCPR although there was a tendency for recovery to increase with increasing particle size of the NCPR.

4.4.4 Recovery of NCPR-P and MCP-P by either single or sequential extraction

Recovery of MCP-P was also very low regardless of whether it was applied to the soil or to the HCl extractant (Table 4.5). Without 1 M NaOH extraction, 80 and 84% of the added MCP-P and NCPR-P was recovered from Sembawa soil in the 1 M HCl extraction following NaCl/TEA pre-extraction from Sembawa soil. These recoveries were higher than the 72 and 64% recovery of MCP-P and NCPR-P, respectively using 1 M NaOH extraction. On the other hand, a single extraction with 1 M HCl gave almost total (95-110%) recovery of added NCPR-P (Table 4.6). These results indicate that the inability of 1 M HCl extractant to recover added NCPR-P occurred whenever NaCl/TEA or NaOH extraction preceded HCl extraction.

4.4.5 Recovery of NCPR-P from Sembawa soil in various concentrations of HCl or H_2SO_4 following 0.5 M NaCl/TEA and 1 M NaOH extractions

In an attempt to select acid extractants capable of achieving complete recovery of NCPR-P from Sembawa soil, various concentrations of HCl (1, 2 and 4 M) and H_2SO_4 (0.5 and 1 M) were used to extract NCPR-P from Sembawa soil following extraction with 0.5 M NaCl/TEA and 1 M NaOH (Table 4.7). Although recoveries of added NCPR-P in HCl extracts increased with increasing HCl concentration (63% in 1 M HCl extract to 87% in 4 M HCl extract), complete recoveries were not achieved. On the other hand, extraction with 0.5 and 1 M H_2SO_4 gave almost total recovery of the added NCPR-P (96 to 104%) indicating that recovery was not affected by the use of alkaline extractants in the earlier stage of the sequential procedure. These results also show that O.5 M H_2SO_4 was strongly enough to recover most of the added NCPR-P in soil.

This same acid proved equally effective when used in the sequential extraction method on Sembawa soil which had been enriched with soluble MCP fertilizer (Table 4.7).

Table 4.4 Recovery of added NCPR-P (500 mg kg^{-1} soil) varying in particle size from Sembawa soil following 0.5 M NaCl/TEA, 1 M NaOH and 1 M HCl extractions.

Particle size (µm)	Extract sequence	Extractable P (mg P kg^{-1})		Recovery[1] (%)
		Soil	Soil+PR	
<106	NaCl/TEA	2.6	2.6	0.0
	NaOH	93.5	118.9	5.1
	HCl	0.0	212.7	42.5
	Total	96.1	334.2	47.6
106-150	NaCl/TEA	2.6	2.6	0.0
	NaOH	93.5	120.9	5.5
	HCl	0.0	315.5	63.1
	Total	96.1	439.0	68.6
150-250	NaCl/TEA	2.6	2.6	0.0
	NaOH	93.5	106.5	2.6
	HCl	0.0	319.3	63.9
	Total	96.1	427.9	66.5
250-500	NaCl/TEA	2.6	2.6	0.0
	NaOH	93.5	131.9	7.7
	HCl	0.0	375.9	75.2
	Total	96.1	510.4	82.9

[1]Means of three replicates, SED<5%

Table 4.5 Recovery of added NCPR-P and MCP-P (500 mg kg^{-1} soil) from Sembawa soil following sequential extraction with or without 1 M NaOH extraction.

Extract sequence	Extractable P (mg P kg^{-1})			Recovery (%)[1]	
	Soil	Soil+PR	Soil+MCP[2]	PR-P	MCP-P
a. Without NaOH extraction					
NaCl/TEA	2.6	2.6	0.0	0.0	0.0
HCl	20.5	439.5	420.5	83.8	80.0
Total	23.1	442.1	423.1	83.8	80.0
b. With NaOH extraction					
NaCl/TEA	1.1	2.6	2.6	0.3	0.3
NaOH	83.7	93.5	97.9	2.0	2.8
HCl	0.0	319.3	357.9	63.9	71.6
Total	84.8	415.3	458.4	66.2	74.7

[1]Means of three replicates, SED<5%.
[2]MCP was added to the HCl extractant.

Table 4.6 Recovery of added NCPR-P (500 mg kg^{-1} soil) from Indonesian soils by single 1 M HCl extraction.

Soil	Extractable P (mg P kg^{-1})		Recovery (%)[1]
	Soil	Soil+PR	PR-P
Sembawa	30.8	504.3	95.0
Prabumulih	38.3	590.1	110.4
Lubuk Linggau	41.9	539.8	99.6

[1]Means of three replicates, SED<5%

Table 4.7 Recovery of added NCPR-P and MCP-P (500 mg kg^{-1} soil) from Sembawa soil by acid extraction following 0.5 M NaCl/TEA and 1 M NaOH extractions.

P source	Final extract	Extractable P (mg kg^{-1})		Recovery[1] (%)
		Soil	Soil+PR	
NCPR	1 M HCl	0.0	317.2	63.4
	2 M HCl	1.2	373.0	74.3
	4 M HCl	15.5	452.3	87.4
	0.5 M H_2SO_4	7.8	482.7	95.5
	1 M H_2SO_4	9.5	531.5	104.4
MCP	0.5 M H_2SO_4	103.9	593.9	98.0

[1]Means of three replicates. SED<5%

4.5 DISCUSSION

Recoveries of P obtained using any sequential extraction method on P fertilized and unfertilized soils will always be subject to sampling and P partitioning errors. In the present procedure, P partitioning errors have reduced the accuracy of the measurement of acid soluble P in soils. However, results of the present study suggest that experimental errors were small with SEM mostly <5%. The experimental techniques were reproducible and consistent results were obtained when the sequential extraction was repeated using the same soil sample (e.g. the recoveries of NCPR-P in 1 M HCl extracts from Sembawa and Prabumulih soils presented in Tables 4.2 and 4.3).

Although the ΔHCl method gave adequate estimate of the amount of residual NCPR in New Zealand soils (Chapter 3, Table 4.2), problems were encountered when the same method was used on Indonesian soils.

Results obtained using tri-acid digestion (Table 4.3) suggest that the low recovery of

NCPR-P from Indonesian soils was caused by the inability of 1 M HCl to extract P from the soil pellets remaining after the 1 M NaCl/TEA and NaOH extractions. The tendency for recovery of added NCPR-P in 1 M HCl extracted increases with increasing NCPR particle size (Table 4.4) initially suggested that the mechanisms inhibiting NCPR-P recovery might be associated with PR surface area. However, the low recoveries of P by 1 M HCl were not confined to NCPR alone. Similar low recovery of P was found when MCP was either applied to the soil or to the HCl extractant (Table 4.5). Formation of an "insoluble P" in 1 M HCl, appeared to be partly due to pre-extraction with NaCl/TEA and NaOH, because extraction with 1 M HCl alone gave total recoveries of added MCP and NCPR-P from Indonesian soils (Table 4.5).

It appears likely that the decrease in extractability of soluble-P and NCPR-P by HCl in the lower pH and more strongly weathered Indonesian soil after NaCl/TEA and NaOH extraction relates to the forms of P in this soil. Highly weathered soils characteristically have a large proportion of their Pi in relatively insoluble Al and Fe associated forms and high activities of Al and Fe oxyhydroxides. Under neutral and alkaline conditions preceding an HCl extraction, some of the extracted organic matter may also have been associated with Al or Fe and P (Levesque, 1969; Sinha, 1971; Jambu *et al.*, 1972). Upon acidification, a portion of the extracted organic matter (humic acid) will precipitate or coprecipitate P onto soil or coat PR surfaces inhibiting their solution in 1 M HCl. One hypothesis therefore is that the poor recovery of P in 1 M HCl probably results from resorption of P by the soil surface or these organic complexes during HCl extraction (Table 4.5). It is unclear why these P loss processes did not occur in H_2SO_4.

Energy dispersive X-ray analysis (EDXA) of the NCPR particles (<500 μm) recovered from soil residue of Indonesian soils prior to 1 M HCl extraction failed to find any evidence for surface coatings of Al and Fe oxides (D.C. Golden, pers. comm.), however, humic coating or coprecipitation of P would be expected to form during the initial stages of the 1 M HCl extraction.

Although the mechanism of the low recovery remains unclear, the problem was overcome by tri-acid digestion (Table 3.3). Tri-acid digestion of the final soil residue, however, makes the sequential extraction procedure tedious and in some soils that have

high levels of recalcitrant residual P (McLaughlin and Alston, 1986; Hedley *et al.*, 1982b) this method is less sensitive to small additions of PR.

Results of the study have not provided a clear explanations as to why H_2SO_4 was a better extractant than HCl for recovering residual NCPR-P from Indonesian soils following 0.5 M NaCl/TEA and 1 M NaOH extraction. Earlier workers who developed or modified P fractionation methods (e.g. Chang and Jackson, 1957; William *et al.*, 1967; Williams and Walkers, 1969; Hedley *et al.*, 1982b) did not report any problem in recovering the apatite (Ca-bound P) fraction in soils. In the procedures proposed by the above workers, both HCl and H_2SO_4 extractants are generally considered to be equally effective in recovering apatite fraction. For example, the earlier procedure developed by Chang and Jackson (1957) uses 1 M H_2SO_4 extractant to assess the apatite fraction in soils. Subsequent workers (e.g. Williams *et al.*, 1967 and Hedley *et al.*; 1982) replaced H_2SO_4 with 1 M HCl when modifying the method of Chang and Jackson. More recently Rajan (1983) and Rajan *et al.* (1991b) used 0.5 M H_2SO_4 for estimating amounts of residual PR in some New Zealand soils.

Overall, the results presented in this chapter show that the earlier method of measuring amounts of residual PR (ΔHCl method), which was developed for use in New Zealand soils, can now be improved for use on a wider range of soils by replacing 1 M HCl with 0.5 M H_2SO_4 as the preferred extractant for recovering the apatite fraction. This newly modified method (ΔH_2SO_4 method) was found to be accurate for use on highly weathered Indonesian soils. It should be pointed, however, that in order to measure amounts of PR accurately, pre-extraction of soil with 0.5 M NaCl/TEA is essential prior to 1 M NaOH and 0.5 M H_2SO_4 as explained in Chapter 3.

4.6 CONCLUSIONS

An evaluation of the sequential extraction method for measuring amounts of residual (undissolved) PR in soil (ΔHCl method) which was developed for use in a range of New Zealand soils shows that this method failed to achieve a complete recovery of residual NCPR in a range of Indonesian soils. The estimate of amount of residual NCPR in the

Indonesian soils from the increase in the acid-extractable P was improved when the 1 M HCl in the NaCl/TEA-NaOH-HCl method was replaced with tri-acid mixture or H_2SO_4 (0.5 or 1 M). For convenience, use of 0.5 M H_2SO_4 instead of 1 M HCl as an acid extractant is recommended.

Although the evaluation of the newly developed method was confined to dry blended of soil/PR mixture, the results show that ΔH_2SO_4 (NaCl/TEA-NaOH-H_2SO_4) method can also be used to measure residual PR in a range of soils under various conditions. Under glasshouse and field conditions, this method can only be accurate if residual PR remains in the sampling zone.

All measurements of amounts of residual PR in subsequent studies involving Indonesian soils reported in the remaining chapters will use ΔH_2SO_4 method.

CHAPTER 5
MEASURING AND MODELLING THE EFFECTS OF SOIL PROPERTIES ON PHOSPHATE ROCK DISSOLUTION

5.1 INTRODUCTION

High soil acidity (Ellis *et al.*, 1955; Peaslee *et al.*, 1962; Kirk and Nye, 1986c; Kanabo and Gilkes, 1987a; Robinson and Syers, 1991), high P sorption capacity and low Ca saturation (Khasawneh and Doll, 1978; Chien *et al.*, 1980; Smyth and Sanchez, 1982; Wilson and Ellis, 1984; Mackay *et al.*, 1986; Kanabo and Gilkes, 1987b; Bolan *et al.*, 1990; Rajan *et al.*, 1991b; Robinson and Syers, 1990; 1991; Wright *et al.*, 1992) appear to be important soil properties promoting phosphate rock (PR) dissolution. Robinson and Syers (1991) recently reported that provided the supply of protons in soil was adequate, PR dissolution was mainly controlled by the size of Ca sink. Results presented in Chapter 3 on PR dissolution in some New Zealand soils amended with either $CaCO_3$ or $NaHCO_3$ showed that dissolution was favoured under soil conditions where pH and exchangeable Ca were both low. The importance of soil solution Ca concentration was discussed, with respect to the stoichiometric equation for PR dissolution, in Chapter 2.

Most studies on PR dissolution have been conducted using temperate rather than tropical soils. As mentioned in Chapter 4, the properties of highly weathered tropical soils are likely to favour PR dissolution. Hughes and Gilkes (1986), for example, found greater PR dissolution in the more acidic Oxisols and Ultisols from Brazil and Colombia than in Entisols from Australia.

While several agronomic studies have shown the potential value of PRs for direct application to Indonesian soils (Harjono, 1987; 1988a; 1988b; Harris *et al.*, 1985), no studies have closely examined the kinetics of PR dissolution in these soils. Such studies may help in identifying soil properties affecting PR dissolution and thereby selecting potential sites for PR application and prescribing the type of PR to be applied.

Studies aiming to quantify effects of soil properties on the extent of PR dissolution in soil so far have relied on simple regression analysis of soil properties against the extent of PR dissolution (Khasawneh and Doll, 1978; Mackay *et al.*, 1986, Robinson and Syers, 1991). Constructing empirical models requires experiments to be conducted across a wide range of soil conditions. This practice is usually expensive and very time consuming.

There is a need to develop less-empirical models which can be used to predict PR dissolution over a wide range of soil conditions and management. Two models, namely Cubic (Rajan and Watkinson, 1988) and Kirk and Nye (Kirk and Nye, 1986b; 1986c) have been proposed for this purpose. Conceptually, both models describe processes of PR dissolution differently. The models are explained in more detail in Section 5.3.4.

Successful simulation of PR dissolution over time would allow identification of the important parameters that are useful in selecting soils and sites for potential PR use.

5.2 OBJECTIVES

The objective of this study were (1) to simulate dissolution of PRs in a range of soils using different models, and (2) to examine the effect of selected soil properties on PR dissolution

5.3 MATERIALS AND METHODS

5.3.1 Soils

Six surface soils, three each from New Zealand and Indonesia, were used in this study. The soils were similar to those used in Chapter 4. Some basic properties of the soils were presented in Table 4.1 (Chapter 4). Additional soil properties required as parameters in the Kirk and Nye model are given in Table 5.10.

5.3.2 Phosphate rocks

The 150-250 μm particle size separate of North Carolina reactive phosphate rock (NCPR) and Moroccan medium reactive phosphate rock (MPR) were used. Some properties of the PR size separates are given in Table 5.1.

Table 5.1 Selected properties of PRs used in the study.

PR	Diameter (μm)	Total P (% w/w)	2% Citric acid soluble-P (% of total P)
NCPR	150-250	13.6	40.6
MPR	150-250	14.4	33.1

5.3.3 Incubation of soil and phosphate rock

Soil samples (8 g) were thoroughly mixed with PR at rates equivalent to either 250, 500 or 1000 mg P kg^{-1} soil. Each soil/PR mixture was moistened with deionized water to 95% of soil field moisture capacity, then repacked in a 10 ml plastic centrifuge tube, which had a small hole at its base and was covered with glass wool. The mixtures were incubated in the dark at 20±2°C for 90 days. The moisture content and bulk density of the repacked soils are given in Table 5.2. The soils were aerated and moistened regularly. Individual samples were withdrawn at 10, 20, 60 and 90 days. For the 500 mg P kg^{-1} treatment, samples were also withdrawn at 30 days. Soil solution was extracted at day 60 by centrifugation (Section 5.3.5.2). After collection of the soil solution, soil samples were oven-dried at 45°C for 16 h.

5.3.4 Models used to evaluate the influence of soil properties on phosphate rock dissolution

The empirical regression model used in this study is a simple exponential regression equation of the modified Mitscherlich equation. The other descriptors used were the pragmatic Cubic (Chatupote, 1990) and the mechanistic Kirk and Nye (1986c; 1986d) models. These models are described briefly in the following sections.

5.3.4.1 Regression analysis

The extent of PR dissolution in a closed system, from which dissolution products are not removed, can be described by using an empirical modified Mitscherlich regression equation (Kanabo and Gilkes, 1987a; 1988; Mackay *et al.*, 1986), written as follows:

$$y=a(1-e^{cx}) \qquad (5.1)$$

where y=percentage of PR dissolved; a=the maximum percent of PR dissolution observed; c=curvature coefficient; and x=incubation time (days). In a closed incubation system the Mitscherlich equation has been shown to closely simulate the dissolution pattern of PR with coefficients of determination (R^2) greater than 0.93 (Kanabo and Gilkes, 1987a).

The values of both a, the maximum dissolution, and c, the curvature coefficients, vary between soils. Simple regression analyses have been used to establish relationships between maximum dissolution (a) and soil properties (Mackay *et al.*, 1986; Robinson and Syers, 1991; Wright *et al.*, 1992).

5.3.4.2 Cubic model

The Cubic model was initially developed for estimating the rate of oxidation of S° in New Zealand soils (Chatupote, 1990). The model is based on the defoliation of a sphere, a method used to describe the dissolution of limestone (Swartzendruber and Barber, 1965). Use of such a model to estimate the dissolution rate of PR over a period of time was first proposed by Rajan and Watkinson (1988).

The Cubic model allows a dissolution rate constant (K) to be calculated per unit surface area of PR. Soil factors affecting the dissolution constant can be studied. Some of the assumptions made in modelling the oxidation of S° (Chatupote, 1990) are also applicable to the present study. These include: (1) dissolution of PR proceeds as a function of its surface area; (2) PR particles are assumed to be spherical in shape; (3) dissolution rate is constant when measured over a period of time.

The proportion of added PR remaining (Pt/Po) after time t is determined by ratio of current to initial mass:

$$\frac{P_t}{P_o}=\frac{4/3\pi r_t^3 \rho N}{4/3\pi r_o^3 \rho N} \qquad (5.2)$$

where r_o (mm) is initial radius; r_t (mm) is radius after time t; N is number of particles applied; and ρ is PR density. From Equation 5.2 it follows that

$$r_t=r_o(P_t/P_o)^{1/3} \qquad (5.3)$$

Since

$$\frac{\Delta r}{\Delta t}=\frac{(r_o-r_t)}{t} \qquad (5.4)$$

then by substituting r_t from Equation 5.3, we obtain,

$$\frac{\Delta r}{\Delta t}=\frac{r_o\left(1-\frac{P_t}{P_o}\right)^{1/3}}{t} \qquad (5.5)$$

In the event that the PR particles vary in sizes, Equation 5.5 can be further modified. However, in the present study using a narrow range of particle size (mean radius = 100 µm), no modification was needed.

An iterative procedure (Chatupote, 1990) was developed to calculate dissolution rates (K) by least square fitting of K values to observed dissolution data. The dissolution rate K per unit surface area of PR particle (µg P cm^{-2} day^{-1}) can be calculated from Δr as follows:

$$K=(\Delta r/\Delta t) \times \rho \times 10^5 \qquad (5.6)$$

It should be noted that this procedure calculates a single mean K value over time for each set of dissolution data.

The model was written in BASICA using QuickBasic (Microsoft Corporation, 1987) and was run on an IBM compatible personal computer.

5.3.4.3 Kirk and Nye model

The mechanistic Kirk and Nye model for predicting PR dissolution was initially developed to describe the dissolution of dicalcium phosphate dihydrate (DCPD) in a single dimensional system. It was then extended to predict the dissolution of DCPD in a three dimensional soil system, and then for the apatitic components of PR. A complete account of the development of the model was described in a series of papers (Kirk and Nye, 1985a; 1985b; 1986a; 1986b; 1986c; 1986d).

According to the Kirk and Nye model, the rate of dissolution of a carbonate fluorapatite is controlled by the diffusion of the products (i.e. calcium, phosphate and base) away from the dissolving particle surface. The concentrations of calcium, phosphate and hydrogen ions in solution at the mineral/soil boundary are found from (a) the ion activity products of calcium phosphate and (b) fluxes of calcium, phosphate and base across the boundary. The model also allows for the diminution of the particles as they dissolve, and the mutual effect of neighbouring particles upon each other.

Basic equations

The basic equations used in the Kirk and Nye model are summarized in Table 5.2. The sequence of calculations performed in estimating the amount of PR dissolved (ΔM_t) for a particular time interval are as follows:

(1) A new value for pH_s is calculated from Equation 5.7 using the values for C_{LS} (P concentration in solution, L, at PR particle surface, S) and $[Ca^{2+}]_{LS}$ (Ca concentration in soil solution, L, at PR particle surface, S).

(2) A new C_{LS} is calculated from Equation 5.8 using the new pH_s and previous C_{LR} (P concentration at edge of zone of particle's influence) and pH_{LR} (pH at edge of zone of particle's influence).

(3) A new $[Ca^{2+}]_{LS}$ is calculated from Equation 5.9.

Table 5.2 Summary of equations used in Kirk and Nye model to calculate PR dissolution.

Calculation of the concentration and activity coefficient of ions at particle surface

$$pH_s = -\log \frac{(K_2 C_{LS} [Ca^{2+}]_{LS} \lambda_I \lambda_{II})}{K_{PR}} \tag{5.7}$$

$$C_{LS} = C_{LR} + \frac{b_{HS}(pH_s - pH_R) R_{HS} \bar{D}_{HS} (R_P - a_s)}{b_P R_P D_P (R_{HS} - a_s)} \tag{5.8}$$

$$[Ca^{2+}]_{LS} = \frac{(C_{LS} + 2[HPO_4^{2-}]_{LS} + [HCO_3^-]_{LS} + z_-[A^{z-}]_{LS} + [H^+]_{LS} - z_+[M^{z+}]_{LS})}{2} \tag{5.9}$$

Calculation of the amounts of phosphate and base dissolved at time t

$$\frac{dM_t}{d_t} = \bar{b}_P (C_{LS} - C_{LR}) 4\pi a_s^3 \left(\frac{R}{R - a_s}\right) \frac{\bar{D}_P}{a_s^2} \tag{5.10a}$$

$$\frac{dMt}{dt} = b_{HS}(pH_s - pH_R) 4\pi a_s^3 \left(\frac{R_{HS}}{R_{HS} - a_s}\right) \frac{\bar{D}_{HS}}{a_s^2} \tag{5.10b}$$

Calculation of the average of P concentration and P concentration at particle surface

$$(\bar{C}_L - C_L') = \frac{3M_t}{4\pi R^3 \bar{b}_P} \tag{5.11}$$

$$C_{LR} = \bar{C}_L \left(1 + \frac{a_s}{2R}\right) - C_{LS} \left(\frac{a_s}{2R}\right) \tag{5.12}$$

Calculation of the average pH and pH at particle surface

$$(\overline{pH} - pH') = \frac{3M_t}{4\pi R^3 b_{HS}} \tag{5.13}$$

Table 5.2 (cont)

$$pH_R=\overline{pH}\left(1+\frac{a_s}{2R}\right)-pH_s\left(\frac{a_s}{2R}\right) \tag{5.14}$$

Calculation of P buffer capacity and average P and base diffusion coefficients

$$\bar{b}_P=\frac{a(C_{LS}-C_{LR}^b)}{(C_{LS}-C_{LR})} \tag{5.15}$$

$$\bar{D}_P=D_{LP}\theta f\frac{(C_{LS}-C_{LR})}{a(C_{LS}^b-C_{LR}^b)} \tag{5.16}$$

$$\bar{D}_{HS}=\frac{\theta f}{b_{HS}\Delta pH}(D_{LH}\Delta[H^+]_L-D_{LC}\Delta[HCO_3^-]_L-D_{LP}\Delta[HPO_4^{2-}]_L) \tag{5.17}$$

Calculation of the new particle radius of PR

$$a_s=\left[\frac{3(m.w)}{4\pi\rho(p.c)n_t}\right]^{\beta} \tag{5.18}$$

Calculation of the rate of P uptake per unit volume of soil (U_v)•

$$U_v=\frac{2\pi D_{LP}\theta f L_v\bar{C}_L}{\ln(x/1.65a_r)} \tag{5.19}$$

Accounting for the effect of acid secretion on PR dissolution•

$$\frac{dM_t}{dt}=4\pi b_{HS}\bar{D}_{HS}(pH_s-pH_R)a_s\left(\frac{R_{HS}}{R_{HS}-a_s}\right)+\frac{2\pi a_r FL_v}{N} \tag{5.20}$$

•Not used in Chapter 5.

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where:

a : parameter "a" in Freundlich equation for phosphate sorption, $C_s=aC_L^b$.

a_s : radius of surface of PR at a particular time, dm.

$[A^{z-}]$: concentration of additional anions as represented by Equation 5.9.
b : parameter "b" in Freundlich equation for phosphate sorption.
b_{HS} : pH buffer capacity.
b_P : phosphate buffer capacity.
C_L : concentration of $H_2PO_4^-$ in soil solution, mol dm^{-3}.
$[Ca^{2+}]_L$: concentration of Ca in soil solution, mol dm^{-3}.
D_{HS} : soil base diffusion coefficient, $dm^2\ s^{-1}$.
D_P : soil phosphate diffusion coefficient, $dm^2\ s^{-1}$.
f : diffusion impedance factor.
$[H^+]$: concentration of H^+ in solution, mol dm^{-3}.
$[HS]$: concentration of titratable acidity with respect to the native soil, mol dm^{-3}.
K_{PR} : solubility products of PR.
K_2 : second dissociation constant of H_3PO_4.
$[M^{n+}]$: concentration of additional cation as represented by Equation 5.9.
M_t : mol of P dissolved at time t.
$(m.w)$: molar weight of calcium phosphate (PR), kg mol^{-1}.
n : mol of phospate per particle.
$(p.c)$: mol of phosphate per mol calcium phosphate.
R : average radius of zone of influence of a particle, dm.
x : radius of zone of root exploitation, dm s^{-1}.
z : ionic valence.
λ : activity coefficient
ρ : density of calcium phosphate, kg dm^{-3}
θ : volumetric moisture content

Subscripts: i initial, L liquid phase, R edge of particle's zone of influence, S native soil, s PR particle surface, t time (second).
Superscripts: $'$ value in native soil, $\bar{}$ average value.

(4) A new M_t (amount of PR remaining) is calculated from Equation 5.10 with the new C_{LS} and previous C_{LR}.

(5) A new C_{LR} is calculated from Equations 5.11 and 5.12 using the new C_{LS} and M_t and a new pH_{LR} is calculated from Equations 5.13 and 5.14 using the new pH_s and M_r.

(6) If any of the boundary conditions have changed over Δt, the whole process is repeated from step (1).

In each time interval the new values for phosphate buffer capacity and coefficients of diffusion of phosphate and soil base are calculated from Equations 5.15, 5.16 and 5.17, respectively. The decrease in particle radius as the PR particle dissolves is calculated from Equation 5.18.

To account for the effect of plant roots on PR dissolution, Equation 5.19 was used. The effect of Ca uptake in the model was accounted for by the value of $[Ca^{2+}]_{LS}$ obtained from the balance of ionic charges as shown by Equation 5.9. The main effect of acid secretion on PR dissolution is through changes in the amount of acid or base in the rhizosphere. In turn this relates to imbalances in the uptake of cations and anions across the root soil-interface, which must of necessity be balanced by the export of H_3O^+ and HCO_3^- to maintain electrical neutrality. Changes in acid or base production depend on the type of plant and its nutritional regime (Chapter 2). The effect of acid secretion on the change in rate of PR dissolution with time can be calculated from Equation 20.

Parameterization

The Kirk and Nye model requires various input parameters describing the soil, PR and plant roots, as outlined below.

Soil parameters

a and ***b***-"a" and "b" coefficients in the Freundlich equation describing the phosphate adsorption isotherm ($C_s=aC_L^b$, Freundlich equation).

$[Ca^{2+}]_L'$-initial calcium concentration in soil solution, mol dm^{-3}.

b_P and b_{HS}-phosphate and pH buffer capacity, mol kg^{-1} soil pH^{-1}.

C_L'-initial P concentration in soil solution, mol dm^{-3}.

D_{LP}, D_{LH} and D_{LC}-diffusion coefficients in water of $H_2PO_4^-$, H_3O^+ and HCO_3^-, respectively, dm^2 s^{-1}.

f-diffusion impedance factor, which is related to ρ_b, soil dry bulk density, by the relationship $f=\theta^{1.49}x\rho_b$ (Nye and Tinker, 1977).

pH_L'-initial pH in soil solution.

θ-volumetric moisture content, dm^3 dm^{-3}.

ρ_b-soil dry bulk density, kg dm^{-3}.

Phosphate rock parameters

a_i-initial radius of PR, dm.

K_{CaF2}-solubility product of CaF_2.

pK_s-solubility product of apatite.

K_{H1}-product of the first dissociation constant of H_2CO_3 x solubility of CO_2 in water x pressure of CO_2 (PCO_2).

K_{H2}-the product of K_{H1} x the second dissociation constant of H_2CO_3.

K_2-the second dissociation constant of H_3PO_4.

($p.c$)-mol of phosphate per mol PR.

nC, nP and nH-coefficients of the activities of Ca^{2+}, $H_2PO_4^-$ and H^+ for apatite in equilibrium with CaF_2.

w-weight of PR per unit of volume soils, kg dm^{-3}.

ρ-density of PR, kg dm^{-3}.

Plant parameters (not used in Chapter 5 simulations)

a_r-average root radius, dm.

F-flux of acid across root surface, mol dm^{-2} s^{-1}.

L_v-rooting density, dm dm^{-3}.

Input parameters such as, a, b, C_L', $[Ca^{2+}]_L'$, b_P, b_{HS}, θ, and ρ_b are determined using analytical procedures described in Section 5.3.5. Values of D_{LP}, D_{LH} and D_{LC} were taken as 8.9 x 10^{-8}, 8.4 x 10^{-7} and 1.08 x 10^{-11} dm^2 s^{-1}, respectively and the values of K_{CaF2}, K_{H1}, K_{H2} and K_2 were taken as 1.45 x 10^{-10}, 8.17 x 10^{-17}, 3.78 x 10^{-21} and 6.12 x 10^{-8},

respectively (Lindsay and Vlek, 1977). Values of pK_s, a_i, $(m.w)$, $(p.c)$, w, and ρ_b were determined for the PR used (Appendix 5.2). In the absence of plant roots, values of a_r, F and L_v were set at close to 0.

Executing the model

The model was originally written in FORTRAN (Kirk and Nye, 1986c), and later modified to BASICA using QuickBasic (Microsoft Corporation, 1987) and the program was run on an IBM compatible personal computer. This version of the model, which was provided by Dr. N.J Barrow, includes an optimization procedure for iteratively estimating the new pH values.

5.3.5 Chemical analysis

5.3.5.1 General soil analysis

The soil properties given in Table 4.1 were determined by methods described in Sections 3.3.3 and 4.3.3. The analytical procedures for soil chemical properties used as model parameters (Table 5.10) are described below.

Initial soil pH

Soil pH was measured in $CaCl_2$ solutions of differing ionic strength (Table 5.9). Soil samples (2 g) were shaken with 10 ml $CaCl_2$ solution for 30 minutes. The pH in the supernatant was measured following centrifugation for 5 minutes at 5000 rpm.

Freundlich a and b coefficients

Five gram samples of air dry soil were shaken with 40 ml of 0.001 M $CaCl_2$ containing varying amounts of P as NaH_2PO_4. One drop of $CHCl_3$ was added and the tubes were shaken on an end-over-end shaker for 20 hours at 20±2°C. After shaking, the tubes were centrifuged for 5 minutes at 6000 rpm and filtered through Whatman No. 5 filter paper. Phosphate concentrations in the supernatant were measured by the method of Murphy and Riley (1962). The amount of adsorbed phosphate was estimated from the difference between the amount added and the amount remaining in the equilibrium

solution. The Freundlich equation was then fitted to the observed data using a curve-fitting program. Least squares regression analysis was used to calculate appropriate values of ***a*** and ***b*** (data not presented).

Soil pH buffer capacity

Soil pH buffer capacity was determined by shaking 2 g soil with 10 ml of 0.01 M $CaCl_2$ containing varying amounts of KOH for 20 h (Kirk and Nye, 1985b). After shaking, the pH of the supernatant was measured. The pH buffer capacity was estimated from the slope of the linear regression of the change in the amounts of base (OH^-) in the supernatant against lime potential. The change in the amounts of base which was assumed to be involved in the neutralization of the protons in the soil was found from the difference between the base added and the base in the equilibrium solution.

Concentration of calcium and phosphate in soil solution

Soil solution was extracted from the unfertilized 3- and PR fertilized 60-day incubated soil (90% of field moisture capacity) using the procedure described in the following section. Concentrations of calcium and inorganic P (Pi) in the soil solution were determined using the procedure described in Section 3.3.3.

5.3.5.2 Soil solution extraction

Soil solution was obtained using a modification of the centrifugation technique of Reynolds (1984). The extraction unit consisted of two centrifuge tubes placed one inside the other. The inner tube, which has a small hole at the base, contained the incubated moist soil sample (see Section 5.3.3). The outer tube collected soil solution when the tubes were centrifuged at 8000 rpm for 15 minutes. From 0.5 to 2 ml of soil solution, depending on the soil, was extracted using this technique. The soil solution was analyzed for pH, phosphate and Ca.

5.3.5.3 Sequential extraction of soil/PR mixtures

Amounts of undissolved PR residue, in samples taken at regular intervals from incubating soil/PR mixtures, were estimated from the increase in amounts of 0.5 M

H_2SO_4-extractable P following extraction of the soil with 0.5 M NaCl/TEA and 1 M NaOH (Chapter 4). The amounts of residual PR in soils was calculated using Equation 3.1.

5.3.5.4 Soil solution ionic strength measurement

For the determination of soil solution ionic strength, a simple leaching column was constructed. Each column consisted of a PVC tube, 100 mm long and 50 mm internal diameter, covered on the bottom end with a nylon mesh (150 μm). A disk of filter paper (Whatman No 5) was placed above the nylon mesh to prevent soil loss during leaching. 100 g of air-dried soil was placed in the column and packed to the same bulk density as in the incubation experiment (Table 5.11). A disc of filter paper was placed on top of the soil to minimize disturbance during leaching.

Soil columns were leached with deionised water until the volume of leachate collected was equivalent to 0.25 pore volumes, after which the columns were allowed to stand for 1 day. Electrical conductivity (EC) of the leachate was determined immediately, and soil solution ionic strength (μ) was estimated by the following equation (Gillman and Bell, 1978).

$$\mu = 0.012EC - 0.004 \qquad (5.21)$$

where EC=leachate electrical conductivity at 25°C (mS cm^{-1}). After EC measurement the leachate was stored at 4°C in sealed centrifuged tubes. Leachate was reapplied to soil columns every 2 days in order to displace the resident soil solution. Leaching and EC measurements of the leachate were repeated over the next 38 days.

5.4 RESULTS AND DISCUSSION

5.4.1 Experimental results

5.4.1.1 Effects of PR reactivity on PR dissolution

The dissolution of NCPR and MPR, applied at 500 mg P kg^{-1} soil, increased rapidly during the first 30 days, after which dissolution rates were much lower (Figure 5.1). Kanabo and Gilkes (1987a) and Syers and Mackay (1986) also reported that, in closed incubation systems, the extent of PR dissolution usually reached a maximum within rather short periods (less than 60 days).

For each soil, the maximum extent of dissolution of the more reactive NCPR was higher than that of the less reactive MPR. For example, 23-56% of NCPR had dissolved at 90 days, but only 11-40% of MPR.

For the same time intervals, the extent of PR dissolution was always higher in Indonesian soils (Sembawa, Prabumulih and Lubuk Linggau) than in New Zealand soils (Tokomaru, Dannevirke and Ramiha). For example, at 90 days, whereas 53-56% of NCPR had dissolved in Indonesian soils only 23-32% had dissolved in New Zealand soils. Corresponding values for MPR were 37-40% for Indonesian soils and 11-24% for New Zealand soils. Reasons for these differences will be discussed in Section 5.4.2.

By 60 days the effects of PR dissolution produced a measurable increase in soil solution pH (Table 5.3). Wright *et al.* (1991) reported similar findings. The magnitude of pH increases due to NCPR dissolution was always higher than for MPR. This was attributed to the higher consumption of protons released from the more reactive NCPR (Smyth and Sanchez, 1982; Kirk and Nye, 1986c). The free calcite content of the NCPR (2%, Syers *et al.*, 1986; Kanabo and Gilkes, 1987a) may also have a liming effect not obtained with MPR. The larger increase in soil solution pH observed in Sembawa soil is attributed to a greater extent of PR dissolution in this soil (Figure 5.2) and its relatively low titratable acidity (Table 4.1).

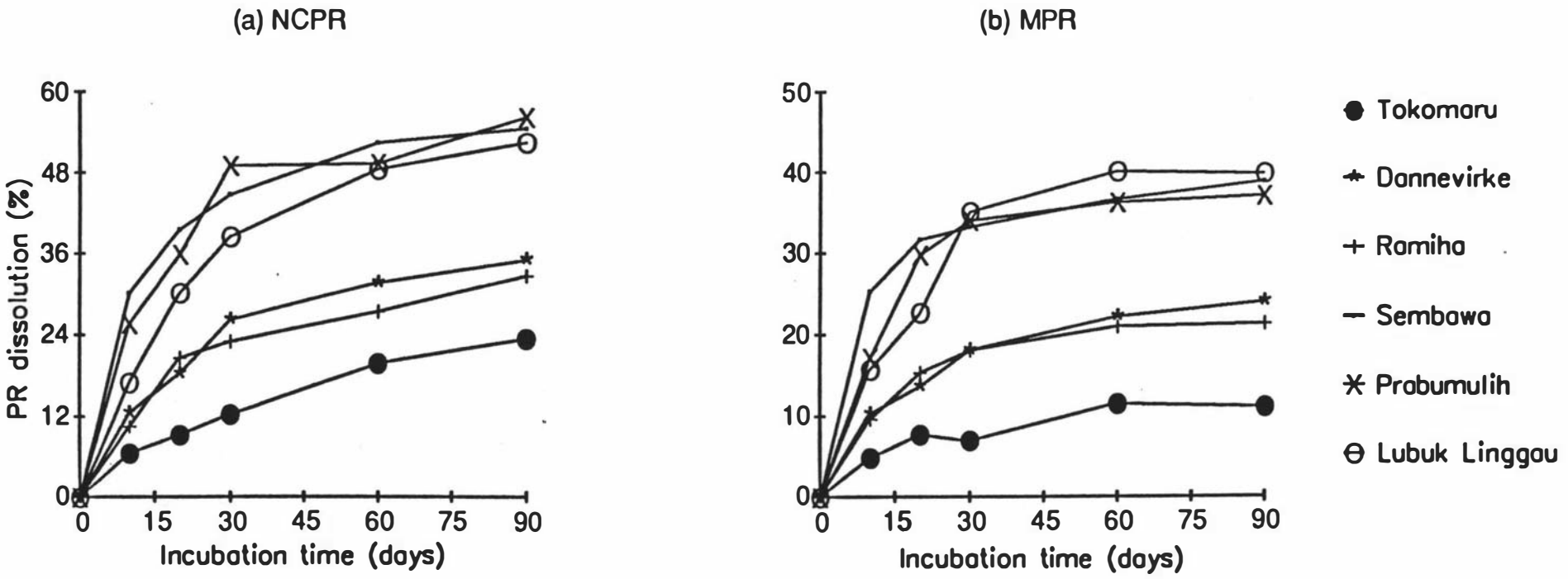


Figure 5.1 Dissolution of (a) NCPR and (b) MPR (applied at 500 mg P kg^{-1} soil) during 90 days of incubation.

Table 5.3 pH of soil solution of the 60 day-incubated soils fertilized with PR (500 mg P kg^{-1} soil).

PR	Solution pH					
	Tokomaru	Dannevirke	Ramiha	Sembawa	Prabumulih	Lubuk Linggau
Control	4.86	4.54	4.80	4.33	4.76	nd
NCPR	5.20	4.84	5.29	5.31	5.05	nd
MPR	5.04	4.80	5.05	5.07	4.94	nd
LSD (P<0.05)	ns	0.07	0.36	0.15	0.25	nd

nd: not determined

5.4.1.2 Effects of rate of application on PR dissolution

For all soils, increases in PR application rate decreased the percentage dissolution of PR (Figure 5.2). At application rates of 250, 500 and 1000 mg P kg^{-1} soil, the extent of NCPR dissolution across all soils ranged between 31-69%, 23-56% and 12-40%, respectively. The corresponding ranges for MPR were 18-44%, 11-40% and 10-32%.

Although the proportion of PR dissolved decreased with increasing rates of application, the absolute amounts dissolved increased. For example, the proportions of NCPR dissolved in Sembawa soil for the application rate of 250, 500 and 1000 mg P kg^{-1} soil after 90 days were 69, 55 and 35%, respectively. These proportions correspond to 172, 273 and 351 mg P dissolved per kg soil. The significance of these increases in terms of the subsequent plant availability of the dissolved P will be discussed in Chapter 6.

At higher PR application rates, diffusion of dissolution products away from the particle surface appears to be limiting (Kirk and Nye, 1986c). The number of PR particles per volume of soil increases as the application rate increases, thus the distance between particle becomes smaller. This results in an overlap of the zones of diffusion from adjacent particles.

Reasons for differences in the extent of PR dissolution in relation to soil properties will be discussed in the following sections.

5.4.2 Evaluation of the influence of soil properties on phosphate rock dissolution using various models

5.4.2.1 Regression analysis

Mitscherlich equations were fitted to data describing the extent of the dissolution of NCPR and MPR during the 90 day incubation. From 93 to 100% of the variation in the extent of PR dissolution over 90 days was accounted for by the Mitscherlich equations for all soils (Table 5.4). The predicted extent of NCPR dissolution (applied at 500 mg P kg^{-1} soil) in soil during 90 days of incubation is shown in Figure 5.3.

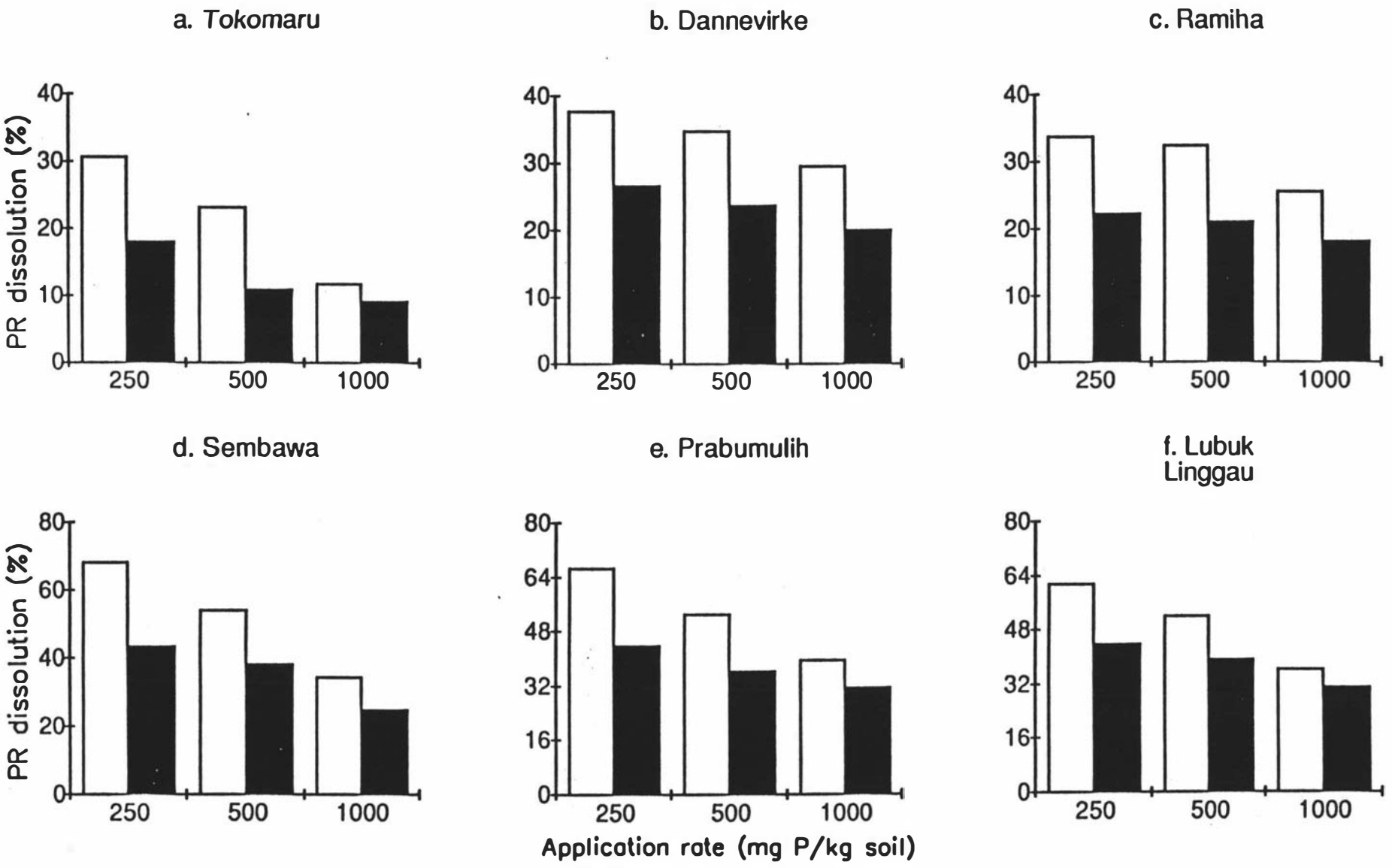


Figure 5.2 Dissolution of NCPR (□) and MPR (■), applied at different rates, in soils after 90 days of incubation.

Table 5.4 Coefficients of the Mitscherlich regression equation describing the dissolution of NCPR and MPR applied at different levels.

Soil	PR rate (mg P kg^{-1} soil)	NCPR			MPR		
		a	*c*	R^2	*a*	*c*	R^2
Tokomaru	250	35.3	-0.023	0.99	17.5	-0.043	0.97
	500	27.2	-0.022	0.99	11.5	-0.047	0.94
	1000	12.5	-0.064	0.99	9.5	-0.077	0.99
Dannevirke	250	38.7	-0.042	0.99	27.1	-0.042	0.99
	500	35.6	-0.040	0.99	23.9	-0.048	0.99
	1000	30.5	-0.043	0.99	19.4	-0.065	0.98
Ramiha	250	34.8	-0.049	0.99	23.0	-0.058	0.99
	500	31.7	-0.045	0.98	21.5	-0.061	0.99
	1000	28.5	-0.048	0.93	18.6	-0.074	0.99

Table 5.4 (Cont)

Soil	PR rate (mg P kg^{-1} soil)	NCPR			MPR		
		a	*c*	R^2	*a*	*c*	R^2
Sembawa	250	67.3	-0.082	0.98	42.4	-0.113	0.99
	500	53.1	-0.073	0.98	36.8	-0.106	0.99
	1000	35.4	-0.129	0.99	26.1	-0.153	0.99
Prabumulih	250	62.1	-0.056	0.99	43.1	-0.062	0.99
	500	54.3	-0.062	0.98	37.4	-0.072	0.99
	1000	39.0	-0.080	0.99	32.6	-0.078	0.99
Lubuk Linggau	250	60.6	-0.052	0.99	45.5	-0.052	0.98
	500	53.7	-0.041	0.99	41.6	-0.048	0.98
	1000	38.2	-0.068	0.99	32.9	-0.066	0.99

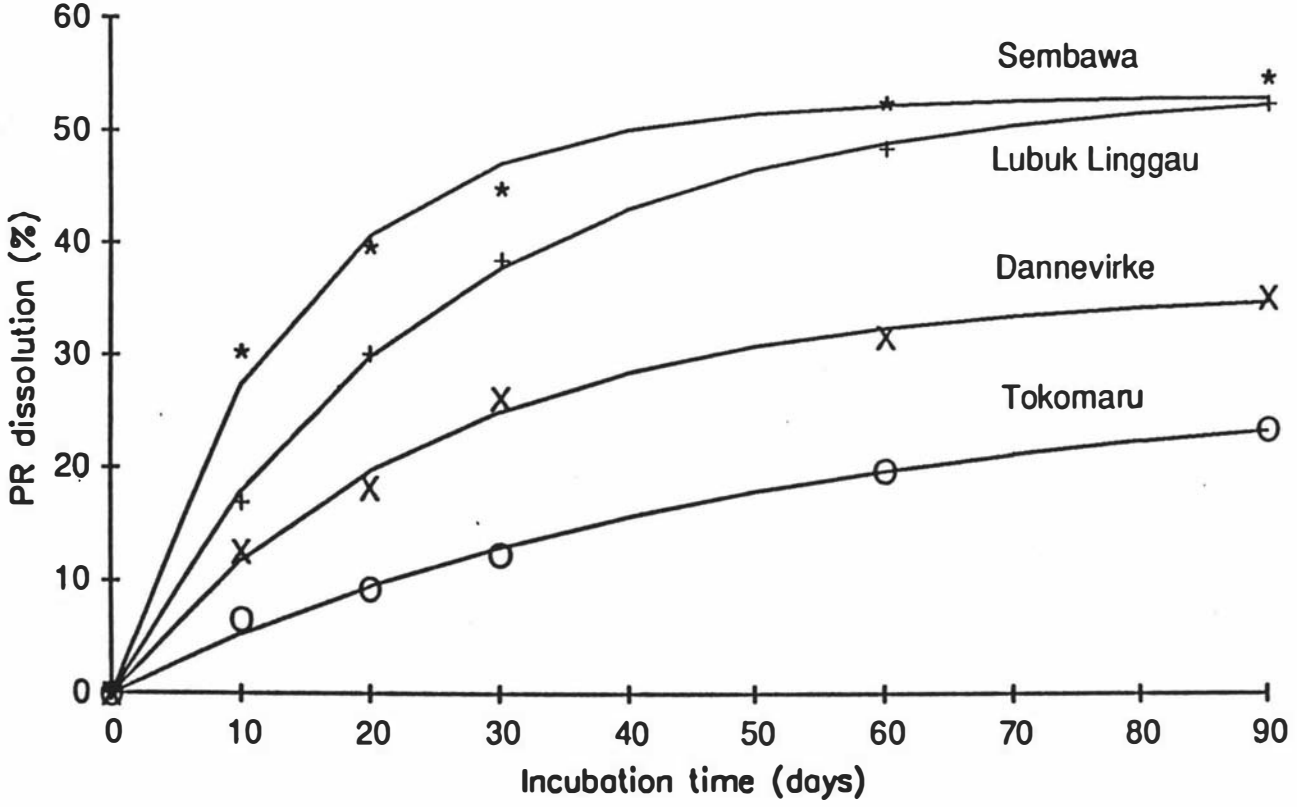


Figure 5.3 Predicted NCPR dissolution (applied at 500 mg P kg^{-1} soil) in Tokomaru, Dannevirke, Sembawa and Lubuk Linggau soils using Mitscherlich equation.

The maximum dissolution predicted by the Mitscherlich equation, as indicated by the *a* values (Table 5.4), ranged from 13 to 62% for NCPR and 10 to 46% for MPR. At each PR application rate, the maximum extent of PR dissolution in Indonesian soils was always higher than in New Zealand soils. Whereas the maximum extent of PR dissolution in all Indonesian soils was almost similar, the values found for New Zealand soils varied more widely. For example, the *a* values in Indonesian soils for the PR application rate of 500 mg P kg^{-1} soil ranged from 53 to 54 and 37 to 42 for NCPR and MPR, respectively. The corresponding values for the New Zealand soils were 27 to 36 and 12 to 24. Among the New Zealand soils, the maximum extent of PR dissolution was always lower in Tokomaru than in both Dannevirke and Ramiha soils.

A simple correlation analysis between the predicted maximum PR dissolution (*a*), over all application rates, and soil properties (as listed in Table 4.1) was carried out (Table 5.5). Strong negative correlations were found between maximum percent PR dissolution (*a* value) and either exchangeable Ca (r=0.83-0.97) or Ca saturation (r=0.78-0.92). Both exchangeable Ca and Ca saturation were not significantly correlated (Appendix 5.3).

Results reported in Chapter 3, together with some published papers (e.g. Mackay *et al.*, 1986), show decreases in the extent of PR dissolution with increasing amounts of exchangeable Ca. In addition to exchangeable Ca, several workers (e.g. Mackay *et al.*, 1986; Robinson and Syers, 1991; Wright *et al.*, 1992) have also noted the importance of Ca saturation on PR dissolution. Both exchangeable Ca and percent Ca saturation largely control the activity of Ca in soil solution which in turn would affect the release of Ca from solid phase Ca phosphate (Chien, 1978, Khasawneh and Doll, 1978; Wilson and Ellis, 1984; Kirk and Nye, 1986a; Mackay *et al.*, 1986; Robinson and Syers, 1991). The high correlations between exchangeable Ca or percent Ca saturation and the extent of PR dissolution appear to be dependent on the rate of PR application. This trend was not unexpected given that the absolute amount of Ca released from PR depends on the application rate. The size of the sink for Ca released from PR applied at low rates does not appear to be limiting. Much of this dissolved Ca would be likely to become exchangeable (Robinson and Syers, 1991). Therefore exchangeable Ca probably exerts the most important influence on PR dissolution. At higher PR application rates, the size of the Ca sink may be controlling PR dissolution because greater amounts of Ca are

Table 5.5 Correlation coefficients (r) for the relationships between maximum percent PR dissolution (*a* in the equation 5.1) and some soil properties.

Soil properties	NCPR (mg P kg^{-1} soil)			MPR (mg P kg^{-1} soil)		
	250	500	1000	250	500	1000
pH (H_2O)	-0.77	-0.67	-0.51	-0.61	-0.57	-0.51
Titratable acidity	-0.19	-0.04	0.08	-0.01	0.08	0.25
Organic C	-0.19	-0.04	0.14	0.04	0.15	-0.29
Exchangeable Ca	-0.97**	-0.95**	-0.87*	-0.94**	-0.87*	-0.83*
CEC	-0.69	-0.58	-0.44	-0.55	0.44	-0.37
Percent Ca saturation	-0.78	-0.87*	-0.92**	-0.88*	-0.92**	-0.92**
P retention	-0.12	0.04	0.16	0.07	0.16	0.29

* and ** indicate significance at $P<0.05$ and $P<0.01$, respectively.

dissolved. Unless the size of the Ca sink increases, a proportionally larger fraction of Ca released from PR at the higher rates would be likely to remain in soil solution.

In contrast to the findings of many workers (e.g. Khasawneh and Doll, 1978; Kanabo and Gilkes, 1987a; Bolan and Hedley, 1990; Robinson and Syers, 1990; and Wright *et al.*, 1992), soil acidity, whether expressed as pH or titratable acidity, was not strongly correlated with the maximum extent of the dissolution of NCPR and MPR in the present study. Soil pH, which is a measure of the intensity factor of soil acidity, may be more related to PR dissolution at initial stages of dissolution. The weak correlation between titratable acidity and percent maximum PR dissolution may be attributed to the fact that titratable acidity (measured in pH 8.2 buffer solution), which is a measure of total acidity in soil, overestimates the actual amount of acidity that may be available for PR dissolution. Amounts of titratable acidity in the pH 6.4-8.2 region would cause little PR dissolution (Kirk and Nye, 1986a). In retrospect a value of titratable acidity measured in pH 6.4 buffer may be suitable.

The importance of P sorption capacity on PR dissolution as suggested by Chien *et al.* (1980), Smyth and Sanchez (1982) and Kanabo and Gilkes (1987b) was not evident in this study. Neither was the importance of soil organic C. It is reasoned that any effects of organic matter and P sorption capacity on the dissolution of NCPR and MPR were probably overridden by the large proton supply available in the soils. Soil P sorption capacity and organic C content, which were not strongly correlated with PR dissolution, were themselves significantly intercorrelated (Appendix 5.3).

5.4.2.2 Cubic model

The modified Mitscherlich equation was fitted to the observed data to produce a "smoothed" data set that could be simulated by the Cubic model. Two approaches were used to predict the dissolution rate constant (K). Firstly, the Cubic model was applied to the data for the entire 90-day dissolution period. Secondly, the model was used to simulate dissolution in 10 day increments. The first procedure generated a single K value, whereas the second procedure produced 5 to 6 values.

Predicted K values for 90-day dissolution

The Cubic model produced a wide range of dissolution rate constants (K) (Table 5.6). It was generally found that the K value decreased with increasing rate of application, and was higher for NCPR than MPR in all comparisons. Reasons for these trends were similar to those discussed in Section 5.4.2.1. It is also evident that, as expected, K values varied from soil to soil. Again, this can be attributed to differences in the soil properties affecting the dissolution process.

The Cubic model did not accurately describe the percentage of PR remaining in soils, particularly at higher rates of application (R^2=0.07-0.65, Table 5.6). Figure 5.4 shows observed and predicted amounts of PR remaining in Tokomaru and Dannevirke soils for the 90-day period at the 500 mg P kg^{-1} application rate. It is clear that the Cubic model did not accurately predicted the amount of PR remaining in soils.

These results suggest that the Cubic model, which uses a single mean dissolution rate constant (K), is of limited use for describing the pattern of PR dissolution in closed soil systems over long incubation periods. For this reason, little confidence can be placed in using the Cubic model to investigate the relationship between various soil properties and PR dissolution.

Predicted K values for separate 10 day intervals

The Cubic model was used to calculate K values at 10 day intervals during the first 40 days of incubation. Using multiple values of K of 10 day intervals (Table 5.7), the model explanied the amounts of PR remaining in soils (R^2 values greater than 0.95).

The calculated K values (only for K_1, K_2 and K_4; Table 5.7) progressively decreased with increasing time of dissolution ($K_1>K_2>K_4$). Under the closed system it was expected that the dissolution rate would decrease with increasing contact time between PR and soil. As described earlier, the activity of Ca in soil solution increases as the PR continues to dissolve thus slowing PR dissolution. As different K values were required for each soil and time period before the Cubic model could give a reasonable description

Table 5.6 The least square fitted K values for NCPR and MPR over 90 days incubation period.

Soil	Rate	K (μg P cm^{-2} day^{-1})	
	(mg P kg^{-1} soil)	NCPR	MPR
Tokomaru	250	5.2 (0.90)[a]	2.8 (0.85)
	500	3.8 (0.90)	2.1 (0.53)
	1000	2.2 (0.26)	1.9 (0.07)
Dannevirke	250	7.3 (0.68)	5.3 (0.65)
	500	6.5 (0.71)	4.7 (0.56)
	1000	5.5 (0.65)	3.9 (0.28)
Ramiha	250	6.6 (0.58)	4.7 (0.41)
	500	5.8 (0.63)	4.4 (0.34)
	1000	4.8 (0.38)	3.8 (0.15)
Sembawa	250	21.3 (0.46)	10.5 (0.27)
	500	12.5 (0.40)	8.7 (0.26)
	1000	7.6 (0.25)	5.8 (0.15)
Prabumulih	250	15.9 (0.73)	10.1 (0.28)
	500	12.5 (0.53)	8.5 (0.30)
	1000	8.3 (0.19)	7.2 (0.18)
Lubuk Linggau	250	14.4 (0.65)	10.4 (0.60)
	500	11.0 (0.77)	9.0 (0.63)
	1000	7.9 (0.35)	7.2 (0.34)

[a] Figure in brackets are R^2 values.

Table 5.7 K values (μg P cm^{-2} day^{-1}) for NCPR and MPR predicted during the first (K_1), second (K_2) and fourth (K_4) 10 day intervals.

Soil	PR	Application rate (mg P kg^{-1} soil)	Interval (days)*		
			0-10	10-20	30-40
Tokomaru	NCPR	250	7.58	6.31	4.25
		500	5.50	4.59	2.59
		1000	6.19	3.35	0.50
	MPR	250	4.52	3.56	1.75
		500	4.93	3.15	0.79
		1000	5.95	2.78	0.29
Dannevirke	NCPR	250	14.6	10.4	3.27
		500	12.6	9.12	3.03
		1000	11.3	7.88	2.42
	MPR	250	10.9	7.53	3.44
		500	10.6	6.89	1.74
		1000	10.8	5.96	0.89
Ramiha	NCPR	250	14.4	9.71	2.50
		500	12.3	8.39	3.65
		1000	12.3	7.19	1.25
	MPR	250	11.8	7.04	1.33
		500	11.6	6.60	1.10
		1000	11.4	5.68	0.62

*The R^2 values of the linear regression between the observed and predicted amount of PR remaining in soil is greater than 0.95.

Table 5.7 (contd)

Soil	PR	Application rate (mg P kg^{-1} soil)	Interval (days)		
			0-10	10-20	30-40
Sembawa	NCPR	250	44.5	25.9	2.96
		500	31.0	17.9	2.48
		1000	28.9	9.16	0.21
	MPR	250	36.1	15.7	0.51
		500	27.9	11.8	0.66
		1000	19.9	5.93	0.14
Prabumulih	NCPR	250	28.9	21.3	6.53
		500	27.9	17.9	3.57
		1000	24.3	12.2	1.16
	MPR	250	28.2	15.2	1.81
		500	23.1	12.7	1.65
		1000	21.2	10.8	1.11
Lubuk Linggau	NCPR	250	28.9	19.9	5.04
		500	19.5	14.7	5.45
		1000	20.8	11.8	1.73
	MPR	250	22.1	14.8	3.72
		500	19.0	13.0	3.54
		1000	19.1	10.8	1.64

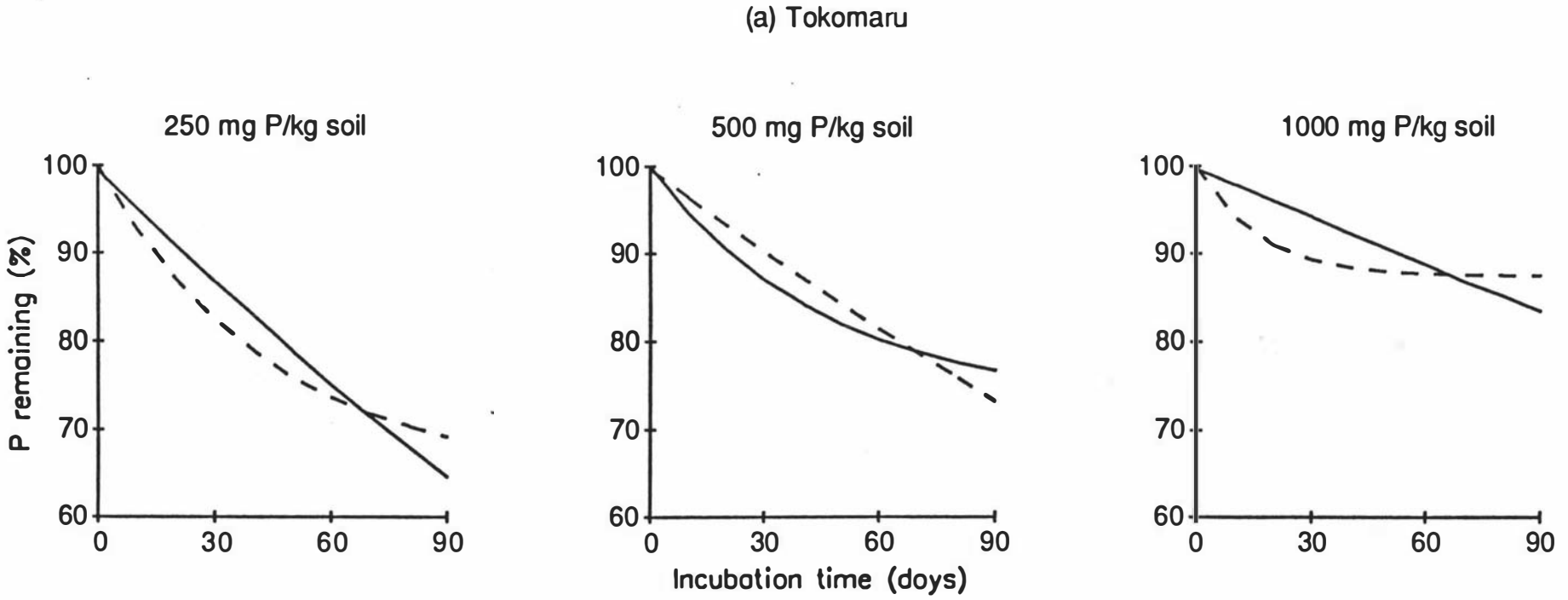
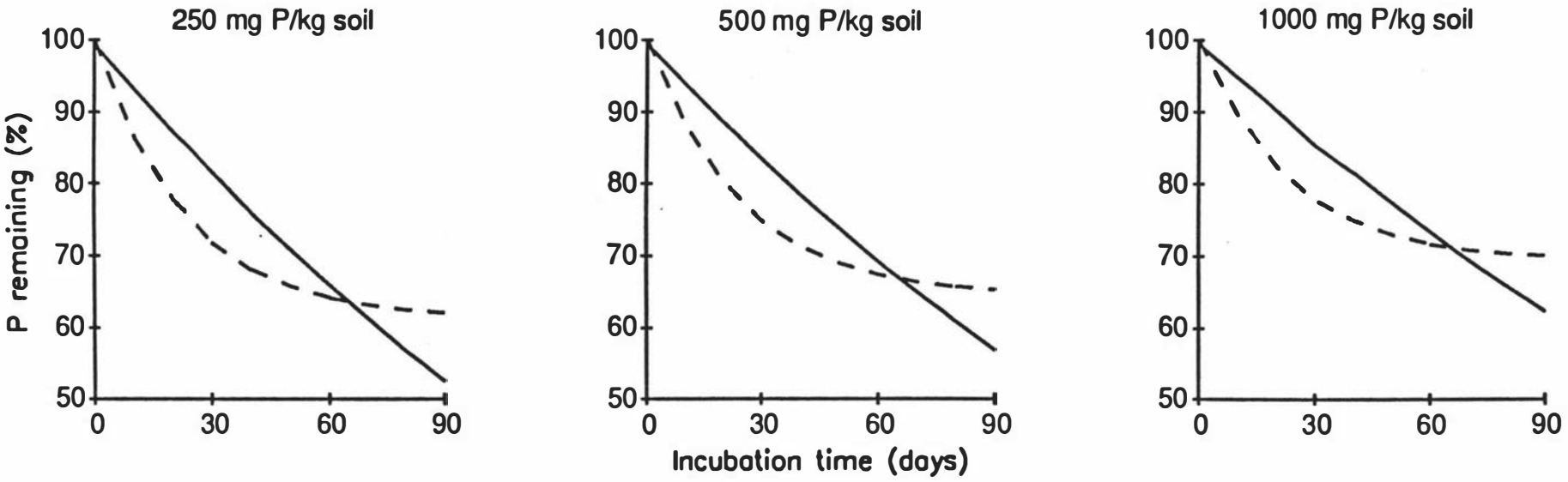


Figure 5.4 Measured (--) and predicted (–) NCPR-P remaining in (a) Tokomaru and (b) Dannevirke soils using the Cubic model. NCPR was applied at rates equivalent to 250, 500 and 1000 mg P kg^{-1} soil.

(b) Dannevirke (Fig. 5.4)



of PR dissolution, the zero order kinetics assumed in this model are not appropriate for the incubation system used.

Results of a simple correlation analysis between soil properties and the K values presented in Table 5.8 show that the K values for the first 10 day interval (K_1) were negatively correlated with both soil pH (r=0.84-0.90) and exchangeable Ca (r=0.80-0.88).

Both simple and multiple regression analysis indicated that none of the soil properties measured were well correlated with the K values predicted for the fourth 10 day interval (K_4), suggesting that at this stage dissolution was probably limited by other factors such as the accumulation of dissolution products and their subsequent diffusion across the PR particle-soil interface.

The results reported above are consistent with the view that dissolution of PR in soil is initiated by the acidity in a soil (Khasawneh and Doll, 1978). At the same time dissolution is also controlled by the activity of Ca in soil solution, which in turn is controlled by exchangeable Ca (Robinson and Syers, 1991). As indicated by the poor relationship between K_1 and percent Ca saturation, the initial PR dissolution rate did not appear to be limited by the size of the Ca sink.

5.4.2.3 Kirk and Nye model

The Kirk and Nye model requires various input parameters to describe soil characteristics (Section 5.3.4.3). The accuracy of the model is very sensitive to the precision with which soil pH is measured (Kirk and Nye, 1985a). Also the selection of the electrolyte in which soil pH is measured becomes extremely important. Electrolyte form and ionic strength should reflect the solution of the soil being studied.

Initial soil pH

Kirk and Nye (1985b) measured the initial soil pH in 0.001 M $CaCl_2$ (μ=0.003) to

Table 5.8 Correlation coefficients (r) for the relationships between soil properties* and PR dissolution rate constant (K) predicted in the first (K_{10}) and fourth 10 day intervals.

Interval K	P Source	Rate	pH_{H2O}	Org.C	P retn.	TA	Exch. Ca	CEC	Ca sat.
		mg P kg^{-1}		(%)		cmol (+) kg^{-1}			(%)
K_1	NCPR	250	-0.84*	-0.23	-0.14	-0.28	-0.85*	-0.54	-0.78
		500	-0.88*	-0.06	-0.06	-0.56	-0.85*	-0.47	-0.76
		1000	-0.86*	-0.01	-0.08	-0.12	-0.87*	-0.52	-0.79
	MPR	250	-0.89*	-0.15	-0.05	-0.17	-0.86*	-0.52	-0.76
		500	-0.90*	-0.21	-0.10	-0.24	-0.80*	-0.49	-0.75
		1000	-0.84*	-0.07	-0.01	-0.09	-0.88*	-0.51	-0.81*
K_4	NCPR	250	-0.12	-0.04	-0.03	-0.16	-0.61	-0.58	-0.23
		500	-0.21	-0.41	-0.02	-0.32	-0.28	-0.08	-0.43
		1000	-0.64	-0.61	-0.78	-0.70	-0.19	-0.59	-0.29
	MPR	250	-0.72	-0.45	-0.35	-0.34	-0.08	-0.17	-0.15
		500	-0.32	-0.38	-0.24	-0.27	-0.38	-0.13	-0.45
		1000	-0.28	-0.57	-0.45	-0.51	-0.34	-0.03	-0.46

*Org.C:organic C; P retn.:P retention capacity; TA:titratable acidity; Exch. Ca:exchangeable Ca; Ca sat.:Ca saturation. *Significant at $P<0.05$.

approximate the ionic strength of soil solution in their studies. In the present study, given the diversity of soils used, 0.001 M $CaCl_2$ may not be appropriate. Also, under a closed incubation system where products are not removed, the ionic strength would be expected to change as a result of mineralisation of organic matter (Ottabong, 1983). Because the pH of variable-charge soils is so dependent on the strength and type of electrolyte used, an attempt was made to estimate the ionic strength of the soil solution as it varies during incubation. A novel sequential leaching technique was employed to follow changes in soil solution ionic strength under laboratory incubation conditions.

The results of this investigation showed that whereas initial ionic strengths of leachate ranged from 0.005 to 0.019 (Figure 5.5), the values decreased sharply as incubation progressed to day 4 and remained essentially constant until day 28. Only after day 28 did the ionic strength tend to increase again. During the 36-day of incubation period, the ionic strength of the leachate averaged 0.015, 0.011, 0.008, 0.003, 0.003 and 0.006 for Tokomaru, Dannevirke, Ramiha, Sembawa, Prabumulih and Lubuk Linggau soils, respectively. Appropriate strengths of the $CaCl_2$, in which the initial pH was measured, were then selected based on the these "averaged" values. Soil pH values varied with the ionic strengths of $CaCl_2$ used (Table 5.9).

Prediction of PR dissolution in soils

The model was used to simulate the dissolution of PRs over 90 days in all soils under laboratory incubation conditions. Input parameters required to test the model for each soil are shown in Table 5.10.

With increasing time, the extent of PR dissolution predicted by the model showed a curvilinear form (Figure 5.6). The predicted PR dissolution decreased with increasing rate of application. Within experimental error (±10%), the model predicted the dissolution of PRs in all soils reasonably well, particularly during the first 30 days. Under-predictions of PR dissolution were, however, observed after 30 days, especially at the highest PR application rates.

Relationships between predicted and measured dissolution of NCPR and MPR by the

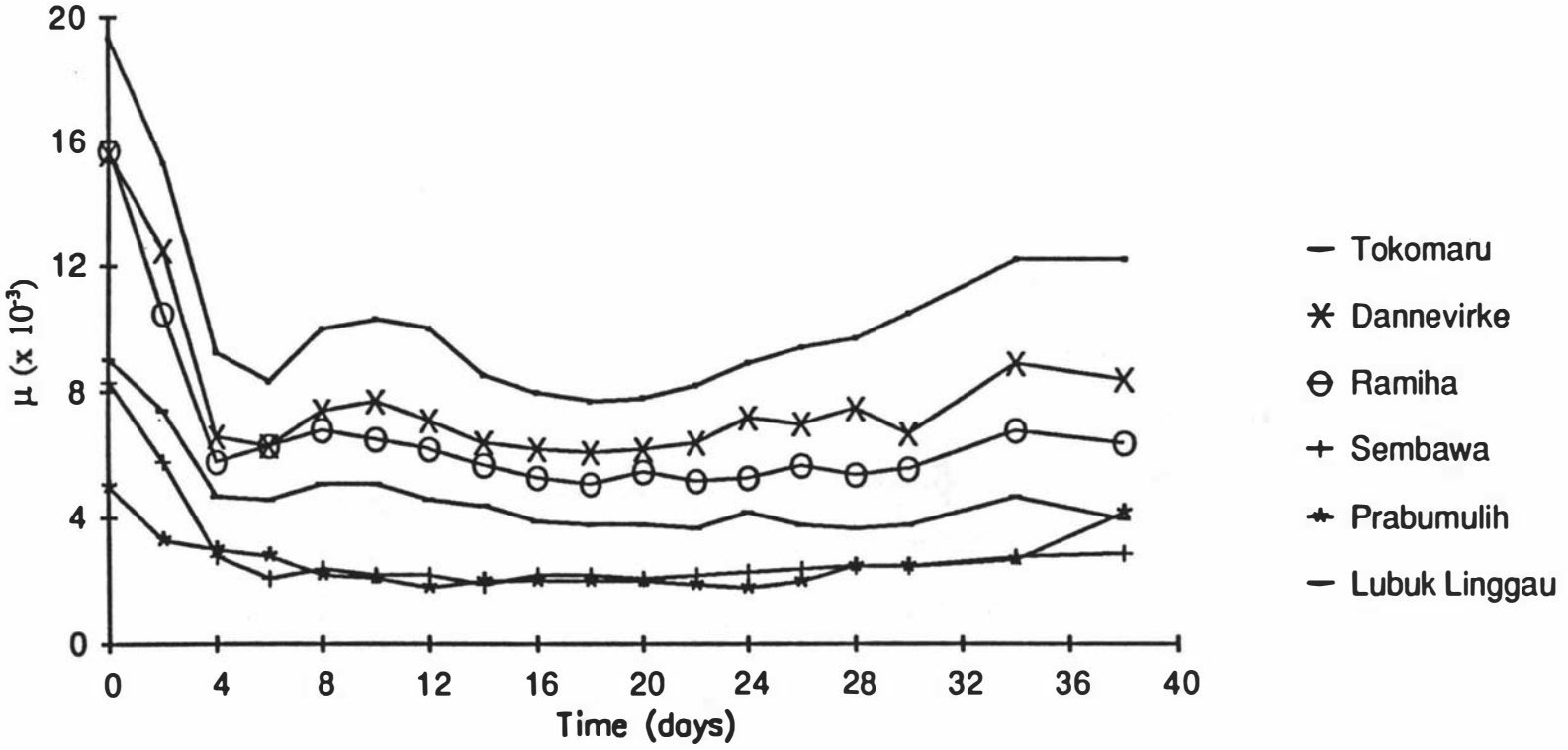


Figure 5.5 Changes in ionic strength (μ) of leachate over time measured after leaching the soil columns.

Table 5.9 Soil pH measured in $CaCl_2$ solution of differing ionic strength (μ).

Soil	Ionic strength (μ) of $CaCl_2$ solution							
	0.030	0.021	0.018	0.015	0.012	0.009	0.006	0.003
Tokomaru	4.76	-	-	4.81*	-	-	-	5.24
Dannevirke	4.75	-	-	-	4.83*	4.95	-	5.19
Ramiha	4.58	4.62	4.68	-	-	4.81*	4.89	4.91
Sembawa	3.97	-	-	3.98	-	4.04	4.29	4.59*
Prabumulih	4.27	-	4.26	4.29	-	-	4.34	4.62*
Lubuk Linggau	4.34	-	4.40	4.44	-	4.47	4.49*	4.78

*Values of pH at an μ close to an estimated "average" μ of each soil solution measured in the leaching study (Figure 5.5).

Table 5.10 Values of input parameters used in Kirk and Nye simulation.

Soil	Input parameters*									
	w**	θ	f	ρ_b	pH'	C_L'	$[Ca^{2+}]L'$	a	b	b_{HS}
Tokomaru	0.32-1.28	0.35	0.27	1.28	4.79	0.0000020	0.0016	0.50	0.62	0.037
Dannevirke	0.21-0.84	0.42	0.23	0.84	4.83	0.0000008	0.0020	2.94	0.70	0.067
Ramiha	0.19-0.76	0.37	0.17	0.76	4.68	0.0000020	0.0010	2.29	0.67	0.11
Sembawa	0.28-1.10	0.30	0.19	1.10	4.59	0.0000030	0.0015	1.71	0.65	0.04
Prabumulih	0.25-0.99	0.42	0.27	0.99	4.52	0.0000009	0.0010	2.08	0.62	0.066
Lubuk Linggau	0.20-0.81	0.38	0.19	0.81	4.45	0.0000010	0.0010	0.96	0.59	0.051

* Symbols and units of each parameter are given in Section 5.3.4.3.

** Application rates (w) of NCPR and MPR, with A_i=0.001 dm, are equivalent to 250 to 1000 mg P kg^{-1} soil.

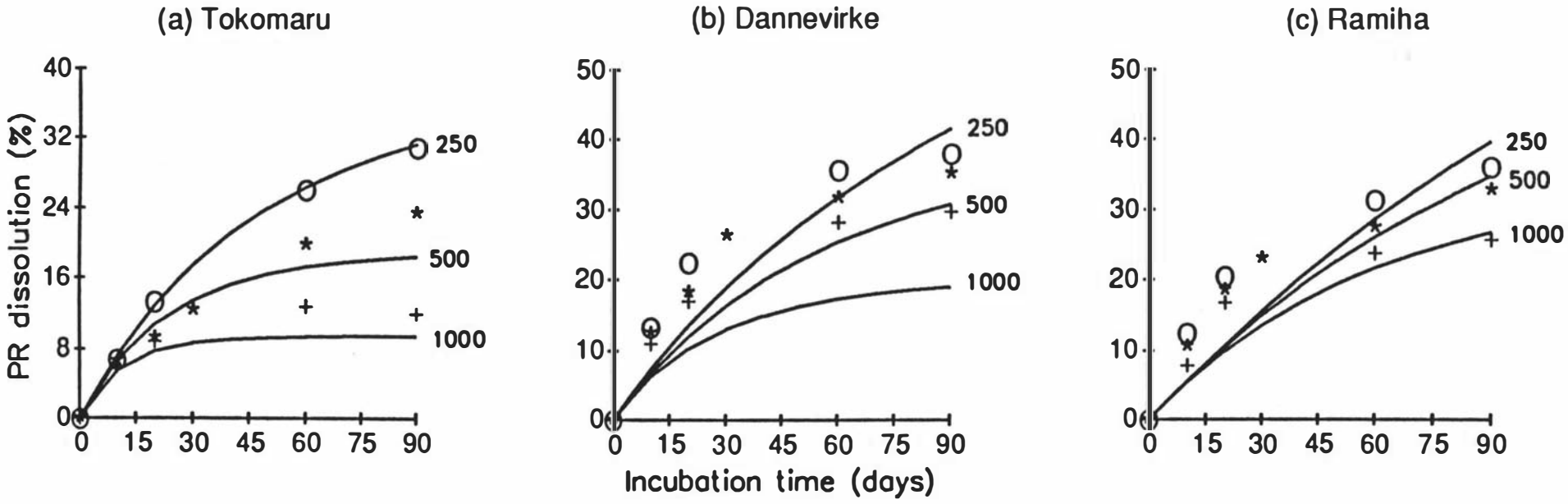
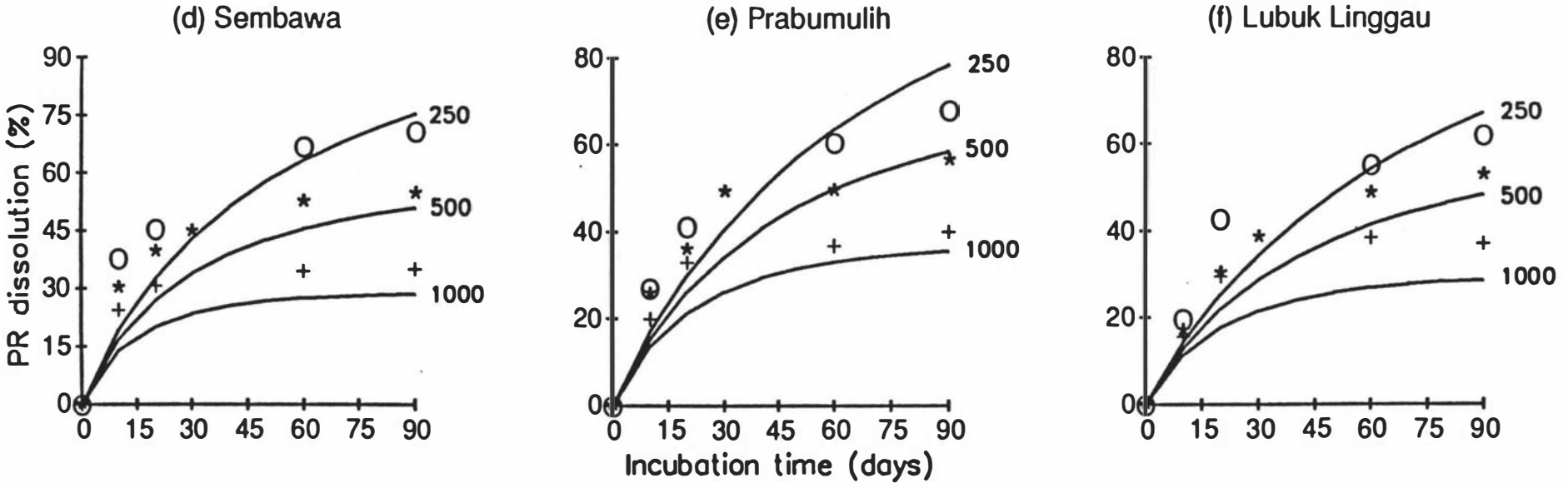


Figure 5.6 Measured and predicted NCPR dissolution in soils using Kirk and Nye model. NCPR was applied at rates equivalent to (o) 250, (*) 500 and (+) 1000 mg P kg^{-1} soil.

(Fig. 5.6)


(d) Sembawa
(e) Prabumulih
(f) Lubuk Linggau
PR dissolution (%)
Incubation time (days)
250
500
1000
0
15
20
30
40
45
60
75
80
90

Kirk and Nye model in Tokomaru and Sembawa soils are shown in Figure 5.7 (for the sake of brevity relationships for Dannevirke, Ramiha, Prabumulih and Lubuk Linggau soils are not presented). The variation in observed data explained by the dissolution predicted by the Kirk and Nye model was tested by examining the goodness of fit of a 1:1 relation of the the following form:

$$y=x \qquad (5.22)$$

where y=observed PR dissolution (%); and x=predicted PR dissolution (%).

The accuracy of the Kirk and Nye model for predicting PR dissolution was similar for most soils. The model gave the best prediction at lower application rates. With increasing application rates, the model tended to under-predict the PR dissolution and the regression lines deviated from the 1:1 target line.

The accuracy of the Kirk and Nye model for predicting extent of PR dissolution obviously depends in part on the accuracy with which the input parameters are measured. To show this, a sensitivity analysis of the model was carried out.

Sensitivity analysis

Dissolution of NCPR was simulated in Dannevirke soil by independently varying soil input parameters. This technique allowed the importance of an individual soil property to be examined. The dissolution of NCPR at an application rate (w) of 250 mg P kg^{-1} (0.2105 kg P m^{-3}) soil was simulated for a 90 day incubation period. Standard input parameters used for Dannevirke soil in the sensitivity analysis are shown in Table 5.10.

Initial soil solution P concentration

Although the dissolution reaction of PR (Equation 2.1) indicates that P concentration in soil solution may affect PR dissolution, the simulation shows that varying P concentration in the soil solution (by ±10%) had a negligible effect on NCPR dissolution (Figure 5.8a). The concentration of P in the solution of most soils is so small compared to the concentration of P on the PR surface as to have no major effect on PR dissolution.

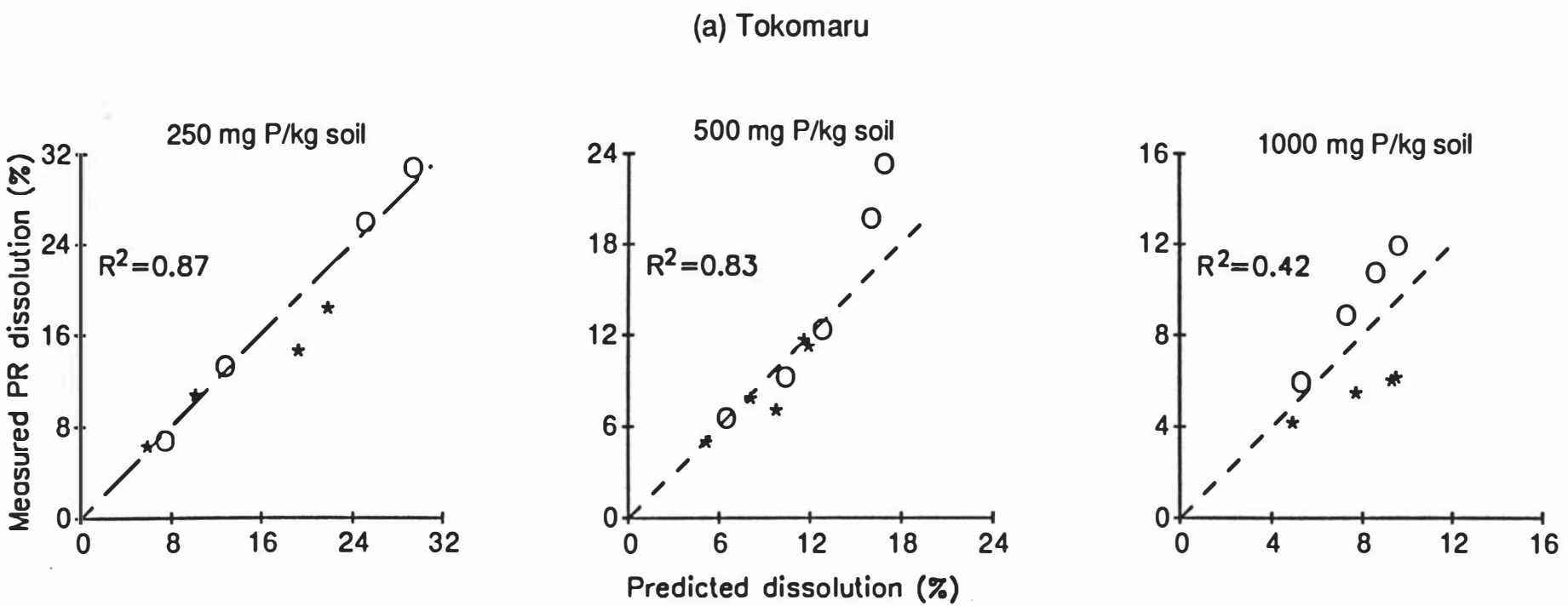
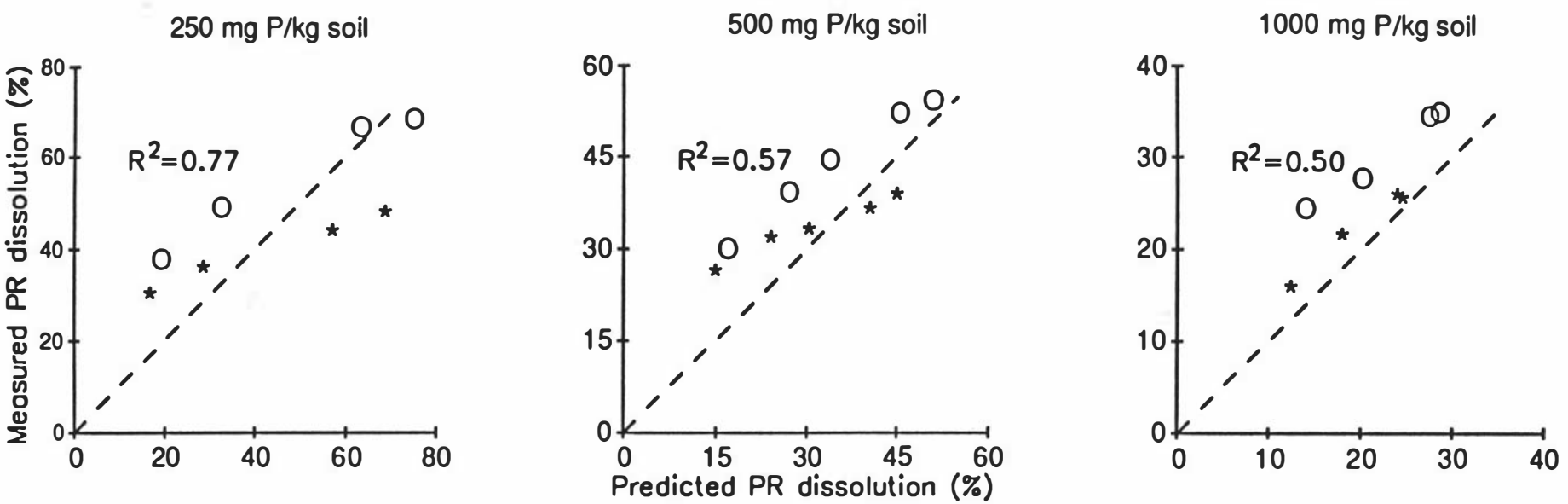


Figure 5.7 The variation in measured dissolution of NCPR (o) and MPR (*) explained (R^2) by the dissolution predicted using the Kirk and Nye model in (a) Tokomaru and (b) Sembawa soils. The PRs were applied at rates equivalent 250 to 1000 mg P kg^{-1} soil. Dotted lines indicate theoretical 1:1 relationships.

(b) Sembawa (Fig. 5.7)



Initial soil pH

The model shows that PR dissolution was highly dependent on the initial soil pH (Figure 5.8b). Increasing soil pH (measured in $CaCl_2$ solution with the ionic strength of 0.012) by 0.05, 0.1, and 0.24 unit decreased the NCPR dissolution by 5, 9 and 19%, respectively, while a decrease in soil pH by 0.05, 0.1 and 0.24 increased dissolution by 4, 9 and 37%, respectively. These results indicate the potential importance of soil pH as a parameter in the Kirk and Nye model.

Initial calcium concentration

Changing the value of initial Ca concentration by ±10% did not cause any major change in NCPR dissolution (Figure 5.8c). Hence the initial Ca concentration in soil solution does not appear to be an important factor controlling the PR dissolution in this soil. However, it should be noted that total Ca concentration in soil solution can show considerable variation. For example, a range of 0 to 0.009 M has been reported in acid soils of the South Pacific area (Naidu and Haynes, 1991). Concentrations of Ca in soil solution increase with use of fertilizers and lime (Edmeades *et al.*, 1985; Naidu and Haynes, 1991; Shamshuddin *et al.*, 1991).

The range of the expected concentration of Ca in solution is much wider than that of phosphate. Where large differences in initial concentration of Ca occur, effects on PR dissolution warrant consideration. For example, a decrease in Ca concentration from 0.002 M to 0.001 M produced a 5% increase in simulated NCPR dissolution (Figure 5.8c).

Phosphate adsorption capacity (Freundlich *a*)

Smyth and Sanchez (1982) and Kanabo and Gilkes (1987b) have noted the importance of P adsorption capacity. Results presented in Figure 5.8d, however, show that varying the value of *a* by ±10% did not produce any major change in NCPR dissolution. Dannevirke soil does however possess a relatively high inherent P sorption capacity.

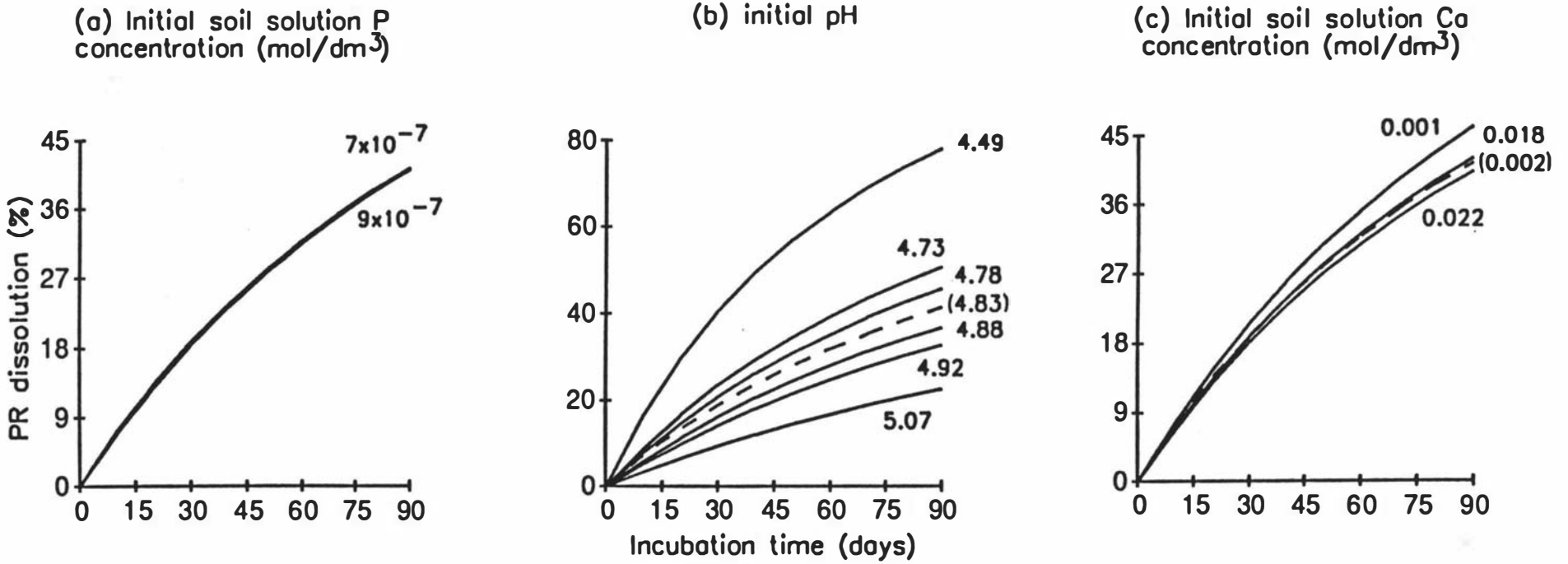
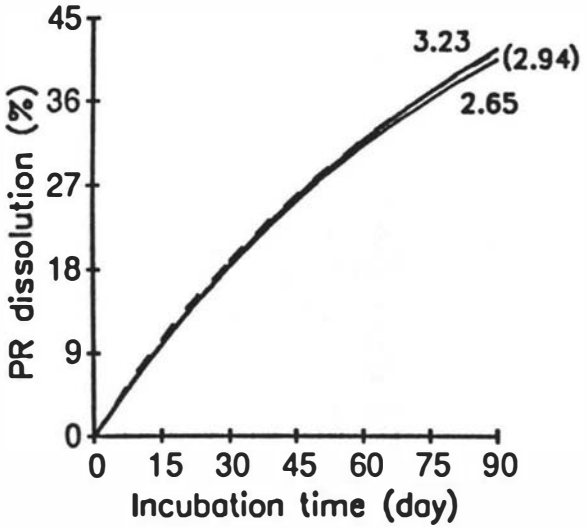
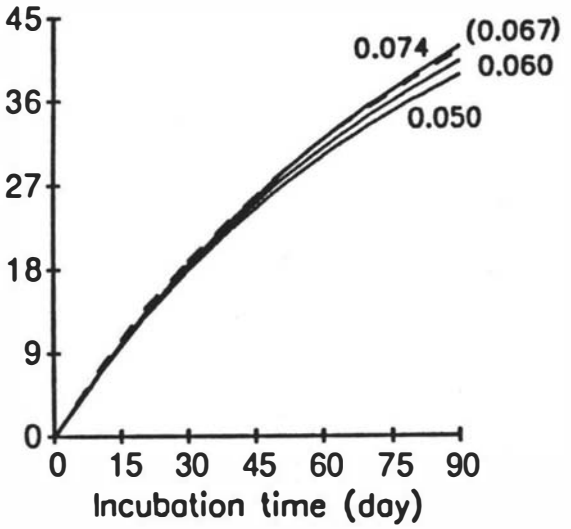


Figure 5.8 Sensitivity analysis showing the effect of changing soil input parameters on the predicted NCPR dissolution [applied at a rate equivalent to 250 mg P kg^{-1} soil (0.2105 kg P m^{-3})] in Dannevirke soil. Bracketed values are unadjusted input parameters.

(d) Phosphate adsorption
(a coefficient, mol P/dm^3)



(e) pH buffering capacity
(mol OH^-/kg soil/pH)



Soil pH buffer capacity

Although the model gave an increased PR dissolution with an increase in soil pH buffer capacity (b_{HS}), the extent of NCPR dissolution predicted in the present soil was not very sensitive to changes in pH buffer capacity values. A large decrease (25%) in pH buffer capacity decreased NCPR dissolution by only 3% (Figure 5.8e). Variations in pH buffer capacity influenced PR dissolution more in soils with lower pH buffer capacity values, such as Tokomaru (b_{HS}=0.037). Soils with low pH buffer capacity are generally less able to neutralize the base released, from the PR, during the dissolution process. The importance of pH buffer capacity becomes apparent in later stages of PR dissolution where the concentration gradient of H^+ around PR particle surface becomes smaller (Kirk and Nye, 1986a).

The importance of pH buffer capacity on PR dissolution has implications for slightly acid soils with high organic matter content, or those that receive regular organic matter additions. In such soils, proton dissociation from acidic functional groups in the organic component contributes substantially to pH buffering capacity (Bache, 1985) and thereby enhances PR dissolution.

5.5 GENERAL DISCUSSION AND CONCLUSIONS

The use of simple and complex dissolution models has enabled soil properties affecting PR dissolution in a range of New Zealand and Indonesian soils to be identified. The maximum extent of PR dissolution in a closed system can be adequately described by a modified Mitscherlich equation. The maximum extent of PR dissolution in the soils studied was found to be negatively correlated to initial amounts of exchangeable soil Ca and percent Ca saturation. This suggests that the size of Ca sinks seems to be a very important factor affecting PR dissolution under closed incubation conditions.

The Cubic model, which allows PR dissolution to be expressed in terms of a single rate constant (K), could not adequately explain the extent of PR dissolution measured in this series of experiments. If K is allowed to decrease with time then the model may be better be able to describe the dissolution results. The initial rate of PR dissolution

during the first 10 days (K_{10}) predicted by the Cubic model appeared to be more influenced by initial soil pH (measured in H_20) and exchangeable Ca than by other soil chemical properties. Soil pH, which is a measure of "active" soil acidity, is the driving force for initial PR dissolution as expected from the stoichiometric equation which describes the PR dissolution process (Equation 2.1).

The mechanistic model of Kirk and Nye, which takes into account many of the important soil and PR properties thought to control PR dissolution, adequately predicted the extent of PR dissolution in the soils used in this study, particularly at low application rates (equivalent to 250 mg P kg^{-1} soil). A sensitivity analysis demonstrated that, when soil moisture is not limiting, differences between simulated and observed PR dissolution can be attributed to problems in determining initial soil pH. Obviously it is important to obtain an accurate measure of soil pH when using this model.

The Kirk and Nye model has the potential to be extended to allow modelling of PR dissolution in environments where moisture content is not held constant. Thus it could be tested in a wide range of field and laboratory situations. In fact this model has been used to simulate PR dissolution under field condition using data from a field experiment in Indonesia. The results are reported in Chapter 9.

CHAPTER 6
THE AVAILABILITY OF PHOSPHORUS IN SOILS FERTILIZED WITH MONOCALCIUM PHOSPHATE AND PHOSPHATE ROCK

6.1 INTRODUCTION

Although dissolution is a prerequisite for phosphorus (P) in a phosphate rock (PR) to become available for plant uptake, increased dissolution may not necessarily result in an increase in plant-available P (Syers and Mackay, 1986). This is because some soil properties which induce dissolution of PR (e.g. low pH and high P adsorption) also promote adsorption of dissolved P and thereby decrease its availability to plants. Syers and Mackay (1986), Kanabo and Gilkes (1987a) and Bolan *et al.* (1990) have shown that only a small fraction (9-15%) of P dissolved from PR may in fact remain available for plant uptake in some soils, and hence the amount of P dissolved from PR can not be taken as a true estimate of plant-available P.

The results in Chapter 3 provide information on the extent of PR dissolution in a range of New Zealand soils varying in pH and exchangeable Ca content. The extent of PR dissolution in New Zealand and Indonesian soils, as affected by its reactivity and rate of application, was discussed in Chapter 5. It is of greater agronomic value to determine how the dissolution of PR in both studies changes the subsequent availability of P.

To date, a number of soil tests have been developed to estimate the size of plant available soil P. For example, 0.5 M $NaHCO_3$ has been used successfully in New Zealand (Saunders *et al.*, 1987) and Australia (Colwell, 1963) to predict the amount of P available to plants in soils fertilized with soluble P fertilizers. In tropical soils, acid extractants, such as Bray 1 and Bray 2, are commonly used. In soils fertilized with water-insoluble P fertilizers, however, such methods may be less accurate for estimating plant-available P. For example, Saggar *et al.* (1991b) found that Olsen test was less successful in predicting plant response in New Zealand soils fertilized with PRs than a resin extractant procedure.

It has been suggested by Hammond *et al.* (1986), Bolland *et al.* (1988) and Rajan *et al.* (1991b) that separate calibrations are required for soils fertilized with different types of P fertilizers, especially those varying in water-solubility. Thus more research is still needed to examine suitable soil P tests for use in soils fertilized with PR.

The new resin-membrane P (resin P) test for extracting soil P (Saggar *et al.*, 1990) has shown promise although the test has been limited so far to a narrow range of soils. In this section a comparison is made of the effectiveness of this new test with the more conventional soil tests, including Olsen (Olsen *et al.*, 1954) and Bray 1 (Bray and Kurtz, 1945), for extracting soil P from New Zealand and Indonesian soils fertilized with PR.

6.2 OBJECTIVE

The objective of this study was to examine the influence of soil chemical characteristics on the potential availability of P from monocalcium phosphate and phosphate rock.

6.3 MATERIALS AND METHODS

6.3.1 Experiment 1

In this experiment, the effects of PR and MCP additions on extractable soil P were examined using three New Zealand soils. The soils were adjusted to different pH and exchangeable Ca levels for this evaluation. The relationship between plant response to P fertilizers and extractable soil P was also investigated.

6.3.1.1 Soils and P fertilizers

Tokomaru silt loam, Dannevirke silt loam and Tihoi sand were the three soils used in this study. Some properties of these soils and are given in Chapter 3 (Table 3.1). The pH of each soil was adjusted to four different levels as described in Section 3.3.2. The range of adjusted pH values is given in Chapter 3 (Table 3.4).

"As received" North Carolina Phosphate Rock (NCPR) and analytical reagent grade monocalcium phosphate (MCP) were used as the two P fertilizers. Some relevant properties of NCPR are given in Chapter 3 (Table 3.2).

6.3.1.2 Incubation of soil and P fertilizer

Soil and P fertilizer (400 mg P kg^{-1} soil) mixtures were incubated as described in Chapter 3 (Section 3.3.2.3). Sub-samples were withdrawn 30 days after incubation and passed through a 2 mm sieve prior to being used in pot experiment or chemical analyses. The remaining samples were left to incubate for further 50 days.

6.3.1.3 Pot experiment

A pot experiment (Stanford and Dement, 1957) was carried out to assess the plant availability of dissolved fertilizer-P. For this purpose, 13 g (air dried) of the 30-day incubated soils were used. Each treatment was replicated three times. Approximately 40 seeds of perennial ryegrass (*Lolium perenne* var. Hewett) were sown in plastic pots (100 mm in diameter, 6 mm deep) containing 300 g washed river sand (150-500 μm portions). Pots were watered twice daily to approximately 80% of saturation water capacity of the sand. A minus-P nutrient solution (Smith *et al.*, 1983) was applied three times each week. After three weeks the herbage was cut 50 mm above the sand surface and the dense mat of root was brought into contact with another pot containing 13 g of pH amended and/or fertilized soil samples.

Watering with minus-P solution was continued until harvest. After 45 days, plant-tops were harvested and the roots in the sand medium were collected and washed with tap, and then distilled water. Shoots and roots for each treatment replicate were combined and dried at 65°C for 48 h before being ground to <1 mm particle size in a Wiley mill.

6.3.2 Experiment 2

In this experiment, the availability of P dissolved from PRs was examined using a range of New Zealand and Indonesian soils. The ability of different soil P tests to extract P from these PR- fertilized soils was investigated.

6.3.2.1 Soils and PRs

Four surface (0-75 mm) soils, two from New Zealand (Tokomaru silt loam and Ramiha silt loam) and two from Indonesia (Sembawa silt loam and Prabumulih sandy loam) were used in this study. Some properties of the soils are given in Chapter 4 (Table 4.1).

A reactive North Carolina phosphate rock (NCPR) and a medium reactive Moroccan phosphate rock (MPR) were used as P sources. The PRs were sieved (150-250 μm) before use. Some properties of the PRs are given in Chapter 5 (Table 5.1).

6.3.2.2 Incubation of soil and PR

Soil samples (8 g) were thoroughly mixed with PR at rates of 250, 500 and 1000 mg P kg^{-1} soil. Details of the incubation and sampling procedures are described in Chapter 5 (Section 5.3.3).

6.3.3 Soil solution extraction

Soil samples pre-incubated with PR for 60 days (Experiment 2, Section 6.3.2.2) were used for extracting soil solutions according to procedure described in Section 5.3.5. Soil solutions were analyzed for inorganic P (Pi) using the Murphy and Riley method described in Chapter 3 (Section 3.3.3).

6.3.4 Soil analysis

Methods for the measurement of pH, organic C, CEC, exchangeable Ca, P retention capacity and titratable acidity are described in Chapters 3 and 4.

Plant-available P was extracted from incubated soils using various methods. In experiment 1, plant-available P was estimated by the Olsen test (Olsen *et al.*, 1954). In experiment 2, plant-available P was estimated by direct measurement of Pi in soil solution (Section 6.3.3) and by three soil tests, namely Olsen (Olsen *et al.*, 1954), Bray 1 (Bray and Kurtz, 1945) and ion-exchange resin membrane (Saggar *et al.*, 1990). The Olsen method is described in Chapter 3 (Section 3.3.3). The Bray 1 extraction involves extraction of 1 g of soil with 7 ml of Bray solution for 5 minutes (Bray and Kurtz, 1945). After centrifugation (8000 rpm, 5 min) and filtering (Whatman No. 41), P concentrations in the extracts were determined by the method of Murphy and Riley (1962).

Details of the resin extraction procedure were described by Saggar *et al.* (1990). The method involves the following steps:

Preparation of resin membrane strips:

The anion exchange resin (AER) and cation exchange resin (CER) membrane (BDH Chemicals Ltd., England) were prepared by cutting into strips (62.5 mm x 25 mm). The exchange capacity of the AER and CER were 0.19 to 0.20 and 0.24 to 0.26 me of charge per strip, respectively.

Conversion of AER to HCO_3^- form and CER to Na^+ form

The AER and CER were soaked in 0.5 M $NaHCO_3$ and 0.5 M NaCl solution, respectively, and stirred occasionally for 1 hour. This treatment was repeated in fresh solutions for another hour, followed by two washing with deionised water. The resins were stored in deionized water prior to use.

Regeneration of resins

Used resin strips were transferred to a beaker and washed thoroughly, 2 to 3 times, with deionised water. Thereafter the resins were converted to the HCO_3^- or Na^+ form as described above.

Extraction and estimation of P

1 g of soil was shaken for 16 h with 30 ml deionised water in a 50 ml centrifuge tube containing one AER and CER strips. After shaking the AER strip was recovered and

rinsed with deionised water to remove adhering soil or root particle and then transferred to a 150 ml plastic beaker containing 84 ml deionised water. This was followed by addition of 16 ml Murphy and Riley's reagent. The solution was stirred from time to time until the colour was fully developed. The concentration of P in solution was measured at 712 nm with a UV spectrophotometer.

6.3.5 Plant analysis

Total P content of plant samples was determined using Kjeldahl digestion following the autoanalyser method of Twine and Williams (1971).

6.4 RESULTS AND DISCUSSION

6.4.1 Experiment 1

6.4.1.1 Dry matter yield

Yield responses to different P treatments are presented in Figure 6.1. Among P treatments, MCP consistently produced higher dry matter yield than NCPR and control treatments. Only for Tokomaru soil with pH 5.6 did NCPR treatment significantly outyielded the unfertilized control. In Dannevirke and Tihoi soils NCPR produced similar yield as the controls at all pH levels. This lack of response may be due to either limited dissolution of PR or strong adsorption of any dissolved Pi in these soils rendering it unavailable for plant uptake. Soil pH had no significant effect on yield.

6.4.1.2 Plant P uptake

Total P taken up by plants was always higher from P-treated than control soils (Figure 6.2). The P uptake from control soils was essentially independent of soil pH. The uptake of P was significantly higher from MCP-fertilized pots than from control pots for all soils at all pH levels, due mainly to differences in dry matter yield (Figure 6.1). Fertilization with NCPR resulted in significantly higher P uptake compared with the

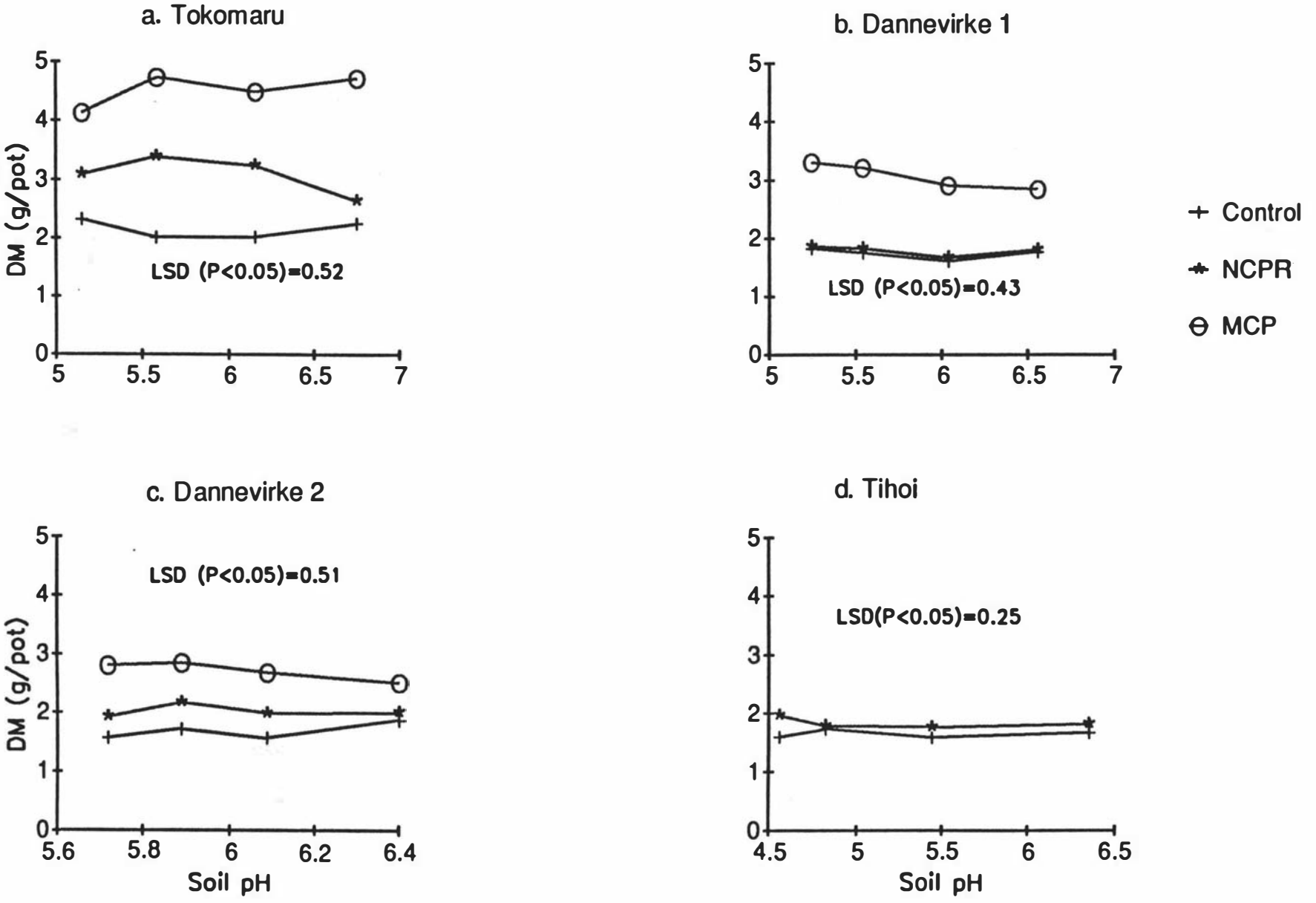


Figure 6.1 Effect of pH on dry matter (DM) yield of ryegrass in soils fertilized with different P sources.

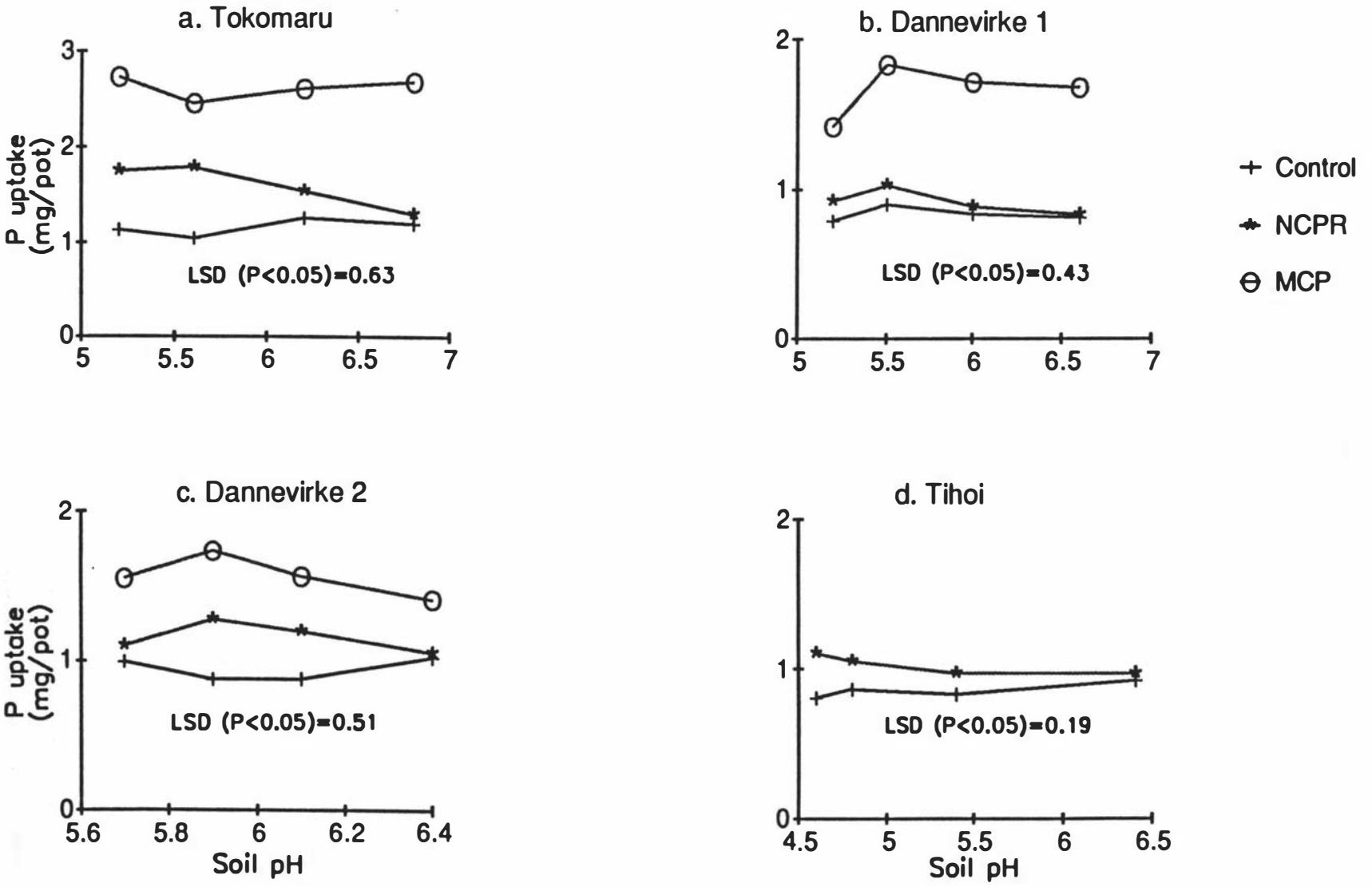


Figure 6.2 Effect of pH on the amount of P taken up by plants from soils fertilized with different P sources.

respective controls, only for Tokomaru soils at the two lowest pH levels (pH 5.2 and 5.6), and for Dannevirke 2 soil at pH 5.9 probably as a result of different extent of PR dissolution and sorption of dissolved P by the soils.

Over the approximate pH range (5.7-5.8 to 6.4-6.5) the amount of P derived from fertilizer (pdf) for NCPR-fertilized soils steadily decreased as pH increased. This was associated with decreased NCPR dissolution (Figure 3.2, Chapter 3). However, at pH's lower than 5.7, pdf for NCPR-fertilized Tokomaru and Dannevirke 2 soils tended to decrease, despite greatest NCPR dissolution occurring in this pH range. These results, in Dannevirke soils, were associated with decreased P uptake of available P in this pH range as evident from similar decreases in the pdf for MCP (Figure 6.3). The reasons for this are either increased sorption of dissolved P at low soil pH (Bolan *et al.*, 1989) or poor plant root growth caused by aluminum toxicity (Alam, 1981).

For the NCPR-treated soils, the decrease in uptake of P with increasing pH tends to confirm the earlier finding of decreased PR dissolution at higher pH's (Figure 3.1, Chapter 3).

6.4.1.3 Olsen-extractable P

The effects of P fertilizer on the amount of Olsen-extractable P (Olsen-P) in soils after 30 and 80 days of incubation are shown in Figure 6.4. Irrespective of soil pH, higher amounts of Olsen-P were found in soils treated with MCP than NCPR. In general, the amounts of Olsen-P decreased with increasing soil pH except in Tokomaru soil treated with MCP. Amounts of Olsen-P found in PR-fertilized soils, at low pH, were significantly higher than in the control soils.

In both Dannevirke soils, the amounts of Olsen-P tended to decrease as the contact time between soil and MCP increased from 30 to 80 days. Prolonged contact between the soil and MCP probably increased adsorption of P from MCP and reduced the amount of readily-available P (Cabala-Rosand and Wild, 1982). It was evident without replotting the figures that the difference (ΔOlsen-P) in Olsen-P values between MCP-

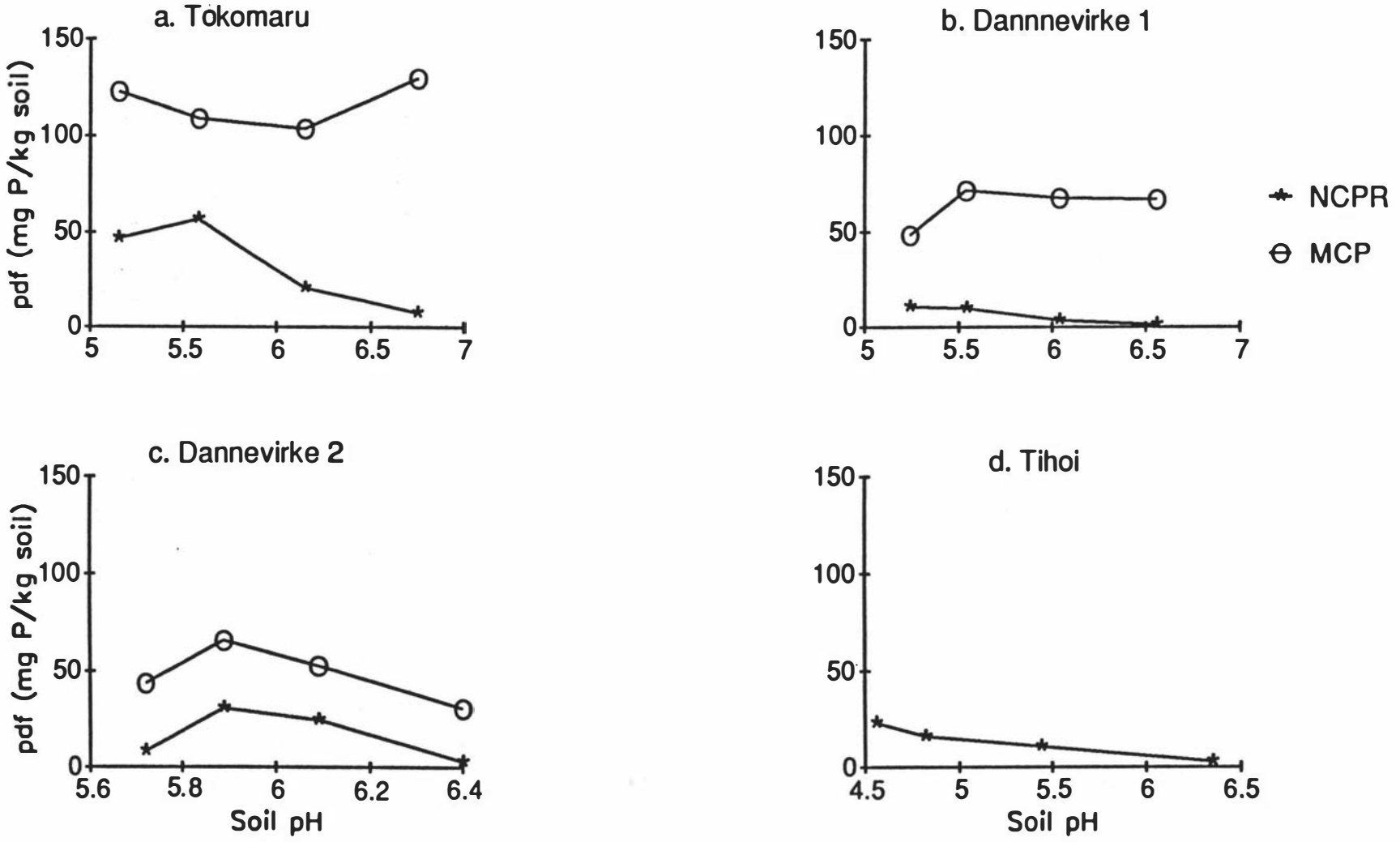


Figure 6.3 Effect of pH on the amount of P derived from P fertilizer taken up by plants (pdf) in soils fertilized with different P sources.

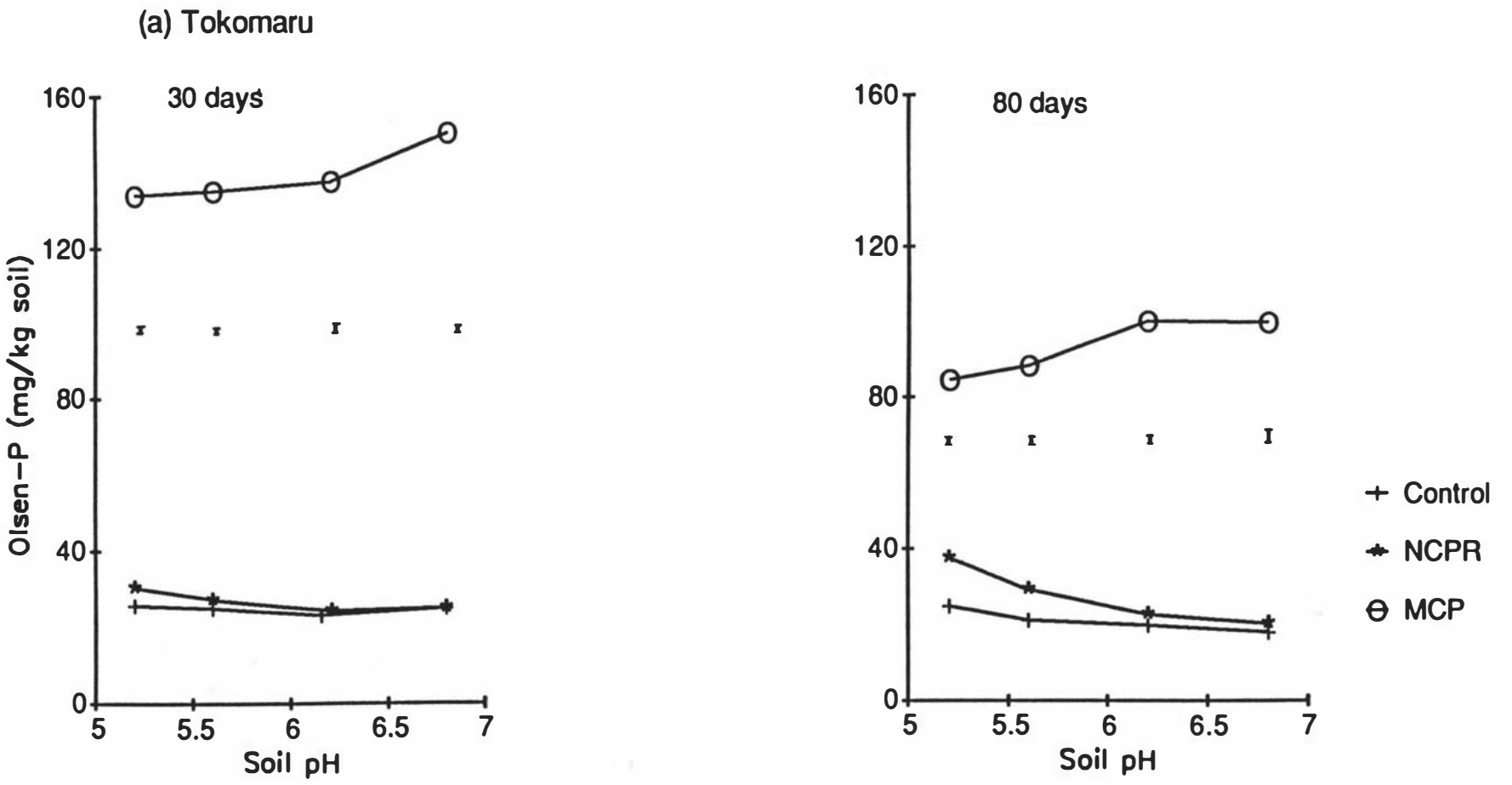
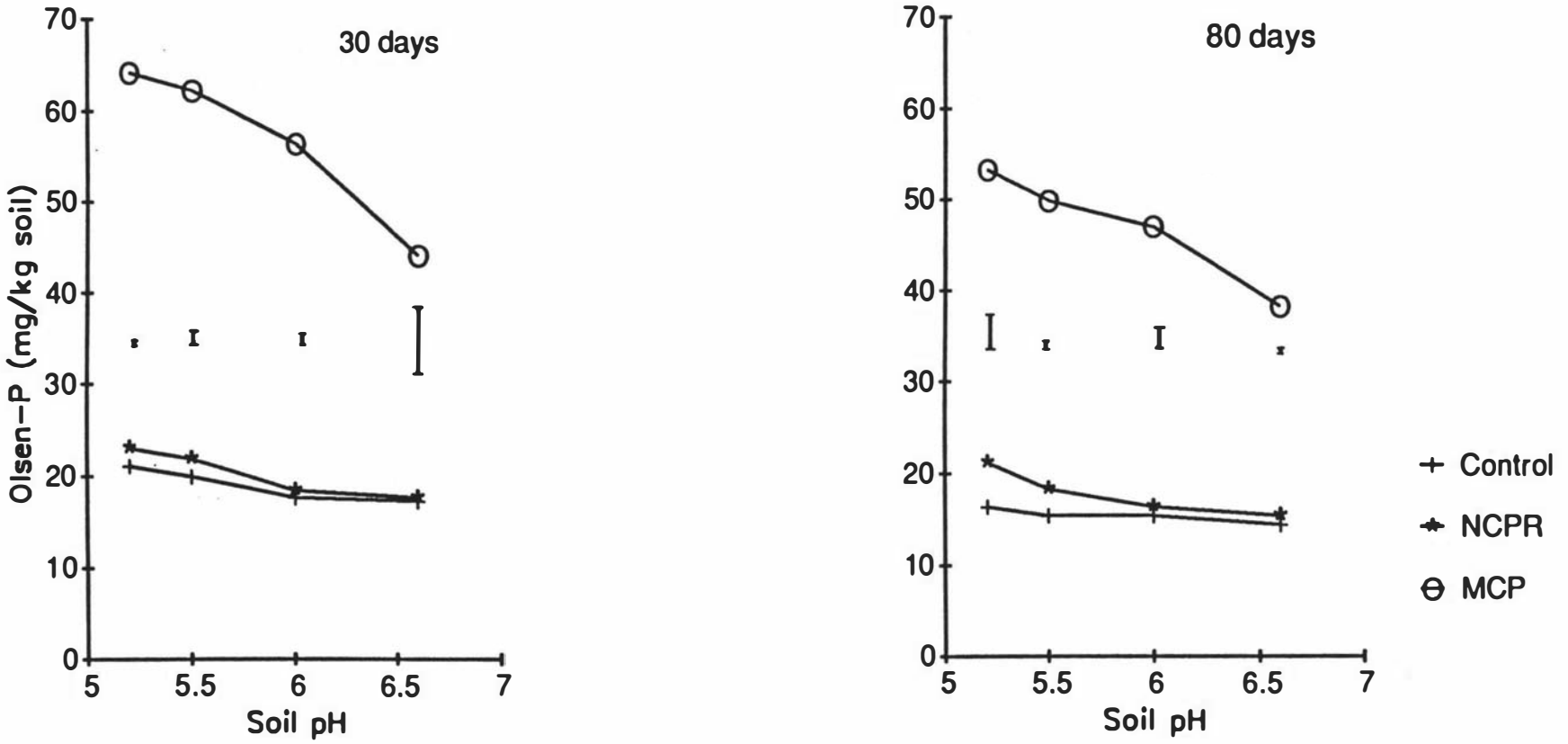
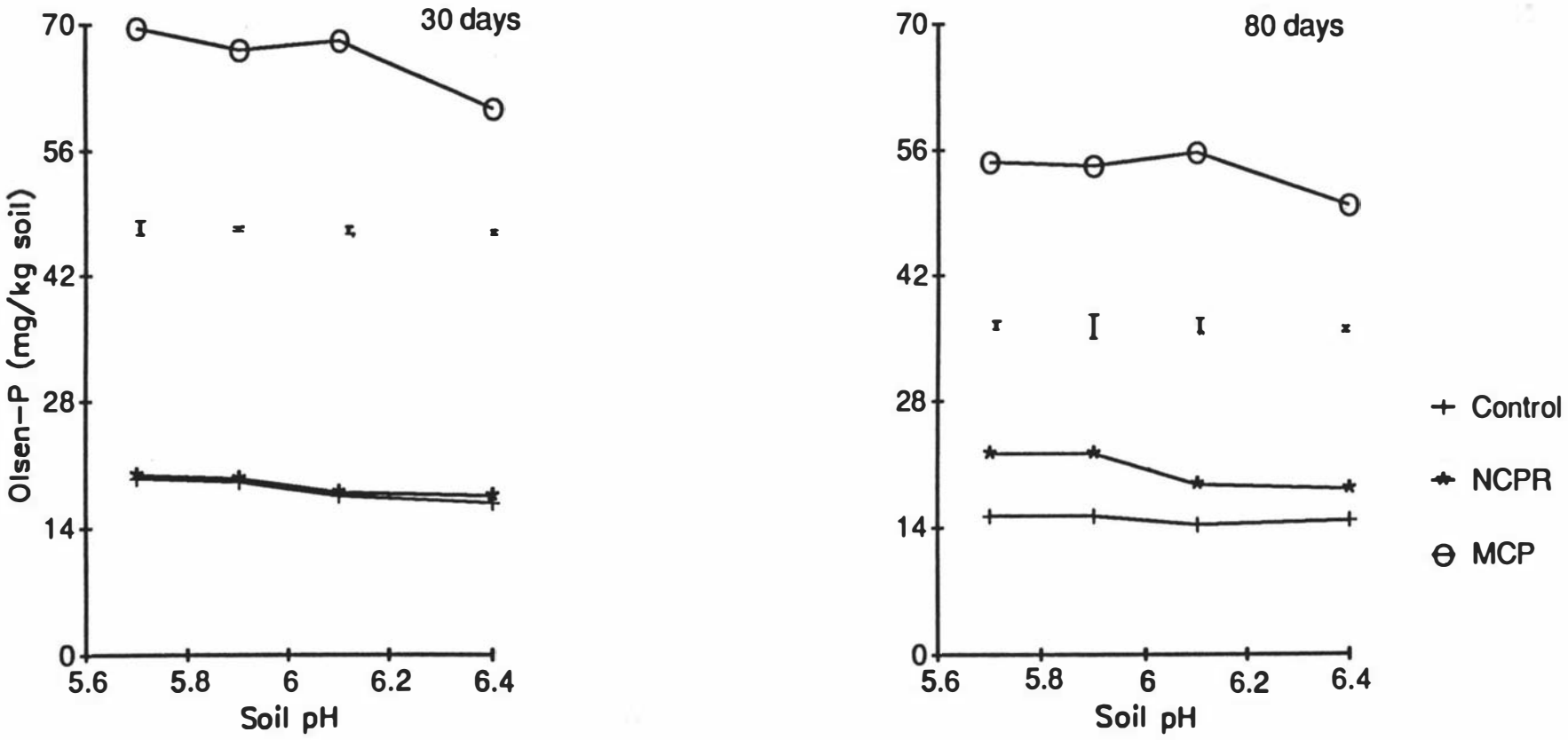


Figure 6.4 Effect of pH on the amount of Olsen-extractable P (Olsen-P) after 30 and 80 days of incubation in soils fertilized with different P sources. Vertical bars are LSD ($P<0.05$) values.

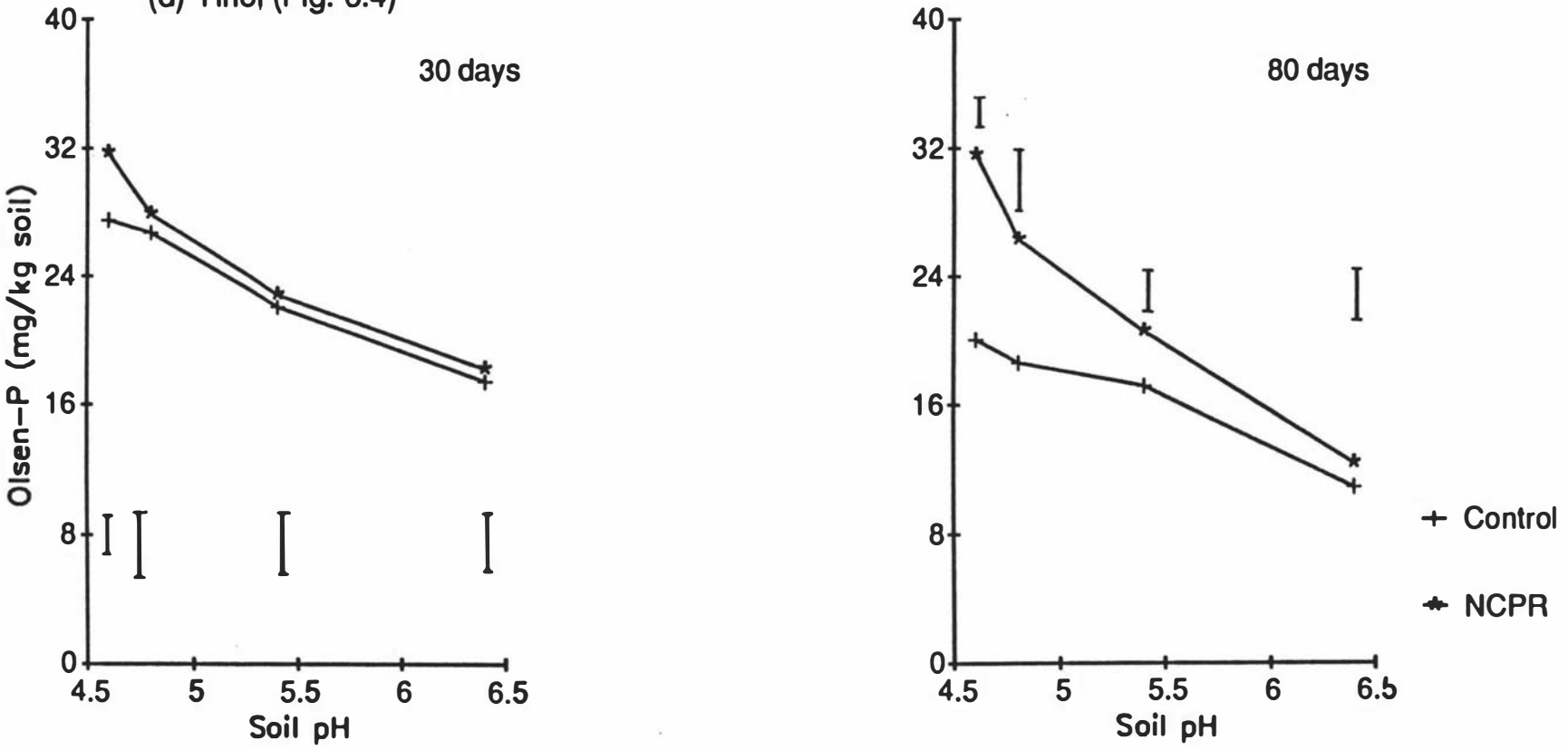
(b) Dannevirke 1 (Fig. 6.4)



(c) Dannevirke 2 (Fig. 6.4)



(d) Tihoi (Fig. 6.4)



fertilized and unfertilized (control soil) decreased with increasing soil pH in all soils except Tokomaru.

Increases in Olsen-P due to PR fertilization (ΔOlsen-P) were generally higher in samples taken at 80 than at 30 days (Figure 6.5). In this case dissolution of PR from 30 to 80 days appears to override P adsorption such that Olsen P values increase with time of incubation. In soils with pH range 4.6 to 5.7, ΔOlsen-P at 30 days ranged from 0.4 to 4.5 mg P kg^{-1}, whereas at 80 days the range was 4.9 to 12.6 mg P kg^{-1}. This increase in ΔOlsen-P with time is small compared to the amount of P dissolved from PR, which ranged from 91.2 to 134.8 mg P kg^{-1}, at the lowest pH for each soil. The relatively small increase in Olsen-P is probably the result of string adsorption of the dissolved P by soil at low pH. Less than 13% of the P dissolved from PR was recovered by the Olsen extractant (0.5 M $NaHCO_3$).

As found with the extent of PR dissolution (see Figure 3.2, Chapter 3), the ΔOlsen-P for both 30 and 80 day incubations decreased with increasing soil pH, in all soils. For example, in the 30 day-incubated Tokomaru soil the ΔOlsen-P decreased from 4.5 to 0.8 mg P kg^{-1} as the pH increased from 5.2 to 6.8. The corresponding values for the 80 day samples were 12.6 and 2.3 mg P kg^{-1}.

Although the extent of PR dissolution across all soils increased with increasing P adsorption capacity of the soils (Figure 3.2. Chapter 3), the ΔOlsen-P values tended to be higher in soils of lower P retention capacity. For example, for the low P retention Tokomaru soil (P retention capacity=18%), the amounts of ΔOlsen-P found after 80 days incubation ranged from 2 to 13 mg P kg^{-1}. The corresponding range for the medium P retention Dannevirke 1 (P retention=74%) soil was 1 to 5 mg P kg^{-1}. Data for the extent PR dissolution shown in Chapter 3 (Figure 3.1) indicate that after 80 days incubation between 38-91 and 61-135 mg P kg^{-1} of the added PR had dissolved in Tokomaru and Dannevirke 1 soils, respectively. These results, taken together with earlier published results (Chien *et al.*, 1980; Syers and Mackay, 1986; Kanabo and Gilkes, 1987b; Smyth and Sanchez, 1987; Bolan *et al.*, 1990) suggest that soil P adsorption capacity may influence not only the extent of the PR dissolution process but also the amount of dissolved P that remains in soil in a plant-available form.

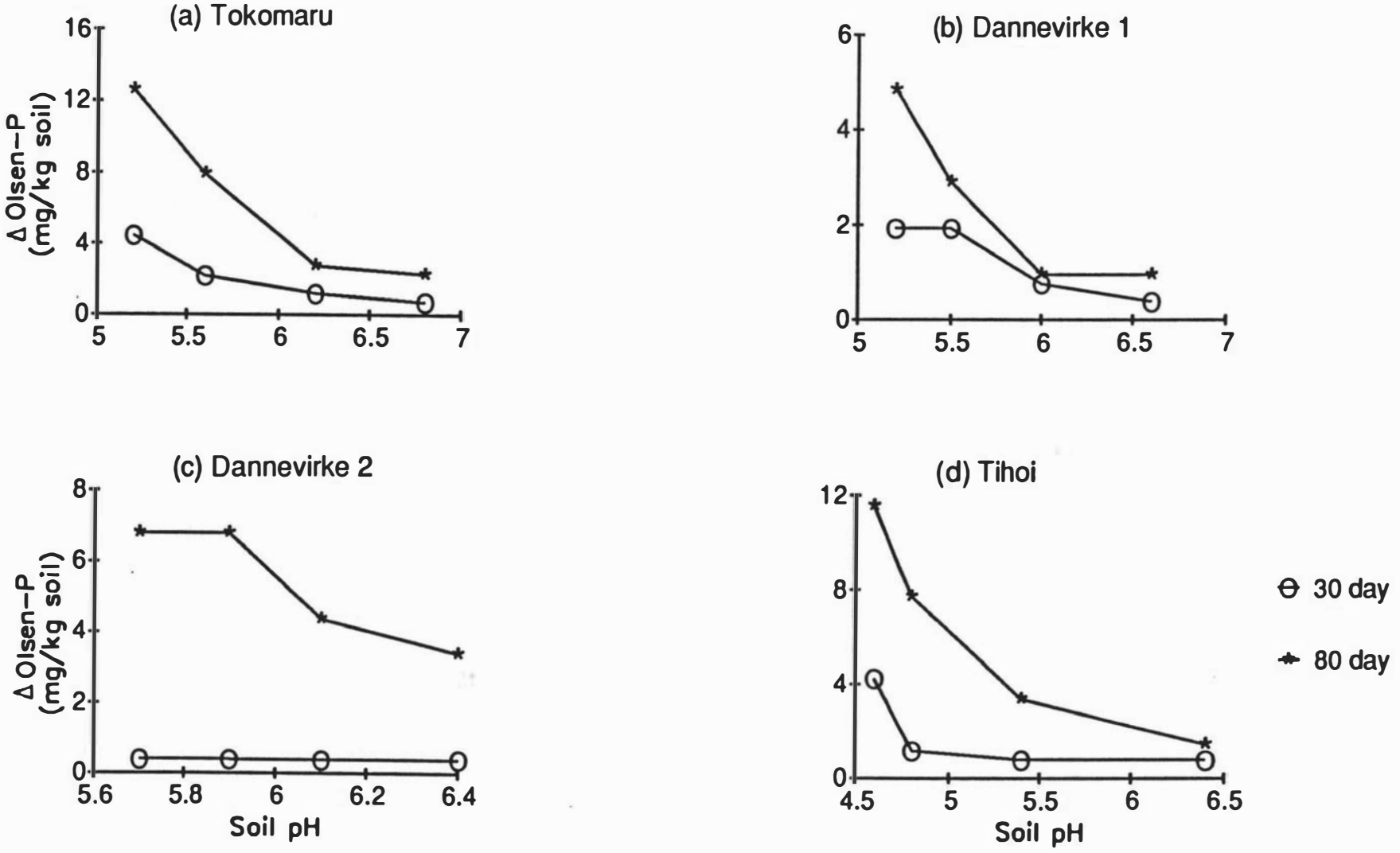


Figure 6.5 Effect of pH on the increase in Olsen-extractable P caused by NCPR (ΔOlsen-P) in soils after 30 and 80 days of incubation.

6.4.1.4 Relationship between plant P uptake and extractable soil P

The amounts of P dissolved from PR after either 30 or 80 days of incubation in soil alone were poorly related to the amounts of plant-P derived from PR (pdf-PR) (Figure 6.6). In fact the relationship shows that the amount of PR-P dissolved tends to overestimate the amount of P available for P uptake by plants. Similar findings were reported by Syers and Mackay (1986) and Bolan *et al.* (1991). Such results suggest that the amount of P dissolved from PR can not be used as a simple index of plant available P. In this case the relationship is further complicated because PR dissolution may have increased during plant growth (day 30 to 85) relative to soil incubation alone (day 30 to 80).

The relationship between P uptake by plants and amounts of Olsen-extractable P (Olsen P) in soils immediately prior to transplanting is illustrated in Figures 6.7 and 6.8. Regression analyses between P uptake and amounts of Olsen P across soils (Figure 6.7a) or within all pH's of each soil (Figure 6.8a) were not performed for soils fertilized with MCP because of the polar distribution of the data points. However, strong relationships are generally found between dry matter yield or P uptake and amounts of Olsen P in soils fertilized with water-soluble P fertilizers (Bolan, 1985; Bolan and Hedley, 1990; Naidu *et al.* 1991; Rajan *et al.* 1991b). In a combined analysis across all soils of all pH's, increases in Olsen P in NCPR-fertilized soils produce 2.8 fold unit increases in plant P uptake (Figure 6.7b). The coefficients of determination (R^2) values for NCPR-fertilized soils were low, with larger variations in the nature of the relationship between soils (Figure 6.7b). Even within NCPR-fertilized soils, little (<50%) of the variation in plant P uptake was accounted for by increases in Olsen P (Figure 6.8b). These results provide evidence that increases in Olsen P do not fairly represent the potential plant available pool in soil to which a PR has been added.

Per unit increase in Olsen P, increased plant P uptake was lower in the Dannevirke 1 ($CaCO_3$ treated) than Dannevirke 2 ($NaHCO_3$ treated) soils fertilized with MCP (Figure 6.8b). Opposite results would be expected for the Dannevirke soils fertilized with MCP (Figure 6.8a). According to Sorn-srivichai *et al.* (1984), Olsen P underestimates plant-available P in limed soils fertilized with soluble P because insoluble Ca-P forms during

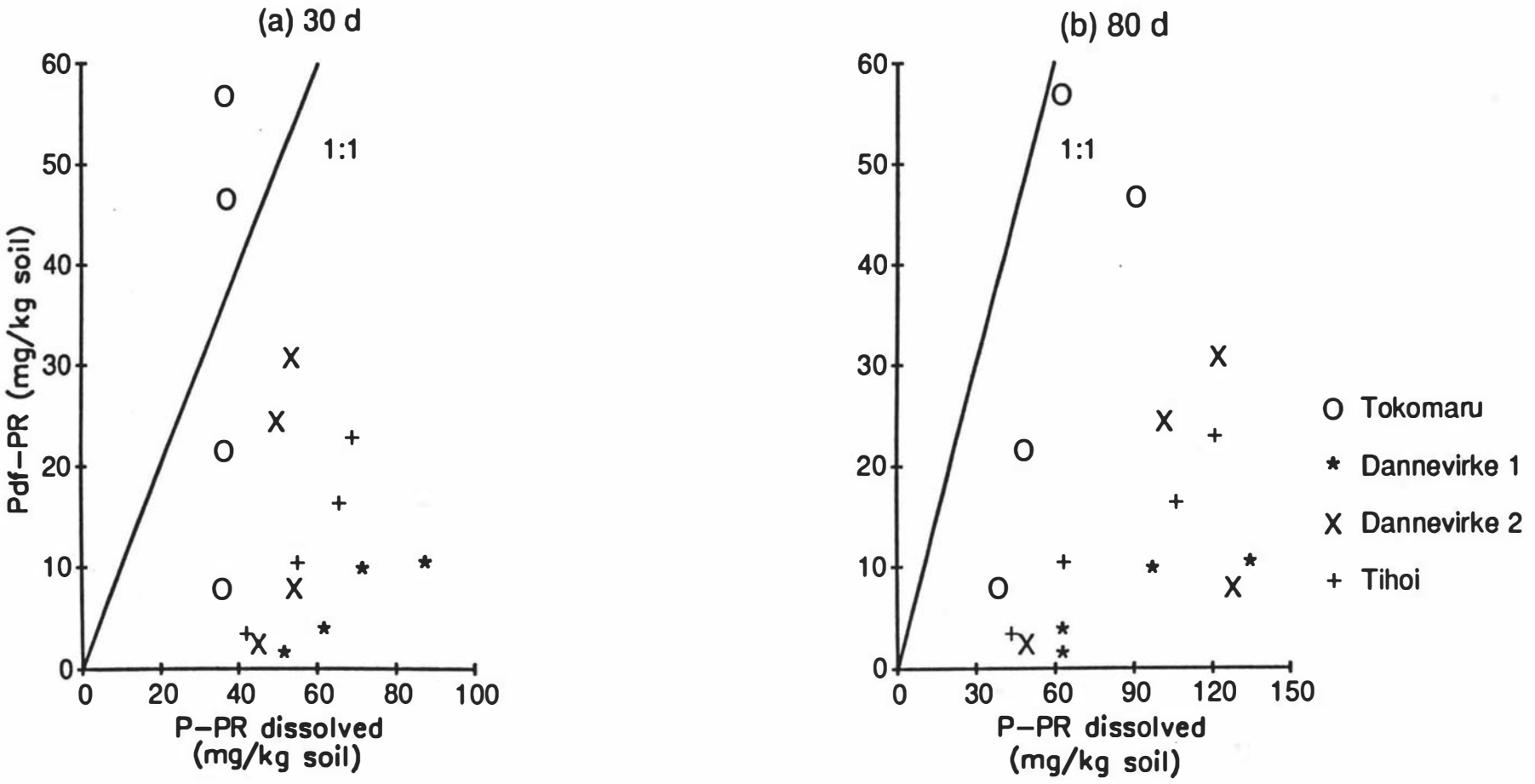


Figure 6.6 Relationship between amounts of P derived from NCPR taken up by plants (pdf-PR) and amounts of P dissolved from NCPR after (a) 30 and (b) 80 days of incubation.

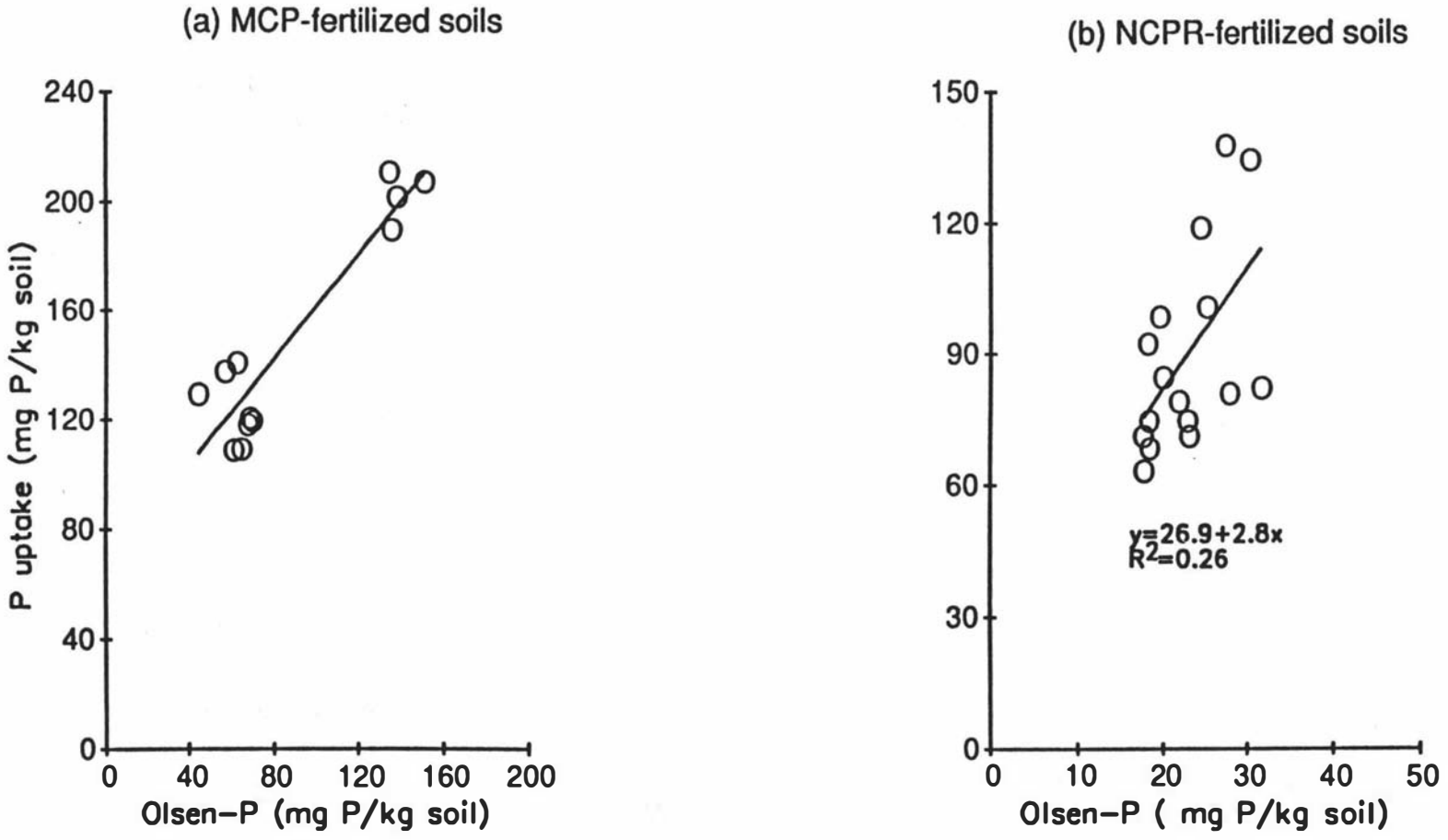


Figure 6.7 Relationship between amounts of Olsen-extractable P (Olsen-P) in all 30-day incubated soils fertilized with (a) MCP or (b) NCPR and amounts of P taken up by plants.

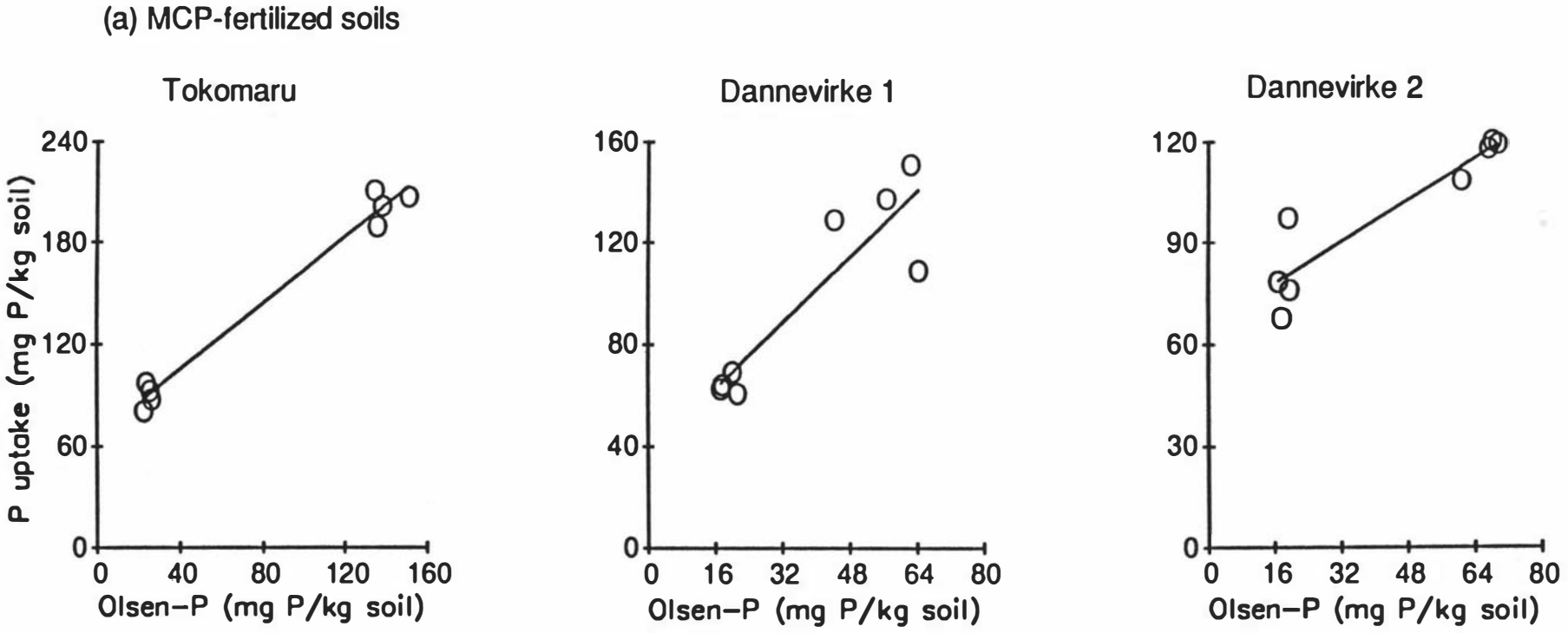
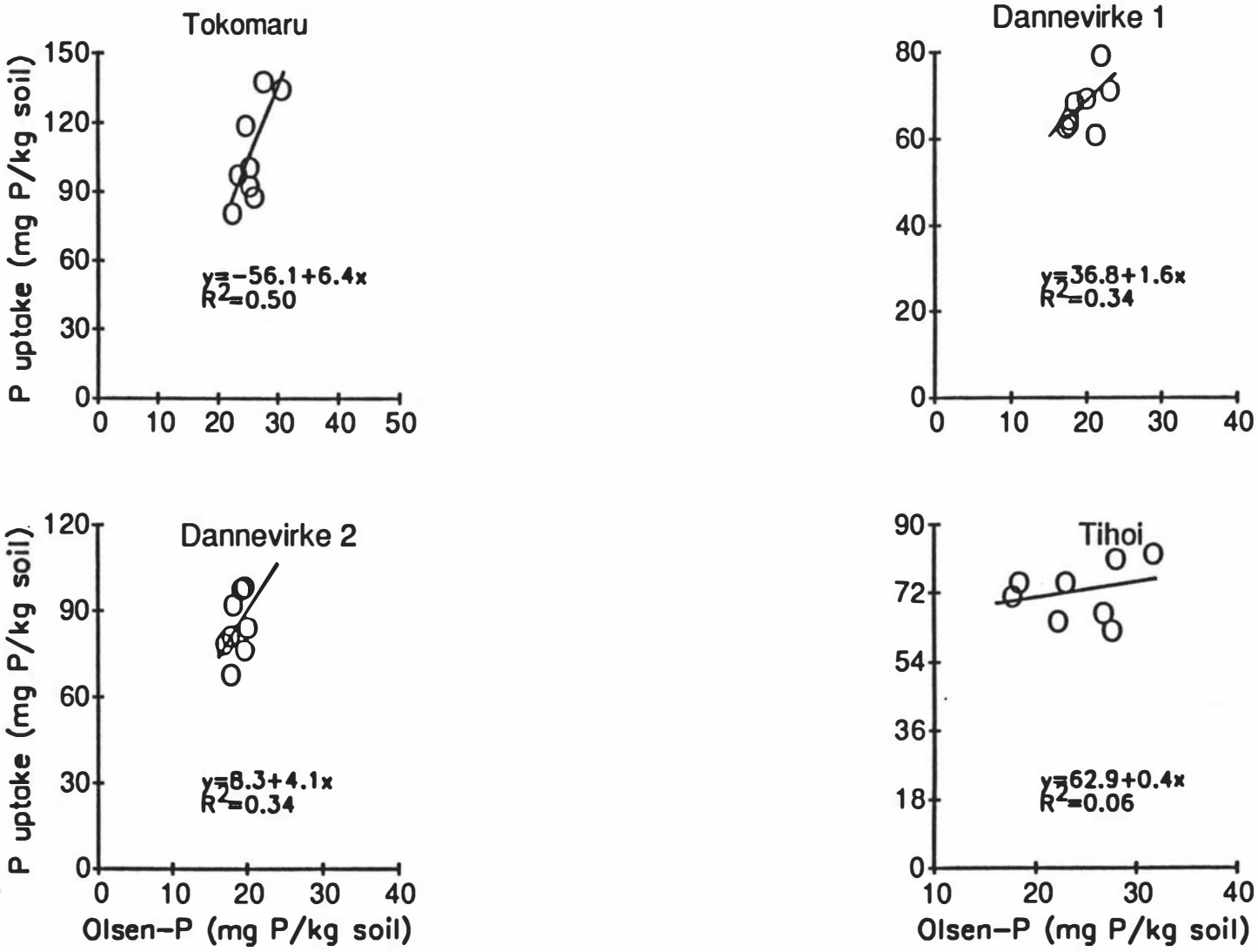


Figure 6.8 Relationship between amounts of Olsen-extractable P (Olsen-P) in each 30 day-incubated soil fertilized with (a) MCP or (b) NCPR and amounts of P taken up by plants.

(b) NCPR-fertilized soils (Fig.6.8)



extraction resulting in reduced P recovery. Results of the present study indicate that Olsen P measured prior to plant growth will underestimate plant-available P to a greater extent in PR-fertilized soil that have high levels of exchangeable Ca (e.g. Danneverke 1). In this case underestimation occurs because the Olsen P measurement will not reflect subsequent PR dissolution during plant growth, and PR dissolution was reduced under higher Ca concentrations in Dannevirke 1 soil, which resulted in a reduction in the plant P uptake relative to Dannevirke 2 (Figure 6.8b).

Bolan and Hedley (1990) have suggested that a close relationship exists between the amount of plant P derived from P fertilizer (pdf) and the increase in Olsen-P resulting from P fertilization (ΔOlsen-P). To test this relationship, the pdf and ΔOlsen-P (measured in the 30 day-incubated soils) values were calculated for each pH value. The results (Figure 6.9) support the previous discussion that an increase in Olsen-P caused by fertilization with MCP increased pdf by a similar margin (slope=0.7), and explained 73% of the variation in pdf (Figure 6.9). However, the increase in Olsen-P caused by NCPR fertilization only explained 27% of the variation in pdf, which on average increased 6.9 times per unit increase in Olsen-P.

The weak relationship found between ΔOlsen-P and pdf in PR- fertilized soils in the present study contrasts with the findings of Syers and Mackay (1986) and Bolan and Hedley (1990) who worked with a range of New Zealand soils. These contrasting results may be due to differences in soil properties and amendments used in the present study. However, Syers and Mackay (1986) worked with a range of unlimed New Zealand soils whose pH and exchangeable Ca content of these soils were generally lower than that used in the present study. Also they used fine materials (60%<150 μm) of reactive Sechura PR as a fertilizer source. Bolan and Hedley (1990) used a soil which varied in pH with a similar amount of exchangeable Ca. It was therefore expected that the soils used by Syers and Mackay (1986) and Bolan and Hedley (1990) would favour greater PR dissolution than those used in the present study.

Overall, the results of the present experiment suggest that Olsen-P may not be a suitable index of plant-available P in soils with significant amounts of residual (undissoved) PR.

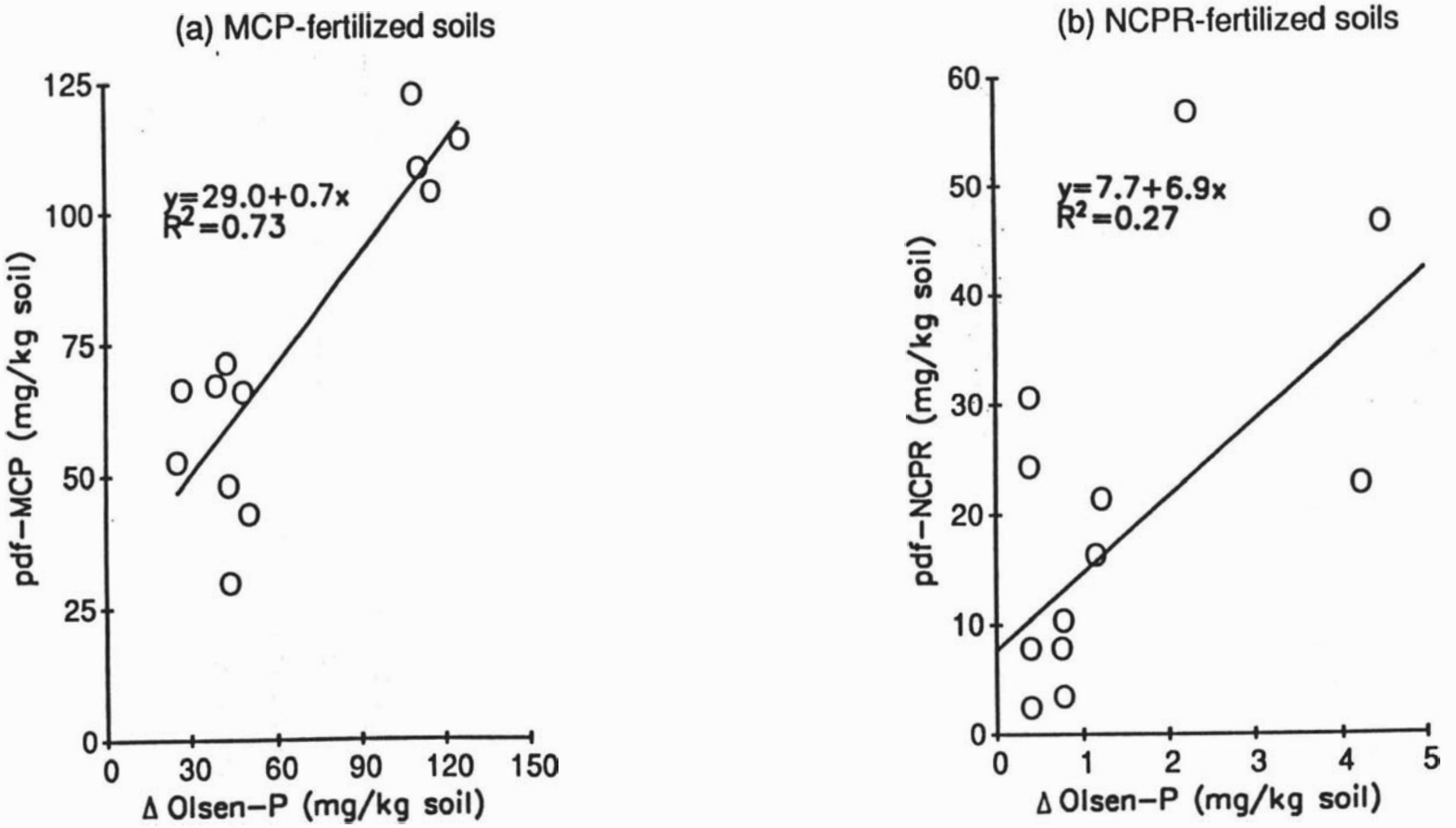


Figure 6.9 Relationship between increases in Olsen-extractable P (ΔOlsen-P) caused by (a) MCP or (b) NCPR fertilization in 30 day-incubated soil and amounts of P taken up by plants derived from MCP (pdf-MCP) or NCPR (pdf-NCPR).

The poor predictive power of the Olsen test is probably because that it removes only part of the sorbed P. Unlike acid extractants, such as Bray 1, the Olsen-P extractant does not dissolve any unreacted PR during the extraction. Thus it does not measure amounts of P in the undissolved form that might dissolve during the plant assay. This probably explains why acid extraction, such as Bray 1, has been found to provide a better index of available P than the Olsen test on a range of New Zealand soils fertilized with PR (Syers and Mackay, 1986).

6.4.2 Experiment 2

6.4.2.1 Inorganic phosphorus concentrations in soil solution

In the four soils to which two PRs (NCPR and MPR) had been added (500 mg P kg^{-1} soil), dissolution of PR had increased soil solution P concentrations (Table 6.1). The exception was in the high P sorbing Ramiha soil. After incubation for 60 days, soil solution P concentrations ranged from 0.037 to 0.202 mg P l^{-1}. The final increase in solution P concentration from PR dissolution was more closely related to the P retention capacity and P status of the soil than to the actual extent of PR dissolution *per se*. For example, the extent of dissolution of NCPR amounted 117 mg P kg^{-1} soil in the high P status, low P sorbing Tokomaru soil, increased in solution P concentration by 0.107 mg P l^{-1}. In the low P status, high P sorbing Prabumulih soil, dissolution of 281 mg P kg^{-1} resulted in an increase by only 0.007 mg P l^{-1}.

Any P dissolved from PR can be quickly removed by various sinks. In the absence of plants, most of the dissolved P is likely to be adsorbed by soil and result in a very low concentration of P remaining in soil solution (Table 6.1). The subsequent availability of this dissolved, but sorbed, P to plants is then controlled by the desorption process (Barrow, 1983).

Table 6.1 Inorganic P (Pi) concentrations of soil solution of 60 day-incubated soils fertilized with 500 mg P kg^{-1} soil of North Carolina (NCPR) and Moroccan (MPR) phosphate rocks.

Soil	Phosphate rock	Pi concentration (mg l^{-1})
Tokomaru	Control	0.095
	NCPR	0.202
	MPR	0.186
	LSD (P<0.05)	0.093
Ramiha	Control	0.037
	NCPR	0.052
	MPR	0.040
	LSD (P<0.05)	ns
Sembawa	Control	0.039
	NCPR	0.169
	MPR	0.129
	LSD (P<0.05)	0.059
Prabumulih	Control	0.026
	NCPR	0.033
	MPR	0.029
	LSD (P<0.05)	ns

6.4.2.2 Olsen-extractable P

Changes in plant-available P estimated by changes in Olsen-extractable P (Olsen-P) over the 90 days of incubation of Sembawa and Prabumulih soils with NCPR and MPR, added at 500 mg P kg^{-1} rate, are presented in Figure 6.10. These two soils were chosen to represent low and high P sorbing soils, respectively. The trends in Olsen-P caused by PR addition were similar for both soils, tending to increase up to 60 days and remain constant thereafter.

Although the extent of PR dissolution was similar for both Sembawa and Prabumulih soils (Figure 4.1, Chapter 4), higher Olsen-P values were found in Sembawa soil which has the lower P adsorption capacity.

During the 90-day incubation, higher Olsen-P values were found in soils treated with NCPR than MPR. This result was expected because NCPR is considered to be the more "reactive" of the two P sources and consequently dissolved to a greater extent during incubation (Figure 5.1, Chapter 5).

After 90 days incubation, amounts of ΔOlsen-P (fertilized soil - control soil) increased with increasing rate of PR applied in all soils (Figure 6.11).

The increase in ΔOlsen-P found with increased PR application rate is evident that the absolute amount (mg P kg^{-1}) of dissolved P increases with increasing PR application rate (Figure 5.1, Chapter 5). However, when expressed as a proportion of both the total PR-P added and dissolved P, the amount of P extracted as Olsen-P decreased with increased rate of PR application. This finding suggest that at higher rates of application the % PR dissolution decreases (Chapter 5), and in addition most of the dissolved P remains Olsen-extractable.

6.4.2.3 Bray 1- and resin-extractable P

Amounts of Bray 1-extractable (Bray 1-P) and resin-extractable (resin-P) P in four selected soils after 30 or 90 days of incubation with NCPR and MPR, at 500 mg P kg^{-1},

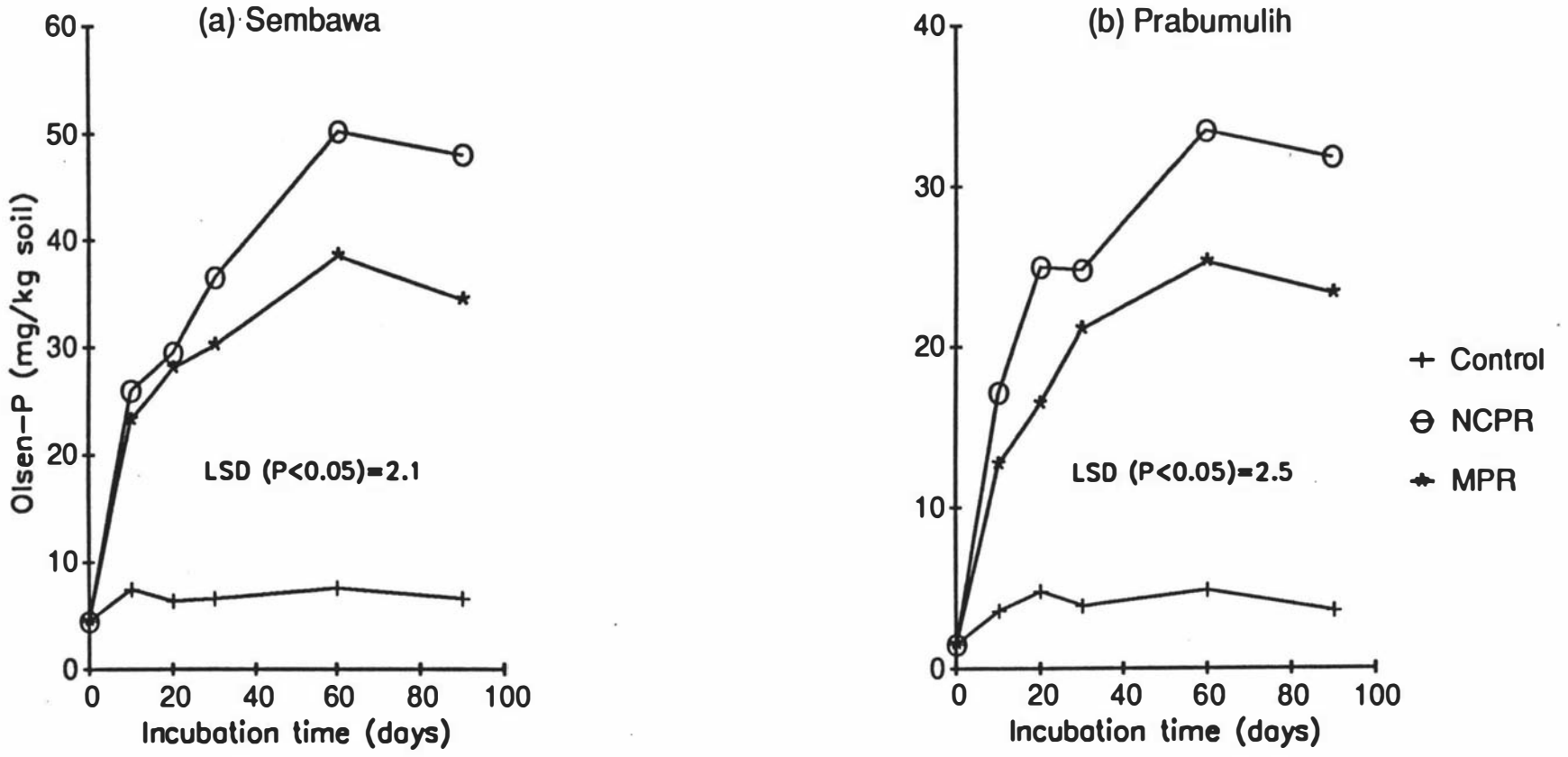


Figure 6.10 Effect of incubation time on changes in Olsen-extractable P (Olsen-P) in (a) Sembawa and (b) Prabumulih soil fertilized with NCPR and MPR (500 mg P kg^{-1} soil).

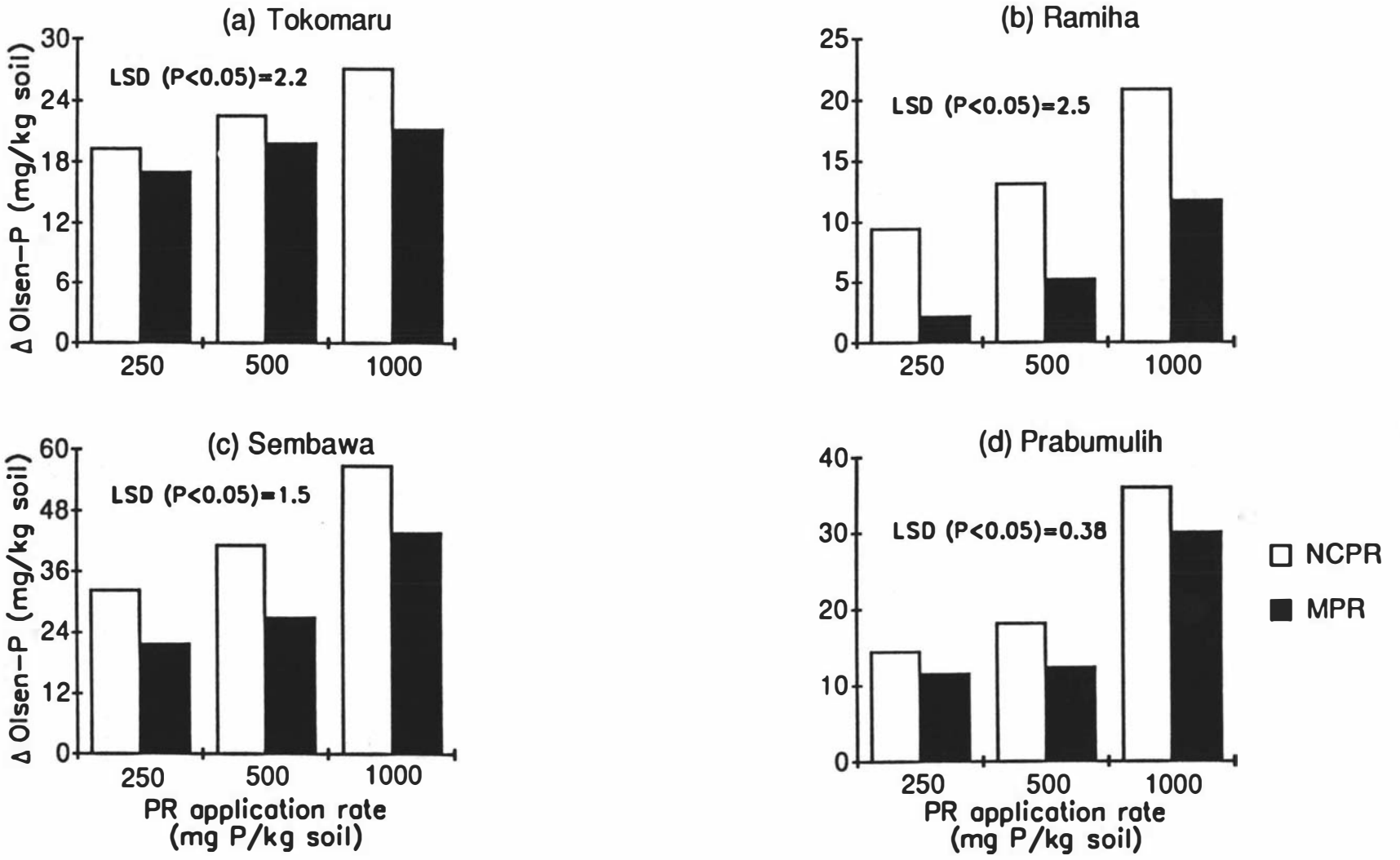


Figure 6.11 Increases in Olsen-extractable P (ΔOlsen-P) in 90 day-incubated soils fertilized with NCPR and MPR at different application rates (250-1000 mg P kg^{-1} soil).

are presented in Figures 6.12 and 6.13. As with Olsen-P (Section 6.4.2.2), additions of either NCPR or MPR significantly increased the level of Bray 1- and resin-P in all soils. The extractability of P in fertilized soils was generally higher in samples taken at 90 days samples than at 30 days.

Higher amounts of extractable soil P were measured in all soils treated with the reactive NCPR than with medium reactive MPR. Again, greater amounts of extractable soil P occurred in soils with low P retention capacity (Tokomaru and Sembawa) than in those with high P retention capacity (Ramiha and Prabumulih).

6.4.2.4 Relationships between amounts of dissolved P from PR and various estimates of plant-available P

This section examines the ability of various soil tests to predict the increase in soil P status as PR dissolves. The absolute input of available P into the soil was taken as the measured amounts of PR-P dissolved as explained in Chapter 4.

There was a close relationship ($P<0.05$) between amounts of dissolved P and available P estimated by various soil P tests (Olsen, Bray 1 and resin). The strength of the relationship, however, varied depending on the soil and P test used (Figures 6.14, 6.15 and 6.16).

For all three soil P tests, the amount of P extracted accounted for more of actual amounts of P dissolved in Indonesian (Sembawa and Prabumulih) than in New Zealand (Tokomaru and Dannevirke) soils. Bray 1 test appeared to be the best method for predicting amounts of P dissolved in the New Zealand soils. Olsen test, in particular, was not very useful in the case of Tokomaru soil. In Indonesian soils, the predictive ability of the three soil tests also varied. Both Bray 1 and resin tests had similar predictive capabilities when used on Sembawa and Prabumulih soils.

The variation in dissolved P accounted by Olsen and Bray 1 tests was affected by the P sorption capacity of the soil. Also slopes of the regression equation relating the Olsen and Bray 1 test versus P dissolved varied with soil P sorption capacity. Between soil,

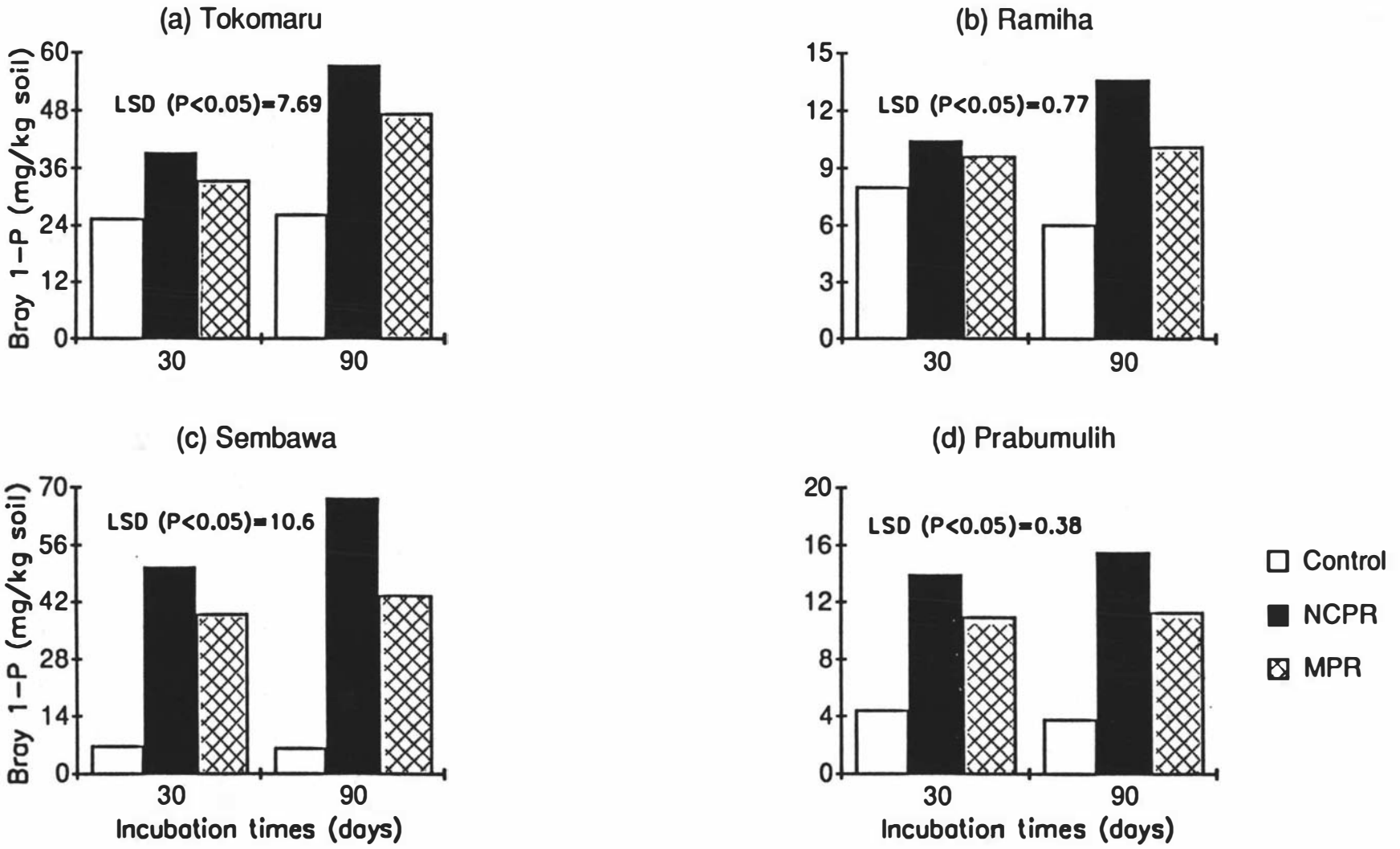


Figure 6.12 Amounts of Bray 1-extractable P (Bray 1-P) after 30 and 90 days of incubation in soils fertilized with NCPR and MPR (500 mg P kg^{-1} soil).

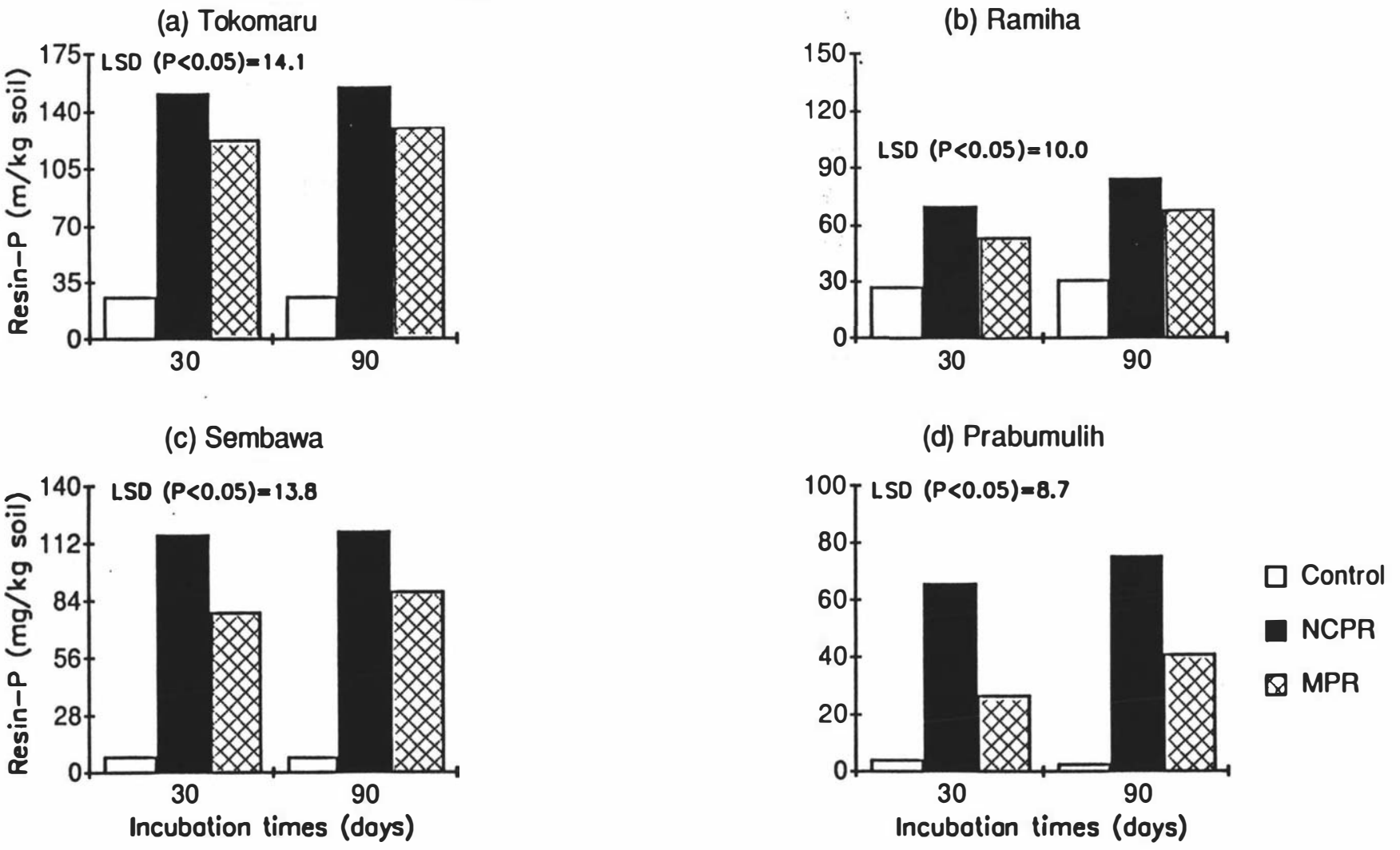


Figure 6.13 Amounts of resin-extractable P (resin-P) after 30 and 90 days of incubation in soils fertilized with NCPR and MPR (500 mg P kg^{-1} soil).

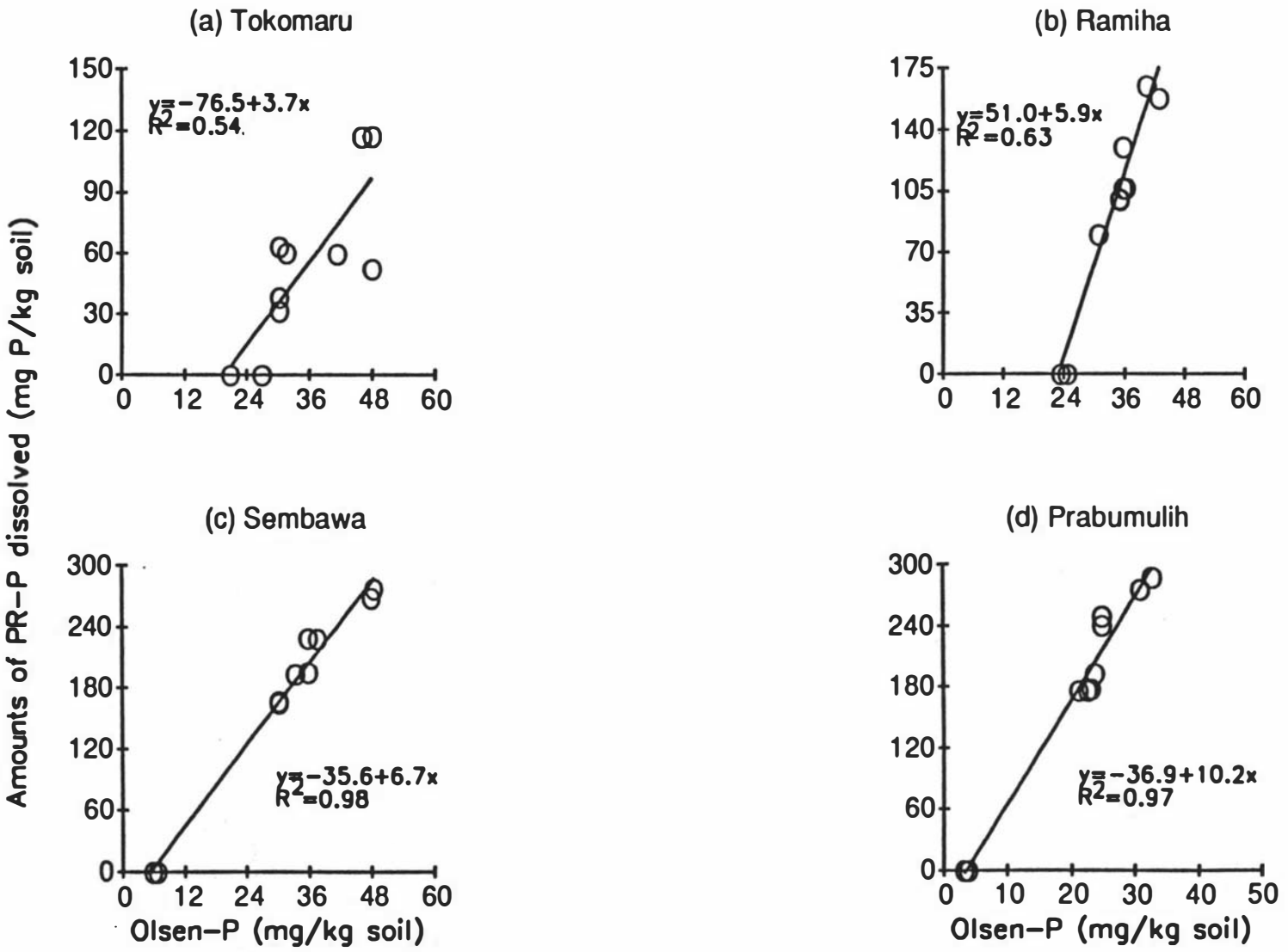


Figure 6.14 Relationship between amounts of Olsen-extractable P (Olsen-P) and amounts of P dissolved from NCPR and MPR (applied at 500 mg P kg^{-1} soil) after 30 and 90 days of incubation.

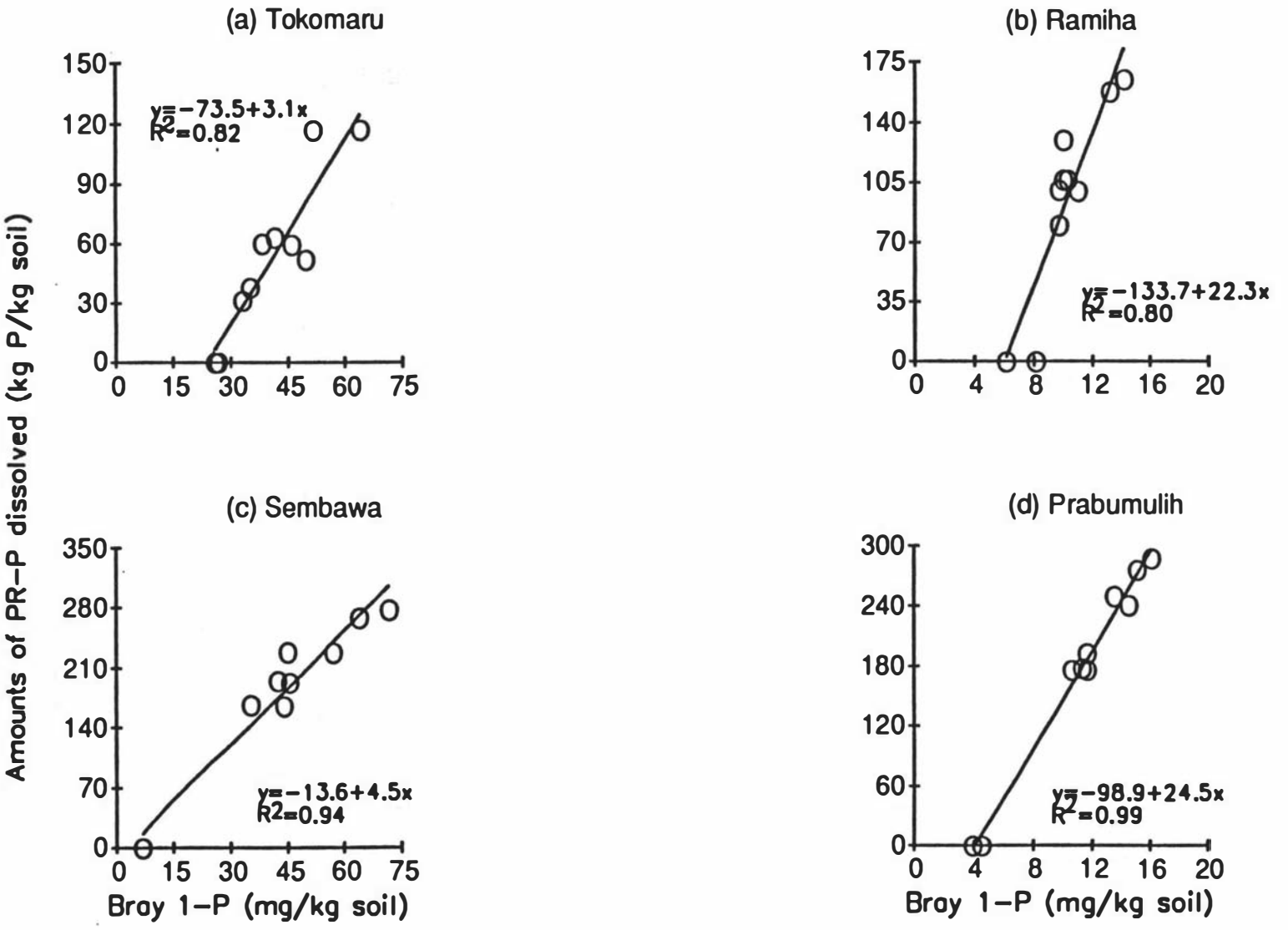


Figure 6.15 Relationship between amounts of Bray 1-extractable P (Bray 1-P) and amounts of P dissolved from NCPR and MPR (applied at 500 mg P kg^{-1} soil) after 30 and 90 days of incubation.

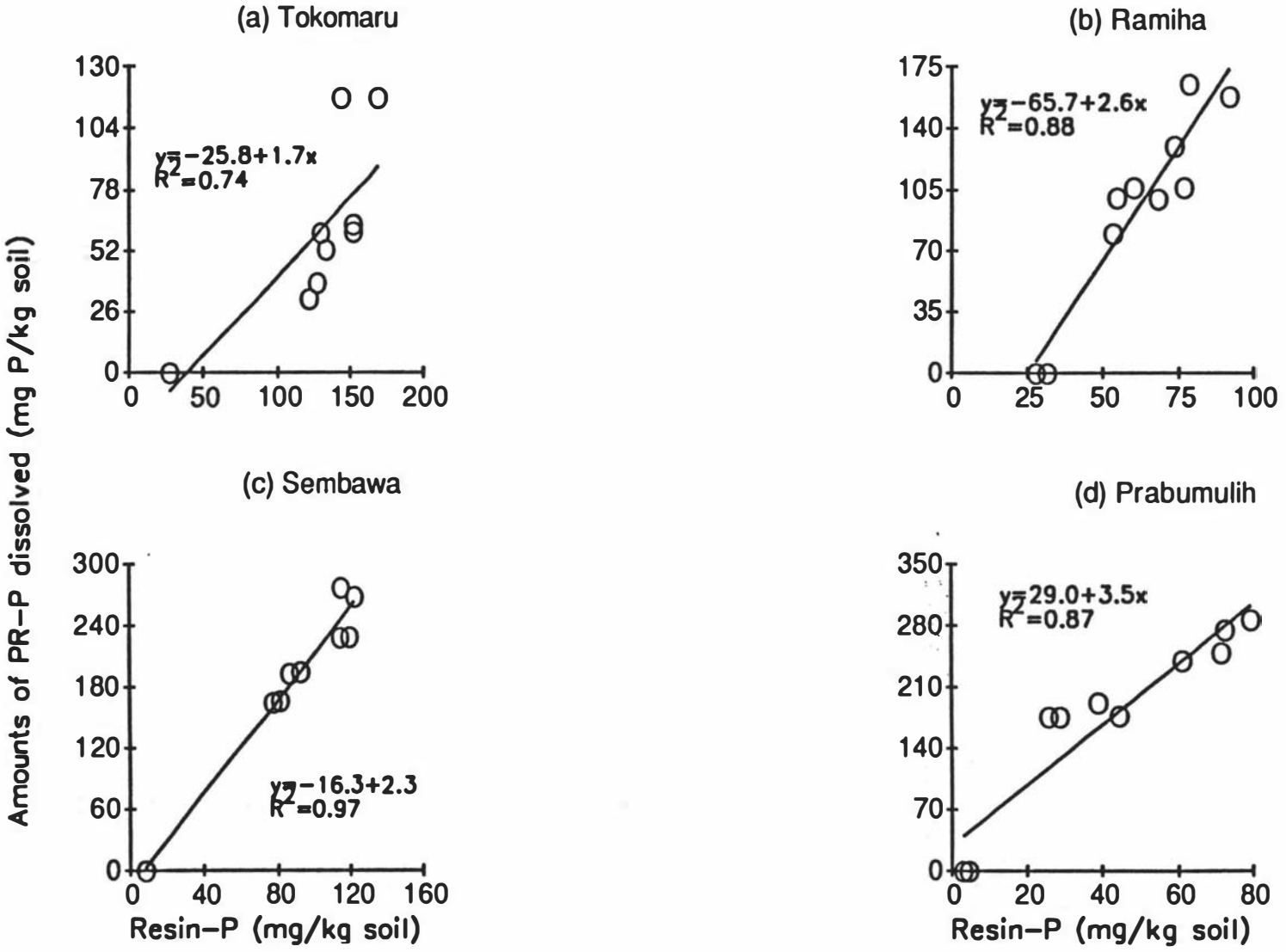


Figure 6.16 Relationship between amounts of resin-extractable P (Resin-P) and amounts of P dissolved from NCPR and MPR (applied at 500 mg P kg^{-1} soil) after 30 and 90 days of incubation.

variation in the slope was less with the resin test.

6.4.2.5 Relationships between various soil testing methods

Relationships between amounts of available P measured by Olsen, Bray 1 and resin tests in soils 90 days after the addition of 500 mg P kg^{-1} of NCPR or MPR are presented in Table 6.2. Olsen-P was positively correlated with both the Bray 1- and resin-P. Except for PRabumulih soil, the relationship between Olsen and resin-P was slightly stronger than between Olsen and Bray 1-P.

It has been shown earlier (Section 6.4.2.4) that resin test extracted greater amounts of dissolved P than either Olsen or Bray 1 test. The presence of a CER in the resin method removes cations contributing to positive charge on soil surfaces, and as a result the extraction of soil P by AER is more effective (Saunders, 1964; Saggar *et al.*, 1990).

The slopes in the regression equations shown in Table 6.2 also indicate that the Olsen test extracted less P from the lower P sorbing soils of Tokomaru and Sembawa soil than the did the Bray 1 test. In high P sorbing Dannevirke and Prabumulih soils, on the other hand, the Olsen test extracted more P than the Bray test. The acid Bray solution is expected to dissolve some of the residual PR in soil (Syers and Mackay, 1986). However the effectiveness of acid extractants, such as Bray 1, can lead to greater resorption of dissolved P in high P sorbing soils (Saggar *et al.*, 1991a). Thus Bray 1 can underestimate the availability of the dissolved P in the high P sorbing soils, such as Dannevirke and Ramiha, used in this study.

6.5 CONCLUSIONS

The effect of soil chemical characteristics on amounts of plant-available P, measured either by plant uptake or soil tests, in a range of New Zealand and Indonesian soils varied with the soil used and form of P fertilizer applied. Across all soils fertilized with PR, the amount of plant-available P was determined more by soil P adsorption characteristics than by the extent of PR dissolution.

Table 6.2 Relationships between amounts of available P extracted by various soil P tests in 90 day-incubated soils fertilized with NCPR and MPR (500 mg P kg^{-1} soil).

Soil	Soil P test	Regression equation	R^2
Tokomaru	Olsen vs Bray	y = -11 + 1.4x	0.87
	Olsen vs Resin	y = -128 + 5.9x	0.90
Dannevirke	Olsen vs Bray	y = -3.1 + 0.4x	0.92
	Olsen vs Resin	y = -37.6 + 2.9x	0.95
Sembawa	Olsen vs Bray	y = -3.7 + 1.4x	0.98
	Olsen vs Resin	y = -8.1 + 2.7x	0.99
Prabumulih	Olsen vs Bray	y = 2.3 + 0.4x	0.99
	Olsen vs Resin	y = -7.7 + 2.5x	0.94
All soils	Olsen vs Bray	y = -8.8 + 1.1x	0.53
	Olsen vs Resin	y = -23.9 + 3.0x	0.82

R^2 values greater than 0.50 and 0.16 are significant at $P<0.05$ for each soil and across all soils, respectively.

Liming of New Zealand soils had small effects on plant availability of P in soil fertilized with MCP but generally decreased the availability of P in soil fertilized with NCPR. These decreases were attributed to decreases in NCPR dissolution caused by increasing soil pH and amounts of exchangeable Ca. In high P sorbing Dannevirke soils fertilized with MCP, the amounts of chemical P availability, as indicated by Olsen P, decreased with increasing rate of lime application. These decreases were not attributed to the effect of increasing soil pH on the efficiency of Olsen test, but was caused by increases in exchangeable Ca probably inducing insoluble P compounds to precipitate.

In limed soils of New Zealand, Olsen-P was a better predictor of plant P uptake from MCP-fertilized soils, but underestimated P uptake from NCPR-fertilized soils.

Among three soil P tests examined in PR-fertilized New Zealand and Indonesian acidic soils, the new resin test developed by Saggar *et al.* (1990) was more effective in extracting P from PR- fertilized soils than either the Olsen or Bray 1 test. Compared to Olsen and Bray 1 tests, the ability of the resin test to predict increases in soil P status due to PR dissolution was less sensitive to the P sorption capacity of the soil. Thus the resin test has potential use across wider range of acid soils fertilized with PRs. However, in terms of usefulness as a predictor of plant available P, further plant growth studies are still needed to calibrate such a soil P test. Results of field studies described in Chapter 8 are used to evaluate in more detail the potential use of these three soil P tests as predictors of potential plant available P in soils fertilized with PR.

CHAPTER 7
EFFECTS OF PLANT RESIDUES ON THE DISSOLUTION AND AVAILABILITY OF PHOSPHATE FROM ^{32}P-LABELLED FRANCOLITE

7.1 INTRODUCTION

Plant residues added to soil, act not only as sources of nutrients (e.g. manures), but also influence the availability of soil nutrients. The addition of plant residues has been reported to increase the availability of soil P to plants (White and Ayoub, 1983; McLaughlin and Alston, 1986; Bumaya and Naylor, 1988; Li *et al.*, 1990).

Several studies have examined the effect of plant residues on the plant availability of P from soluble fertilizers (Till and Blair, 1978; McLaughlin and Alston, 1986; McLaughlin *et al.*, 1988a; 1988b; Friesen and Blair, 1988; Thibaud *et al.*, 1988) but few have studied their influence on P availability from phosphate rock (PR). The yield and P uptake of lowland rice significantly increased when plant residues were added to soil fertilized with Mussoori PR (Ranjan and Kothandaraman, 1986; Sreekantan and Palaniappan, 1990). The increased P availability was attributed to the production of organic acids during plant residue decomposition which increased the solubility of the PR in soil.

Mineralisation of organic N in soil may also increase the dissolution of PR. Nitrogen mineralisation starts with the hydrolysis of protein to form ammonia. Solution of ammonia in soil water raises the pH but the ammonium ion is subsequently oxidized to nitrate ions by chemolithotropic bacteria. During the nitrification process, two H^+ ions are produced when one NH_4^+ ion is oxidized to a NO_3^- ion. The supply of protons can enhance the dissolution of PR in soil (Chapter 3). The enhanced PR dissolution in the presence of organic materials may also be brought about by the action of organic acids, such as citric, oxalic, malonic, malic and lactic acids, produced during the decomposition of organic materials (Struthers and Sieling, 1950). Additionally, the ability of organic acids or hydrolized soil organic matter to chelate the dissolved Ca^{2+} from PR may increase the extent of PR dissolution.

7.2 OBJECTIVE

The objective of the study reported in this Chapter was to investigate the effect of plant residue addition on the extent of PR dissolution in soil and the subsequent availability of the P dissolved from PR. The use of ^{32}P-labelled francolite as the PR source allowed the contribution of P from PR to the available P pool to be determined.

7.3 MATERIALS AND METHODS

7.3.1 Plant residues

Shoots and leaves of white clover (*Trifolium repens*) were used as plant residues. The fresh shoots and leaves of white clover were chopped and sieved to pass a 5 mm sieve. The chopped leaves were immediately placed in a sealed bag and stored overnight in a fridge prior to use in the incubation experiment. Subsamples of chopped plant materials were analysed for dry matter content and total N, P and C contents. For this purpose, the subsamples were oven-dried at 70°C for 12 hours, reground and then sieved to pass a 150 µm sieve. The chemical composition of the plant residues is given in Table 7.1.

Table 7.1 Chemical composition and moisture content of white clover.

C	N	P	C/N	C/P	Moisture content
%					%
84.9	5.57	0.44	15.2	192.9	82.5

7.3.2 Soils

Two surface (0-75 mm) soil materials, one each from New Zealand (Dannevirke silt loam, Typic Eutrochrept) and Indonesia (Prabumulih loamy sand, Typic Paleudult), were used in this study. Prior to use, the soils were air-dried and sieved to pass through a 2 mm sieve. Some properties of the soils are given in Tables 4.1 (Chapter 4) and 5.10 (Chapter 5).

7.3.3 Preparation of ^{32}P-labelled synthetic francolite

Synthetic francolite, radioactively labelled with ^{32}P, was used as a P source in this study. The ^{32}P-labelled francolite was synthesized using the technique developed by Resseler and Warner (1989). Protective clothing and perspex shields were used in manipulations involving the ^{32}P tracer solution and radioactive francolite.

7.3.3.1 Reagents

The following reagents were used in preparing the synthetic francolite:

(1) 20% NH_4OH solution.
128 ml of deionised water was added to 284 ml of NH_4OH (specific gravity 0.88; assay 33% w/w). The pH of this solution was 13.5.

(2) Solution A.
61.336 g $Ca(NO_3)_2.4H_2O$ was dissolved in approximately 180 ml of 20% NH_4OH solution with constant stirring.

(3) Solution B.
(i) 17.857 g of $(NH_4)_2HPO_4$ was dissolved in 50 ml deionised water.
(ii) 5.3107 g of Na_2CO_3 anhydrous and 2.4414 g of NaF were dissolved in each 75 ml of deionised water with slight warming.
Solutions (i) and (ii) were mixed and the pH was adjusted to 10 using 20% NH_4OH solution to form solution B.

(4) ^{32}P stock solution.
0.1 ml of stock ^{32}P carrier free solution (74 MBq) was diluted to 100 ml. 13.7 ml of this diluted solution was added to solution B while stirring.

7.3.3.2 Synthesis

Solution B was added to solution A while stirring was continued for 2 hours. After 18 hours the suspension was filtered through a Buchner funnel using a Whatman filter paper (No. 5). To remove large amounts of NH_4NO_3, 700 to 1000 ml of deionised water was added to the solution and the precipitate was washed 4 times by allowing it to settle

followed by decantation of the supernatant. The residual precipitate on the funnel was transferred into a silica crucible and was sequentially heated at 100°C for 12 hours, 200°C for 2 hours, 400°C for 2 hours and 600°C for 90 minutes in a stepwise fashion to obtain a desirable solubility of francolite. As an alternative procedure to heating,the precipitate can be autoclaved at 150°C for 24 hours. The final product was ground on a mortar to obtain particle sizes ranging from 150 to 250 µm. Some chemical properties of the synthetic francolite are given in Table 7.2. Citric acid solubility test indicated that this material has a reactivity similar to that of medium reactive PR. The X-ray diffraction pattern of the synthetic francolite was similar to that of North Carolina phosphate rock (Figure 7.1).

Table 7.2 Some properties of the ^{32}P-labelled synthetic francolite used in the study.

Properties of francolite		
Particle size range (µm)	Total P (w/w)	2% citric acid solubility (% total P)
150 - 250	16.1	35.2
Amount of francolite added to soil (mg P kg^{-1} soil)	^{32}P activity added to soil (KBq g^{-1} soil)	
250	1.16	
500	2.32	
1000	4.64	

7.3.4 Incubation of soil, francolite and plant residue

Soil (10 g), francolite and plant residue were thoroughly mixed in a plastic bag and moistened to approximately 80% of the soil moisture "field capacity". The francolite was added at rates equivalent to 0, 250, 500 and 1000 mg P kg^{-1} soil. At these rates, the activity of the ^{32}P of the fertilizer was 1.16, 2.32 and 4.64 KBq g^{-1} soil, respectively. Plant residues were added at rates equivalent to 2500 and 5000 kg DM ha^{-1}. The mixtures were then transferred into sealed plastic bags (3 replicates per treatments) and incubated in an incubator at 30°C for 40 days. Moisture content of the mixture was checked by weighing the bag every day, and deionised water was added when necessary.

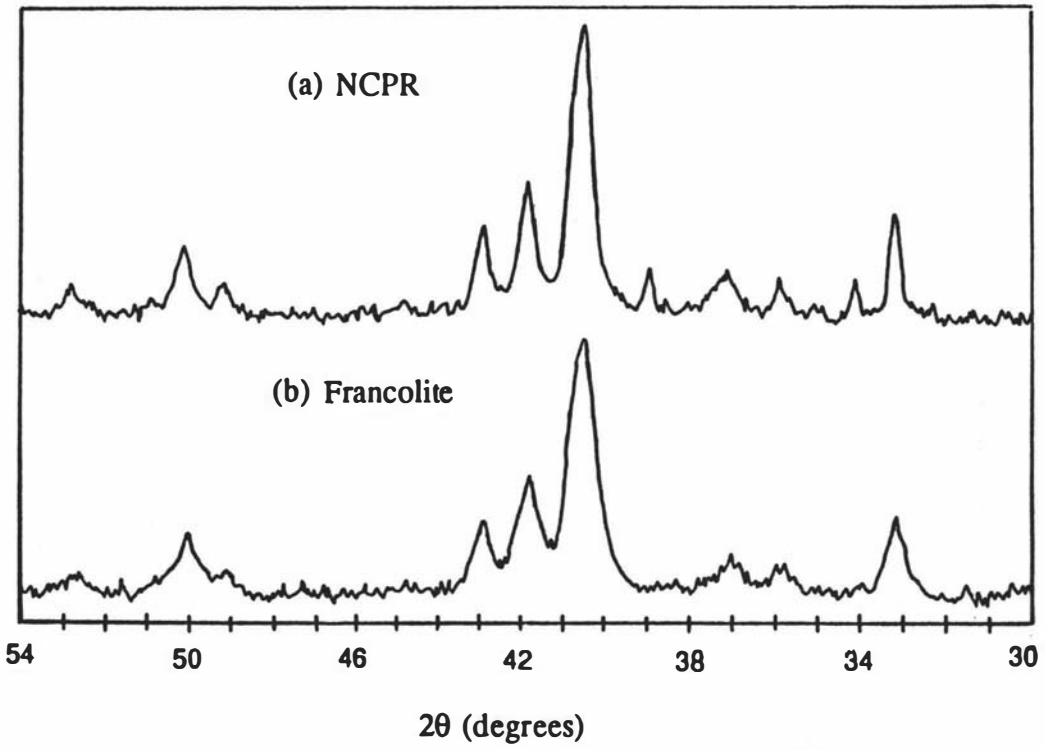


Figure 7.1 X-ray diffractograms of powdered materials of (a) North Carolina phosphate rock (NCPR) and (b) synthetic francolite (N.S. Bolan, unpublished data).

Individual samples withdrawn at 10, 20 and 40 days were immediately oven-dried at 50°C for 24 hours and ground in a coffee grinder.

7.3.5 Analytical measurements

7.3.5.1 Fertilizer analysis

The francolite was analysed for total P content following a tri-acid digestion and 2% citric acid extraction as described in Section 3.3.4 (Chapter 3). The activity of ^{32}P in the francolite was measured in the tri-acid digest using the Cerenkov counting method as described later in Section 7.3.5.4.

7.3.5.2 Soil analysis

Soils were characterised using the procedures described in Chapters 3 and 4. The plant availability of P in soils during the incubation study was estimated using an Olsen (O.5 M $NaHC0_3$) extraction (Section 3.3.3, Chapter 3). The amount of available P derived from fertilizer was estimated from the activity of the ^{32}P in the Olsen extract. The extent of francolite dissolution was estimated using Δ0.5 M H_2SO_4-^{31}P and Δ0.5 M H_2SO_4-^{32}P methods as described in Section 4.3.4 (Chapter 4).

7.3.5.3 Plant analysis

Concentrations of N and P in plant residues were measured following Kjeldahl digestion (Section 6.3.5, Chapter 6). The total C content in the leave residues were determined by dry combustion using Leco furnace (Tabatabai and Bremner, 1970).

7.3.5.4 Radioisotope analysis

The activity of the ^{32}P in the H_2SO_4 and Olsen extracts was measured using the Cerenkov counting method in a Beckman LS 3801 liquid scintillation counter. All counts were corrected for background radiation and colour quenching. No significant effect of chemical quench was found. The colour quenching was estimated by spiking

the non-labelled H_2SO_4 and Olsen extracts with 0.1 ml water containing a known quantity of ^{32}P. All measurements of radioactivity were also corrected for decay and normalized to the day on which the ^{32}P-labelled francolite was applied.

The percentage of inorganic P (Pi) derived from francolite (%Pidff) which is extractable in Olsen solution was calculated using the following equation:

$$\%Pidff = Olsen\text{-}^{32}P\ (KBq\ g^{-1}) / Initial\ ^{32}P\ total\ (KBq\ g^{-1}) \times 100 \quad (7.1)$$

Where Olsen-^{32}P is the activity of ^{32}P in the Olsen extract. The absolute amount of Pidff (mg P kg^{-1}) was calculated as follows:

$$Pidff\ (mg\ P\ kg^{-1}) = \%Pidff \times {}^{31}P\ applied\ (mg\ P\ kg^{-1}) \quad (7.2)$$

Amount of ^{31}Pi derived from soil or soil plus plant residue (Pidfs) which is extractable in Olsen solution was calculated as follows:

$$Pidfs\ (mg\ P\ kg^{-1}) = Total\ Olsen\text{-}Pi\ (mg\ P\ kg^{-1}) - Pidff\ (mg\ P\ kg^{-1}) \quad (7.3)$$

Amount of Olsen-extractable Pi (Olsen-Pi) derived from francolite, expressed as a percentage of the total Olsen-Pi (%PifNa), was calculated from the amount of Pidff by the following relation:

$$\%PifNa = Pidff\ (mg\ P\ kg^{-1}) / Total\ Olsen\text{-}Pi\ (mg\ P\ kg^{-1}) \times 100 \quad (7.4)$$

7.4 RESULTS

7.4.1 Relationship between the extent of francolite dissolution estimated by Δ0.5 M H_2SO_4-^{31}P and Δ0.5 M H_2SO_4-^{32}P methods

The extent of PR dissolution in Dannevirke and Prabumulih soils over 40 days estimated by the Δ0.5 M H_2SO_4-^{31}P and Δ0.5 H_2SO_4-^{32}P methods was closely related (Figure 7.2). Within the experimental error (±10%), the slope coefficient for the regression equation, together with the very low intercept, indicate that the extent of francolite dissolution estimated by the two methods was similar. These results derived from the use of radioactive francolite confirms, for the first time, that Δ0.5 M H_2SO_4-P method should be suitable for estimating the extent of francolite dissolution in similar acid soils.

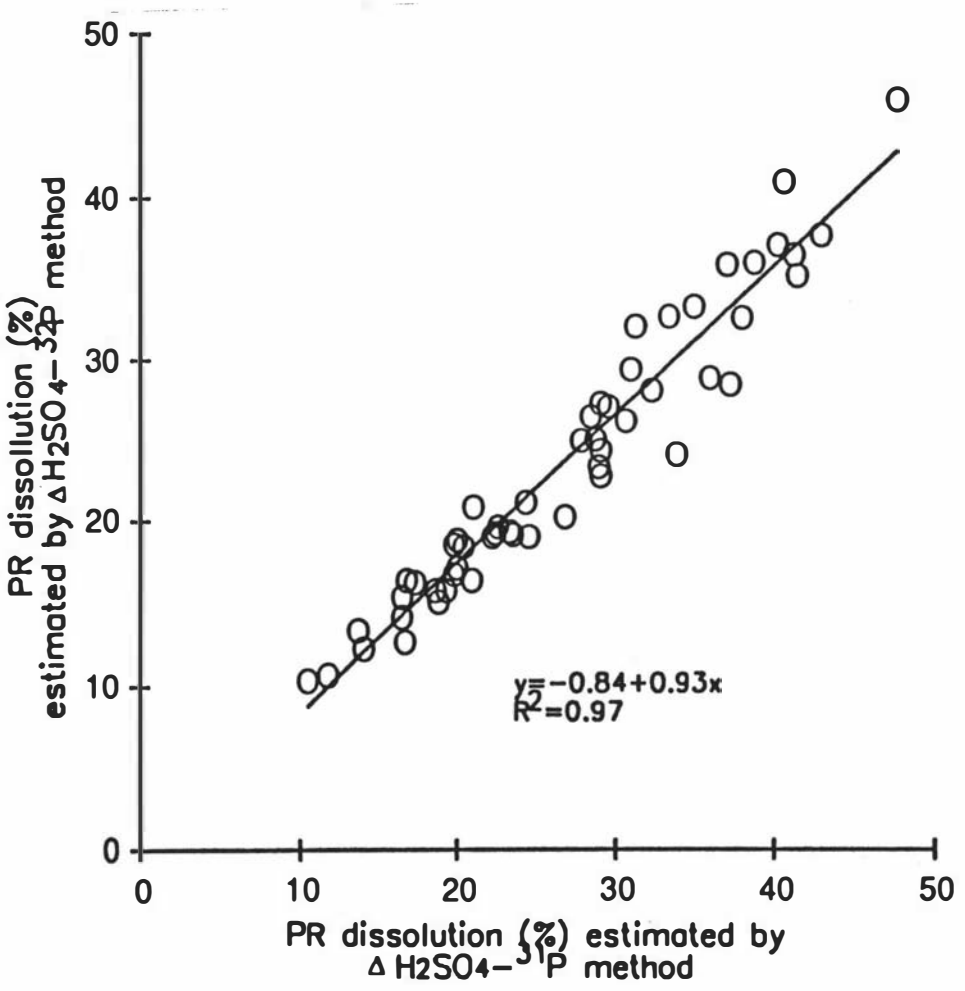


Figure 7.2 Relationship between the extent of francolite dissolution (applied at 250, 500 and 1000 mg P kg^{-1} soil) in Dannevirke and Prabumulih soils estimated by ΔH_2SO_4-^{31}P and ΔH_2SO_4-^{32}P methods.

Data of PR dissolution estimated by the Δ0.5 M H_2SO_4-^{31}P, subsequently referred to as the Δ0.5 M H_2SO_4-P, will be used in the remaining chapter.

7.4.2 Francolite dissolution

The extent of francolite dissolution in soils estimated from the increase in the H_2SO_4-extractable P (ΔH_2SO_4-P) in francolite-fertilized soil over control soil are shown in Figure 7.3. Plant residues had a marked effect on the extent of francolite dissolution in both soils. Irrespective of the francolite application rates, significant decreases in francolite dissolution were observed with increasing rates of plant residues. As the application rate of plant residues increased from 0 to 5000 kg ha^{-1}, the extent of francolite dissolution in Dannevirke soil after 40 days decreased from 32.2 to 20.9, 28.8 to 19.9 and 19.9 to 16.5 for the francolite application rate of 250, 500 and 1000 mg P kg^{-1}, respectively. The corresponding values for Prabumulih soil were 47.6 to 34.9, 47.7 to 34.9 and 28.4 to 35.9%.

The extent of francolite dissolution decreased with increasing its application rates. This trend was noted earlier (Chapters 3 and 5) for NCPR and MPR.

There was a significant interaction between increasing levels of plant residue and francolite dissolution in both soils (Table 7.3). The extent of PR dissolution after 40 days consistently decreased with increasing rate of plant residue and francolite applications. At the lowest rates of plant residue and francolite application (0 kg DM ha^{-1}, 250 mg P kg^{-1}), 32 and 48% of francolite had dissolved after 40 days of incubation in Dannevirke and Prabumulih soils, respectively. The corresponding values at the highest application rates (2500 kg DM ha^{-1}, 1000 mg P kg^{-1}) were 17 and 27%. Increased PR application rate caused a greater decrease in PR dissolution in the absence of plant residue.

7.4.3 Olsen-extractable Pi

Phosphorus availability in the soil-francolite-plant residue mixtures was assessed using Olsen extraction (Olsen *et al.*, 1954). The amount of Olsen-Pi derived from francolite

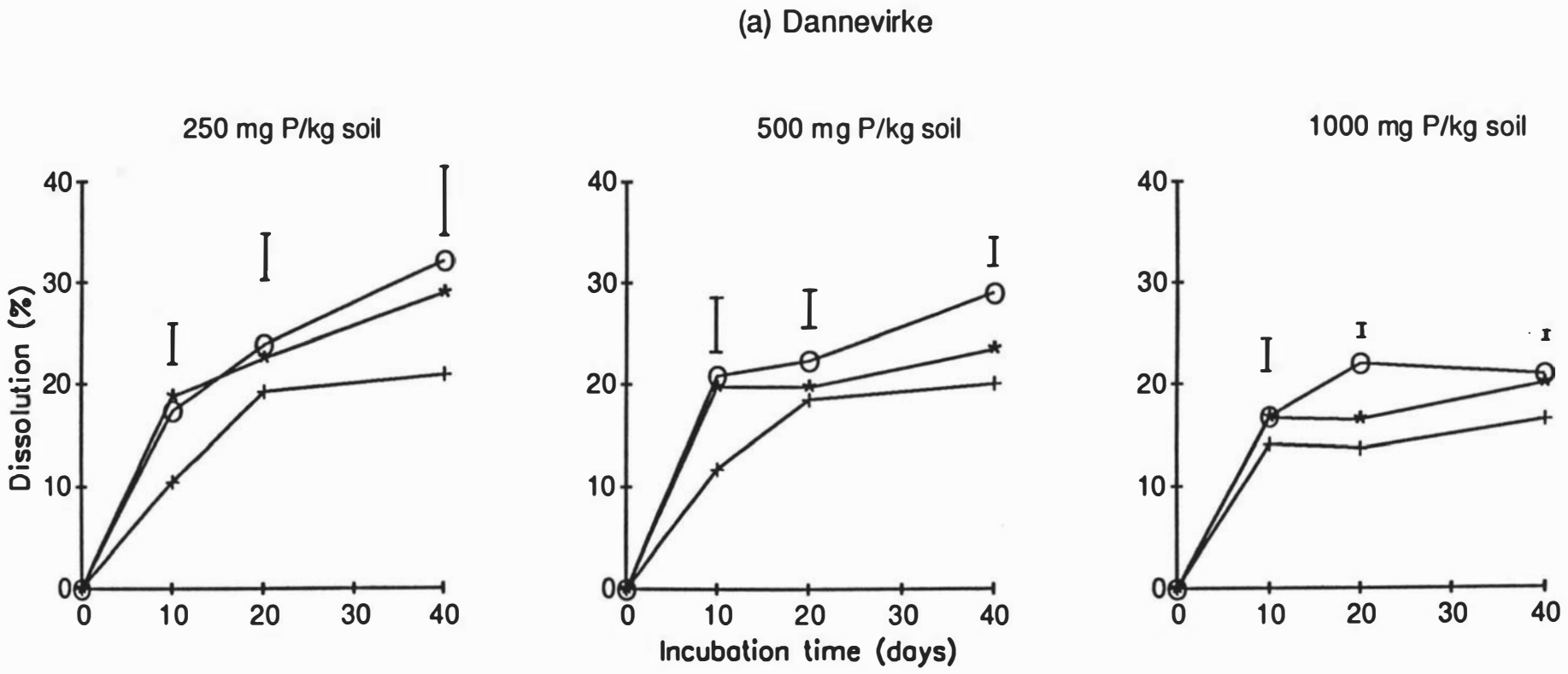


Figure 7.3 Effect of incubation time on the extent of francolite dissolution (applied at 250, 500 and 1000 mg P kg^{-1} soil) in (a) Dannevirke and (b) Prabumulih soils amended with (o) 0, (*) 2500 and (+) 5000 kg dry matter ha^{-1} of plant residue. Vertical bars are LSD ($P<0.05$) values.

(b) Prabumulih (Fig. 7.3)

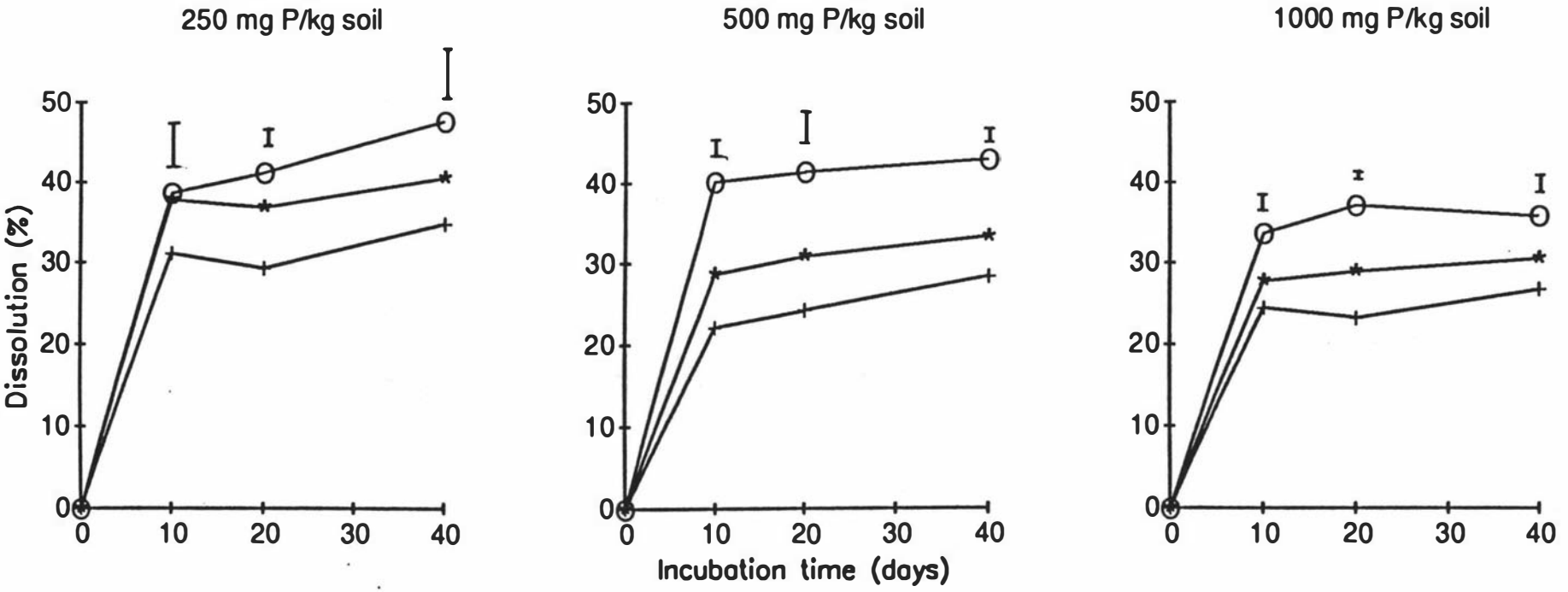


Table 7.3 Effect of plant residue and francolite application on the dissolution of francolite in Dannevirke and Prabumulih soils after 40 days of incubation.

Treatment		Francolite dissolution (%)	
Plant residue (kg DM ha^{-1})	Francolite (mg P kg^{-1} soil)	Dannevirke	Prabumulih
0	250	32.2	47.7
	500	29.0	42.9
	1000	20.9	35.9
2500	250	29.0	40.6
	500	23.5	33.3
	1000	20.0	30.6
5000	250	21.0	34.9
	500	20.0	28.4
	1000	16.5	26.8
LSD(P<0.05)	Plant residue (P)	3.1	2.7
	Francolite (F)	3.1	2.8
	P x F	1.8	1.6

is expressed as either the percentage of the added P (%Pidff) or the percentage of the total Olsen-Pi (%PifNa).

7.4.3.1 Amount of Olsen-extractable Pi

Marked changes in the amounts of Olsen-Pi occurred in both soils over the 40 day incubation (Figure 7.4). In the presence of plant residue and/or francolite, amounts of Olsen-Pi reached maximum after 10 days of incubation and subsequently tended to decrease with time reflecting the increased adsorption of P released to soil solution. After 40 days of incubation, the amounts of Olsen-Pi in Dannevirke soil fertilized with 0, 250, 500 and 1000 mg P kg^{-1} ranged from 10 to 19, 14 to 20, 17 to 21, and 21 to 22 mg P kg^{-1}. The corresponding values for the Prabumulih soils were 1 to 9, 11 to 12, 16 to 18, and 21 to 23 mg P kg^{-1}.

In the absence of francolite, amounts of Pi extracted by Olsen from both soils significantly increased with increasing rates of plant residues (Figure 7.4). After 40 days of incubation, increases in the rate of plant residue application from 0 to 5000 kg DM ha^{-1} increased the amounts of Olsen-Pi from 11 to 19 and 1 to 9 mg P kg^{-1} in Dannevirke and Prabumulih soils, respectively. In the presence of increasing amounts of francolite and plant residue, there was no consistent change in the amounts of Olsen-Pi. However, increases in Olsen-Pi in the francolite-fertilized samples over their respective control (ΔOlsen-Pi) at each francolite application rate (Figure 7.5) clearly show that increased plant residue additions decreased the availability of P. For example, by 40 days, the amounts of ΔOlsen-Pi in the Dannevirke soil fertilized with 500 mg P kg^{-1} of francolite decreased from 7 to 2 mg P kg^{-1} as the rates of plant residue application increased from 0 to 5000 kg DM ha^{-1}. The corresponding values for the Prabumulih soils decreased from 10 to 3 mg P kg^{-1}.

7.4.3.2 Amount of Olsen-extractable Pi derived from francolite

The amount of Pi derived from francolite in the Olsen extracts, expressed as a percentage of the added francolite-P (%Pidff), are presented in Table 7.4. In general Olsen reagent extracted only a small fraction (<4%) of the added francolite-P. By 40

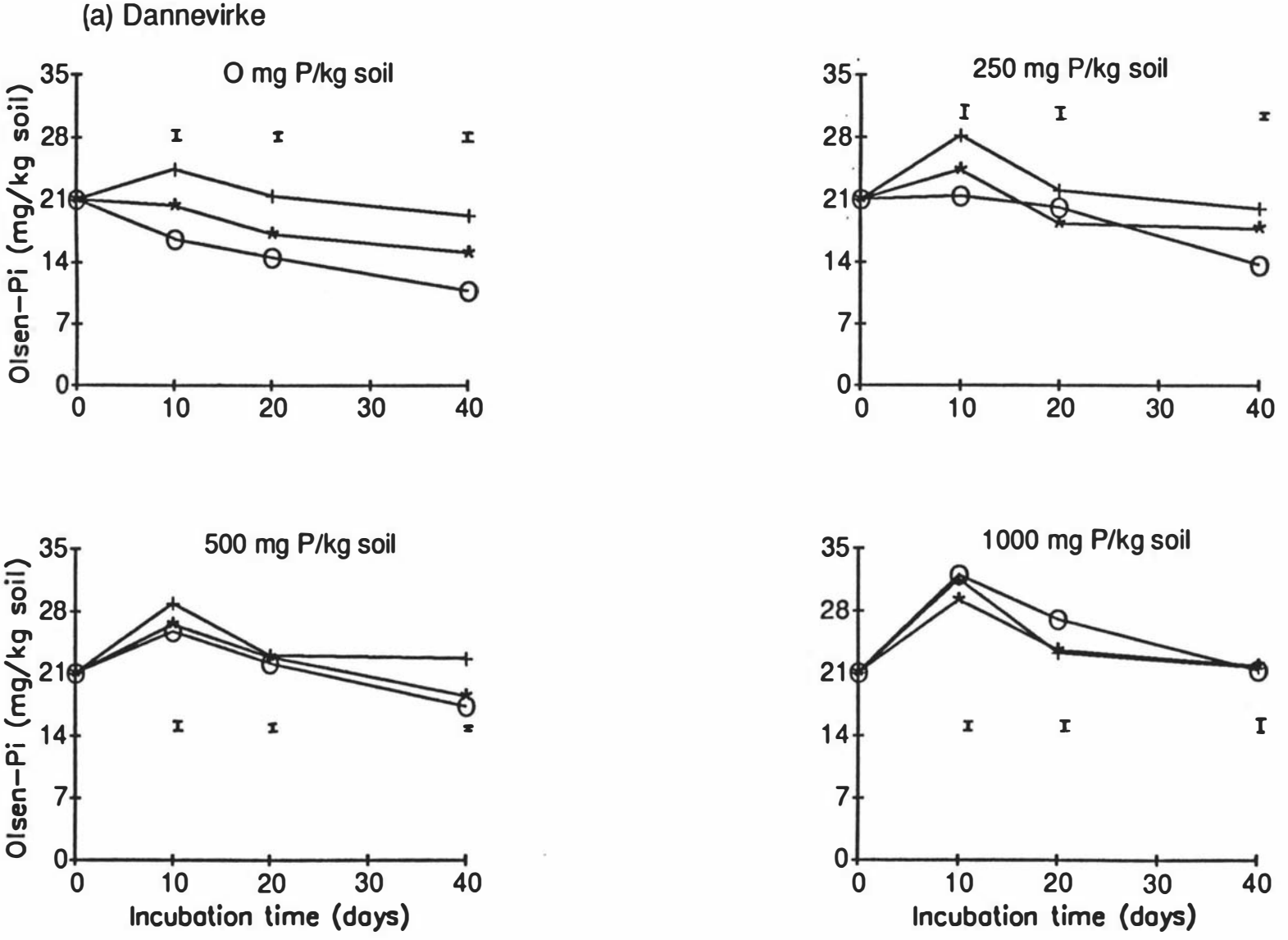
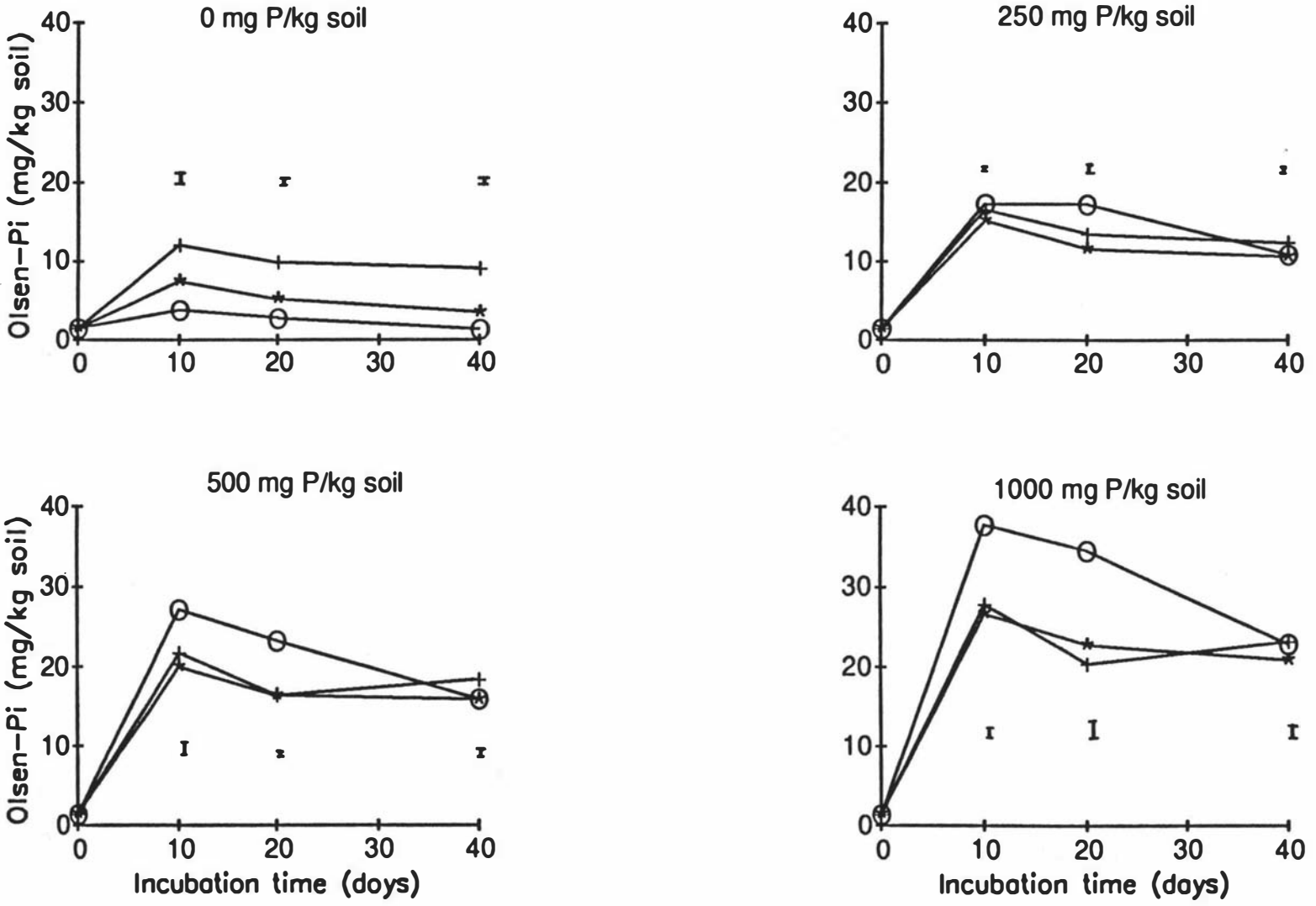


Figure 7.4 Effect of incubation time on changes in amounts of $NaHCO_3$-extractable Pi (Olsen-Pi) in (a) Prabumulih and (b) Dannevirke soils fertilized with 250, 500 and 1000 mg P kg^{-1} of francolite and amended with (○) 0, (*) 2500 and (+) 5000 kg dry matter ha^{-1} of plant residue. Vertical bars are LSD ($P<0.05$) values.

(b) Prabumulih (Fig. 7.4)



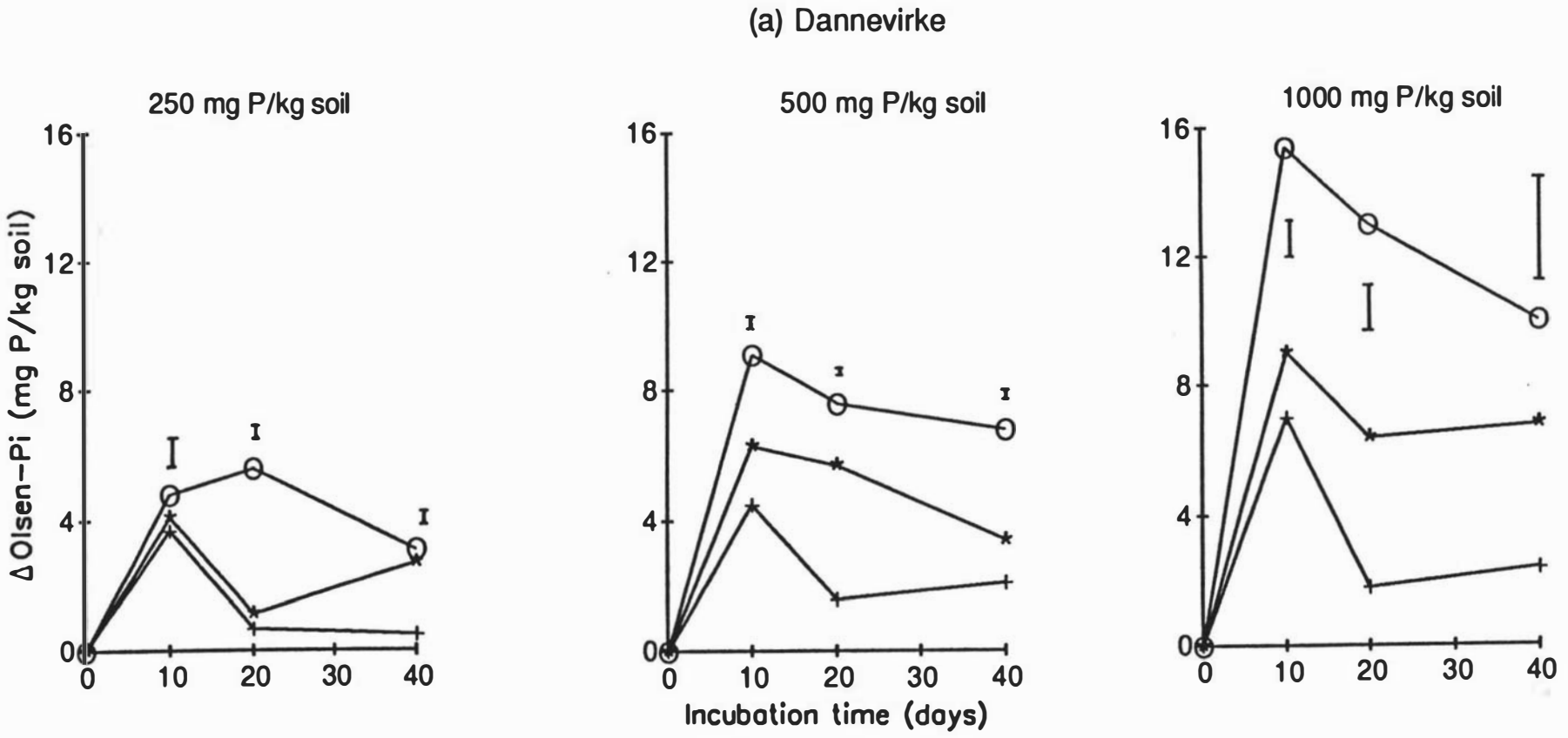


Figure 7.5 Effect of incubation time on increases in amounts of $NaHCO_3$-extractable Pi (ΔOlsen-Pi) in (a) Dannevirke and (b) Prabumulih soils fertilized with 250, 500 and 1000 mg P kg^{-1} of francolite and amended with (o) 0, (*) 2500 and (+) 5000 kg dry matter ha^{-1} of plant residue. Vertical bars are LSD ($P<0.05$) values.

(b) Prabumulih (Fig. 7.5)

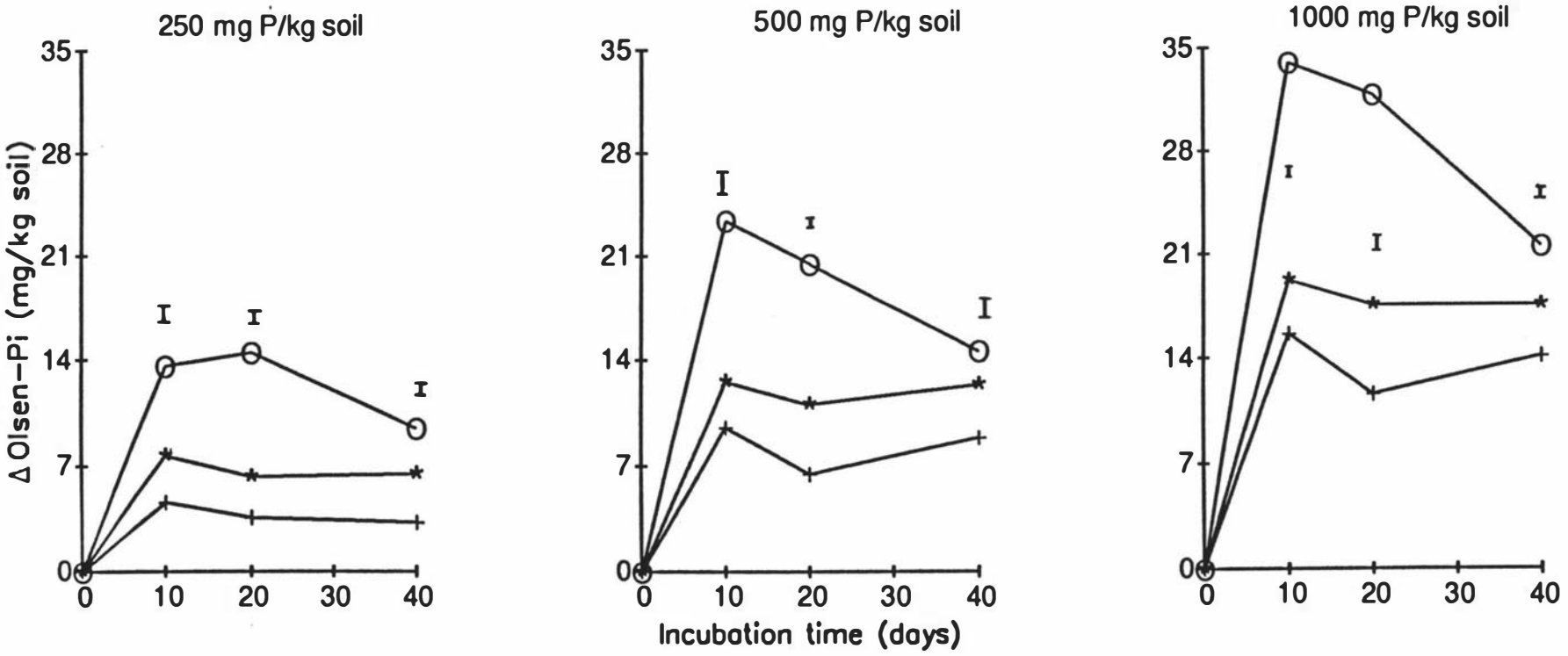


Figure 7.4 The activity of ^{32}P in Olsen extract and the percentage of Olsen-Pi derived from francolite relative to total francolite-P added (%Pidff) in Dannevirke (a) and Prabumulih (b) soils.

(a) Dannevirke

Treatment		^{32}P activity (Bq g^{-1} soil)			%Pidff*		
Francolite (mg P kg^{-1})	Plant residue (kg DM ha^{-1})	10d	20d	40d	10d	20d	40d
250	0	25.40	24.63	20.99	2.20	2.13	1.82
	2500	3.76	7.08	18.32	0.32	0.61	1.58
	5000	0.80	3.16	9.98	0.07	0.28	0.86
LSD(P<0.05)		6.72	2.64	2.49	0.57	0.22	0.21
500	0	26.32	29.73	29.10	1.14	1.28	1.26
	2500	13.67	16.62	24.24	0.59	0.72	1.05
	5000	7.65	7.95	13.21	0.33	0.34	0.57
LSD(P<0.05)		5.98	5.34	3.53	0.26	0.23	0.16
1000	0	60.96	56.81	51.00	1.32	1.23	1.10
	2500	23.67	27.10	43.36	0.51	0.59	0.94
	5000	18.70	13.90	31.48	0.40	0.30	0.68
LSD(P<0.05)		9.37	6.59	8.45	0.20	0.14	0.18

*%Pidff=^{32}P activity in Olsen extracts/Total activity applied x 100

Table 7.4 (contd)

(b) Prabumulih

Treatment		^{32}P activity (Bq g^{-1} soil)			%Pidff		
Francolite (mg P kg^{-1})	Plant residue (kg DM ha^{-1})	10d	20d	40d	10d	20d	40d
250	0	58.28	52.18	45.4	5.04	4.51	3.93
	2500	32.83	33.96	33.6	2.84	2.93	3.08
	5000	26.30	22.60	23.96	1.93	1.95	2.08
LSD(P<0.05)		8.44	6.49	8.84	0.73	0.57	0.77
500	0	103.90	89.14	83.77	4.49	3.85	3.62
	2500	53.70	53.48	59.12	2.32	2.31	2.56
	5000	39.72	32.53	48.29	1.72	1.41	2.09
LSD(P<0.05)		9.97	5.21	9.75	0.43	0.22	0.42
1000	0	157.2	135.07	110.44	3.40	2.92	2.27
	2500	88.57	78.18	84.79	1.92	1.45	1.83
	5000	72.82	57.79	79.77	1.60	1.25	1.73
LSD(P<0.05)		14.9	34.12	18.73	0.32	0.74	0.41

days, the %Pidff in Dannevirke soil ranged from 0.9 to 1.8, 0.6 to 1.3 and 0.7 to 1.7% at the francolite application rates of 250, 500 and 1000 mg P kg^{-1}, respectively. The corresponding ranges for the Prabumulih soil were 2.1 to 3.9, 2.1 to 3.6 and 1.7 to 2.3%. In both soils, the %Pidff values consistently decreased with increasing plant residues or increasing PR application rates (Table 7.4).

The amount of Olsen-Pi derived from francolite, expressed as a percentage of the total Olsen-Pi (%PifNa), increased consistently with increasing incubation time (Table 7.5), partly reflecting the decrease in the total amount of Olsen-Pi as the incubation proceeded (Figure 7.4) and the increased dissolution of the francolite (Figure 7.2).

Addition of plant residues significantly ($P<0.05$) increased the amount of Olsen-Pi and decreased the %PifNa (Table 7.5). As the application of plant residue was increased from 0 to 5000 kg ha^{-1}, the %PifNa in Dannevirke soil after 40 days decreased from 33 to 11, 36 to 13 and 52 to 32% at the francolite application rate of 250, 500 and 1000 mg P kg^{-1}, respectively. The corresponding ranges for the Prabumulih soil were 90 to 42, 94.5 to 59 and 99 to 75%.

After 40 days of incubation, less than 6 and 8% of the francolite-P dissolved was extracted by Olsen reagent in Dannevirke and Prabumulih soils, respectively (Figure 7.6) indicating that most of the dissolved P was adsorbed or immobilized by the soil. With increasing rate of francolite application, the relationship between amount of P dissolved and the amount of dissolved P extracted by Olsen reagent differed between soils (Figure 7.6). In general, increasing application rate of francolite in Prabumulih soil caused the percentage of dissolved P extracted by Olsen reagent to decrease. There was no clear trend in Dannevirke soil. In both soils, however, the percentage of dissolved francolite-P extracted by Olsen reagent decreased with increasing application rate of plant residue.

Table 7.5 Amounts of Olsen-Pi derived from francolite (Pidff), and soil or soil plus plant residues (Pidfs) and percentage of Olsen-Pi derived from francolite relative to total Olsen-Pi (%PifNa) in (a) Dannevirke and (b) Prabumulih soils.

(a) Dannevirke

Treatment		Olsen-Pi*						%PifNa##		
		Pidff** (mg P kg^{-1})			Pidfs# (mg P kg^{-1})					
Francolite (mg P kg^{-1})	Plant residue (kg DM ha^{-1})	10d	20d	40d	10d	20d	40d	10d	20d	40d
0	0	0	0	0	16.7	14.6	10.6	0	0	0
	2500	0	0	0	20.3	17.2	15.1	0	0	0
	5000	0	0	0	24.5	21.5	19.3	0	0	0
LSD(P<0.05)					0.7	0.3	0.7	-	-	-
250	0	5.5	5.3	4.6	16.0	14.9	9.1	8.5	26.4	33.3
	2500	0.8	1.5	4.0	23.6	16.8	14.5	3.3	8.3	21.4
	5000	0.2	0.7	2.1	28.0	21.5	17.7	0.6	3.1	10.9
LSD(P<0.05)		1.5	0.6	0.5	2.9	1.4	0.9	-	-	-
500	0	5.7	6.4	6.3	20.1	15.8	11.1	22.1	28.9	36.2
	2500	3.0	3.6	5.3	23.7	19.3	13.3	11.1	15.7	31.9
	5000	1.7	1.7	2.9	28.5	21.4	18.6	5.6	7.4	13.4
LSD(P<0.05)		2.7	1.1	0.8	1.7	1.4	1.5	-	-	-
1000	0	13.2	12.3	10.5	18.9	15.3	10.3	41.1	44.4	51.6
	2500	5.1	5.9	9.4	24.2	17.7	12.5	17.5	24.9	42.9
	5000	4.0	3.0	6.8	27.5	20.3	14.8	12.8	12.9	31.8
LSD(P<0.05)		2.0	1.4	1.7	2.5	1.8	ns	-	-	-

* Total Olsen-Pi data are shown in Figure 7.4

** Pidff (mg P kg^{-1}) = %Pidff x Initial P added (mg P kg^{-1})

Pidfs = Total Olsen-Pi (mg P kg^{-1}) - Pidff (mg P kg^{-1})

%PifNa = Pidff (mg P kg^{-1})/Total Olsen-Pi (mg P kg^{-1}) x 100

Table 7.5 (contd)
(b) Prabumulih

Treatment		Olsen-Pi						%PifNa		
		Pidff (mg P kg^{-1})			Pidfs (mg P kg^{-1})					
Francolite (mg P kg^{-1})	Plant residue (kg DM ha^{-1})	10d	20d	40d	10d	20d	40d	10d	20d	40d
0	0	0	0	0	3.8	2.8	1.4	0	0	0
	2500	0	0	0	7.5	5.3	3.5	0	0	0
	5000	0	0	0	12.1	9.9	9.1	0	0	0
LSD(P<0.05)					2.1	1.2	2.6			
250	0	12.6	11.3	9.8	4.8	6.7	1.1	72.2	62.7	89.9
	2500	7.1	7.4	7.7	8.1	4.3	2.3	46.8	63.0	76.9
	5000	4.8	4.9	5.2	11.9	7.6	7.2	28.9	39.9	41.8
LSD(P<0.05)		1.8	1.4	1.9	1.1	ns	2.2	-	-	-
500	0	22.5	19.3	17.2	4.7	4.0	1.0	82.7	82.9	94.5
	2500	11.6	11.6	12.8	8.4	4.9	3.1	57.8	70.5	80.4
	5000	8.6	7.0	10.4	13.1	9.4	7.6	39.8	42.8	58.5
LSD(P<0.05)		2.1	1.1	2.1	2.8	1.5	3.51	-	-	-
1000	0	34.0	29.2	22.7	3.8	5.3	0.2	89.9	84.5	99.1
	2500	19.2	16.9	18.3	7.5	5.9	2.6	71.6	73.9	88.1
	5000	16.0	12.5	17.3	11.9	9.0	6.0	57.4	58.1	74.6
LSD(P<0.05)		3.2	3.1	4.0	2.9	ns	5.3	-	-	-

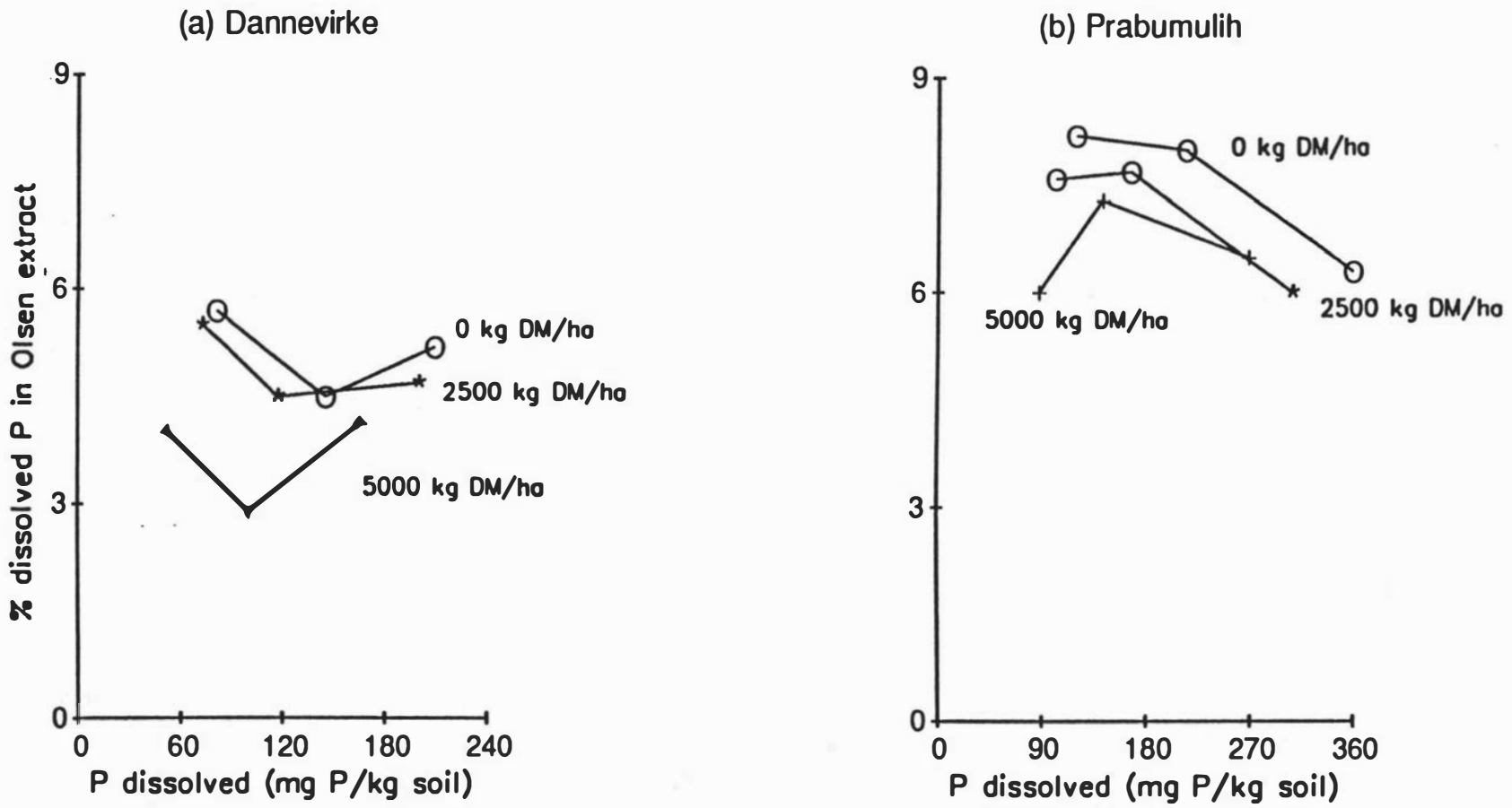


Figure 7.6 Relationship between amounts of P dissolved from francolite and percentage of the dissolved P extracted by Olsen reagent from (a) Dannevirke and (b) Prabumulih soils amended with different rates of plant residue.

7.5 DISCUSSION

7.5.1 Francolite dissolution

Two reasons can be given for the decreased francolite dissolution observed with increasing rates of plant residue application rates.

Firstly, the increased pH in soil amended with plant residue (as shown for Dannevirke soil, Figure 7.7), particularly during the first two weeks, decreased the supply of protons. Increases in soil pH generally decrease the extent of PR dissolution (Chapters 3 and 5). The increase in pH of soil amended with plant residue is attributed to the net production of OH^- ions resulting from the ammonification process (Floate and Torrance, 1970). The ammonification rate during the decomposition of organic materials having low C/N could be expected to be high during the first two weeks (Sutopo and Kawatsuka, 1990). Figure 7.7 shows that after 10 days the pH decreased with increasing incubation period suggesting that nitrifying bacteria became more active resulting in increased production of protons from nitrification.

Secondly, the decomposition of plant residue will have increased the concentrations of P and Ca in soil solution. During plant residue decomposition, considerable amounts of plant P (Till and Blair, 1978; Dalal, 1979; White and Ayoub, 1983; McLaughlin and Alston, 1986; Pathiratne *et al.*, 1987; Bumaya and Naylor, 1988; Thibaud *et al.*, 1988; Li *et al.*, 1990) are released to soils. The Olsen-Pi data shown in Figure 7.5 support this finding. In addition to P, considerable amounts of Ca may have also been released to soil during plant residue decomposition (Kalburtzi *et al.*, 1990). Most legumes generally accumulate larger quantities of Ca than non legumes (Bolan *et al.*, 1990). In contrast to P, much of the Ca released to soil would remain in soil solution because the concentrations of Ca in solutions are generally higher than P, and Ca would be required to balance anions, such as NO_3^- and SO_4^{2-}, remaining in soil solution. Most of the released plant P was immediately immobilized either by chemical (adsorption, precipitation) or by biological processes in the soil (White and Ayoub, 1983). Thus, increased solution Ca concentrations during plant residue decomposition was expected to affect francolite dissolution because solution Ca concentrations modify the solubility

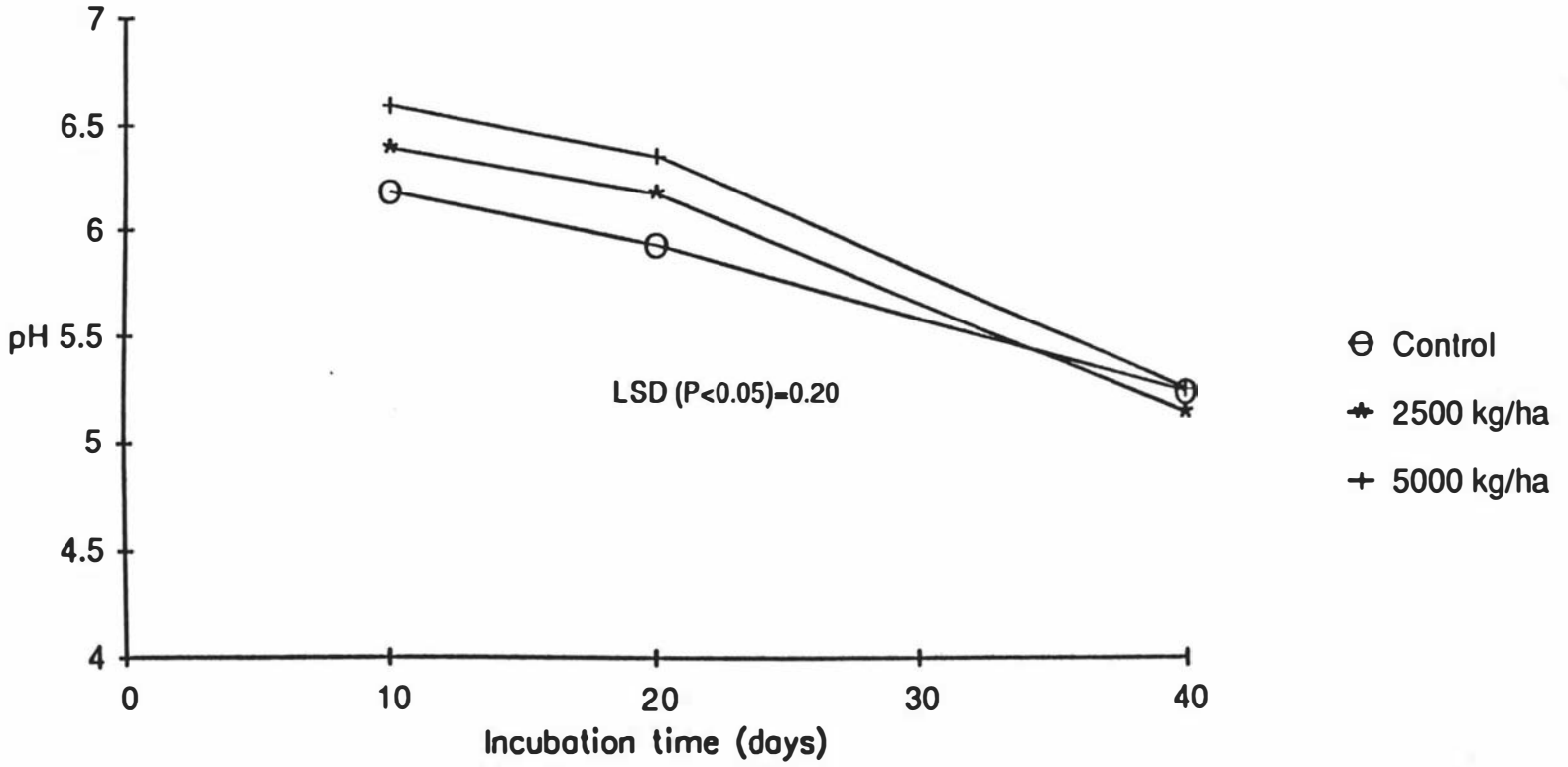


Figure 7.7 Effect of incubation time on pH_{H2O} of unfertilized Dannevirke soil amended with different rates of plant residue.

product for francolite by approximately a power of 10.

Additions of organic matter to soil are reported to either decrease (Dalton *et al.*, 1952; Singh and Jones,1976; Sanchez and Uehara, 1980; Bumaya and Naylor, 1988) or increase (Field *et al.*, 1985; Bumaya and Naylor, 1988) P sorption by soil constituents. In PR-fertilized soil, such changes may affect the extent of PR dissolution (Smyth and Sanchez, 1982; Mackay *et al.*, 1986; Kanabo and Gilkes, 1986). There was good evidence of decreased dissolution through plant residue addition. This, however, may not be necessarily associated with changes in P sorption in soil caused by additions of plant residue. Bumaya and Naylor (1988) have demonstrated that additions of plant residue with P content greater than 0.1% at application rates equal to or greater than 5% (w/w) decrease P sorption of a volcanic soil. While the P content of plant residue used in the present study is high (0.44%), the plant residue was added to soil at rates less than 2% (w/w).

7.5.2 Olsen-extractable Pi

Amounts of Olsen-Pi in both soils decreased with time (Table 7.5) indicating that the released P from francolite and plant residue became more strongly adsorbed by the soil, making it less extractable in Olsen reagent. Similar findings were reported in Chapter 6 when North Carolina and Moroccan PRs were incubated in a range of New Zealand and Indonesian soils.

Although the extent of PR dissolution decreased with increasing francolite application rates (Figure 7.3), the amounts of Olsen-Pi derived from francolite, either expressed as %Pidff or %PifNa, increased (Table 7.5). This is because the absolute amount of P released (mg P kg^{-1} soil) from francolite increased with increasing its application rate. However, the effect of francolite application rate on the percentage of dissolved francolite-P extracted in Olsen reagent did not show a clear trend (Figure 7.6). These results were different from the finding of Kanabo and Gilkes (1988b) showing that the percentage of dissolved NCPR-P extracted in Olsen reagent decreases linearly with increasing PR application rate.

During the 40 days of incubation, the amount of Olsen-Pi derived from francolite, expressed either as the percentage of total francolite-P (%Pidff) or as the percentage of total Olsen-Pi (%PifNa), was higher in Prabumulih soil than in Dannevirke soil (Tables 7.4 and 7.5). The main reasons for this are the higher extent of francolite dissolution in Prabumulih soil which has a lower pH.

Decreases in the availability of the P dissolved from francolite and its contribution to Olsen-Pi with increasing additions of plant residues agree with the findings of Pathiratne *et al.* (1987). Reasons for this can be given by (a) decreases in francolite dissolution, and (b) increased chemical and microbial immobilization of the dissolved P. Whereas the first reason has been proven (Figure 7.3), no experimental data in the present study directly supported the latter reason. Increases in microbial immobilization of the dissolved P from francolite is possible. Several workers (e.g. McLaughlin and Alston, 1986; Thibaud *et al.*, 1988) have shown that microbial immobilization of P from MCP increased with addition of plant residues. However, these workers observed that most of soil P originating from MCP remained in soil inorganic P fractions. The addition of litter of leaves of *Hevea brasiliensis* (Pathiratne *et al.*, 1987) and medic residues (McLaughlin and Alston, 1986) produced similar result. A study by McLaughlin *et al.* (1988a) shows that most of the medic residue P was inorganic when it was added to an Australian solonized brown soil, but only 7 days later more than 50% had been incorporated into organic fractions in the soil. The total P content of the clover residue used in the present study was 0.44%. Thus immobilization of native P was unlikely to occur because Fuller (1956) demonstrated that the immobilization of native P in soil amended with plant residue is more likely to occur when the added residue contains less than 0.2% P (i.e. has a wide C:P ratio). The net effect of plant residue decomposition in soils was to increase Olsen-Pi content (Figure 7.4).

7.6 CONCLUSIONS

Radioisotope data have shown that ΔH_2SO_4-extractable Pi provides an accurate measure of the amount of undissolved francolite remaining in soil.

The results from this experiment demonstrated that, under short-term laboratory incubation conditions, the extent of a synthetic francolite dissolution, which has the characters similar to a medium reactive PR, decreased with increasing rates of plant residue application. Increases in soil pH and concentration Ca in soil solution are the main reasons for these decreases.

Less than 4% of the P added as francolite was Olsen-Pi extractable after 40 days of incubation. The majority of the dissolved francolite-P was adsorbed by soil surfaces. The availability of P dissolved from francolite generally decreased with increasing rates of plant residue application. Results from this study indicate that incorporation of P rich crop residues into soils will increase the available P content of the soil but, in PR-fertilized soils, may not enhance PR dissolution in the short-term.

CHAPTER 8
AGRONOMIC EFFECTIVENESS OF PHOSPHATE ROCKS IN INDONESIAN SOILS

8.1 INTRODUCTION

A large number of studies have been carried out to examine the residual effect of fertilizer P in acidic tropical soils (e.g. Widjaya-Adhi *et al.*, 1985; Fox *et al.*, 1971). Most of this research, however, has been focused on the residual effectiveness of water-soluble P fertilizers, such as single superphosphate (SSP) and triple superphosphate (TSP). Information on residual effectiveness of phosphate rocks (PRs) in different cropping systems is still limited.

As discussed in Chapter 2, several studies have shown that PRs can be used as alternatives to soluble fertilizers in Indonesia. These studies, however, have evaluated only the potential agronomic effectiveness of PR and have not investigated more closely the relationship between the amount of P taken up by plants in relation to the amount of PR-P dissolved. In addition, research is required to provide information on suitable rates and frequencies of PR application.

It has been recognized that P fertilizer recommendations based on soil P test data require different tests or different calibration curves for soils fertilized with P fertilizers of differing solubility (Hammond *et al.*, 1986; Rajan *et al.*, 1991b). Assessments of the ability of soil P tests to predict PR fertilizer requirements in acidic tropical soils, especially in Indonesian soils, are scarce.

Hammond *et al.* (1986) suggested that new soil tests are required for soils fertilized with P fertilizers of varying solubility. Some new soil P tests have been proposed. These include the Pi (Menon *et al.*, 1989c) and the mixed ion-exchange resin membrane (Saggar *et al.*, 1990) tests. The accuracy of these new soil tests, particularly the resin membrane test, in predicting yield has not been examined extensively.

8.2 OBJECTIVES

The main objectives of this study were:

1. To evaluate the influence of soil-fertilizer contact time on residual effectiveness of TSP and various PRs in two contrasting Indonesian soils. The influence of lime on residual fertilizer value was also investigated;

2. To measure the effect of soil-PR contact time on the extent of PR dissolution; and

3. To compare the ability of different soil P tests to predict the residual agronomic effectiveness of TSP and PR fertilizers.

8.3 MATERIALS AND METHODS

8.3.1 Field trial site selection

Two field trials were conducted at Sembawa and Serong, South Sumatra province, Indonesia. The Sembawa trial was established at the Research Institute for Estate Crops (RIEC), Sembawa. The Serong trial was established on a farmer's property. The map showing the study areas is shown in Figure 8.1. Both sites were initially covered with shrubby vegetation, with a predominance of *alang alang* (*Imperata cylindrica*), which commonly invades low fertility and deforested sites. Site descriptions are given in Table 8.1. The field trial sites were selected based on differences in soil properties relevant to PR dissolution and P availability. These include pH, P retention capacity, CEC and soil texture. Some properties of the soils are given in Table 8.2.

8.3.2 Phosphate fertilizers

North Carolina phosphate rock (NCPR), Moroccan phosphate rock (MPR), Pati phosphate rock (PPR) and triple superphosphate (TSP) were used as P fertilizers. Some

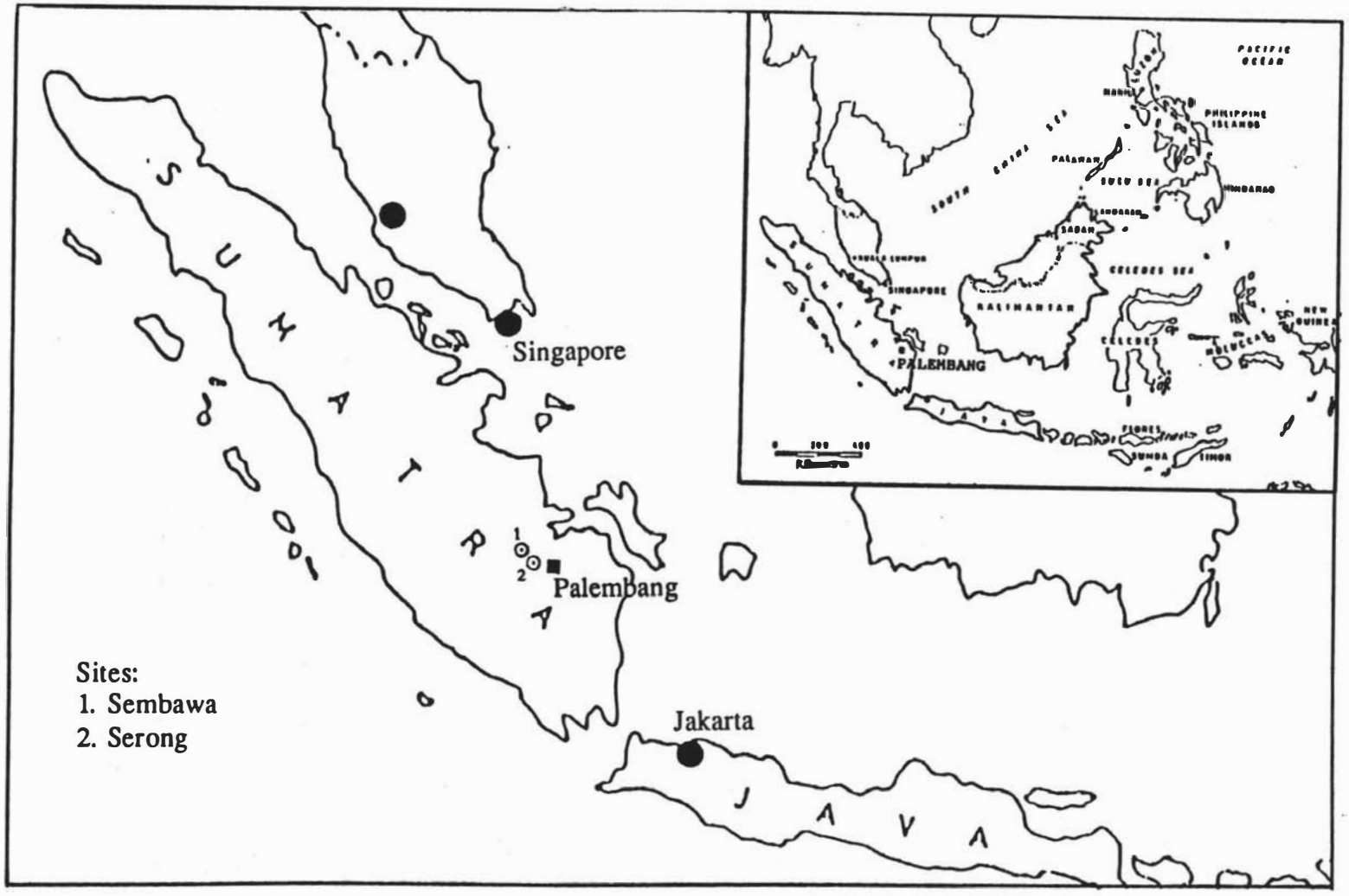


Figure 8.1 Map of Sumatra Island showing the location of field trials.

Table 8.1 Description of field trial sites.

	Field trial site	
	Sembawa	Serong
Location	10 km north west of Palembang, South Sumatra province	25 km north west of Palembang, South Sumatra province
Estimated annual rainfal (mm)	2263	2154
Vegetation	*Imperata cylindrica*, mixture of shrubs	*Imperata cylindrica*, mixture of shrubs
Classification:		
1. Soil Taxonomy	Typic Paleudult	Typic Fluvaquent
2. Indonesian Soil Group	Red yellow podzolic	Brown alluvial

Table 8.2 Selected properties of the soil (0 - 75 mm) used in the study.

Field trial site	pH (H_2O)	Organic C (%)	Olsen P (mg kg^{-1})	Exchangeable cations (cmol (+) kg^{-1})				CEC	TA*	P retention (%)	Bd (g cm^{-3})	Soil textural class
				Ca	Mg	K	Na	cmol (+) kg^{-1}				
Sembawa	4.8	2.8	4.5	0.5	0.1	0.3	0.1	9.0	13.2	32	1.1	clay loam
Serong	5.3	1.6	2.3	0.1	<0.1	<0.1	<0.1	5.0	12.7	19	1.4	sand

* TA: Titratable acidity.

properties of the P fertilizers are given in Table 8.3. Whilst the first two fertilizers are reactive and medium reactive PRs imported to Indonesia, PPR is an indigenous material mined from a deposit located in Pati region, Central Java province, Indonesia. According to its citric solubility (33.3% total P), the finely divided PPR behaves as a medium reactive PR (Bolan *et al*,. 1990). The TSP is a locally manufactured product used as the main P fertilizer in Indonesia.

8.3.3 Conduct of the experiment

8.3.3.1 Land clearing and plot layout

Following the removal of weeds by hand cutting, the sites were ploughed with a tractor and then levelled with a hoe. The area was divided into two sections (Appendices 8.1a and 8.1b). The first section (A), designated for the main treatments, was divided into 4 blocks, each comprising 16 and 14 experimental treatment plots (2 m x 3 m) at Sembawa and Serong, respectively. The second section (B), designated for the response curve plots, was divided into 16 and 14 experimental plots (2 m x 3 m) at Sembawa and Serong, respectively. Each plot represented a fertilizer treatment.

8.3.3.2 Phosphate fertilizer treatments

The P fertilizer treatments used in Section A and B were as follows:

Section A (main plots)

The treatments in Section A, comprising a single application rate (80 kg P ha^{-1}) of four P fertilizer forms at four application times, were designed to test the residual agronomic effectiveness of different fertilizer materials.

1. Phosphate fertilizers

Phosphate fertilizers used in this trial were triple superphosphate (TSP), North Carolina (NCPR), Pati (PPR) and Moroccan (MPR) phosphate rocks. Each fertilizer was applied at 80 kg P ha^{-1}. A control (no P) treatment was also included as a check. All plots received a basal dressing of N, K and S fertilizers at the rate of 30 kg N ha^{-1} and 15 kg

Table 8.3 Several characteristics of P fertilizers used in the field trials

P fertilizer	Particle size	P total (% w/w)	2% citric acid solubility	2% formic acid solubility
			(% of total P)	
Triple superphosphate (TSP)	Conventional granular	20.8	86.9	87.2
North Carolina PR (NCPR)	20%<150 µm, 80%<250 µm	13.0	41.7	70.5
Moroccan PR (MPR)	30%<150 µm, 73%<250 µm	13.6	31.3	50.8
Pati PR (PPR)	90%<60 µm	14.1	33.3	53.8

S ha^{-1} as Urea and Ammonium Sulphate, and 20 kg K ha^{-1} as KCl prior to P fertilizer incorporation at T_1.

2. Phosphate application times

The timing of P fertilizer application was a treatment, and four single applications were made at 0 (T_1), ~6 (T_2), ~18 (T_3) and ~19 (T_4) months after transplanting Calopogonium (*Calopogonium caeruleum*) seedlings in May 1989. Plots receiving TSP and NCPR were fertilized at T_1, T_2, T_3 and T_4, and plots receiving PPR and MPR were fertilized at T_1, T_3 and T_4. Immediately after the fertilization of the T_4 plots, a second crop (maize) was sown.

On T_1 plots, P fertilizers were broadcast onto the surface of the plots and forked into a the soil to a depth of 100 mm. Prior to P fertilizer applications at T_2 and T_3 Calopogonium plants were mown to a height of 80 mm above the ground. Cuttings were removed from the plots prior to fertilizer application and were later returned to each plot after P fertilizer application. On T_4 plots, P fertilizers were broadcast onto the plot, forked into a soil depth of 100 mm one day prior to sowing maize. Similarly, all T_1, T_2, and T_3 plots were also forked at T_4.

All P fertilizer treatments, including the control, were replicated four times. The P fertilizers and application times at Sembawa and Serong are given in Table 8.4.

Section B (response curve plots)

The treatments in Section B comprised triple superphosphate (TSP) and North Carolina phosphate rock (NCPR) applied at several rates ranging from 0 to 240 and 0 to 560 kg P ha^{-1}, respectively. All P fertilizers were broadcast at T_1 and forked into the soil to a depth of 100 mm. The treatments in Section B were not replicated.

8.3.3.3 Lime application

It is common practice to apply lime in order to overcome problems associated with soil acidity. The effect of lime on the residual value of P fertilizers was examined as follows:

Table 8.4 Forms and application times of P fertilizer in Section A (main plots) and Section B (response curve plots) at Sembawa and Serong field sites.

P fertilizer application time			P fertilizer applied to main plots	P fertilizer applied to response curve plots	Cropping sequence
Code	Sembawa	Serong			
T_1	26 May 1989	28 May 1989	TSP, NCPR, PPR, MPR	NCPR, TSP	Calopogonium (*Calopogonium caeruleum*)*
T_2	26 Nov 1989	28 Nov 1989	TSP, NCPR	-	
T_3	26 May 1990	28 May 1990	TSP, NCPR, PPR, MPR	-	
T_4	23 Dec 1990**	18 Dec 1990	TSP, NCPR, PPR, MPR	-	Maize

* The Calopogonium failed to grow at Serong.
**T_4-P fertilizers were applied two weeks after lime (1000 kg ha^{-1}) was applied to 1/2 of the area of each plot.

Two weeks prior to sowing maize at the Sembawa site, the plots in Section A were divided in half. Lime (1000 kg ha^{-1}) was broadcast onto one half of each plot, and forked into the top 100 mm.

8.3.3.4 Transplanting of Calopogonium seedlings

Two week old seedlings of Calopogonium (*Calopogonium caeruleum*) were transplanted following P fertilizer application at T_1, at a spacing of 0.5 x 1.0 m within and between rows, respectively. Due to the prevailing dry conditions at the beginning of the experiment, some seedlings were damaged and had to be replaced. Irrigation was applied daily around each plant during the first 16 days after transplanting at Sembawa to avoid water stress. At the Serong site, water stress was severe and most plants died. The plots at Serong were finally left bare for 18 months before maize was sown at T_4.

During the 18 months of the Calopogonium growth at Sembawa, plants were mown four times at 4, 6, 9, 12 and 18 months after transplanting to a height of 80 mm above the ground. Mowing at 6 and 12 months after transplanting coincided with P fertilizer applications at T_2 and T_3, respectively. Cuttings taken prior to T_4 were returned to the plots after fertilizer application.

At the end of the 18 months of Calopogonium growth, plants were mown and the cuttings were removed from the plots. The herbicide, Paraquat, was sprayed to kill the legume stubble.

8.3.3.5 Sowing maize

Following the final mowing of the Calopogonium, the plots were ploughed to a 100 mm depth and levelled using a hoe. Fertilizer treatments at T_4 were applied on 18 and 23 December 1990 at Serong and Sembawa, respectively. Two days after P fertilizer application, maize seeds (cv. Pioneer) were direct drilled in all plots at spacings of 300 mm x 200 mm and 500 mm x 250 mm at Sembawa and Serong, respectively.

To overcome the effect of variable N supply from uneven Calopogonium growth, starter

and sidedressed fertilizers were applied at final rates of 160 kg N, 100 kg K and 18 kg S ha^{-1}, and 360 kg N, 240 kg K and 36 kg S ha^{-1} at Sembawa and Serong, respectively in four split dressings at 0, 2, 4 and 6 weeks after emergence (Appendix 8.2). The fertilizer dressings were split based on differences in nutrient requirements at different stage of maize growth (Hanway, 1962a). All plots also received Boron (5 kg B ha^{-1} as Borax) at maize planting.

Pesticides (Darmabas, Dithane and Mancozeb) were applied at a recommended dose during early stages of the maize growth. Weeding was done using a hoe when necessary.

8.3.4 Harvesting

Dry matter yield and P uptake of Calopogonium at the final mowing (18 months after transplanting) were initially planned to be measured, however, at this stage the growth of Calopogonium was poor and no measurements were made.

Maize plants were harvested at tasselling on 5 and 7 February 1990 at Serong and Sembawa, respectively. Plants were cut from areas of 1.7 m^2 within plots at the Sembawa and 2.5 m^2 at Serong. The harvested plants from each plot or subplot were weighed and subsampled before being oven-dried at 70°C. The oven-dried plants were once again weighed to determine the moisture content of the fresh harvested plants before milling and storage for chemical analysis.

8.3.5 Soil sampling

Soil samples were taken on three occasions: prior to ploughing at the beginning of the experiments, after harvesting the Calopogonium at Sembawa (26 September 1990) and at Serong (28 November 1990), and one day after harvesting the maize on 5 and 7 February 1990 at Serong and Sembawa, respectively. Initial soil samples were taken from 0 - 75 mm soil depth. On the second and third occasions, 10 to 12 soil cores per plot were sampled from the 0 - 50 mm, 50 - 100 mm and 100 - 150 mm soil depths at Sembawa, and 0 - 50 mm, 5 - 100 mm and 100 - 200 mm soil depths at Serong. Soil

samples were bulked for each depth increment at each plot, air-dried and sieved to pass through a 2 mm sieve.

8.3.6 Soil analysis

Soil samples were analysed for pH, organic C, CEC, exchangeable bases, P retention capacity and titratable acidity as described in Chapters 3, 4 and 5. Amounts of plant-available P in soil were estimated by three soil tests, namely Olsen (Olsen *et al.*, 1954), Bray 1 (Bray and Kurtz, 1945) and ion-exchange resin membrane (subsequently referred to as resin) (Saggar *et al.*, 1990) extractions, as described in Section 6.3.4 (Chapter 6).

To estimate the dissolution of P fertilizers, soil samples taken from three depths (Section 8.3.5) were sequentially extracted using the ΔH_2SO_4-P method (Chapters 4 and 5). For the calculation of the extent of PR dissolution, values for H_2SO_4-extractable P were converted to kg P ha^{-1} using bulk densities determined for each sampling depth.

Soil bulk densities were measured using soil cores, 50 mm long and 50 mm diameter, taken at each soil depth (Section 8.3.5).

8.3.7 Plant analysis

Total P concentrations of composite plant samples were determined following Kjeldahl digestion as described in Section 6.3.5 (Chapter 6).

8.3.8 Meteorological data

Records of daily rainfall and monthly potential evaporation (measured by Penman) at Sembawa were obtained from the Research Institute for Estate Crops (RIEC), Sembawa. Meteorological data were not available at Serong.

8.4 RESULTS AND DISCUSSION

Dry matter yields and P uptake of maize, dissolution and availability of P dissolved from P fertilizers are discussed with respect to, firstly, the residual effect of TSP and NCPR applied at different rates to the response curve plots (Section B of each trial) in the beginning of the experiment (T_1), and secondly, the residual effect of various P fertilizers applied at 80 kg P ha^{-1} (Section A of each trial) at different application times (T_1-T_4).

8.4.1 Rainfall data

In the warm and humid tropics, soil moisture availability places the only climatological constraint on plant growth. Plant growth is highly dependent upon the rainfall pattern.

The long-term average annual rainfall at Sembawa and Serong are 2263 and 2154 mm, respectively (Table 8.1). Monthly rainfall data (for the experimental period) at Serong were not available. However, both Sembawa and Serong field sites, which were 15 km apart, have almost similar climatic conditions (I. Boerhendy, pers. comm.). The monthly rainfall data for Sembawa during the experimental period (May 1989 - February 1991) are presented in Figure 8.2. There was a total of 932 mm rainfall during the growing season in 1989. In 1990, a total of 2155 mm of rainfall was recorded. In the first two months of 1991, 409 mm of rainfall was recorded. The monthly rainfall at Sembawa generally decreases from June to September. The lowest monthly rainfall recorded in 1989 and 1990 occurred in July (116 mm) and September (2 mm), respectively.

The amount of rainfall was quite high during the first two months after transplanting the Calopogonium in May 1989. A total of 370 mm of rainfall was recorded between 26 May and 26 July 1989. However, the daily rainfall was unevenly distributed during the first two months after Calopogonium transplanting (Appendix 9.3). This appeared to have affected the plant growth because at both sites water deficits occurred. Whereas at Sembawa the plants were irrigated when the rainfall was minimal, there was not enough water available for irrigation at Serong. As a result, very few of the plants survived. It was regularly observed that the soil at Serong dried very quickly following

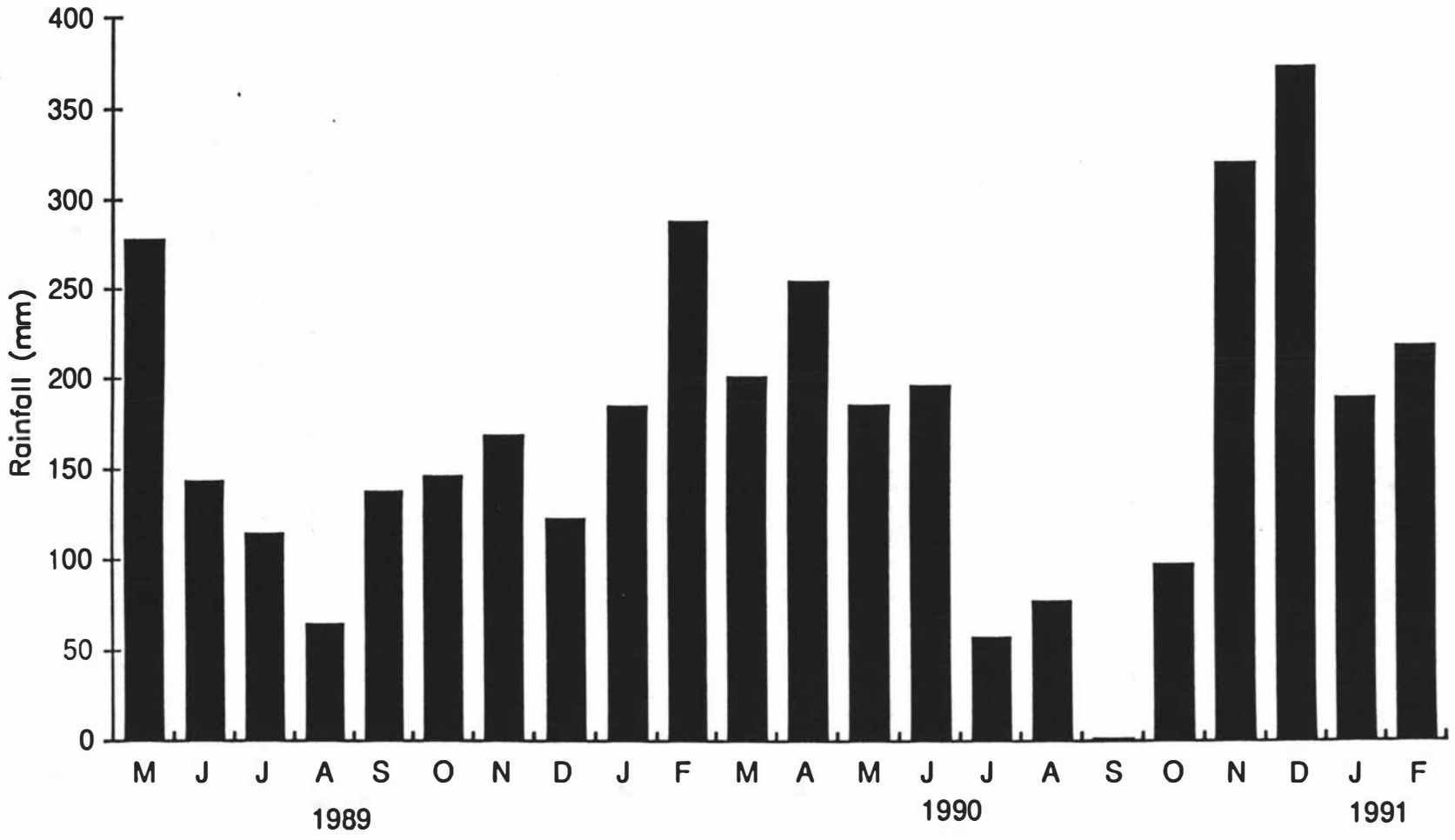


Figure 8.2 Rainfall distribution for Sembawa during May 1989 - February 1991.

rain events. This may be attributed to its low water holding capacity.

The average monthly Penman evaporation data at Sembawa during 1989 - 1991 was 127 mm $month^{-1}$, and was evenly distributed throughout the year. The daily evaporation rate at Sembawa can be as high as 5 to 7 mm day^{-1}. The potential evaporation at Serong, being relatively close to Sembawa, was expected to be as high as that at Sembawa. Such high evaporation rates, coupled with low water holding capacity, caused severe water deficit at Serong.

The growth of the Calopogonium at Sembawa was very slow following the mowing of Calopogonium and application of P fertilizers at T_3 (26 May 1990). Prolonged dry periods and uneven distribution of rainfall occurred more frequently between July and September 1990. The total monthly rainfall in September 1990 was only 2.3 mm. This was one of the lowest values ever recorded at Sembawa. During the prolonged dry periods, the plants were irrigated either once or twice a week during prolonged dry periods between August and September 1990. No records were made on the amounts of irrigation water applied.

During the period of maize growth at Sembawa (December 1990 to February 1991), a total of 294 mm of rainfall was recorded. The daily rainfall was evenly distributed during this growing season.

8.4.2 Dry matter yield of maize

8.4.2.1 Residual effect of TSP and NCPR applied at different rates

At both sites yield response of maize to increasing rates of NCPR and TSP fertilizers applied at T_1 (Figure 8.3) were marked. Increases in dry matter yield with increasing rates of both fertilizers were effectively simulated by exponential Mitscherlich type functions of the form described by Barrow and Campbell (1972):

$$y=a-b\ \exp(-cx) \qquad (8.1)$$

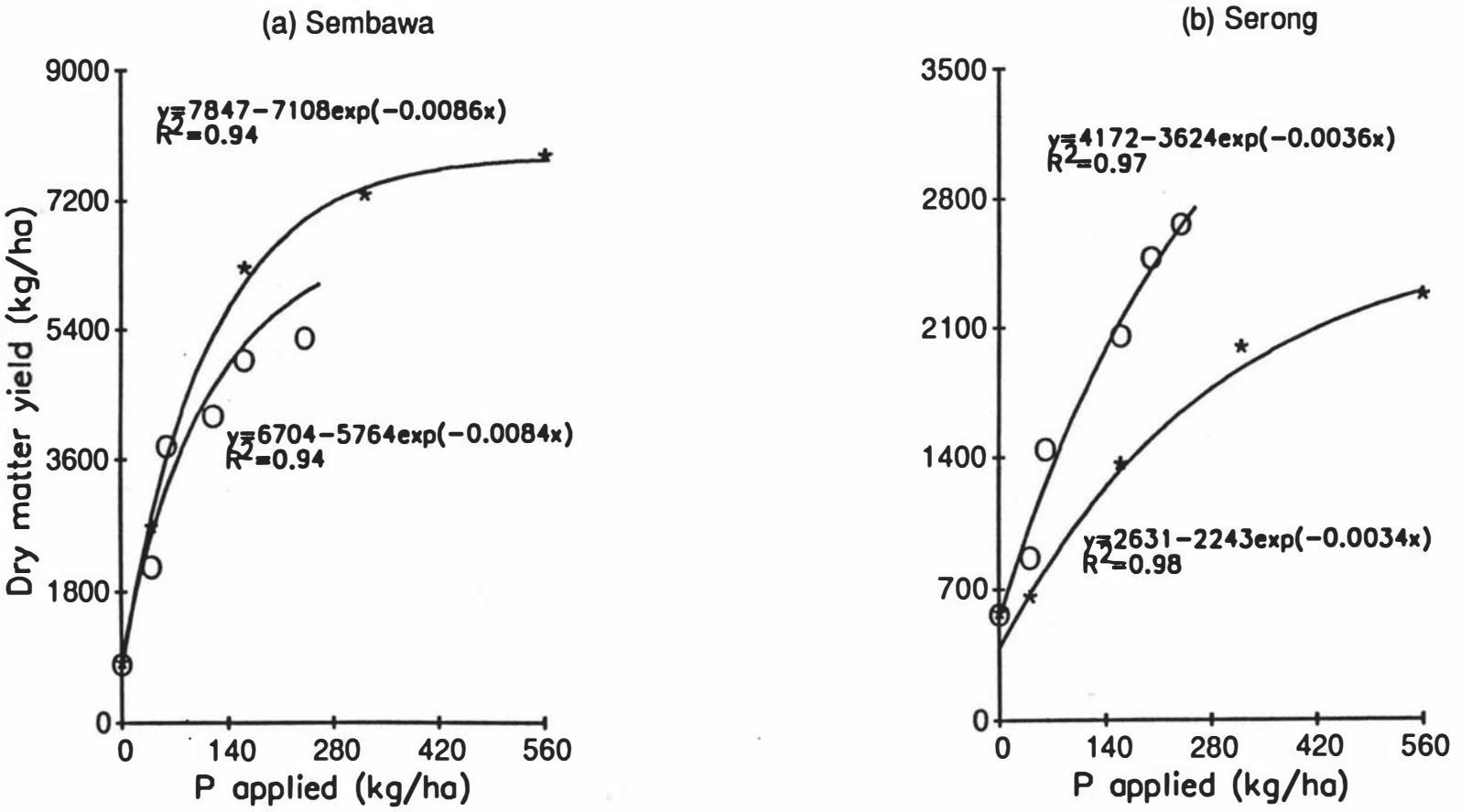


Figure 8.3 Residual effects of TSP (o) and NCPR (*) applied at T_1 (18 months prior to sowing maize) on dry matter yield of maize in unlimed plots at (a) Sembawa and (b) Serong.

where y = dry matter yield (kg ha^{-1}), x = P applied (kg P ha^{-1}), a = maximum dry matter yield, b = the difference between maximum yield and yield measured when no P is applied, and c = curvature coefficient. In this equation, dy/dx approximates to cb as x approximates zero, and thus cb can be used as an estimate of the slope in the linear response phase (Barrow and Campbell, 1972). The value of the coefficients obtained from Equation 8.1 for the relationships between yield and the level of P applied are listed in Figure 8.3. The estimated maximum yield responses and shape of the relationship differed between fertilizers and sites. At Sembawa, TSP residues produced smaller (85%) maximum yields than NCPR residues. At Serong, on the other hand, the maximum yield produced by TSP residues was almost two times higher than that produced by NCPR residues. Notably, Serong was the drier, less acidic site, and hence less suited to PR dissolution (Chapter 2, Section 2.3.7).

8.4.2.2 Effect of P fertilizer form and application time

Dry matter yield responses of maize to P residues and fresh P fertilizers, applied at a single level (80 kg P ha^{-1}), are summarized in Table 8.5. Overall, maize yield at both sites increased 4 to 5 fold on plots containing P residues or freshly applied P fertilizers. The size of the response varied markedly depending upon the site, P fertilizer form and time of P application.

In general, the increases in maize yields at Serong were much lower than that of Sembawa. Yield differences between sites were attributed to the differences in the chemical and physical properties of the soils (Table 8.2). The maize growth in the sandy soil of Serong was constrained by the low availability of soil moisture during the maize growing period. The smaller responses of dry matter yield to P at Serong than at Sembawa was attributed to the lower dissolution of the P fertilizers at Serong (see Section 8.4.4.2), thereby decreasing supply of P to plants during the growing season.

Phosphate fertilizers applied during the preceding crop (Calopogonium) showed significant residual effects on maize growth. At Sembawa, freshly applied TSP gave significantly higher dry matter yield than the other P treatments. The residues of the three PRs, however, tended to produce higher maize yields than TSP residues. Improved

Table 8.5 Mean dry matter yield of maize at Sembawa and Serong as influenced by form and application time of P fertilizer (80 kg P ha^{-1}).

P application time	P fertilizer form	Dry matter yield (kg ha^{-1})*		
		Sembawa (limed)	Sembawa (unlimed)	Serong
-	Control	1181	814	569
T_1	TSP	4206	4016	1201
	NCPR	5074	4971	1315
	PPR	4341	4443	1258
	MPR	4772	4121	1309
T_2	TSP	4614	4198	1451
	NCPR	4978	5036	1400
T_3	TSP	4456	4846	1898
	NCPR	5652	5463	1408
	PPR	5394	5323	1504
	MPR	5547	5165	1232
T_4	TSP	5950	5872	1519
	NCPR	3696	4895	1142
	PPR	3932	4004	1012
	MPR	3173	3906	1003
LSD (P<0.05)		835	847	285

*Means of 4 replicates.

residual value of PR fertilizers compared to soluble P fertilizers has been reported for a range of soils and crops (e.g. Mackay *et al.*, 1984b; Harris *et al*,. 1985; Gregg *et al.*, 1988; Mackay and Wewala, 1990; Fageria *et al.*, 1991; Rajan *et al.*, 1991a). The differences in yield between plots containing TSP and PR residues tended to increase with time since application and was mostly attributed to the residual value of TSP decreasing with time to a greater extent than that of PR residues (Table 8.5).

Among the PR residues, yield responses to the more reactive NCPR were higher than responses to PPR and MPR at Sembawa. With respect to application time, dry matter yields due to PR residues were highest for fertilizers applied at T_3, followed by T_2 and T_1.

At Serong, the highest yield response to P residues was obtained in plots that received TSP at T_3. The yield responses to PR residues were generally similar, irrespective of their application time.

8.4.2.3 Effect of liming

At Sembawa, application of lime (1000 kg ha^{-1}) prior to sowing maize did not significantly affect yield responses to P fertilizer residues (Table 8.6). This is probably because significant amounts of P had been dissolved from the P fertilizers applied during the first crop (Calopogonium) prior to liming.

Liming tended to decrease maize yield in plots treated with fresh PRs. Increased soil pH and exchangeable Ca in limed plots probably decreased PR dissolution (particularly for freshly applied PRs) during maize growth. Rajan *et al.* (1991b) and Thibaud *et al.* (1992) have also reported similar decreases.

The inhibitory effect of liming on PR dissolution in acid soils may not necessarily cause adverse effects on plant growth. This is because liming may decrease concentrations of soluble Al (Kamprath, 1970) and create favourable soil conditions for plant roots to absorb nutrients. Development of more effective root systems will increase the dissolution of PR (Kirk and Nye, 1986d) thereby increasing its availability to plants.

The availability of residual P from P fertilizer applied prior to liming may be increased through a stimulatory effect of lime on root exploitation of soil-fertilizer reaction products or on the mineralisation of organic P (Trasar-Cepeda and Carballas, 1991) and desorption of inorganic P (Sanchez and Uehara, 1980).

Thibaud *et al.* (1992) have suggested that liming may be still beneficial to plant growth in very acid soils fertilized with PR provided that it is not applied excessively. It has also been suggested that inhibitory effects of lime on PR dissolution can be reduced by adding the lime in advance (Mackay *et al.*, 1984; Moersidi and Adiningsih, 1988). The results of the present study indicate if PR is added more than six months prior to liming some beneficial effects can occur.

8.4.3 Uptake of P by maize

8.4.3.1 Residual effect of TSP and NCPR applied at different rates

The residual effect of P fertilizer, applied at different rates at T_1, on amounts of P taken up by maize can also be described by Equation 8.1 (Figure 8.4). The pattern for the P uptake response was similar to that obtained for the dry matter yield data (Figure 8.3). Values for the slope (*bc*) in the regression equations show the P uptake response to TSP residues to be smaller than that of the NCPR residues at Sembawa and higher than those at Serong. The ratios of the slopes (*bc*) explaining P uptake for NCPR and TSP (0.72-1.96), however, were similar to the ratios calculated for yield (0.79-1.93)(compare Figures 8.3 and 8.4). Reasons for this are not clear except that the physiological maturity of plants in plots receiving different P treatments may differ affecting their total P content. Normally, physiologically older maize plants have lower tissue P concentrations (Hanway, 1962b).

8.4.3.2 Effect of P fertilizer form and application times

Trends on the effect of P fertilizer form and application time on P uptake by maize (Table 8.6) generally followed the trends in dry matter yield (Table 8.5). At both sites, the total P uptake in P treated plots was significantly higher than that in control plots.

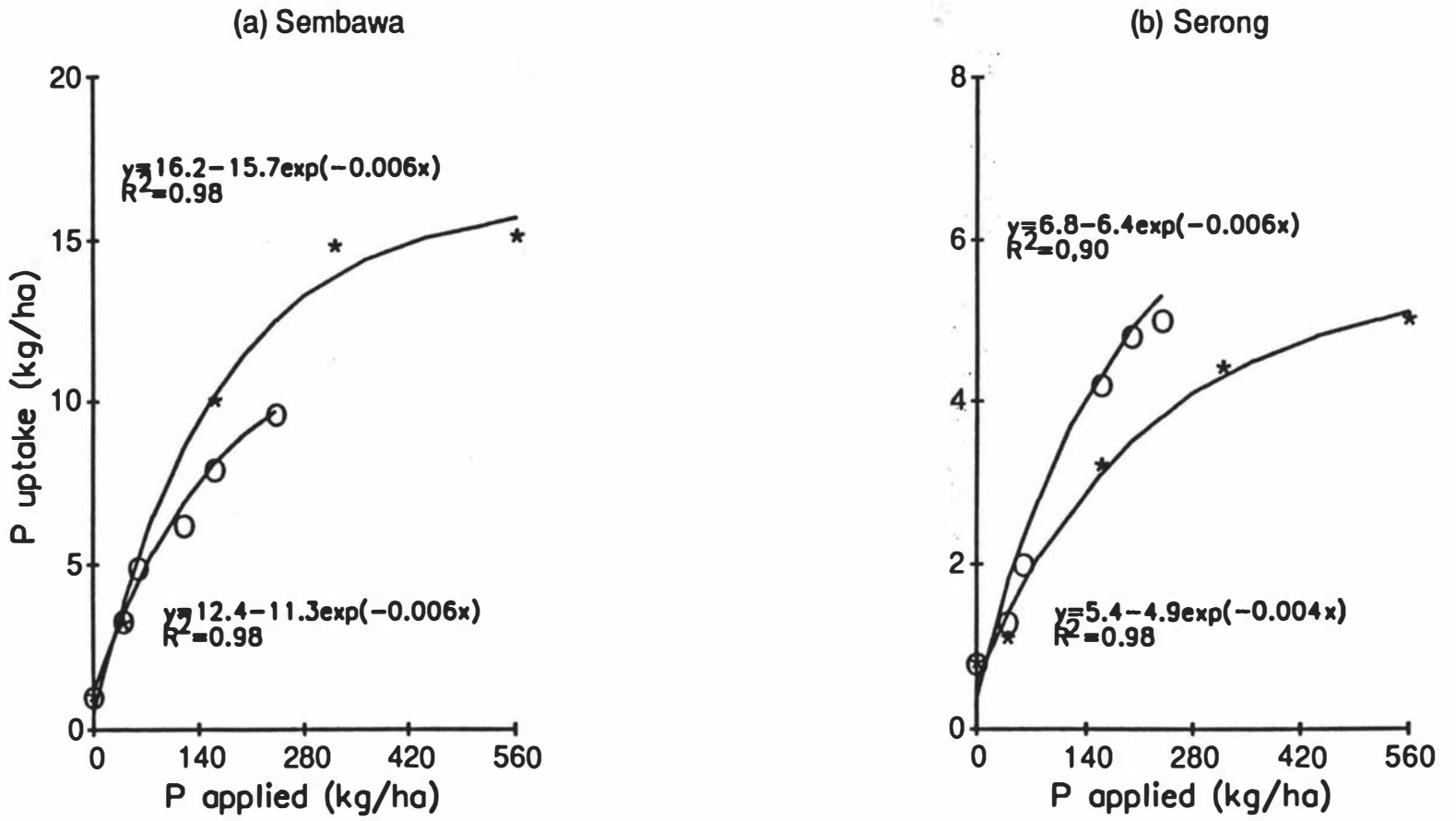


Figure 8.4. Residual effects of TSP (o) and NCPR (*) applied at T_1 (18 months prior to sowing maize) on P uptake by maize in unlimed plots at (a) Sembawa and (b) Serong.

Table 8.6 Effect of form and application time of P fertilizer (80 kg P ha^{-1}) on P uptake by maize at Sembawa and Serong.

P application time	P fertilizer form	P uptake (kg ha^{-1})		
		Sembawa (limed)	Sembawa (unlimed)	Serong
-	Control	1.4	1.0	0.8
T_1	TSP	7.6	5.5	2.2
	NCPR	8.4	7.6	2.2
	PPR	6.9	7.1	2.0
	MPR	7.5	6.2	1.9
T_2	TSP	7.6	7.1	2.9
	NCPR	8.6	7.8	2.7
T_3	TSP	7.7	8.7	4.0
	NCPR	9.9	8.4	2.7
	PPR	9.1	9.1	2.4
	MPR	9.1	8.6	2.6
T_4	TSP	11.1	10.2	3.9
	NCPR	5.8	7.9	2.3
	PPR	6.2	6.2	1.9
	MPR	5.3	5.8	1.6
LSD(P<0.05)		1.7	1.9	0.4

For TSP-fertilized plots at Sembawa, P uptake was highest in plots that received fresh P fertilizer at T_4, followed by those received at T_3, T_2 and T_1. In Serong, the total P uptake in plots receiving TSP at T_2, T_3 and T_4 was similar, but was higher than that at T_1.

For PR-fertilized plots at Sembawa, the P uptake was generally higher when the PRs were applied at T_3, while plots receiving PRs at T_1, T_2, and T_4 gave similar results. In general, the P uptake from the more reactive NCPR treatments tended to be higher than that from PPR and MPR. Except in the T_3 limed plot, uptake of P was slightly higher in PPR than in MPR treated plots.

Application of lime at Sembawa prior to sowing maize did not significantly affect P uptake (Table 8.6).

8.4.4 Relationship between P uptake and dry matter yield

Relationships between P uptake and dry matter yields of maize in plots fertilized with TSP or PRs were similar ($P<0.05$) and linear (Figure 8.5) indicating that, at each site, the internal P use efficiency of maize, defined as the ratio of dry matter yield to P uptake by plants (Khasawneh and Doll, 1978), was similar irrespective of P fertilizer form. This similarity allows the relative agronomic effectiveness of P fertilizers to be calculated (Section 8.4.5). Values of the internal P use efficiency of TSP and NCPR-fertilized plots were greater at Sembawa than at Serong probably because water shortages at Serong limited the maize yield.

The internal efficiencies of various P fertilizer form were similar (Figure 8.5), therefore a single linear regression equation was used to describe the effect of liming on the relationship between dry matter yield and P uptake from various P treatments at Sembawa (Figure 8.6). The slopes of the regression equation for limed and unlimed plots were similar indicating that liming did not significantly effect the internal efficiency of plants fertilized with various P fertilizers.

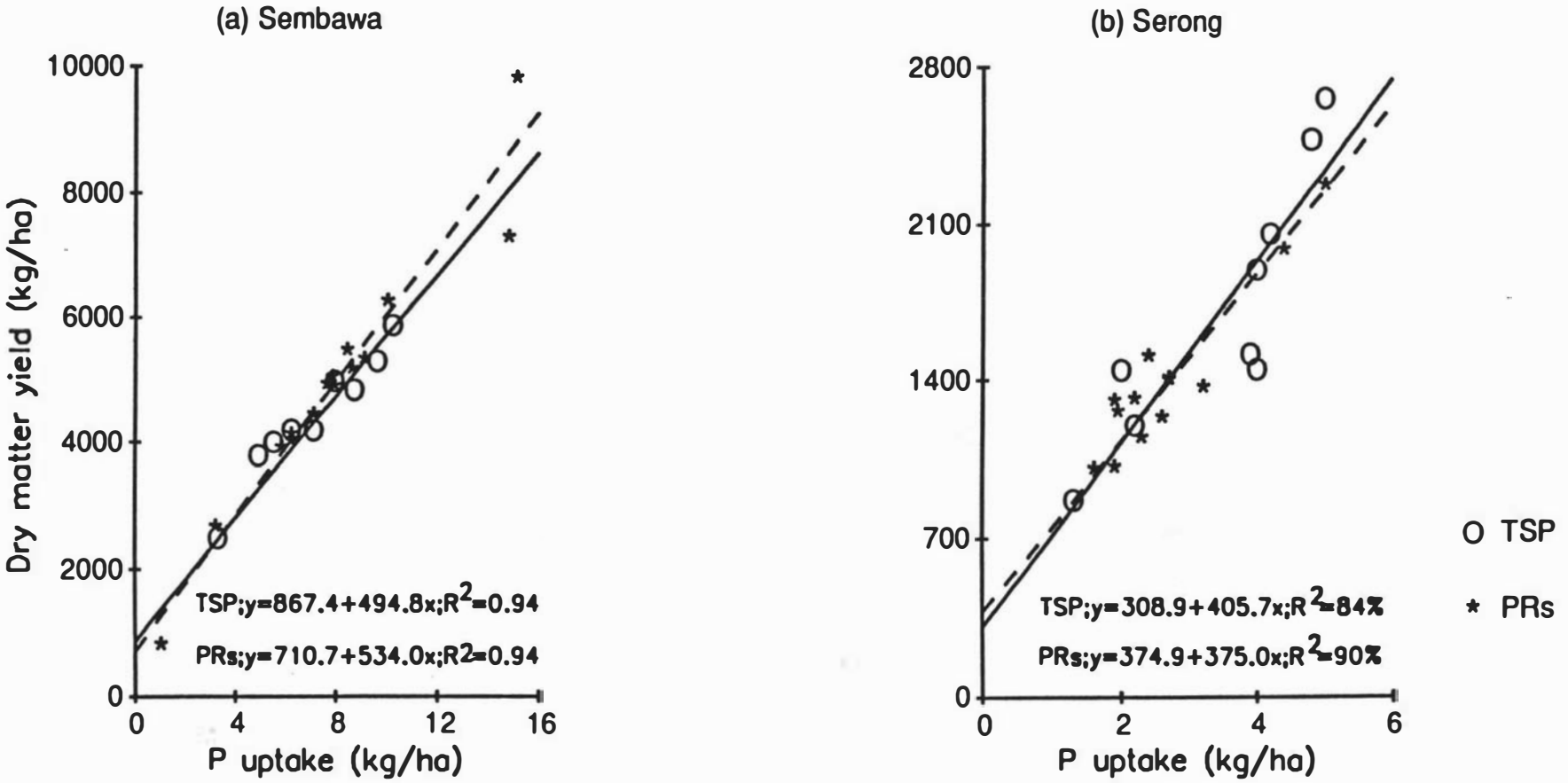


Figure 8.5 Relationship between P uptake and dry matter yield of maize in unlimed plots at (a) Sembawa or (b) Serong fertilized with TSP (—) or PRs (--).

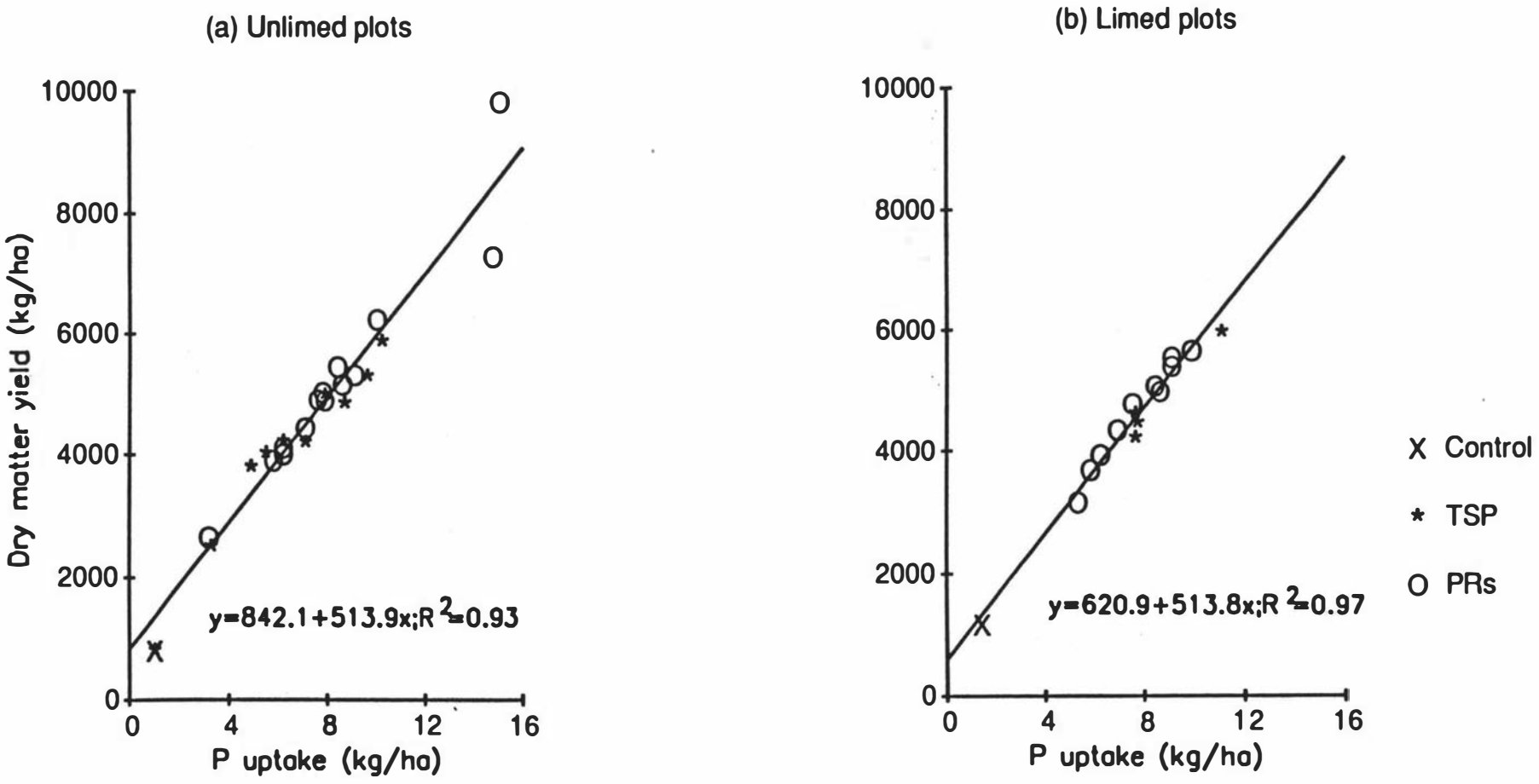


Figure 8.6 Relationship between P uptake and dry matter yield of maize in (a) unlimed or (b) limed plots at Sembawa.

8.4.5 Relative agronomic effectiveness (RAE) of phosphate fertilizers

8.4.5.1 Residual effect of TSP and NCPR applied at different rates

Initial slopes (*bc*) of the Mitscherlich functions fitted to the yield response data were used to calculate the relative agronomic effectiveness (RAE) of the P fertilizers applied at T_1 at different rates. The RAE of a test fertilizer (i.e. PR), relative to a standard P fertilizer (i.e. TSP), is calculated as follows (Barrow, 1985):

$$\text{RAE } (\%) = b_1c_1/b_2c_2 \times 100 \qquad (8.2)$$

where the subscripts 1 and 2 refer to PR and TSP, respectively.

From the maize yield response curve, shown in Figure 8.3, the calculated RAE of NCPR residue relative to TSP residue (Table 8.7) indicates that the NCPR was 26% more effective than the TSP at Sembawa, but 42% less effective than the TSP at Serong. Yield maximas and the response coefficients for each fertilizer are different and influenced by site conditions. Thus, a more accurate estimate of RAE, relative to TSP, must consider fertilizer application rate of target yield (Bolan *et al.*, 1990; Chien *et al.*, 1990).

8.4.5.2 Effect of P fertilizer form and application time

The agronomic effectiveness of residues of P fertilizers or freshly applied PRs (applied at 80 kg P ha^{-1}), relative to fresh TSP, was calculated using the following equation:

$$\text{RAE} = \frac{\text{yield from P fertilizer - control yield}}{\text{yield from fresh TSP - control yield}} \times 100 \qquad (8.4)$$

Note that "P fertilizer" refers to all P treatments other than fresh TSP. This equation assesses the RAE of TSP residues relative to fresh TSP. The RAE calculated for different P fertilizers at Sembawa and Serong are presented in Figure 8.7.

The results at Sembawa show that while the effectiveness of fresh TSP was higher than PRs, the effectiveness of TSP residues decreased progressively with increasing reaction time in soil and was lower than that of PR residues (Figure 8.7a). The effectiveness of

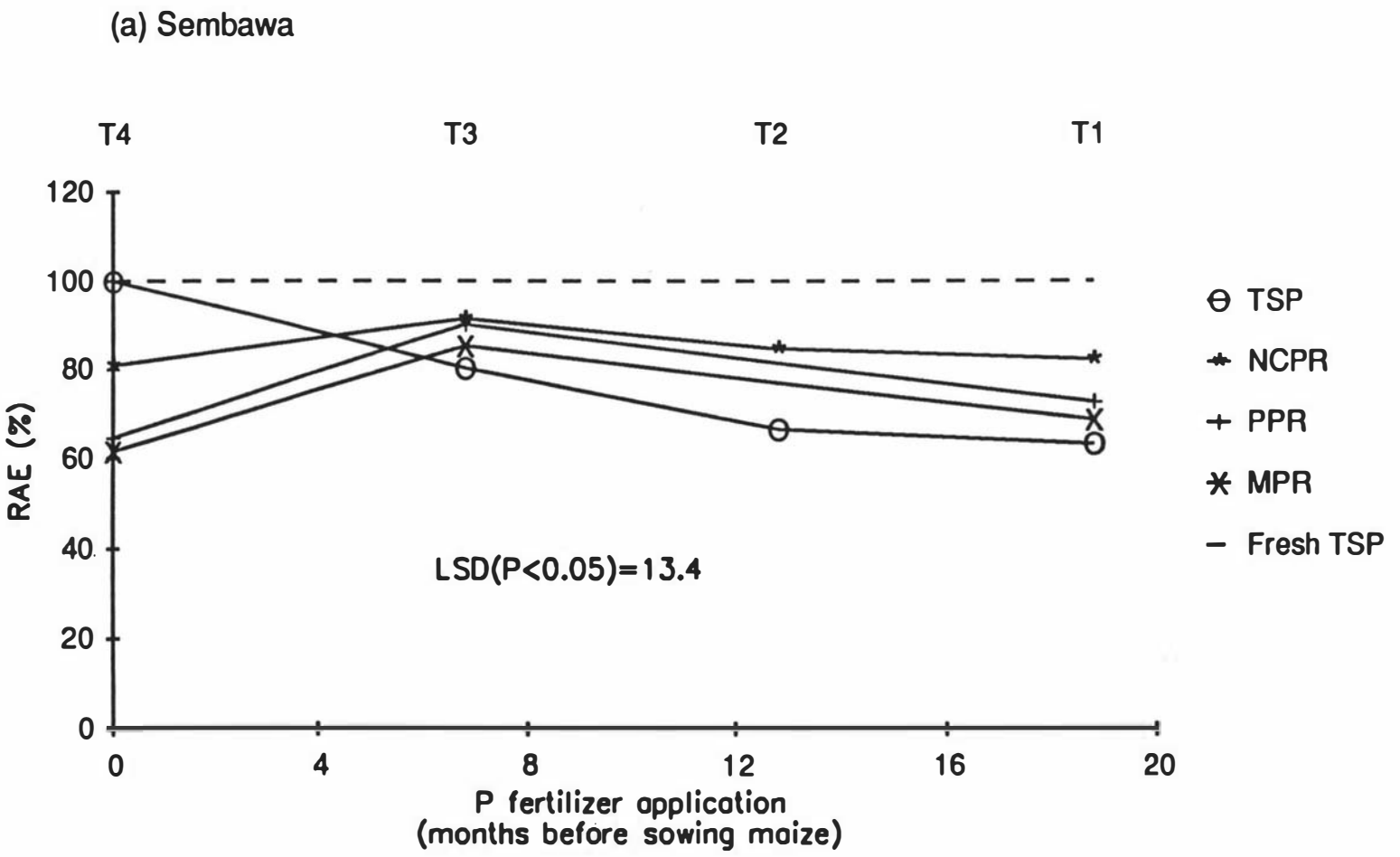


Figure 8.7 Relative agronomic effectiveness (RAE) of fertilizers (80 kg P ha^{-1}) at (a) Sembawa (unlimed) and (b) Serong, relative to fresh TSP. T_1, T_2, T_3 and T_4 indicate P application times.

(b) Serong

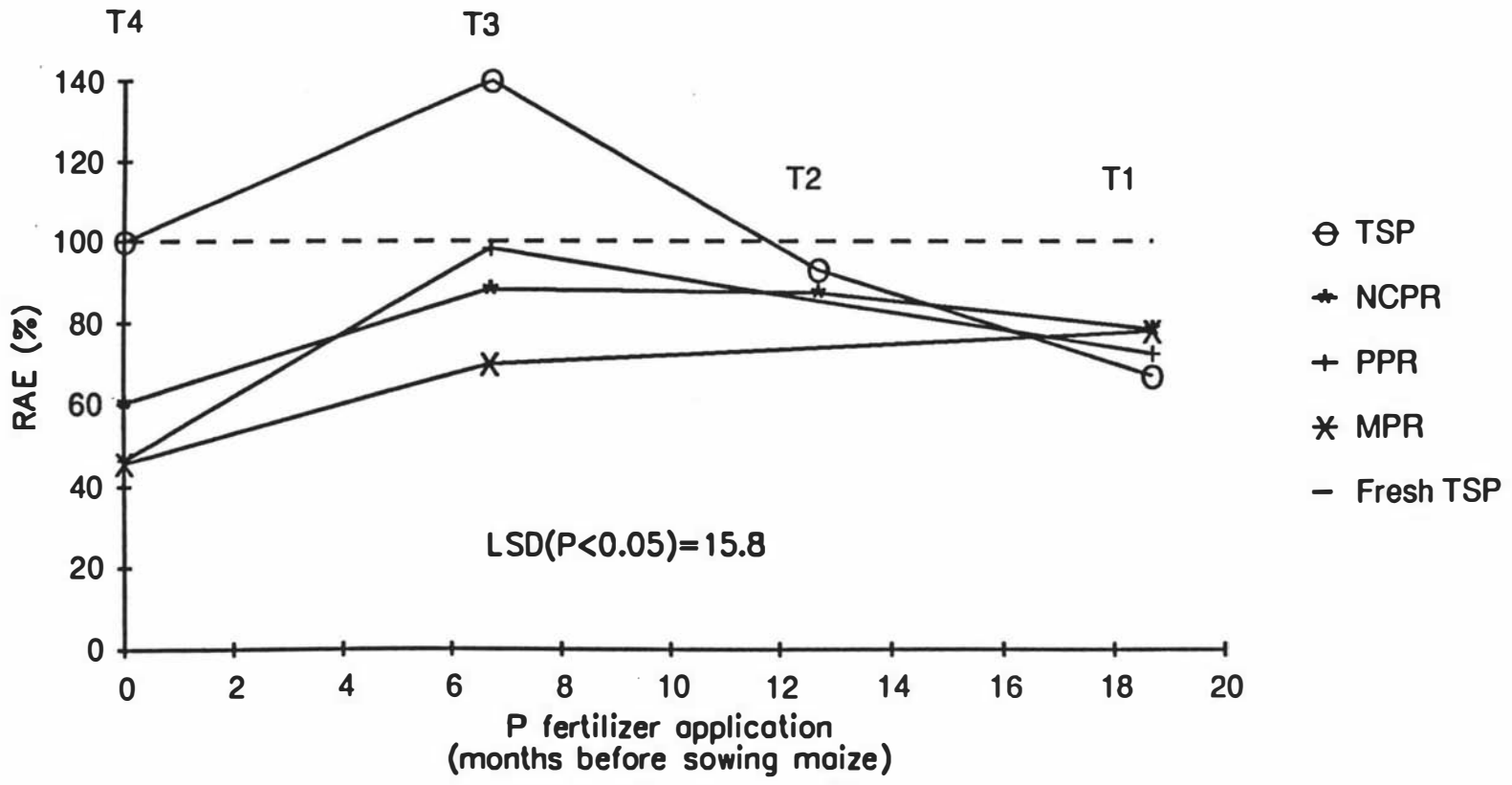

T4
T3
T2
T1
140
120
100
80
60
40
20
0
RAE (%)
LSD(P<0.05)=15.8
0
2
4
6
8
10
12
14
16
18
20
P fertilizer application
(months before sowing maize)
TSP
NCPR
PPR
MPR
Fresh TSP

Table 8.7 Relative agronomic effectiveness (RAE) of TSP and NCPR residues, applied at different rates at T_1, for maize at Sembawa and Serong.

Site	P fertilizer	Coefficients of response curve equation			Initial slope (*bc*)	RAE (%)*
		a	*b*	*c*		
Sembawa	TSP	6703.5	5763.5	0.0084	48.4	100
	NCPR	7847.2	7107.6	0.0086	64.1	126
Serong	TSP	7172.6	3623.8	0.0036	13.0	100
	NCPR	2631.2	2243.2	0.0034	7.62	58

*RAE is calculated using Equation 8.2.

PR at each application time at Sembawa consistently was in the order of NCPR>PPR>MPR. However, these differences were only significant for T_1 applications. Although the effectiveness of PR residues decreased with increasing reaction time (T_3-T_1), PR residues had comparable or higher effectiveness than that of fresh PRs applied at T_4. This can be attributed to the greater dissolution of PRs applied at T_1-T_3 than the fresh PRs (see Table 8.9).

At Serong, TSP applied at T_3 had highest effectiveness followed by fresh TSP applied at T_4 (Figure 8.7). Except at T_1, PRs generally had lower effectiveness than TSP at each application time. Fresh application of PRs were generally less effective than the PRs applied prior to sowing maize. At Serong, the lower effectiveness of PRs than TSP, irrespective of the application time, can be attributed to the lower dissolution of PRs on this drier, less acidic site (Table 8.8).

8.4.6 Dissolution of phosphate fertilizers in soil

8.4.6.1 Measurements at the end of Calopogonium growth

The extent of dissolution of P fertilizers at the end of Calopogonium growth was measured using soil samples from plots fertilized with a single level (80 kg P ha^{-1}) of TSP, NCPR and MPR. The extent of dissolution was affected by P fertilizer form and reaction time (Table 8.8). The dissolution of all PRs increased with increased contact times with soil. For example, the dissolution of NCPR during the first (545 days), second (360 days) and third (180 days) time periods was 98, 82 and 40%, respectively (Table 8.8).

For each time period, the extent of dissolution of P fertilizers generally followed their citric acid solubility (Table 8.3). Their dissolution was in the order of TSP>NCPR>MPR. Considering the standard error of the measured values, differences in dissolution between NCPR and MPR for each time period were very small. The dissolution of both PRs were favoured by the soil and climatic conditions at Sembawa. Hanafi *et al.* (1992b) observed that the extent of dissolution of Christmas Island unreactive PR (CIPR) and Gafsa reactive PR (applied at 500 mg P kg^{-1}) were similar

Table 8.8 Dissolution of P fertilizers (applied at 80 kg P ha^{-1}) in Sembawa soil measured at the end of the Calopogonium growth.

Application time	Duration (days)	P fertilizer	Dissolution (%)*
26 May 1989 (T_1)	545	TSP	97.1±0.5
		NCPR	97.6±0.7
		PPR	nd
		MPR	93.8±0.5
26 Nov 1989 (T_2)	360	TSP	nd
		NCPR	81.7±1.4
26 May 1990 (T_3)	180	TSP	86.4±2.1
		NCPR	40.3±5.4
		PPR	nd
		MPR	36.3±6.8

*SEM
nd: not determined.

(91-95% over 49 days) in a Malaysian Ultisol under an open-leaching system was similar.

8.4.6.2 Measurements after harvesting maize

The extent of dissolution of freshly applied and residual TSP and PRs was measured again after harvesting the maize (Table 8.9). Irrespective of P fertilizer form, the extent of dissolution of the residues and freshly applied P fertilizers was higher at Sembawa than at Serong. For example, the dissolution of fresh NCPR (applied at T_4) during maize growth at Sembawa was 32%. The corresponding value at Serong was 13%, reflecting less suitable soil conditions for PR dissolution.

Table 8.9 also shows that the dissolution of medium reactive PPR during the maize growth at both sites was similar to that of the more reactive NCPR. This is probably because the finer particle size of the PPR (Table 8.3) compensates for its lower chemical reactivity.

At Serong, only 68% of freshly applied (T_4) TSP (citric acid P solubility=87%, Table 8.3) dissolved (Table 8.9) during 48 days of maize growth. Lindsay *et al.* (1962) suggest that a precipitate of calcium ferric phosphate ($CaFe_2O_3(HPO_4)_8.8H_2O$) will form immediately following the reaction of MCP, which is the main component of TSP or SSP, with soil that contains $Fe_2O_3.H_2O$. The formation of calcium ferric phosphate, which is soluble only in acid extraction, in the drier and less acidic Serong soil fertilized with fresh TSP may partly explain the high amount of the "undissolved" TSP measured by the Δ0.5 M H_2SO_4-P method. Over a longer soil contact time (T_1-T_4) and in Sembawa soil, acid soluble TSP residues did not remain (Tables 8.8 and 8.9).

8.4.7 Plant-available P

Amounts of plant-available P, as measured by three soil tests namely Olsen, Bray 1 and resin, in all plots were determined prior to sowing maize using soil samples (0 - 50 mm soil depth) taken prior to sowing maize. Values of these three soil tests were used to predict subsequent maize yields.

Table 8.9 Dissolution of P fertilizers (applied at 80 kg P ha^{-1}) in Sembawa and Serong soils measured at the end of maize growth.

Application time	Duration (days)*	P fertilizer	Dissolution (%)	
			Sembawa	Serong
T_1	616, 613	TSP	96.1±1.0	93.9±5.8
		NCPR	96.8±1.7	61.0±7.1
		PPR	95.4±3.4	67.4±9.4
		MPR	94.8±1.8	57.7±2.5
T_2	433, 429	TSP	nd	nd
		NCPR	92.7±3.1	49.9±6.2
T_3	253, 249	TSP	nd	nd
		NCPR	66.5±8.9	31.6±4.5
		PPR	nd	nd
		MPR	53.9±8.7	28.3±8.5
T_4	45, 48	TSP	91.6±2.9	68.0±8.2
		NCPR	32.4±6.3	13.1±5.2
		PPR	30.0±1.9	15.6±5.6
		MPR	27.9±4.3	8.6±3.9

*Values indicate the duration of P fertilizer in Sembawa and Serong soils, respectively; nd : not determined.

8.4.7.1 Residual effect of TSP and NCPR applied at different rates

Amounts of extractable soil P in plots receiving TSP and NCPR at T_1 increased with increasing application rate of P fertilizer (Figure 8.8). Increases in soil P with increased P application rate were generally higher at Sembawa than at Serong. The effect was more pronounced for the NCPR- than TSP- fertilized plots. This is probably because of the higher dissolution of NCPR at Sembawa. Irrespective of soil test, the relationship between amounts of extractable P and level of P application can be described by linear and exponential regression equations for the TSP and NCPR treated plots, respectively.

At both sites, a single relationship between amounts of P fertilizer added (up to 240 kg P ha^{-1}) and amounts of resin-extractable P (resin-P) applied equally well to plots fertilized with NCPR and TSP. This feature did not apply to Olsen and Bray 1 tests which required two separate relationships to describe the effects of NCPR and TSP on soil test levels (Figure 8.8). Similar results were found for Sechura PR- and TSP-fertilized New Zealand soils (Saggar *et al.*, 1991b).

8.4.7.2 Effect of P fertilizer form and application time

Regardless of soil test, the application of P fertilizers at 80 kg P ha^{-1} at different times generally increased the amounts of extractable soil P at both sites (Table 8.10). Except for Olsen-P, values for Bray 1- and resin-P at Sembawa were generally higher than at Serong. It was also observed that whereas at Sembawa all three tests extracted similar amounts of P, at Serong the resin test extracted smaller amounts of soil P than the Olsen and Bray 1.

Forms of P fertilizer and their application times influenced the amounts of soil P extracted by all three soil tests. At Sembawa, a comparison between P fertilizers shows that increases in the extractable P from soil fertilized with PRs at T_1 were slightly higher for NCPR than for TSP treated plots. In plots that received P fertilizer at T_2 and T_3, NCPR and TSP values were almost the same.

With the exception of the resin-P, amounts of extractable soil P in the Serong soil

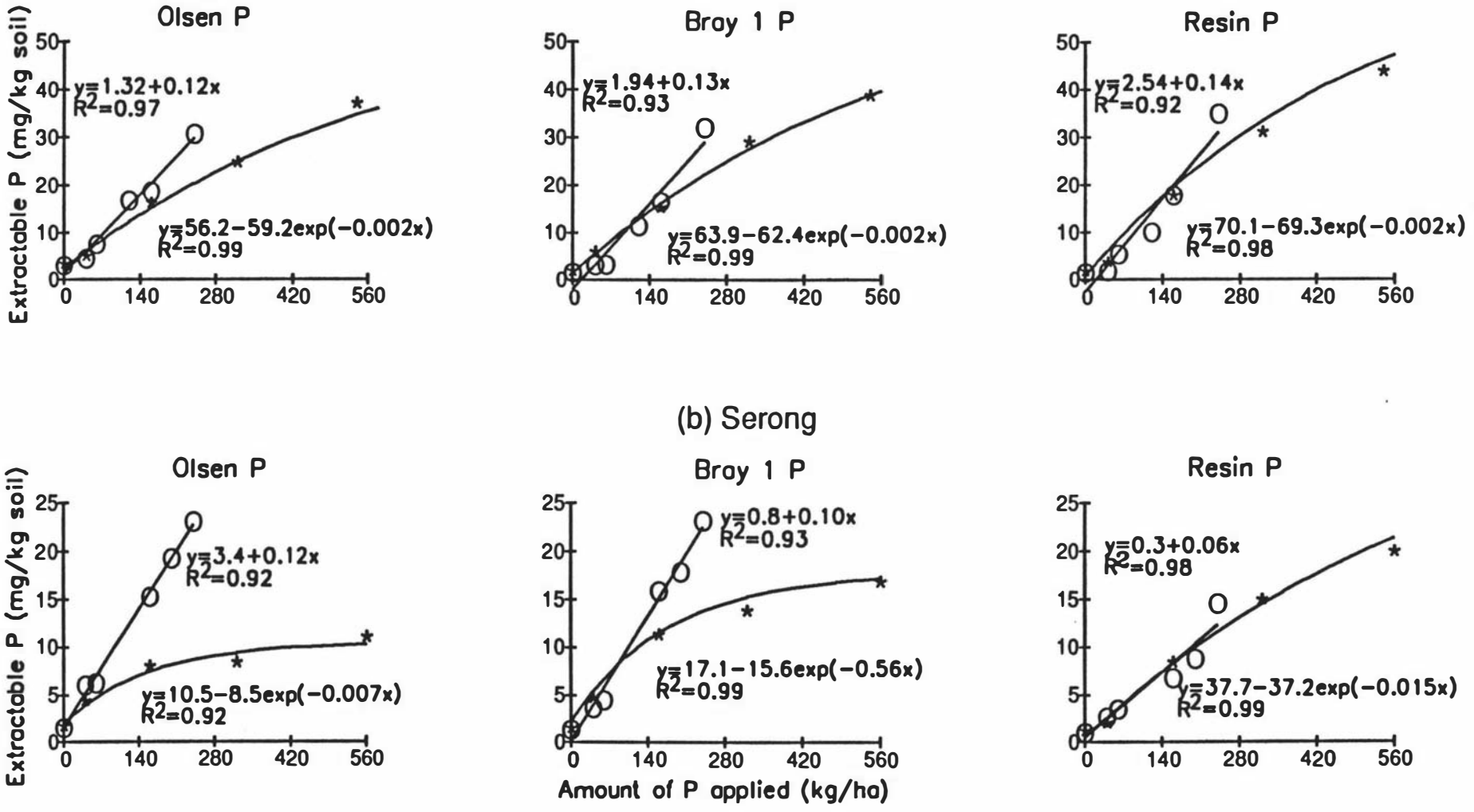


Figure 8.8 Effect of rate of application of TSP (o) and NCPR (*) at T_1 (18 months prior to sowing maize) on amounts of soil P extracted by different soil tests from samples taken prior to sowing maize.

Table 8.10 Amounts of extractable soil P (0 - 50 mm) in (a) Sembawa and (b) Serong samples taken prior to sowing maize.

(a) Sembawa

P application time	P fertilizer	Extractable P (mg kg^{-1} soil)		
		Olsen-P	Bray-P	Resin-P
-	Control	3.1	1.7	1.6
T_1	TSP	7.3	6.0	5.6
	NCPR	9.8	10.1	12.6
	PPR	8.2	8.9	7.8
	MPR	6.9	6.1	10.0
T_2	TSP	9.5	8.5	9.6
	NCPR	10.6	10.5	10.6
T_3	TSP	8.9	10.4	11.5
	NCPR	10.3	9.9	11.0
	PPR	10.1	10.2	12.8
	MPR	7.9	7.5	10.3
LSD(P<0.05)		4.0	2.3	4.5

(b) Serong (Tab. 8.10, contd)

P application time	P fertilizer	Extractable P (mg kg^{-1} soil)		
		Olsen-P	Bray-P	Resin-P
-	Control	1.6	1.4	1.1
T_1	TSP	8.0	7.6	2.7
	NCPR	5.9	5.1	3.0
	PPR	6.2	4.5	2.6
	MPR	5.0	3.5	2.8
T_2	TSP	10.3	6.4	3.3
	NCPR	6.1	3.7	3.4
T_3	TSP	10.8	7.5	6.9
	NCPR	6.3	6.2	4.1
	PPR	6.1	4.0	4.1
	MPR	6.1	4.6	3.7
LSD(P<0.05)		2.4	2.8	1.2

fertilized with TSP were higher than those fertilized with PRs. In general, amounts of extractable soil P in TSP-fertilized plots were in the order of $T_3>T_2>T_1$.

In general, NCPR produced slightly higher amounts of extractable soil P than other PRs. Time of PR application did not affect the amounts of extractable soil P at Serong.

8.4.7.3 Relationship between extractable soil P and dry matter yield of maize

The relationships between dry matter yield and P extracted by the three soil tests are described by Mitscherlich equations (Figure 8.9). For each extractant different coefficients were required to gain best fits of TSP and PR data. Hammond *et al.* (1986) and Rajan *et al.* (1991b) note that separate calibration curves of soil P test levels against yield are required for P fertilizers of differing solubility. This indicates that some P fertilizer-soil reaction products are solubilized differently by plants and P test extractants.

Coefficients of determination of the Mitscherlich relationships between amounts of P extracted by soil test and maize dry matter yield varied between forms of P fertilizer and sites. At Sembawa, the resin test accounted for more of the variation in the dry matter yield for the TSP treated plots than Bray 1 and Olsen tests. For the PR-fertilized plots, the Bray 1 test accounted for more of the variation in the dry matter yield than the Olsen and resin tests. In general the ability of the three soil tests to predict maize yield at Sembawa was in the order of Bray 1>resin>Olsen.

At Serong, the resin test was better than both the Olsen and Bray 1 tests in predicting the dry matter yield in plots treated with TSP. However, for the plots fertilized with PRs, the Olsen test accounted for more variation in dry matter yield than the Bray 1 and the resin tests. For all plots, the Olsen test accounted for more variation in dry matter yield than the other two tests.

Saggar *et al.* (1991b) observed that the resin test was better than the Olsen test in predicting the residual effectiveness of PRs in a range of New Zealand pastoral soils. This finding contradicts the results of the present study in which the resin test was found

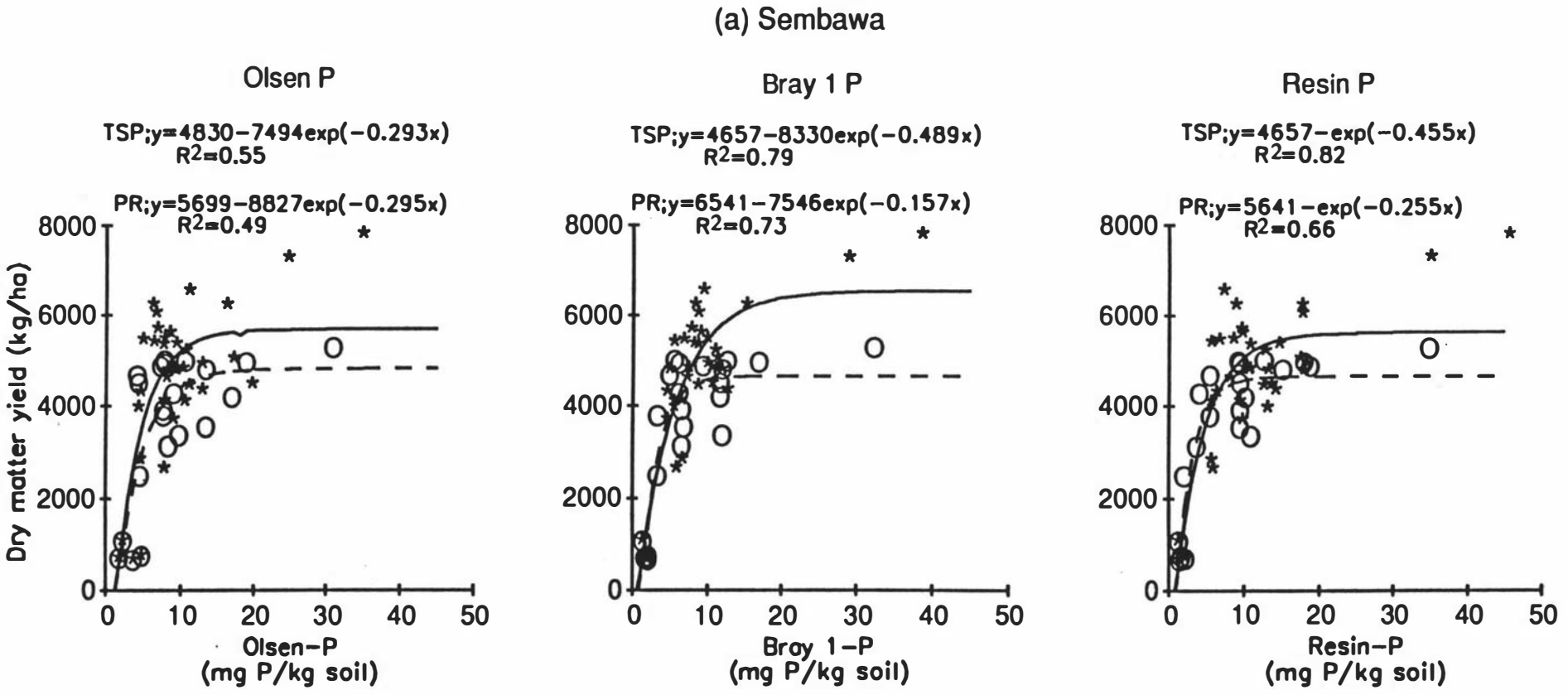
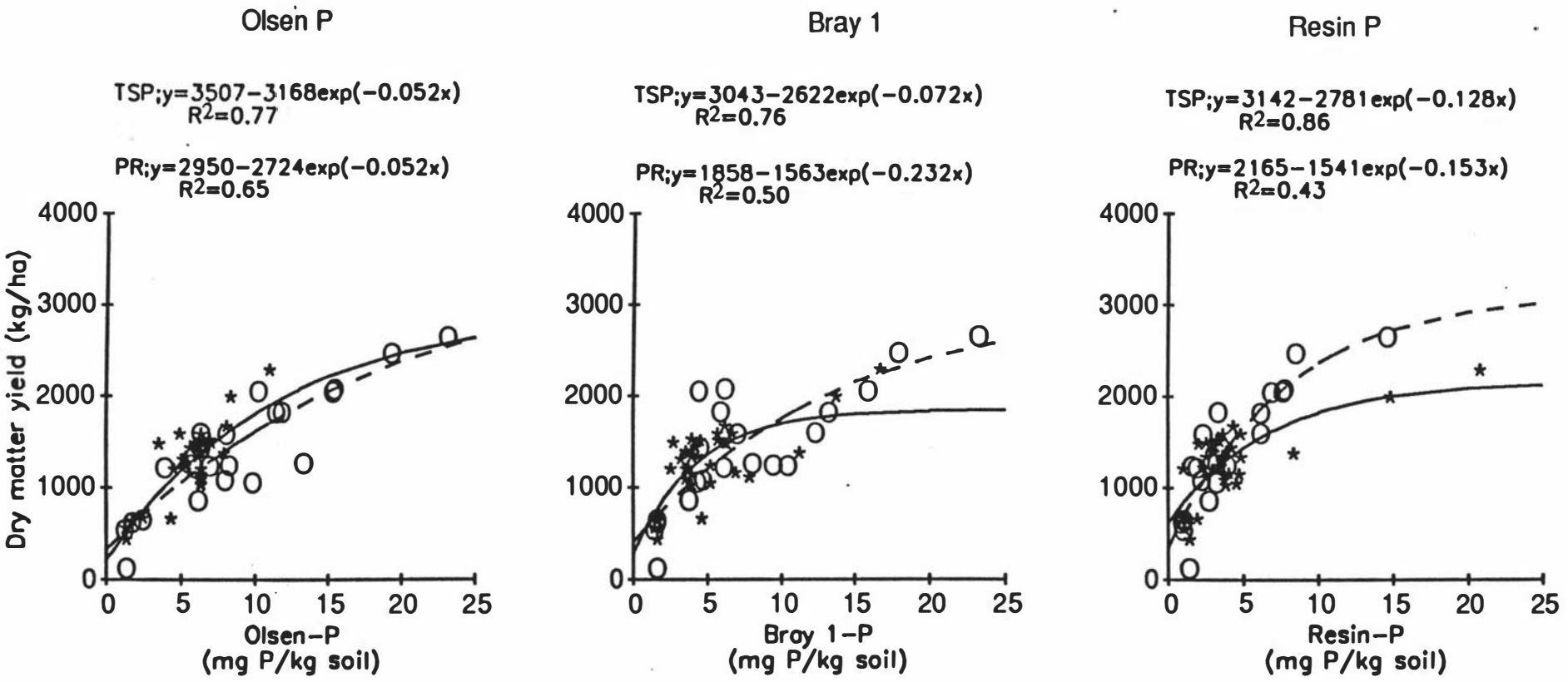


Figure 8.9 Relationship between amounts of soil P extracted by different soil tests from samples taken prior to sowing maize and dry matter yield of maize at (a) Sembawa and (b) Serong plots fertilized with TSP (o) or PRs (*). Solid (—) and dotted (--) lines indicate the fitted relationship for PRs and TSP fertilized plots, respectively.

(b) Serong (Fig. 8.9)



to be better than the Olsen test only in soil treated with TSP. These differences are probably attributed to differences in soil and crop properties used in both studies.

The Bray 1 test was better than the Olsen test in predicting dry matter yield in the more acidic Sembawa soil in both TSP- and PR-fertilized soils. The better ability of the Bray 1 test over the Olsen test in predicting dry matter yield or P uptake has been demonstrated in acidic soils fertilized with water-soluble P sources (Agboola and Oko, 1976; Oyodele, 1986; Bationo *et al*, 1991; Naidu *et al*, 1991) or PRs (Smith *et al*., 1957; Mackay *et al*., 1984d; Syers and Mackay, 1986). MacKay *et al*. (1984d) suggested that the better predictive ability of Bray 1 over Olsen test in PR-fertilized soils may be attributed to the dissolution of some undecomposed (unreacted) PR during the extraction process. According to Chien (1978), both the undecomposed and the dissolved PR-P can provide available P to plant.

8.5 GENERAL DISCUSSION AND CONCLUSIONS

The results obtained from the present field trials show that maize yield responses to P fertilizers differed between sites. However, all of the P fertilizers used, irrespective of their form and application time, increased the growth of maize.

While PRs have been considered as effective fertilizers on tropical acidic soils for various perennial crops, results of the present study demonstrate that they can also be effective fertilizers for annual crops grown on very acidic soils. The present study shows that medium and highly reactive PRs were effective fertilizers for maize in the more acidic Sembawa soil. Greater effectiveness of these PRs than TSP occurred only when the PRs were applied more than six months prior to sowing maize. Additionally, liming of very acidic soil did not reduce the effectiveness of PR in acid soil provided that the PR was allowed to react with soil prior to lime application.

Phosphate rocks of varying solubility can have a higher residual effectiveness than TSP or SSP for annual crops in many tropical acidic soils in Indonesia (Harris *et al*., 1985; Moersidi *et al*., 1982; Hakim and Moersidi, 1982; Widjaya-Adhi *et al*., 1985), the

Philippines (Briones and Vincente, 1985), Brazil (Fageria *et al.*, 1991), and in Kenya (Bromfield, 1981). Most of these studies show that the effectiveness of PR is improved in the second or third season. Harris *et al.* (1985), however, showed Jordan PR to be an effective fertilizer in a very acidic Indonesian Ultisol during first growing season. The residual effectiveness of PR was also found to increase with time.

Soil properties (acidic and high P retention) and climatic conditions in many tropical areas favour the dissolution of PRs. Thus the effectiveness of a PR for annual crops can be less dependent on its chemical reactivity. Results from the present study show that the effectiveness of North Carolina reactive and Moroccan and Pati medium reactive PRs were rather similar. Similarly, Harris *et al.* (1985) showed that both North Carolina reactive and Central Florida medium reactive PRs were as effective as TSP for annual crops in an Indonesian Ultisol for three consecutive seasons. Unreactive PRs, such Christmas Island PR (CIPR), have also been reported to be as effective as TSP in some Indonesian Ultisols from the first growing season (Hakim and Moersidi, 1982; Moersidi *et al.*, 1982). Fageria *et al.* (1991) reported improved effectiveness of some Brazilian unreactive PRs after the second year in rice-bean rotations in a Brazilian Oxisol. It appears that properties of many tropical soils can overcome the effect of fertilizer solubility (Harris *et al.*, 1985).

Because the dissolution rate of PR in the field is generally slow, PR may be unable to supply the crop P requirement at early stages. As mentioned earlier, the application of PR several month prior to planting may overcome this problem in some acidic soils, especially in soils with low and medium P retention capacity. Additionally, soluble P can be applied as a basal fertilizer.

It should be noted, that the high effectiveness of PR in tropical acid soils as a direct fertilizer is obtained only when optimum level of other fertilizers, particularly N and K, are applied (Briones and Vincente, 1985).

The present study has measured for the first time the extent of dissolution of different PRs in tropical soils in the field over different time periods using the Δ0.5 M H_2SO_4-P method. The extent of dissolution of PRs in the more acidic Ultisol from Sembawa was

found to be greater than that in the Entisol from Serong. The present study also provides evidence to suggest that the rate of dissolution of PRs in an acidic tropical Ultisol is faster than that in temperate soils. The present study showed that almost all (94-98%) of the PRs applied (80 kg P ha^{-1}) to the Sembawa Ultisol had dissolved 18 months after application, whereas only 48% of the added Sechura PR (119 kg P ha^{-1}) had dissolved in a New Zealand Inceptisol (pH 5.3) three years after application (Rajan *et al.*, 1991b). Chien *et al.* (1987) observed that between 80 and 98% of the PRs applied (176 kg P ha^{-1}) to a Colombian Oxisol (pH 4.2) had dissolved 5 years after application. Measurements of PR dissolution in soil, either by chemical extractions or using models as discussed in Chapters 5 and 9, might be very useful in making further fertilizer recommendations for PR use.

Results from the present study show that Bray 1 was a better predictor of dry matter yield than Olsen and resin tests in the acidic Sembawa soil fertilized with PRs. The use of the Bray 1 test is, however, disadvantaged by the requirement for two calibration curves for PR- and TSP-fertilized soils. There is a need to examine further the predictive ability of newly developed soil P tests, such as the resin (Saggar *et al.*, 1990) or the Pi (Menon *et al.*, 1989c) test, in a wider range of acidic soils that are potentially suitable for PR application.

CHAPTER 9
MODELLING THE DISSOLUTION OF PHOSPHATE ROCK UNDER FIELD CONDITIONS

9.1 INTRODUCTION

The mechanistic Kirk and Nye model (Kirk and Nye, 1986c) has been shown to predict dissolution of PR in soil in a closed incubation system reasonably well (Chapter 5). The model which is able to predict the relative importance of various soil and rock properties on phosphate rock (PR) dissolution in laboratory experiments is capable of being extended to simulate PR dissolution under field conditions.

Under field conditions a model must simulate not only the influence of the soil and PR materials on the rate of PR dissolution, but also take into account plant and climate factors. One of the limitations of the current Kirk and Nye model is that it does not consider fluctuating soil water contents or the influence of leaching (particularly Ca) that occurs under field conditions. Thus, there is a need to modify the model for its use in the field by including at least a climate-dependent soil water content.

9.2 OBJECTIVES

The objective of this study was to test the value of a "field" modified Kirk and Nye model for predicting the dissolution of PRs of varying reactivity under field conditions. The model was also used to indicate the required accuracy of each input parameter under field conditions.

9.3 MATERIALS AND METHODS

A field trial was conducted in Sembawa, South Sumatra province, Indonesia. Details of the trial, described fully in Chapter 8, are summarized below.

9.3.1 Phosphate rock materials and application times

Although three PRs were used in the field trial, only dissolution of North Carolina (NCPR) and Moroccan (MPR) phosphate rocks was modelled in this experiment. These two PRs were used because, as well as representing PRs of different reactivity, all input parameters required by the model were available. Relevant properties of the PRs are described in Table 8.1 (Chapter 8).

During 18 months of Calopogonium (*Calopogonium caeruleum*) growth, PR (80 kg P ha^{-1}) was broadcast onto individual plots on 26 May 1989 (T_1) for NCPR and MPR, 26 November 1989 (T_2) for NCPR, and 26 May 1990 (T_3) for NCPR and MPR. Plants were mown at 8 cm above the ground prior to fertilizer application at T_2 and T_3. Cuttings were immediately returned after fertilizer application. Plots were irregularly irrigated once or twice a week during the prolonged dry season which occurred between August 1990 and October 1990. Amounts of irrigated water applied were small, relative to total rainfall received, and were not measured.

The trial, which ended on 26 November 1990, was arbitrarily divided into three time periods (see later in Figure 9.7) based on the extent of PR reaction time (days) in soil as follow:

1. First time period (545 days), from 26 May 1989 (T_1) to 26 November 1990 (T_4).
2. Second time period (360 days), from 26 November 1889 (T_2) to 26 November 1990 (T_4).
3. Third time period (180 days), from 26 May 1990 (T_3) to 26 November 1990 (T_4).

9.3.2 Measured data on phosphate rock dissolution

Data on measured PR dissolution used in this Chapter has been reported earlier (Table 8.6, Chapter 8). This data represents dissolution of PRs at the end of the three periods.

9.3.3 Meteorological data

Information on daily rainfall, sunshine hours and maximum and minimum temperatures during the experimental period was supplied by the Research Institute for Estate Crops (RIEC) Sembawa, Indonesia.

9.4 DEVELOPMENT OF WATER BALANCE SUBMODEL

The Kirk and Nye model was briefly described in Section 5.3.4. For the model to simulate PR dissolution under field conditions it needs to take into account the effects of fluctuating soil water content and perhaps leaching (particularly Ca) on the diffusive flux of dissolution products away from the dissolving PR particle. Modification of the model began by including a variable to allow for fluctuating soil water content based on a water balance drainage submodel (L.K. Heng and D.R. Scotter, pers. comm.) (Appendix 9.1).

9.4.1 Accounting for changes in soil water content

9.4.1.1 Calculating drainage volume

Daily drainage water volumes for a soil column of known depth were predicted using the following simple water balance equation:

$$W_f = W_i + R - EP \qquad (9.1)$$

Where W_i is the initial depth of water (mm) in a soil column of a specified depth (z, mm), W_f is the final depth of water (mm) in a soil column of the same depth, R is daily rainfall (mm day^{-1}), and EP is daily potential evapotranspiration (mm day^{-1}) calculated from daily air temperatures and sunlight hours by the method of Priestly and Taylor (1972). EP is later replaced with AEP (actual evapotranspiration rate) which is regulated by root distribution and W_f

The model assumes that rainfall intensity does not exceed the infiltration rate of water

into the soil and that surface run-off does not occur. Assuming that drainage occurs only when the soil reaches its "field capacity", the amount of drainage (D, mm) leaving a certain soil depth (z) is given by the equation

$$D=W_f-W_{fc} \qquad (9.2)$$

where W_{fc} is depth of soil water at field capacity (mm) in soil depth z (mm), and $W_f>W_{fc}$.

9.4.1.2 Estimating daily evapotranspiration

In the field trial, the soil was fully covered by Calopogonium crop. As with pasture plants (Coulter, 1973; McNaughton *et al.*, 1979; and Payne, 1988), it was assumed that all of evapotranspiration (EP) occurred from the leaves of the legumes and none from the soil itself.

In the simple model for the movement of soil water through a plant-soil system, Scotter *et al.* (1979) assumed that the amount of water removed by plants from soil depends only upon the relative distribution of root weight in each soil depth. Under the present experimental condition it was assumed that Calopogonium root mass distribution was 60%, 20%, 15% and 5% for 0-100 mm, 100-200 mm, 200-300 mm and 300-550 mm soil depths, respectively. Hairiah *et al.* (1991) showed that the roots of creeping legumes, of *Mucuna* species, grown in an Indonesian Ultisol, were distributed mainly in the top 55 cm. Total EP was partitioned to draw water from each depth relative to the percentage root distribution in each soil layer. The EP from i^{th} soil layer was calculated as follows:

$$EP_i=EP(r_i) / (\Sigma r_T) \qquad (9.3)$$

where Σr_T is total root mass for all the soil layers (i=1 to 4), r_i is root mass for the i^{th} layer. Actual evapotranspiration (AEP) from each depth was calculated from EP_i using a relationship between AEP/EP and soil water deficit in each depth derived by Scotter *et al.* (1979). This takes the form modified by Sakadevan (1991) as follows:
If $W_{fi}\geq 0.65W_{fci}$, then

$$AEP_i=EP_i \qquad (9.4a)$$

and if $0.30W_{fci} \leq W_{fi} \leq 0.65W_{fci}$, then

$$\frac{AEP_1}{EP_1} = \frac{W_{f1} - (0.30W_{fc1})}{0.35W_{fc1}} \qquad (9.4b)$$

and if $W_{fi} \leq 0.30W_{fci}$, then

$$AEP_1 = 0 \qquad (9.4c)$$

A complete account of the estimation of daily evapotranspiration was given by Sakadevan (1991). In summary, the depth of water (W_{fi}) remaining in a soil layer i is calculated using the following equation:

$$W_{f1(t+1)} = W_{f1t} + R_t - EP_{1t} \qquad (9.5)$$

where t is time (day), and R_t becomes D_i in the $i+1$ soil layer.

9.4.2 Estimating volumetric water content

New daily volumetric water contents for the ith soil layer (θ_i) throughout the experiment were estimated using the following equation:

$$\theta_1 = W_{f1} / z_1 \qquad (9.6)$$

The PR had been mixed with the surface (0-100 mm) soil only (Chapter 8), therefore θ_i calculated for the first layer (i=1) was used as an input parameter for the Kirk and Nye model. As reported in Chapter 5, the impedance factor (f) was estimated from the θ_i and soil bulk density (ρ_b)data by the relationship $f = \theta^{1.49} \times \rho_b$ (Nye and Tinker, 1977).

9.4.3 Executing the model

As reported in Chapter 5, the model was written in BASICA using QuickBasic (Microsoft Corporation, 1987). The simulation was run on an IBM compatible personal computer.

9.5 PARAMETERIZATION

Unless otherwise stated, symbols and units for the input parameters used in this Chapter are same as those used in the Kirk and Nye simulation study reported in Chapter 5.

9.5.1 Soil parameters

Values of a, b, $[Ca^{2+}]_L'$, C_L, ,b_P, b_{HS} and ρ_b for Sembawa soil (Table 5.2) were again used here. The value of initial pH measured in 0.001 M $CaCl_2$ was 4.60.

To calculate the simple water balance of the soil, a top soil depth (z) of 0-100 mm was used. From the relationship $\theta=W_{fi}/z_i$ (Equation 9.6), the value of the maximum content of soil water at field capacity (W_{fc}) was found to be 30 mm (maximum θ_i= 0.30). Since at day O, θ_i was arbitrarily set at as 0.25, W_i, estimated using Equation (9.6), is 25 mm. Daily values for θ were calculated using daily inputs rainfall and *AEP* was calculated from daily maximum and minimum temperature, sunshine hours and θ from the previous day. Initial θ and *f* at the beginning of the experiment were set at 0.25 and 0.139, respectively. Values for θ and *f* at the beginning of the second and third periods were predicted from the drainage submodel.

9.5.2 Phosphate rock parameters

Values of D_{LP}, D_{LH}, D_{LC}, K_{CaF2}, K_{H1}, K_{H2}, K_2 are the same as those used earlier (Chapter 5). Values of a_i, (m.w), (p.c) and ρ were determined for the PR used (Appendix 9.1). Assuming that the applied PR (80 kg P ha^{-1}) was mixed thoroughly through the soil to 100 mm depth, the value of *w*, the application rate per unit soil volume was taken as 0.08 kg P m^{-3}, for both NCPR and MPR.

9.5.3 Plant parameters

The root density (L_v) of Calopogonium was assumed to be similar to that of *Mucuna* species. Using a pinboard technique, Hairiah *et al.* (1991) reported the average value of L_v of *Mucuna* species of 52 dm dm^{-3} in the top 100 mm.

The average root radius (a_r) was taken as 0.002 dm. The flux of acid across root surface (F) during the Calopogonium growth was assumed to be $3x10^{-12}$ mol dm^{-2} s^{-1}. This level of acid secretion, which is considered low for legumes, was selected because N_2 fixation by Calopogonium under the experimental conditions is probably not active due to Al toxicity (H. Sihombing, pers. comm.).

9.6 RESULTS AND DISCUSSION

9.6.1 Prediction of soil volumetric water content

Under field conditions, values of soil water content change with time. An accurate prediction of soil volumetric water content (θ) is very important in order to provide an adequate simulation of PR dissolution because low values of θ severely restrict diffusion of P and base in soil (Equations 5.16 and 5.17, Chapter 5).

Figure 9.1 shows the predicted values of θ in the top 100 mm during the experimental period. Relating this data to the rainfall data (Appendix 9.2), shows that the experiment θ was loosely related to rainfall intensity and distribution. During the experimental period θ ranged from 0.091 to 0.30. Periods with low θ were found mainly in the May/June to October months of each year. In the prolonged dry period from July to October 1990 (Appendix 9.2) θ decreased its lowest level, 0.091, for the whole experimental period.

9.6.2 Prediction of phosphate rock dissolution

Predicted dissolution patterns of NCPR and MPR during the three time periods are shown in Figure 9.2. As expected, the extent of dissolution of the more reactive NCPR was always higher than MPR in each time period. For NCPR applied at T_1, complete dissolution was predicted 380 days after its application. For MPR applied at T_1, 97% of PR was predicted to have dissolved by day 545 after application. The predicted dissolution of NCPR and MPR applied at T_2 at the end of the experiment (360 days) was 94 and 81%. The corresponding values for NCPR and MPR applied at T_3 were 42

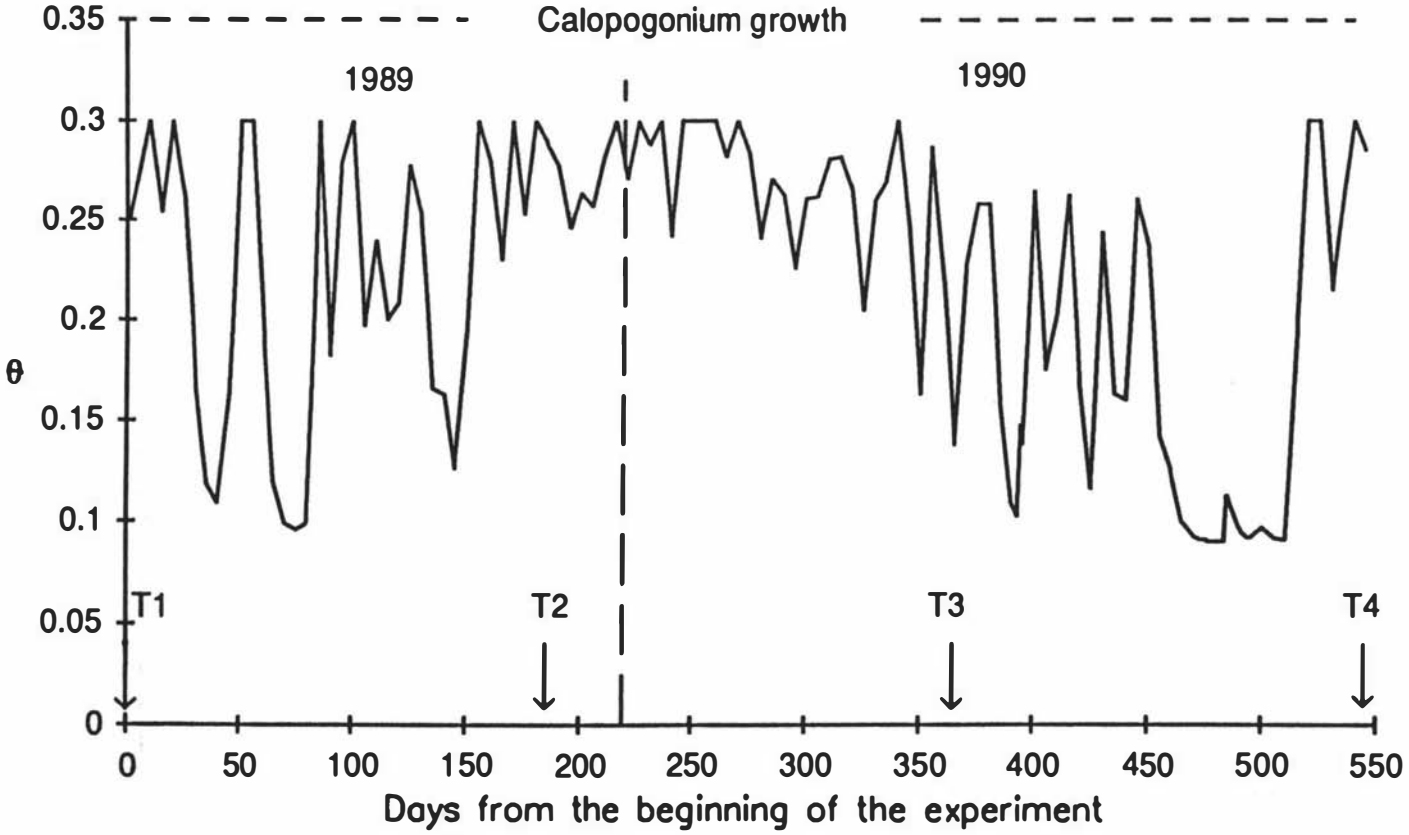


Figure 9.1 Predicted soil volumetric water content (θ) in Sembawa topsoil (0 - 100 mm) during the experimental period (May 1989 to November 1990). T_1, T_2, and T_3 indicate PR application times. T_4 indicates the end of experimental PR dissolution for three separate applications (80 kg P ha^{-1}) during 545 days.

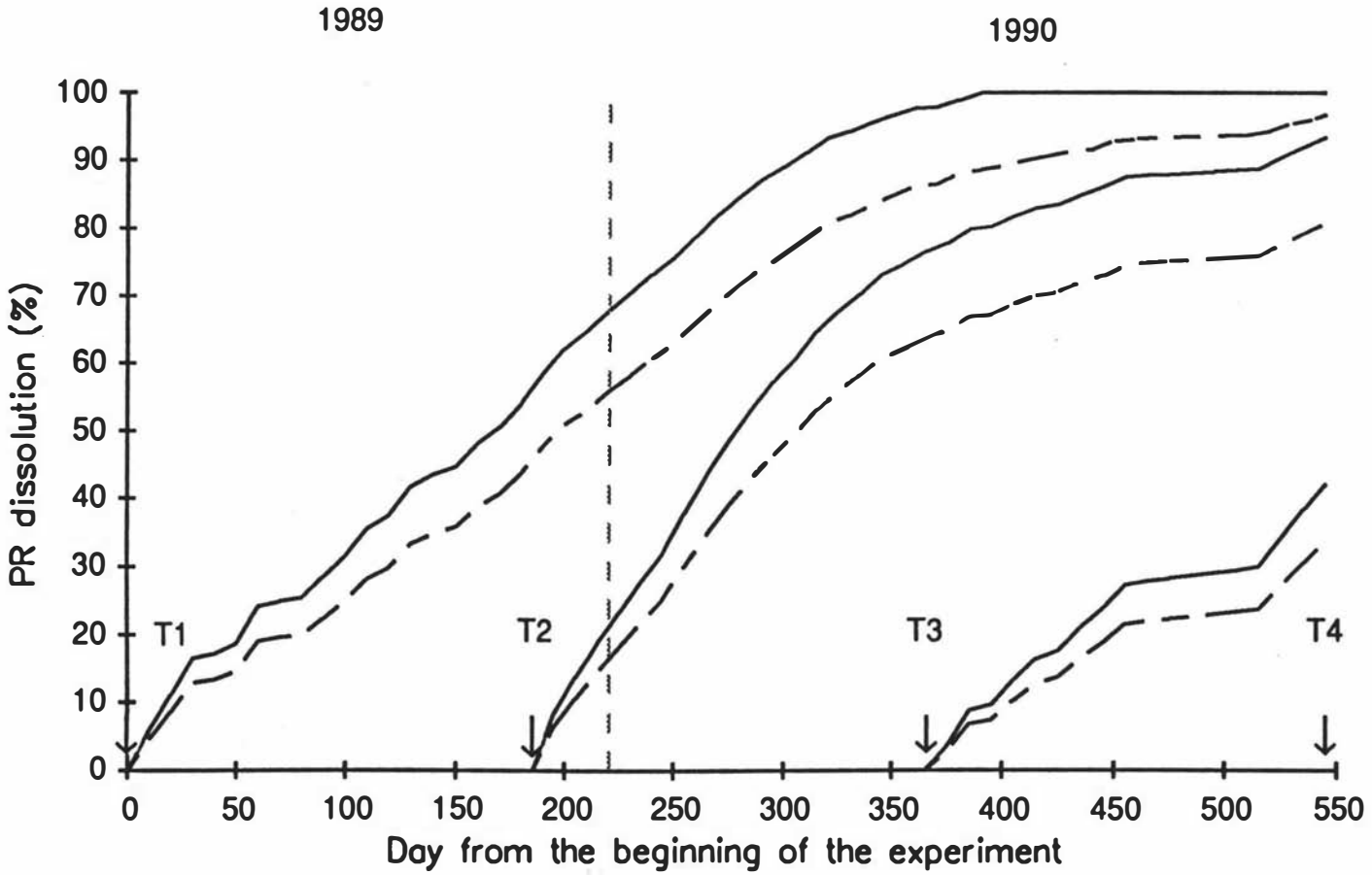


Figure 9.2 Predicted dissolution of NCPR (–) and MPR (--) during the three time periods.

and 34%, respectively.

The fluctuation in the rate and extent of predicted PR dissolution over a short period of time is attributed to changes in soil water (θ) content. Generally the rate of PR dissolution with time decreased with decreasing soil water content. The rate of PR dissolution was negligible when θ was <0.2 (Figures 9.1 and 9.2). Equations 5.16 and 5.17 (Table 5.2, Chapter 5) show diffusion coefficients of phosphate (D_P) and base (D_{HS}) approaches zero as θ approaches zero. Hence the rate of dissolution of PR also approaches zero (Equation 5.10, Chapter 5).

Comparisons between values of predicted and measured (Table 8.4, Chapter 8) PR dissolution at the end of the experiment are presented in Table 9.1. On average the model slightly over predicted PR dissolution, particularly for NCPR applied at T_2 where 94% was the predicted dissolution value, which was 12% less than the measured value. The model gave a satisfactory simulation of PR dissolution over the 180 day period after the T_3 application (Table 9.1).

Differences in predicted and measured amounts of PR dissolution are partly due to the difficulty in assessing values for some input parameters used in the model. Further discussion on this problem is covered in Section 9.7.

9.6.3 Prediction of the amount of the dissolved P taken up by plant

Uptake of P by Calopogonium was not measured, as explained earlier in Chapter 8. However, the Kirk and Nye model can also be used to give indication of the impact of PR form on plant P uptake (Equation 5.19, Chapter 5). Predicted amounts of P taken up from the dissolved PR (PR-P) during three experimental periods are shown in Figure 9.3. Differences between amounts of PR-P predicted to be taken up by plants in plots treated with NCPR or MPR were small despite their markedly different dissolution rates of the two PRs (Figure 9.1). For example, 7.7% (6.1 kg P ha^{-1}) and 6.3% (5.1 kg P ha^{-1}) of the NCPR and MPR applied at T_2, respectively, were taken up by plants before the end of the experiment (360 days). When applied at T_3, the corresponding values were only 0.9% (0.8 kg P ha^{-1}) and 0.8% (0.6 kg P ha^{-1}). The low rooting density of the

Table 9.1 Comparison between measured and predicted PR dissolution over three time periods

Application time	Time period	Duration of each period (days)	PR	PR dissolution (%)	
				Measured*	Predicted
T_1 (May 1989)	May 1989 - Nov 1990	555	NCPR	97.6±0.7	100.0
		555	MPR	93.8±0.5	96.7
T_2 (Nov 1989)	Nov 1989 - Nov 1990	360	NCPR	81.7±1.4	93.5
		360	MPR	-**	80.9
T_3 (May 1990)	May 1990 - Nov 1990	180	NCPR	40.3±5.4	42.3
		180	MPR	36.3±6.8	33.9

* ± indicates SEM
** MPR was not applied at T_2

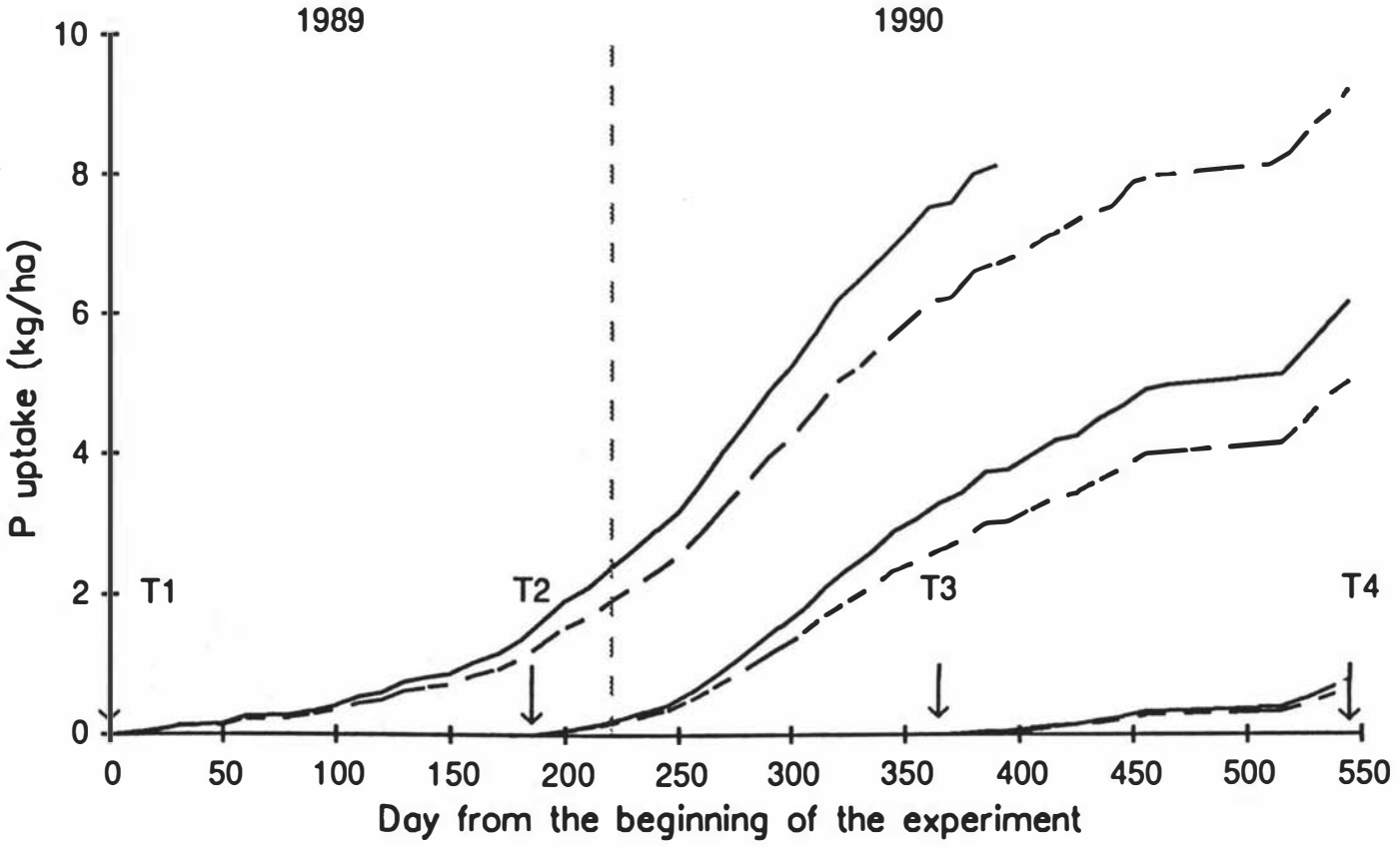


Figure 9.3 Predicted plant uptake of P (kg P ha^{-1}) during the three time periods.

Calopogonium, which was estimated to be 52 dm dm^{-3} is critical in determining the simulated amount of P taken up by plant, particularly in strongly buffered soils (Kirk and Nye, 1986d) (see later discussion in Section 9.6.4.4).

9.6.4 Sensitivity Analysis of the "field' modified Kirk and Nye model

In the following section a sensitivity analysis of the PR dissolution model is conducted to indicate which input parameters are important and need accurate measurements.

In order to test the sensitivity of model, a series of simulations were conducted in which the value of selected input parameters was varied independently. In Chapter 5, it was found that the prediction of PR dissolution in a closed system was sensitive to changes in soil input parameters, such as pH. Under field conditions, accurate simulation of the actual volumetric water content is expected to be important. In addition to soil factors, the effects of plant and PR input parameters on the prediction of PR dissolution were also investigated.

Unless otherwise stated, the input parameters used in the sensitivity analysis are similar to those used for predicting NCPR dissolution during the second time period (26 November 1989 to 26 November 1990).

9.6.4.1 Effect of initial soil pH

Figure 9.4 shows the effect of changing the initial soil pH on the simulated NCPR dissolution. Increasing the initial soil pH (measured in 0.001 M $CaCl_2$) of 4.60 by 0.05 to 0.23 unit decreased the predicted PR dissolution by 7 to 29%, respectively, whereas 0.05 unit decrease in pH increased the predicted PR dissolution by 6%. The NCPR dissolution rate doubled when soil pH was decreased by 0.23 unit to 4.37. It should be noted that changes in pH represent logarithmic changes in H^+ concentration. Hence, decreases in pH have the potential to logarithmically increase PR dissolution. In addition, higher solution calcium concentrations are supported by dissolving PR at lower pH values (Kirk and Nye, 1986c). These results show that a precise in measure of actual soil pH is required if accurate simulations of PR dissolution are to be achieved.

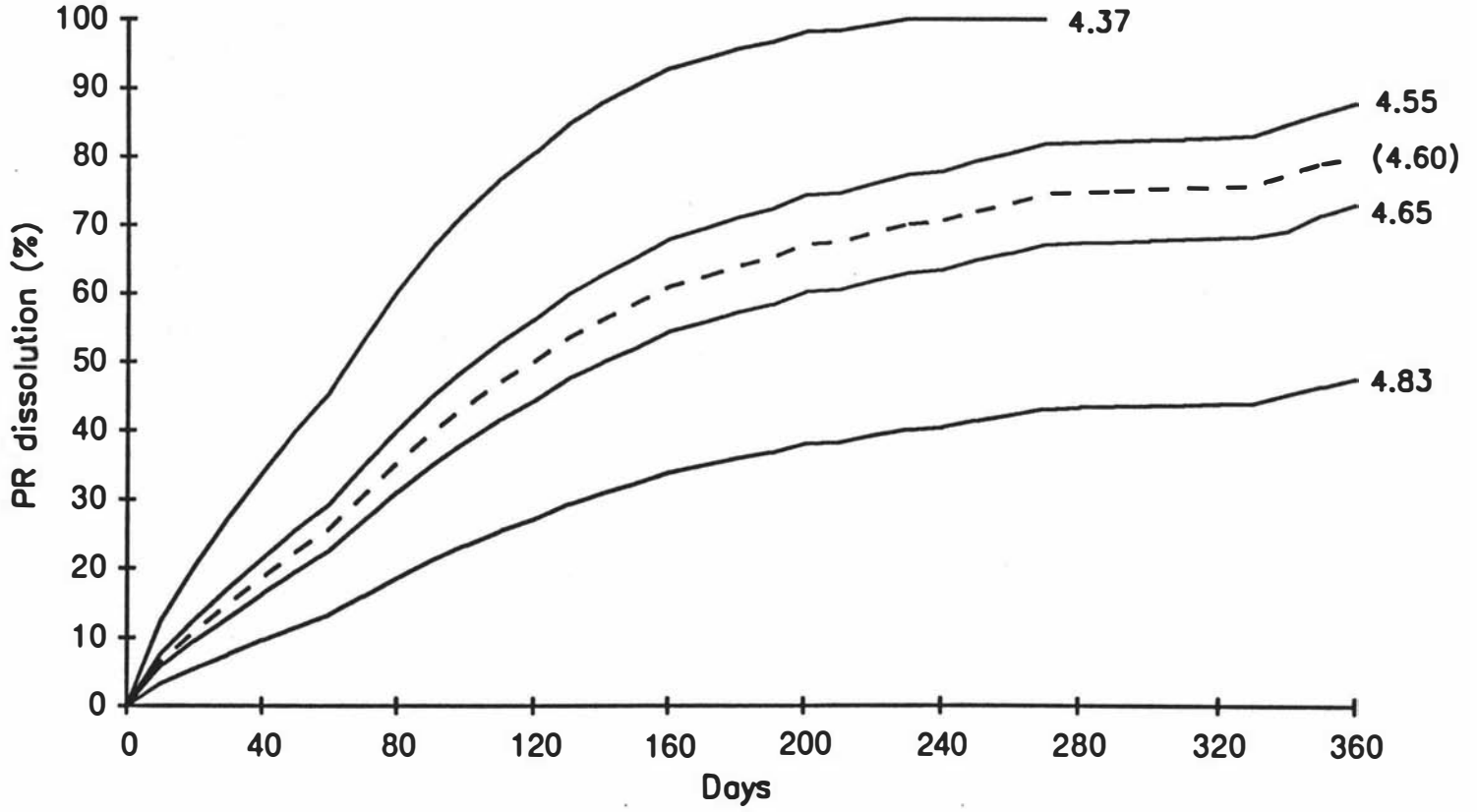


Figure 9.4 Effect of a change in initial (at T_2) soil pH on predicted dissolution of NCPR (T_2-T_4). Initial unadjusted pH is 4.60.

9.6.4.2 Effect of initial concentration of Ca in soil solution

Variations in initial Ca concentration in soil solution, in the range between 0.001 and 0.002 mol dm^{-3}, had minimal effect on PR dissolution (Figure 9.5) suggesting that the choice of value for this parameter in the low concentration range is not so critical for the prediction of PR dissolution in strongly weathered and low pH soils. In less weathered soils with higher concentrations of Ca, variation in initial solution Ca concentration will be more important if it is close to the equilibrium Ca concentration for PR dissolution at that particular soil solution pH and P concentration.

9.6.4.3 Effect of volumetric water content

Effect of variation in distribution and intensity of rainfall

At the present field site, air temperature and sunshine hours varied little during the experimental period. Thus the variation in soil water content throughout the experiment depends largely on rainfall.

As shown earlier (Figure 9.2) the predicted volumetric water content (θ) varied with changes in intensity and distribution of rainfall particularly between T_2-T_3 and T_3-T_4. A total of 1228 mm of rainfall with 99 rain events fell in the first 180 days (T_2-T_3) of the second time period (Appendix 9.2), during which time values of predicted θ of soil ranged from 0.149 to 0.300 (average θ=0.269). During the third time period (T_3-T_4), cumulative rainfall amounted to 552 mm with 36 discrete rain events with almost half of the rainfall recorded in the last 32 days. The predicted value of θ for the third time period ranged from 0.091 to 0.300 (average θ=0.179). Dissolution of PR over 180 days of the second period was always higher than that which occurred over the same interval in the third period (Figure 9.6), although the predicted PR dissolution in both periods showed a different pattern due to differences in the intensity and distribution of the rainfall in both periods (Appendix 9.2). Dissolution of PR was almost negligible during the dry periods in the third time period (T_3-T_4) when θ was reduced to 0.091 (Figures 9.1 and 9.2). In Figure 9.6, this effect is evidenced by the flat portions of the

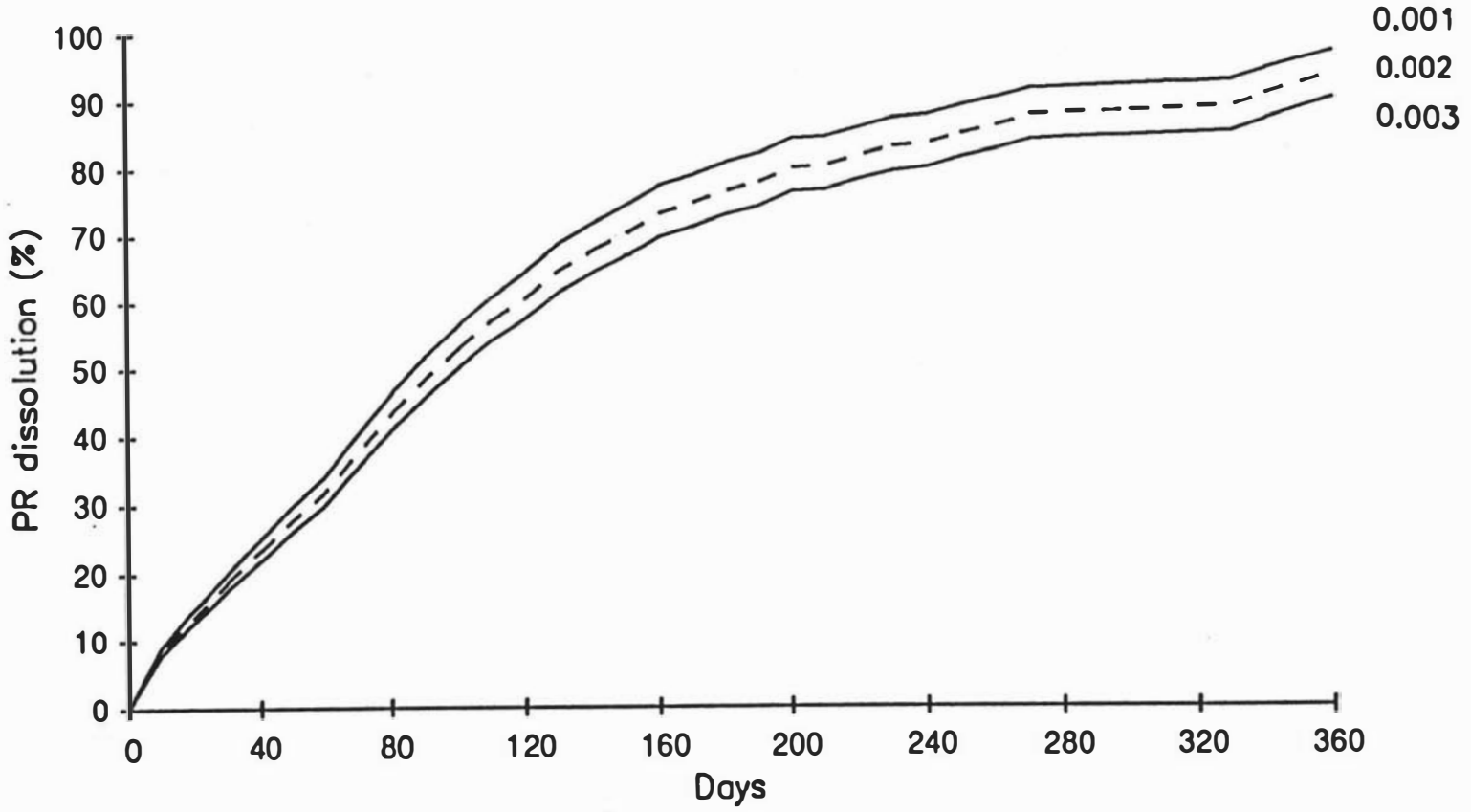


Figure 9.5 Effect of a change in initial (at T_2) soil solution Ca concentration on predicted dissolution of NCPR (T_2-T_4). Initial unadjusted Ca concentration is 0.002 mol dm^{-3}.

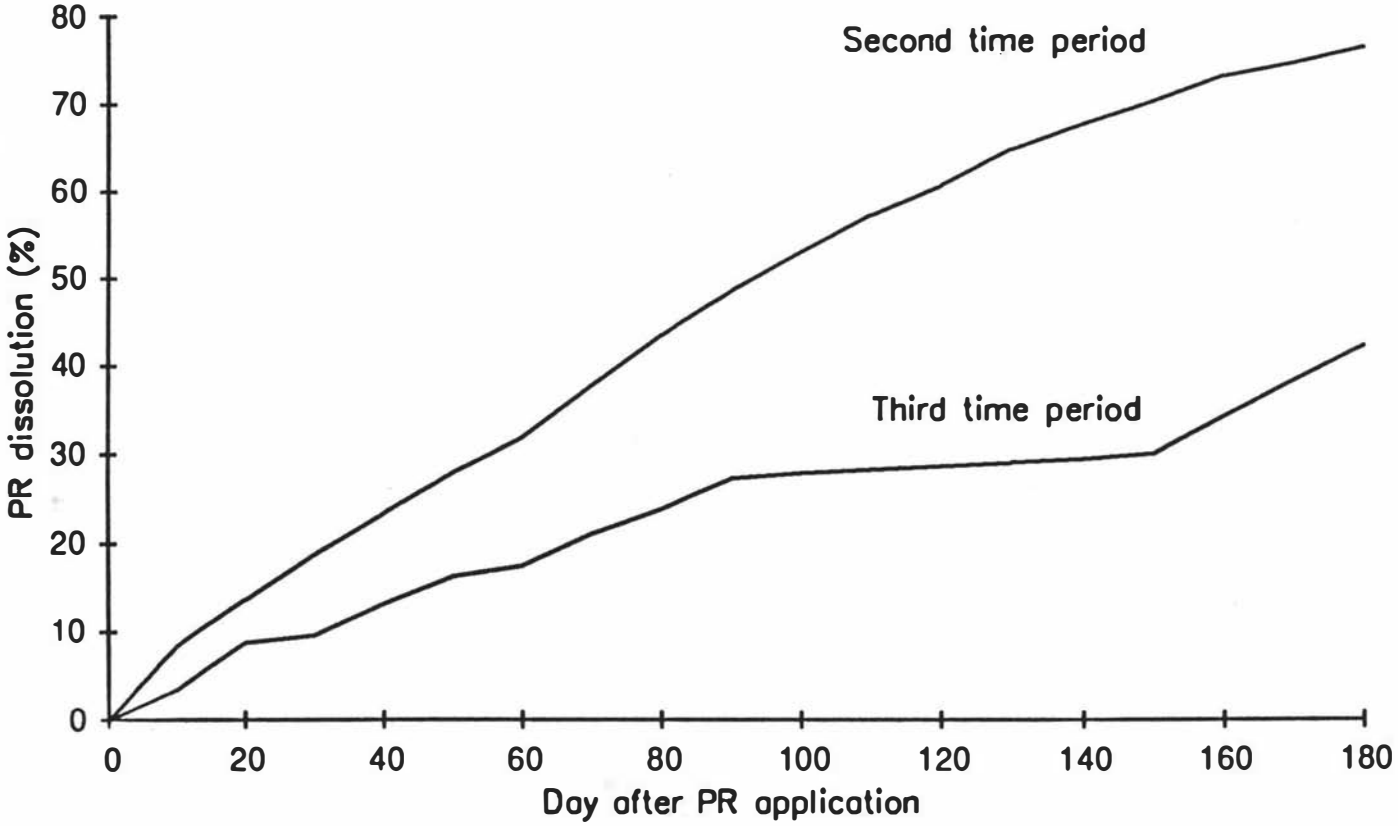


Figure 9.6 Predicted dissolution of NCPR in the first 180 days of the second and third time periods.

dissolution curve between 90 and 150 days after PR application. Differences in soil water content account for the different patterns of PR dissolution observed in both time periods. For example, predicted PR dissolution was small when the soil volumetric water content was less than 0.2.

Effect of the use of a single θ *on PR dissolution*

Addition of the drainage submodel to the Kirk and Nye model has enabled changes in volumetric water content, θ, of a soil layer to be simulated from daily climate data. From the practical point of view, however, use of daily climate data complicates the model for use at a large number of soils. More often, only seasonal rainfall are available as input data rather than daily figures, particularly for remoter regions. The sensitivity of predicted PR dissolution to the use of a seasonal average value for θ was investigated.

An average θ (θ_{av}) was calculated for the predicted θ from actual climate data (Figure 9.1) for a particular time period. Alternatively, this could have been measured during occasional visits to the field site. Values for θ_{av} in the top 100 mm for the first, second and third time periods were 0.221, 0.224 and 0.179, respectively. These values of θ_{av} were used to predict PR dissolution using the Kirk and Nye model without the addition of the drainage submodel.

Results of predicted of NCPR dissolution using "actual" and "average" θ for the three time periods are presented in Figure 9.7. Differences in dissolution patterns are attributed to the fact that the "actual" θ varied during the season depending on the distribution and intensity of rainfall (Figure 9.2). As expected, using θ_{av}, the extent of PR dissolution predicted at the end of each time period was close to the values obtained using actual θ. The use of average θ values, however, slightly underestimates dissolution in the period from day 225 to 475.

9.6.4.4 Effect of plant root density

At a low level of acid secretion (F=3x10^{-12} mol dm^{-2} s^{-1}), the effect of root density, L_v,

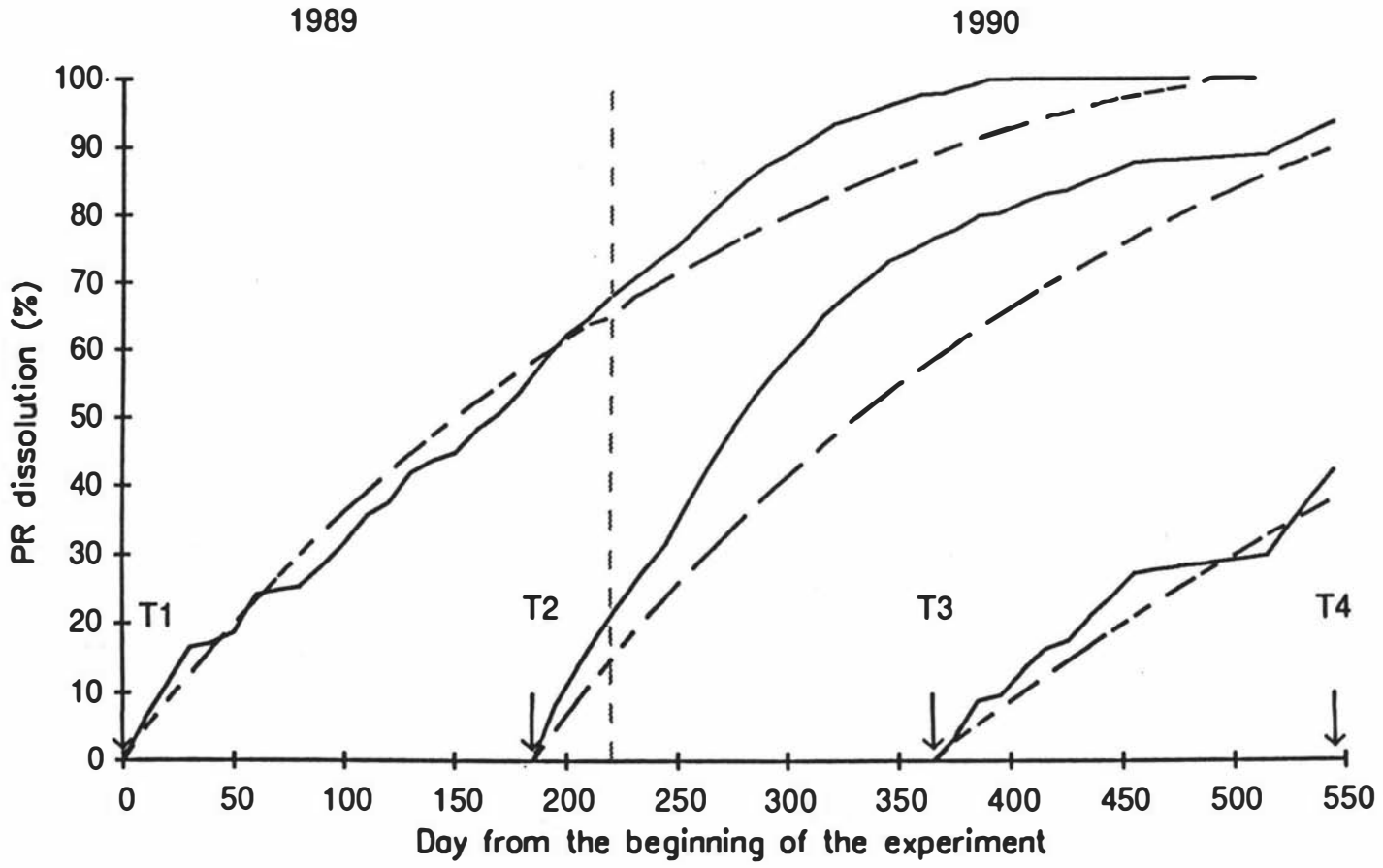


Figure 9.7 Comparison between the predicted dissolution of NCPR during the three time periods using the "actual" (—) and "average" (--) values of θ. T_1, T_2, and T_3 indicate PR application times. T_4 indicates the end of experimental PR dissolution for 3 separate applications.

on PR dissolution was found to be small (Figure 9.8). Varying root density from 52 to 260 dm dm^{-3} increased PR dissolution by only 8%. This is attributed to the high basal soil acidity compared to the extra amounts of produced by roots. Also soil has a high buffering capacity (b_{HS}=0.04 mol kg^{-1}). Root density was found to be more important in affecting P uptake after dissolution rather than the breakdown process it self (Figure 9.8). The amount of P taken up by plant roots in 360 days growth was predicted to increase by 38% when the root density was increased from 52 to 260 dm dm^{-3}. In the present study, prediction about P uptake could not be tested because Calopogonium yields were not measured.

9.6.4.5 Effect of acid secretion

The effect of acid secretion rate, F, on PR dissolution was tested by varying the rate over 10-fold range (Figure 9.9). Increasing F 10-fold from 3 x 10^{-12} to 3 x 10^{-11} mol m^{-2} s^{-1} increased PR dissolution by only 6%. These results suggest that under the present field conditions where root density and amount of acid secretion were both low, root density was not likely to have an important effect on PR dissolution. At a soil pH of 4.6, the amount of acid released by the root in the present study was probably much lower compared to the acid already present in the soil (see earlier discussion). It should be noted however, that the F value used in the model is much lower than the quoted for well nodulated root system, which is 3 x 10^{-11} dm dm^{-2} s (Nye, 1981). A low F value was used here because Calopogonium is expected to fix little N in this acid soil environment (Munns, 1978).

9.6.4.6 Effect of PR particle size

The effect of particle size on the predicted dissolution was assessed by changing the mean radius of PR particle (A_i) by ±10%. Figure 9.10 shows that increasing the average radius of particles by 10% from 0.000915 to 0.001 dm decreased dissolution by 8%. A 10% decrease in radius increased dissolution by 7%. As expected, fine materials with large specific surface areas dissolve quickly in soils. Under field conditions, a typical Sechura PR granule with an average radius of 0.000478 dm (Officer, 1989) dissolved completely within 90 days. Phosphate rock materials that have different ranges of

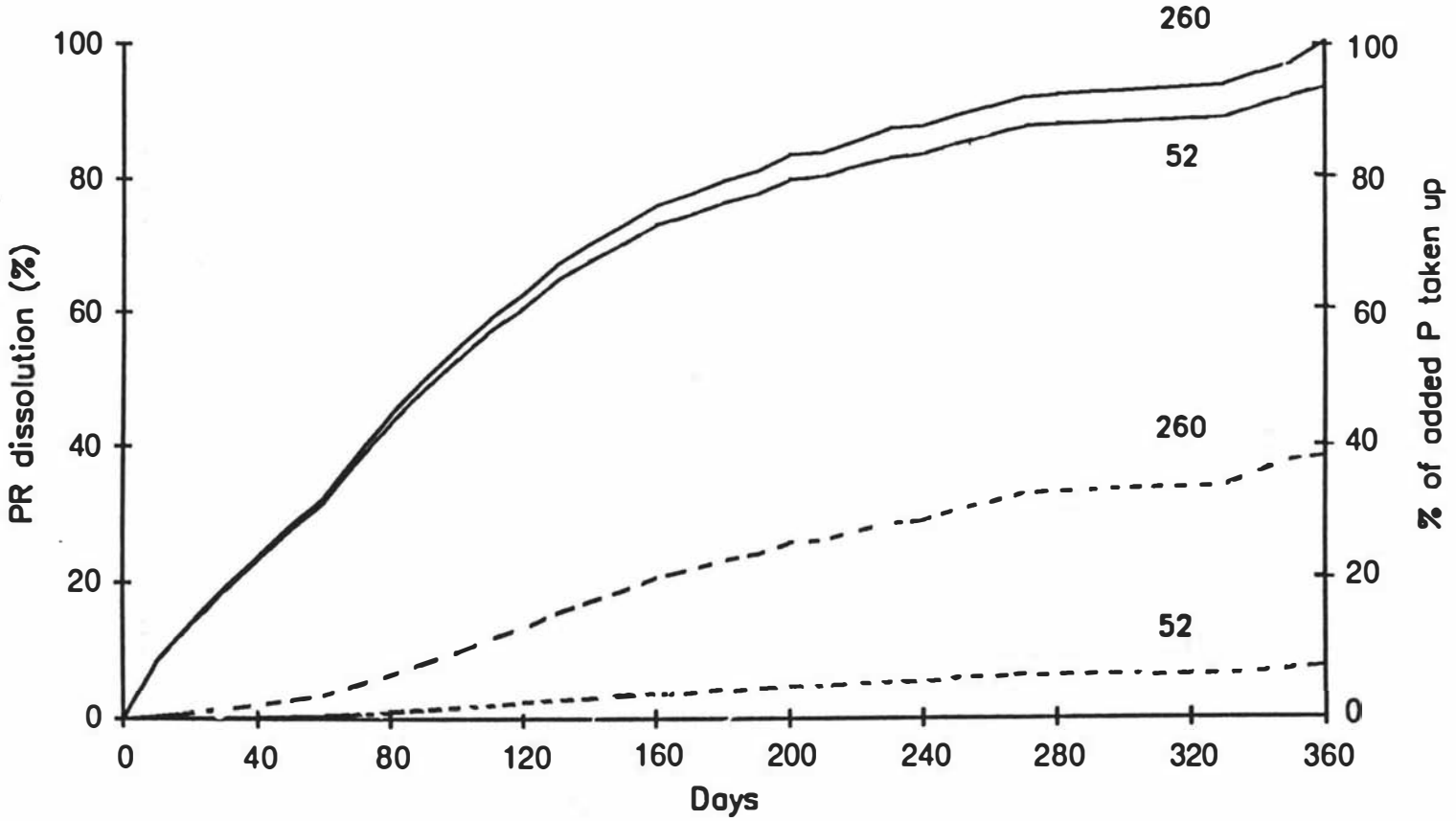


Figure 9.8 Effect of a change in root density (*Lv*) on predicted NCPR dissolution (—) and proportion of PR-P taken up by plant (--) assuming an initial value of *Lv*=52 dm dm^{-3}.

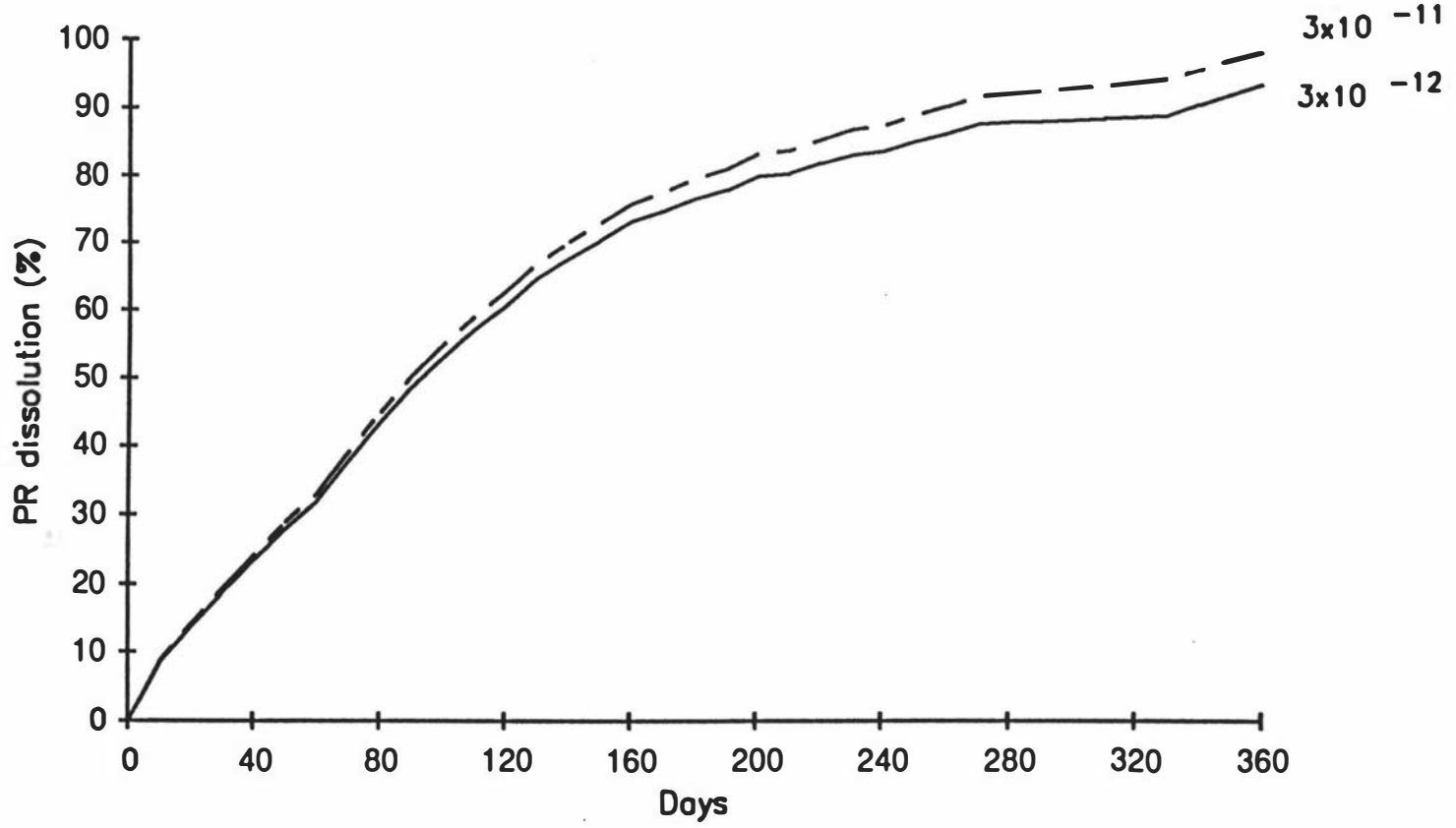


Figure 9.9 Effect of a change in amount of acid excreted by roots (F) on predicted dissolution of NCPR assuming an initial value of $F=3 \times 10^{-12}$ mol dm^{-2} s^{-1}.

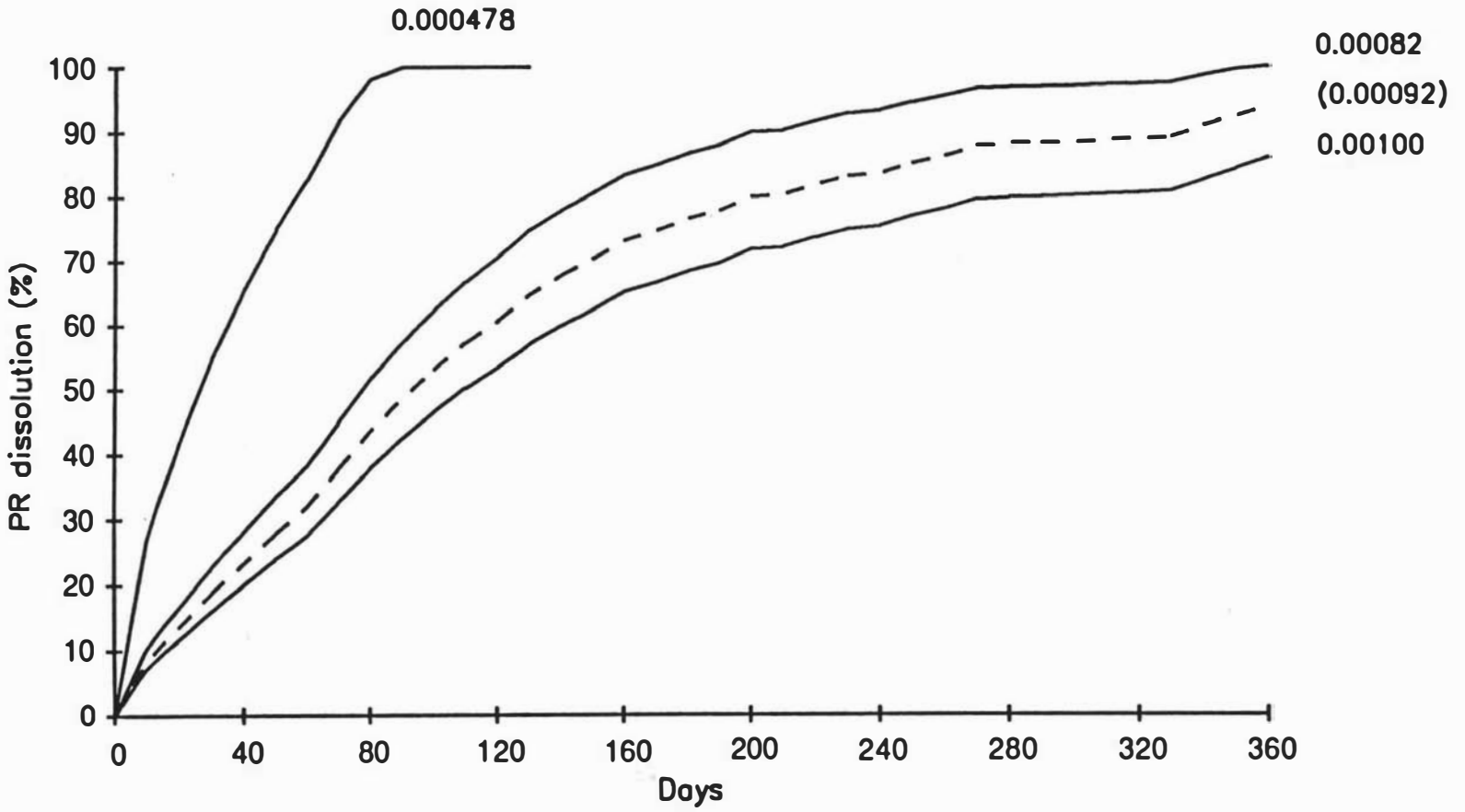


Figure 9.10 Effect of a change in particle size of PR (A_i) on predicted dissolution of NCPR. Initial average of A_i is 0.00092 dm.

particle size will have different dissolution patterns. For materials with a range of particle size, the initial rate of dissolution is generally faster in the presence finer particles. Once these have dissolved, the rate will slow because only the larger particles remain. This suggests that the model should be modified to accommodate the range of particle sizes found in a direct-application PR material.

9.6.4.7 Effect of application rate

The model predicted that varying the application rate (w) by 20% had only minimal effect on PR dissolution (Figure 9.11). Halving the application rate from 0.08 to 0.04 kg m^{-3}, for example, increased PR dissolution by only 5%. It was expected that under these experimental conditions where proton supply is large and Ca sinks are not limiting, PR dissolution would be less affected by w than under conditions of limited proton supply or limited Ca sinks. The effect of application rate on PR dissolution is also expected to be more important when plant roots, with high root densities and high acid secretion rates are high.

9.7 GENERAL DISCUSSION

The sensitivity analysis above suggests that an accurate simulation of PR dissolution is very dependent on initial soil pH and volumetric water content. For this strongly weathered tropical soil other input parameter apparently influence the model's outcome to a less extent.

In addition to the need to accurately determine initial soil pH in all soils, in less acidic soils gains and losses of protons in soil throughout the season due to plant and other processes (e.g. nitrogen fixation, organic matter oxidation, nitrification for NH^{+4} and urea based fertilizers) need to be taken into account.

Under the present field conditions, the decomposition of plant residues returned after each cut may have affected the pH of the top soil during the growing season. Results of the laboratory study reported in Chapter 7 showed that additions of fresh white clover

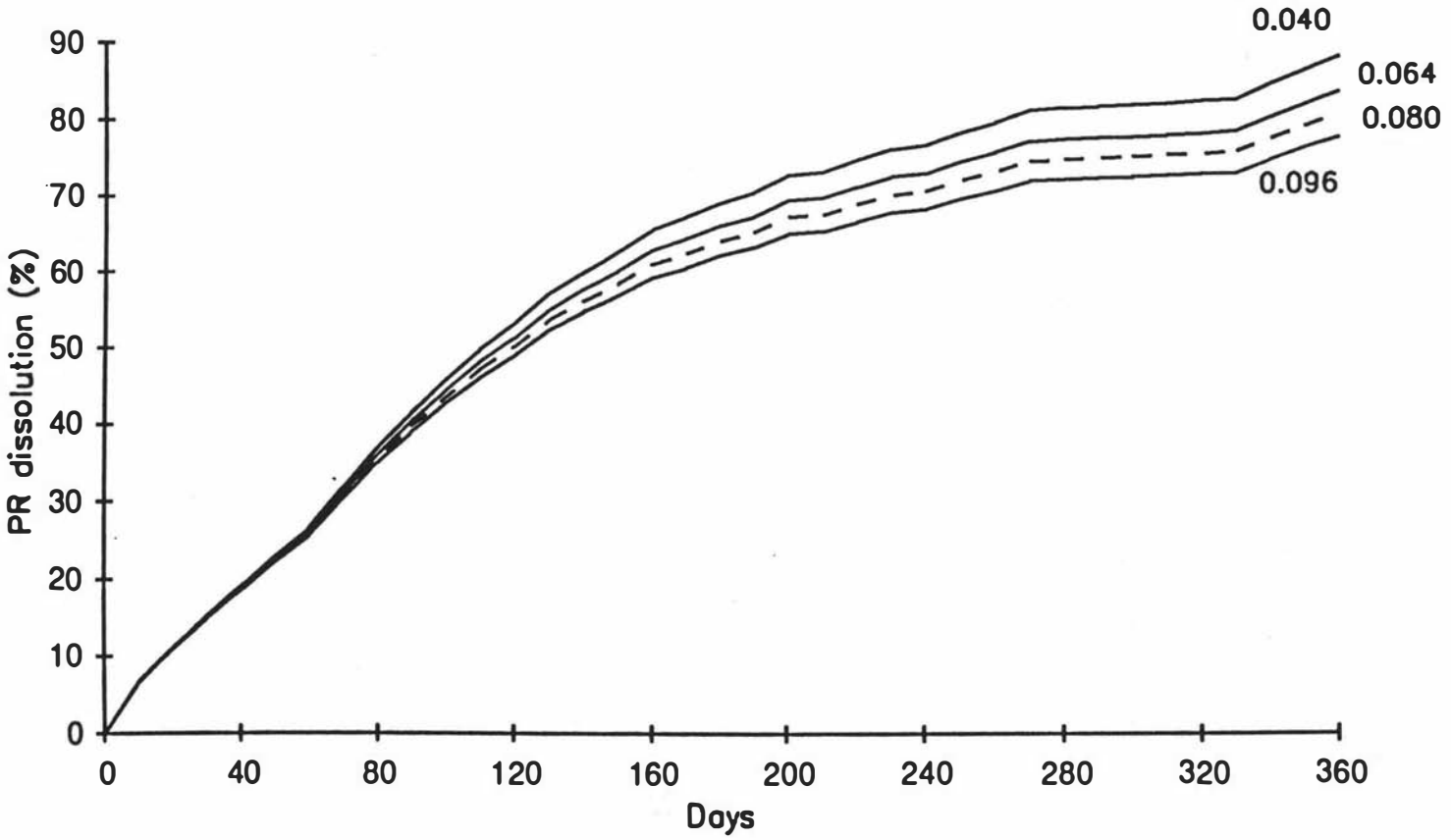


Figure 9.11 Effect of a change application rate (w) on predicted dissolution of NCPR. The measured w is 0.08 kg P m^3 for the field experiment.

residues temporarily increased the soil pH during the first 30 days. Nitrification and organic acid production during decomposition would then be expected to subsequently decrease pH again.

The results of this study also show that dry periods will decrease PR dissolution. In the present study, significant PR dissolution occurred only when the soil water content (θ) was above 0.156. Below this the diffusive flux of PR dissolution products away from the particle is expected to be restricted. This suggests that the effectiveness of PR for direct fertilizer application will be affected by the distribution of rainfall during the growing season. Phosphate rock needs to dissolve continuously during the growing season to meet plant P requirements. Bolland *et al.* (1988) have shown that under a mediterranean climate where the soils are dry for much of the year, PRs were less effective than SSP as P fertilizers. On the other hand, the adequate performance of reactive phosphate rock (RPR) for pasture production in moist climates in New Zealand (Gregg *et al.*, 1988; Mackay *et al.*, 1984b) is primarily because the soils are wet for much of the year and the C, N and S cycles in perennial pastures continually generate protons (Heylar, 1976; Bolan *et al.*, 1992). Indeed, one of the criteria used for direct application of RPR on New Zealand pastures is that the mean annual rainfall in the area selected be >800 mm (Bolan *et al.*, 1990).

In Sembawa soil, PR dissolution was very dependent upon soil water content (θ) in the fertilized zone. Errors in the calculation of soil water content using the water balance submodel may lead to poor prediction of PR dissolution by this model. The prediction of soil water content is strongly dependent on the estimate of water holding capacity (W_{fc}), the depth of soil assumed (z) and root distribution in that zone. For example, it was assumed that the estimate of W_{fc} of the topsoil layer (0-100 mm depth) under the field condition was 30 mm. Thus, according to Equation 9.6, the maximum soil water content, W_f, predicted during the experimental period was 0.30. Values of W_f or θ should be verified by field experiments, as should plant root density.

In other areas the water balance submodel may need to consider infiltration rate and run-off although in many situations run-off will not occur until $W_f=W_{fc}$ and will last no more than 1 day with the soil quickly returning to W_{fc}.

9.8 CONCLUSIONS

The Kirk and Nye model was successfully modified to simulate PR dissolution in an acidic tropical soil by incorporating a water balance model to predict daily soil volumetric water content, θ. The simulation study has shown that the prediction of PR dissolution under a particular set of experimental conditions depends largely on an accurate estimation of initial soil pH and changes in soil volumetric water content during the growing season. Provided that these input parameters are accurately estimated, the model will predict PR dissolution reasonably well.

In the acidic Sembawa soil, a more complex "field" PR dissolution model is not required, presumably because sinks for Ca and the supply of protons are large compared to the those present in soil or generated by soil processes. There is still a need to test the capability of this model to simulate PR dissolution over longer periods of time with different crops grown in other soils with different properties or under different system of management.

In soils with smaller Ca sinks and limited proton supplying power, effects of leaching, soil drying and proton generating processes on important input parameters in the model may also need to be considered.

CHAPTER 10
SUMMARY

The studies presented in this thesis can be summarised as follows.

10.1 REVIEW OF LITERATURE

A review of literature indicated that the chemical nature of phosphate rocks (PRs) is well understood and a significant amount of literature exists on the agronomic value of various PRs as direct-application fertilizers. Despite qualitative information being available on factors influencing the rate of PR dissolution in soil, quantitative descriptions of PR dissolution in soil, particularly field soil, were lacking. Lack of such information precludes formulation of accurate recommendations for appropriate use of PR fertilizer.

The major objective of this thesis was to measure PR dissolution in a range of temperate (New Zealand) and tropical (Indonesian) soils and to use this information to evaluate quantitative methods for describing PR dissolution and subsequent P availability. In this context PR dissolution, P availability and agronomic value of a range of PRs were studied in laboratory, glasshouse and field trials.

10.2 DEVELOPMENT OF METHODS FOR MEASURING RESIDUAL PHOSPHATE ROCK IN SOIL

A soil P fractionation, using 1 M NaCl, 1 M NaOH and 1 M HCl extractions, to measure amounts of residual (undissolved) PR in soils from the increase in HCl-extractable P (ΔHCl-P) between PR-fertilized and unfertilized (control) soils was found to be inaccurate when used on New Zealand soils (Chapter 3). Inaccuracies arose when PR dissolution occurred during the 1 M NaCl pre-extraction of soil/North Carolina phosphate rock (NCPR) mixtures, particularly in acidic soils with low amounts of native exchangeable Ca. In the absence of 1 M NaCl pre-extraction, precipitations of $CaCO_3$ or $Ca(OH)_2$ occurred during 1 M NaOH extraction of soil/PR mixtures, particularly in

the soils with high native exchangeable Ca content. These precipitates adsorb or coprecipitate the P dissolved from PR material causing the amount of residual NCPR, measured by ΔHCl-P, to be underestimated. An improved sequential extraction method (ΔHCl-P method), involving a pre-extraction of the soil/PR mixture with NaCl buffered with TEA (0.5 M NaCl/TEA, pH 7) followed by 1 M NaOH and 1 M HCl extractions, was developed to overcome the two problems mentioned earlier.

The ΔHCl-P method was subsequently evaluated using a range of acidic New Zealand and Indonesian soils (Chapter 4). Although this method provided accurate estimates of amounts of residual NCPR in New Zealand soils, it recovered less than 87% of residual PR in Indonesian soils indicating that it underestimated amounts of residual PR present. Replacement of 1 M HCl with tri-acid (HNO_3, HCl and $HClO_4$) or M H_2SO_4 (0.5-1 M) in the sequential extraction procedure, however, achieved a complete recovery of residual PR in Indonesian soils. It is not clear at this stage why H_2SO_4 is better than HCl for recovering residual PR from Indonesian soils. Use of ^{32}P-labelled francolite (Chapter 7) confirmed that Δ0.5 M H_2SO_4-extractable P (ΔH_2SO_4-P) was an accurate measure of amounts of residual PR in both acidic New Zealand and Indonesian soils. The new ΔH_2SO_4-P method was recommended for measuring residual PR in both temperate and tropical soils.

10.3 DISSOLUTION OF PHOSPHATE ROCK IN SOILS

The effect of soil properties on PR dissolution was examined in both laboratory incubation and field studies. In the first study (Chapter 3), the dissolution of North Carolina phosphate rock (NCPR) and monocalcium phosphate (MCP) was examined in a range of New Zealand soils amended with different amounts of $CaCO_3$ and $NaHCO_3$. Whereas dissolution of MCP in the soils studied was not dependent on soil properties, NCPR dissolution, in general, decreased with increasing soil pH. Increasing amounts of $CaCO_3$ in soils, rather than $NaHCO_3$, decreased NCPR dissolution to a greater extent at similar pH values. In soils amended with $CaCO_3$ the decreases in NCPR dissolution was related to an increase in amounts of exchangeable Ca and a decrease in soil proton supplies.

In a range of acidic soils from New Zealand and Indonesia, the extent of dissolution of the highly reactive North Carolina phosphate rock (NCPR) was greater than that of the medium reactive Moroccan phosphate rock (MPR), and decreased with increasing rate (250 to 1000 mg P kg^{-1}) of PR application (Chapter 5). The maximum extent of PR dissolution occurring in the soils studied was found to be negatively correlated with both initial amounts of exchangeable soil Ca and percentage of the CEC saturated with Ca (Ca saturation). Both exchangeable Ca and Ca saturation control the activities of Ca in soil solution and hence the concentration gradient of Ca away from the PR particle's surface. The latter is one of the major factors controlling the rate of PR dissolution. Additions of plant residue to soils fertilized with synthetic francolite under a short-term (30 days) incubation study (Chapter 7) increased soil pH, and probably solution Ca concentration, thereby decreasing the extent of francolite dissolution.

In all the above experiments, decreased PR dissolution in soil was attributed to increases in soil pH and concentrations of Ca in soil solution. Likewise, long-term field studies conducted in Indonesia at Sembawa and Serong (Chapter 8) showed that the extent of dissolution of medium and highly reactive PRs varied between field sites. Greater dissolution of PRs was measured at Sembawa, which was more acidic and had higher soil moisture content, than at Serong. It was also found that the extent of PR dissolution in Sembawa soil was less affected by the chemical reactivity of PR. At the Serong site, the soil was left fallow for 18 months. This may have limited the extent of dissolution of PR.

10.4 AVAILABILITY OF P DISSOLVED FROM P FERTILIZERS

A series of laboratory (Chapters 6 and 7) and glasshouse (Chapter 6) studies were undertaken to evaluate the effect of soil properties on the plant- and chemical-availability of P derived from PRs and soluble P fertilizers, such as MCP and triple superphosphate (TSP). Soil tests (Olsen, Bray 1 and resin), which measure amounts of P availability, varied in their ability to extract P from PR-fertilized soils. Under laboratory incubations, the amounts of P extracted by soil P tests were generally in the order resin>Bray 1>Olsen. Depending on the soil, rate of P fertilizer addition and

nature of soil test, between 3 and 35% of the P dissolved from P fertilizers was chemically-available (i.e. extractable with Olsen, Bray 1 and resin tests). The greatest proportion of the P dissolved from fertilizers was strongly adsorbed by soil. The availability of the dissolved P in soils was generally more dependent on soil pH and P adsorption characteristics than on other soil properties. Results of these studies indicated that the extent of PR dissolution is a poor indicator of the availability of PR-P in soil.

In New Zealand soils fertilized with MCP, amounts of P taken up in a glasshouse study correlated well with amounts of Olsen-extractable P present prior to plant growth (Chapter 6). In these soils, however, the Olsen test was found to underestimate amounts of plant P taken up from NCPR-fertilized soils.

10.5 FIELD EVALUATION OF PHOSPHATE ROCKS IN INDONESIA

Two long-term (21 months) field trials were conducted to evaluate the effect of soil fertilizer contact time on residual effectiveness of TSP and both medium (Moroccan and Pati) and highly (North Carolina) reactive PRs in two contrasting Indonesian soils (Sembawa Ultisol and Serong Entisol). Maize yield responses to P fertilizers differed between the sites. However, all P fertilizers used, irrespective of source and application time, increased the growth of maize.

The greater dry matter yield or plant P uptake by maize in PR-fertilized plots at Sembawa than at Serong were associated with higher soil P test values, which were attributed to greater dissolution of PRs in the more acidic Sembawa soil, where PRs were found to be most effective. The effectiveness of PRs for maize in this soil was higher than TSP only when the P fertilizers were applied to *Calopogonium caeruleum* cover crop 6 to 18 months prior to sowing maize. Higher effectiveness of PRs resulted from the rapid decrease in the residual fertilizer value of the TSP than that of the PRs with increasing P fertilizer-soil contact time. Results of this study also showed that liming of the acidic Sembawa soil did not reduce the residual effectiveness of PRs provided that the PRs were allowed to react 6 to 18 months prior to lime application.

At Sembawa, where there was a good potential for PR use, Bray 1 test was found to be

a better predictor of plant growth responses to PR fertilizers than either Olsen or resin tests. A limitation in using Bray 1 test to predict maize growth response was that two separate calibration curves were required for soils fertilized with TSP or PRs.

Results of these field trials indicate that acidic soils in the warm and humid tropical, such as Ultisols, are potentially suitable for PR application.

10.6 MODELLING PHOSPHATE ROCK DISSOLUTION

Mitscherlich, Cubic or Kirk and Nye models were used to predict PR dissolution in a range of New Zealand and Indonesian soils incubated in the laboratory (Chapter 5). The empirical Mitscherlich model was found to adequately predict PR dissolution. The Cubic model, which allows PR dissolution to be expressed in terms of a single rate dissolution constant (K), could not adequately explain the extent of PR dissolution measured. Under a closed incubation system, the accumulation of dissolved products, particularly Ca, in soil-PR system increasingly inhibits PR dissolution with time. Therefore, several K values, instead of a single value, were necessary to improve the predicted rate of PR dissolution. Use of the Cubic model with a single K value to describe PR dissolution may be more appropriate in the field situations where increases in the concentrations of dissolution products in soil solution may be minimized by plant uptake and/or leaching.

The mechanistic model of Kirk and Nye, which takes into account many of the important factors controlling PR dissolution, was able to predict closely the extent of PR dissolution in the soils used in this study, particularly at low application rates equivalent to 250 mg P kg^{-1} (0.19 to 0.32 kg P m^{-3}). When soil moisture is not limiting, any differences between simulated and observed PR dissolution in the soils studied was mostly attributed to problems in obtaining a representative measure of soil solution pH as an input parameter in the model. In comparison to the previous two models, the Kirk and Nye model is more complex in terms of input parameters required. Nevertheless, the mechanistic nature of the model makes it possible to extend the model to describe PR dissolution under field conditions.

In order to predict PR dissolution under field conditions, the Kirk and Nye model was modified by incorporating a water balance submodel to simulate changes in daily soil water content (Chapter 9). The modified model adequately simulated NCPR and MPR dissolution in the top 100 mm of field soil at Sembawa in Indonesia.

10.7 SUGGESTIONS FOR FUTURE WORK

The newly developed ΔH_2SO_4-P method enables the extent of PR dissolution to be estimated under laboratory, glasshouse and field conditions. This method can be used to provide data to test the Kirk and Nye PR dissolution model.

The field PR dissolution model may require further modifications for use in other soil-plant-climate environments. In these environments, the effect of varying soil moisture content on soil pH or soil solution concentration of Ca may need to be considered, as well as the leaching and removal of solution Ca. For long-term simulations, the effect of Ca and nitrate leaching, and the role of organic matter decomposition are among several factors that may need to be considered.

Laboratory incubation study showed that additions of plant residue decreased francolite dissolution. Further studies, particularly under open conditions, are required to determine the long-term effects of plant residue additions to PR fertilized soils. In these studies, measurements of concentration of Ca in soil solution, and amounts of acid and organic anions produced during plant residue decomposition may need to be considered.

The ability of different soil P test to predict dry matter yield or P uptake from PR-fertilized soils needs further evaluation in a wider range of soils. Newly developed soil P test, such as Pi (Menon *et al.*, 1989c) and ion-exchange resin membrane (Saggar *et al.*, 1990), have the potential to be successful tests, equally effective in soils fertilized with either PR or soluble P fertilizers.

Improved procedures for measuring amounts of residual (undissolved) PR and available P in soil, in association with a suitable PR dissolution model, will provide an effective basis for formulating recommendations for PR use.

REFERENCES

Agboola, A.A. and Oko, B. 1976. An attempt to evaluate plant available P in Western Nigerian soils under shifting cultivation. *Agronomy Journal* 68: 798-801.

Aguilar, S.A. and Van Diest, A. 1981. Rock phosphate mobilization induced by the alkaline uptake pattern of legumes utilizing symbiotically fixed nitrogen. *Plant and Soil* 61: 27-42.

Alam, S.M. 1981. Influence of aluminum of plant growth and mineral nutrition of barley. *Communications in Soil Science and Plant Analysis* 12: 121-138.

Amberger, A. 1978. Experience with soft rock phosphates for direct fertilizer application. In *Seminar on Phosphate Rock for Direct Application.* IFDC, Muscle Shoals, Alabama. USA, p349-366.

Anderson, D.L., Kussow, W.R. and Corey, R.B. 1985. Phosphate rock dissolution in soils: Indication from plant growth studies. *Soil Science Society of America Journal* 49: 918-925.

A.O.A.C. 1975. *Association of Official Analytical Chemists.* Official Analysis, 12th Edition. Washington, D.C.

Apthorp, J.N., Hedley, M.J. and Tillman, R.W. 1987. The effects of nitrogen fertilizer form on the plant availability of phosphate from soil, phosphate rock and mono-calcium phosphate. *Fertilizer Research* 12: 269-284.

Armiger, W.H. and Fried, M. 1957. The plant availability of various sources of phosphate rocks. *Soil Science Society of America Proceedings* 21: 183-188.

Bache, B.W. 1985. Soil acidification and aluminum toxicity. *Soil Use and Management* 1(1): 10-14.

Ballard, R. and Fiskell, J.G.A. 1974. Phosphorus retention in coastal plain forest. I. Relationship to soil properties. *Soil Science Society of America Proceedings* 38: 250-255.

Barber, S.A. 1984. *Soil Nutrient Bioavailability.* John Wiley & Sons, Inc, New York, 398p.

Barnes, J.S. and Kamprath, E.J. 1975. Availability of North Carolina rock phosphate applied to soils. North Carolina Agricultural Experimental Station. Technical Bulletin 229.

Barrow, N.J. 1983. A mechanistic model for describing the sorption of phosphate by soil. *Journal of Soil Science* 34: 733-750.

Barrow. N.J. 1985. Comparing the effectiveness of fertilisers. *Fertilizer Research* 8: 85-90.

Barrow, N.J. and Campbell, B.A. 1972. Methods of measuring residual value of fertilizers. *Australian Journal of Experimental Agriculture and Animal Husbandry* 21: 502-510.

Bascomb, C.L. 1964. Rapid method for the determination of cation exchange capacity of calcareous and non-calcareous soils. *Journal of the Science of Food and Agriculture* 15: 821-823.

Bationo, A., Baethgen, W.E., Christianson, C.B. and Mokwunye, A.U. 1991. Comparison of five soil testing methods to establish phosphorus sufficiency levels in soil fertilized with water-soluble and sparingly soluble-P sources. *Fertilizer Research* 28: 271-279.

Bekele, T., Cino, B.J., Ehlert, P.A., Van der Maas, A.A. and Van Diest, A. 1983. An evaluation of plant-borne factors promoting the solubilization of alkaline rock phosphates. *Plant and Soil* 75: 361-378.

Blakemore, L.C., Searle, P.L, and Daly, B.K. 1987 Methods for chemical analysis of soils. *NZ Soil Bureau Scientific Report 80*, p102.

Bolan, N.S. and Hedley, M.J. 1989. Dissolution of phosphate rock in soils. 1. Evaluation of extraction methods for the measurement of phosphate rock measurements of phosphate rock dissolution. *Fertilizer Research* 19: 65-75.

Bolan, N.S. and Hedley, M.J. 1990. Dissolution of phosphate rock in soils. 2. Effect of pH on the dissolution and plant availability of phosphate rock in soil with pH dependent charge. *Fertilizer Research* 24: 125-134.

Bolan, N.S., White, R.E. and Hedley, M.J. 1990. A review of the use of phosphate rocks as fertilisers for direct application in Australia and New Zealand. *Australian Journal of Experimental Agriculture* 30: 297-313.

Bolan, N.S., Hedley, M.J.H. and White, R.E. 1991. Process of soil acidification during nitrogen cycling with emphasis on legume based pasture. In *Plant-Soil Interactions at Low Ph* (Eds. R.J. Wright, V.C. Baligar and R.P. Murrmann). Kluwer Academic Publisher, The Netherlands, p169-179.

Bolland, M.D.A. 1985. Residual value for wheat of phosphorus of from Calciphos, Duchess rock phosphates and triple superphosphate on a lateritic soil in south-western Australia. *Australian Journal of Experimental Agriculture* 25:198-208.

Bolland, M.D.A. 1988. Effect of level of application on the relative effectiveness of rock phosphate. *Fertilizer Research* 15: 181-192.

Bolland, M.D.A., Gilkes, R.J. and D'Antuono, F.D. 1988. The effectiveness of phosphate fertilisers in Australian agriculture: A review. *Australian Journal of Experimental Agriculture* 28: 655-668.

Braithwaite, A.C., Eaton, A.C. and Groom, P.S. 1989. Some factors associated with the use of the extractants 2% citric acid and 2% formic acid as estimates of available phosphorus in fertiliser products. *Fertilizer Research* 19: 175-181.

Bray, R.H. and Kurtz, L.T. 1945. Determination of total organic and available forms of phosphorus in soil. *Soil Science* 59: 39-45.

Bremner, J. M. and Jenkison, D. S. 1960. Determination of organic carbon in soil. I. Oxidation by dichromat of organic matter in soil and plant materials. *Journal of Soil Science* 11: 394-402.

Briones, A.M. and Vincente, P.R. 1985. Fertilizer usage of indigenous phosphate deposits. I. Application of apatitic phosphate rock for corn and upland rice in a Hydric Dystrandept. *The Philippine Agriculturist* 68: 1-17.

Bromfield. A.R., Hancock, I.R., and Debenham, D.F. 1981. Effects of ground phosphate and elemental S on yield and P uptake of maize in Western Kenya. *Experimental Agriculture* 17: 383-387.

Bumaya, A.H. and Naylor. D.V. 1988. Phosphorus sorption and extractability in Andic soil incubated with plant residues of variable P content. *Plant and Soil* 112: 77-81.

Bungar, K.C., Yadav. K.S. and Mishra, M.M. 1985. Transformation of rock phosphate during composting and the effect of humic acid. *Plant and Soil* 85: 259-266.

Burnett, W.C. 1977. Geochemistry and origins of phosphorite deposits from off Peru and Chile. *Bulletin of Geological Society of America* 88: 813-823.

Cabala-Rosand, P. and Wild, A. 1982. Direct use of low grade phosphate rock from Brazil as a fertiliser. I. Effect of reaction time in soil. *Plant and Soil* 65: 351-362.

Caro, J.H. and Hill, W.L. 1956. Characteristics and fertilizer values of phosphate rock from different sources. *Agriculture and Food Chemistry* 4: 684-687.

Cathcart, J.B. 1980. Word phosphate reserves and resources. In *The Role of Phosphorus in Agriculture* (Eds. F.E. Khasawneh., E.C. Sample, and E.J. Kamprath), ASA-CSSA-SSSA, Madison, Wisconsin, USA, p1-18.

Chang, S.C. and Jackson, M.L. 1957. Soil phosphorus fraction in some representative soils. *Soil Science* 84: 133-144.

Chatupote, W. 1990. An investigation of some factors influencing the rate of oxidation of elemental sulphur fertilisers. PhD thesis, Massey University, Palmerston North, New Zealand.

Chien, S.H. 1977a. Dissolution rates of phosphate rocks. *Soil Science Society of America Journal* 41: 656-657.

Chien, S.H. 1977b. Thermodynamics considerations on the solubility of phosphate rock. *Soil Science* 123: 117-121.

Chien, S.H. 1978. Interpretation of Bray 1-extractable phosphorus from acid soil treated with phosphate rocks. *Soil Science* 126: 34-39.

Chien, S.H. and Black, C.A. 1976. Free energy of formation of carbonate apatites in some phosphate rocks. *Soil Science Society of America Journal* 40: 234-239.

Chien, S.H. and Hammond, L.L. 1978. A comparison of various laboratory methods for predicting the agronomic potential of phosphate rocks for direct application. *Soil Science Society of America Journal* 42: 935-939.

Chien, S.H., Leon, L.A. and Tejda. H.R. 1980. Dissolution of North Carolina phosphate rock in acid Columbian soils as related to soil properties. *Soil Science Society of America Journal* 44: 1267-1271.

Chien, S.H., Hammond, L.L. and Leon, L.A. 1987. Long-term reactions of phosphate rocks with an Oxisol in Columbia. *Soil Science* 144: 257-265.

Chien, S.H., Sale, P.W.G. and Friesen, D.K. 1990. A discussion of the methods for comparing the relative effectiveness of phosphate fertilizers varying in solubility. *Fertilizer Research* 24: 149-157.

Chu, C.R., Moschler, W.W. and Thomas, G.W. 1962. Rock phosphate transformations in acid soil. *Soil Science Society of America Proceedings* 26: 476-478.

Colwell, J.D. 1963. The estimation of phosphorus fertilizer requirements of wheat in southern New South Wales by soil analysis. *Australian Journal of Experimental Agriculture and Animal Husbandry* 3: 190-197.

Coulter, J.D. 1973. Prediction of evapotranspiration from climatological data. *Proceedings of Soil and Plant Water Symposium.* Information Series No. 96, p38-45.

Dalal, R.C. 1979. Mineralisation of carbon and phosphorus from carbon-14 and phosphorus-32 labelled plant material added to soil. *Soil Science Society of America Journal* 43: 913-916.

Dalton, J.D., Russel, G.C. and Sieling, D.H. 1952. Effect of organic matter on phosphorus availability. *Soil Science* 73: 173-181.

Desai, G.M. and Gandhi, V. 1990. Phosphorus for sustainable agricultural growth in Asia: an assessment of alternative sources and management. In *Phosphorus Requirements for Sustainable Agriculture in Asia and Oceania.* IRRI, Manila, Philippines, p73-83.

Edmeades, D.C., Wheeler, D. M. and Clinton, O.E. 1985. The chemical composition and ionic strength or soil solutions from New Zealand top soils. *Australian Journal of Soil Research* 23:151-165.

Ellis, R., Quader, M.A. and Troug. E. 1955. Rock phosphate availability as influenced by soil Ph. *Soil Science Society of America Proceedings* 19: 484-487.

Fageria, N.K., Baligar, V.C., and Wright, R.J. 1991. Influence of phosphate rock sources and rates on rice and common bean production in an Oxisol. *Plant and Soil* 134: 137-144.

Fertiliser Regulation. 1969. *Document 1969/68.* Wellington, Government Printer.

Field, J.A., Reneau, R.B.Jr. and Kroontje, W. 1985. Effects of anaerobically digested poultry manure on soil phosphorus adsorption and extractability. *Journal of Environmental Quality* 14: 105-107.

Floate, M.J.S. and Torrance, C.J.W. 1970. Decomposition of the organic materials from hill soils and pastures. I. Incubation method for studying the mineralisation of carbon, nitrogen and phosphorus. *Journal of the Science of Food and Agriculture* 21: 116-121.

Fox, R.L. and Hasan, S.M. and Jones, R.C. 1971. Phosphate and sulphate sorption by Latosols. *Proceedings of the International Symposium on Soil Fertility Evaluation* (New Delhi), 1: 857-864.

Friesen, D.K. and Blair, J.G. 1988. A dual radiotracer study of transformations of organic, inorganic and plant residue phosphorus in soil in the presence and absence of plants. *Australian Journal of Soil Research* 26: 355-366.

Fuller, W.H., Nielsen, D.R. and Miller, R.W. 1956. Some factors influencing the utilization of phosphorus from crop residues. *Soil Science Society of America Proceedings* 20: 218-224.

Gregg, P.E.H., Mackay, A.D., Currie, L.D. and Syers, J.K. 1988. Application strategies for Sechura phosphate rock use on permanent pasture. *Fertilizer Research* 17: 219-243.

Gillman, G. P. and Ball, L.C. 1978. Soil solution studies on weathered soils from tropical North Queensland. *Australian Journal of Soil Research* 16: 67-77.

Hairiah, K., Van Noordwijk, M. and Setijono, S. 1991. Tolerance to acid soil conditions of the velvet beans *Mucuna pruriens* var. utilis and *M. deeringiana*. I. Root development. In *Plant-Soil Interactions at Low Ph* (Eds. R.J. Wright, V.C. Baligar and R.P. Murrmann). Kluwer Academic Publisher, The Netherlands, p227-237.

Hakim, L.S. and Moersidi, S. 1982. Comparison and observation of residues of phosphate rocks (in Indonesian). In *Prosiding Pertemuan Teknis Penelitian Tanah* (Ed. M. Sudjadi). Pusat Penelitian Tanah, Bogor, Indonesia, p135-150.

Hammond, L.L., Chien, S.H. and Mokwunye, A.U. 1986. Agronomic value of unacidulated and partially acidulated phosphate rocks indigenous to the tropics. *Advances in Agronomy* 40: 89-140.

Hanafi, M.M., Syers, J.K. and Bolan, N.S. 1992a. Effect of leaching on the dissolution of two phosphate rocks in acid soils. *Soil Science Society of America Journal* (accepted).

Hanafi, M.M., Syers, J.K. and Bolan, N.S. 1992b. Effect of lime on the dissolution of two phosphate rocks in acid soils. *Journal of the Science of Food and Agriculture* (submitted).

Hanway, J.J. 1962a. Corn growth and composition in relation to soil fertility. II. Uptake of N, P and K and their distribution in different plant parts during the growing season. *Agronomy Journal* 54: 217-222.

Hanway, J.J. 1962b. Corn growth and composition in relation to soil fertility. III. Percentages of N, P and K in different plant parts in relation to stage of growth. *Agronomy Journal* 54: 222-229.

Hardjono, A. 1981. Fertilization of rubber seedlings of GT1 clone grown on a Red Yellow Podzolic soil of South Sumatra (in Indonesian). *Menara Perkebunan* 49(6): 143-151.

Hardjono, A. 1987. Agronomic effectiveness of phosphate rocks for *Calopogonium caeruleum* (in Indonesian). *Menara Perkebunan* 55(4): 69-74.

Hardjono, A. 1988a. Agronomic effectiveness of phosphate rocks for cacao grown on some acidic soils (in Indonesian). *Menara Perkebunan* 56(2): 38-43.

Hardjono, A. 1988b. Response of oilpalm to phosphate rock additions (in Indonesian). *Menara Perkebunan* 56(40): 106-109.

Harris, D.J., Briones, A., Hammond, L.L., Manuelpillai, R.G., Raymundo, M. E., Silva, J.A., Soleh, Ir., G. Uehara., and Vincente, P.R. 1985. Comparison of phosphate rock sources in two Benchmark soils. In *Soil-Based Agrotechnology Transfer* (Ed. J.A. Silva). University of Hawaii, Honolulu, p117-125.

Hartatik, W. and Adiningsih, S.R. 1987. Comparison of the residual effectiveness of P fertilizers in a Red Yellow Podzolic soil from Terbanggi, Lampung (in Indonesian). In *Prosiding Pertemuan Teknis Penelitian Tanah* (Ed. M. Sujadi). Pusat Penelitian Tanah, Bogor, Indonesia, p116-125.

Haynes, R.J. 1990. Active ion uptake and maintenance of cation-anion balance: A critical examination of their role in regulating rhizosphere pH. *Plant and Soil* 126: 247-264.

Hedley, M.J., Stewart, J.B.W. and Chauhan, B.S. 1982a. Changes in inorganic and organic phosphorus fraction induced by cultivation and laboratory incubations. *Soil Science Society of America Journal* 46: 970-976.

Hedley, M.J., White, R.E. and Nye, P.H. 1982b. Plant introduced changes in the rhizosphere of rape (*Brassica napus* var. Emerald) seedlings. II. Origin of the pH change. *New Phytologist* 91: 31-44.

Heylar, K.R. 1976. Nitrogen cycling and soil acidification. *Journal of Australian Institute of Agricultural Science* 42: 217-221.

Hughes, J.C. and Gilkes, R.J. 1984. The effect of chemical extractant on the estimation of rock phosphate fertilizer dissolution. *Australian Journal of Soil Research* 22: 475-481

Hughes, J.C. and Gilkes, R.J. 1986a. The effect of rock phosphate properties on the extent of fertiliser dissolution in soil. *Australian Journal of Soil Research* 24: 209-217.

Hughes, J.C. and Gilkes, R.J. 1986b. The effect of soil properties and level of fertilizer application on dissolution of Sechura rock phosphate in some soils from Brazil, Columbia and Nigeria. *Australian Journal of Soil Research* 24: 219:227

Jambu, P., Dupuis, T. and Dupuis, J. 1972. A study of some aspects of iron fixation by humic acids. *Annales Agronomique* 23: 333-354.

Johnson, C.M. and Ulrich, A. 1959. Analitycal methods for use in plant analysis. *California Agricultural Experimental Station Bulletin* 766.

Juo, A.S.R. and Kang, B.T. 1979. Availability and transformation of rock phosphate in three forest soils from southern Nigeria. *Communications in Soil Science and Plant Analysis* 10: 493-505.

Kalburtzi, K.L., Varesoglou, D.S. and Vokou, D. 1990. Decomposition and nutrient release from wheat and fababean straw under field conditions. *Agriculture, Ecosystems and Environment* 30: 107-120.

Kamprath, E.J. 1970. Exchangeable aluminum as a criterion for liming leached mineral soils. *Soil Science Society of America Proceedings* 24: 252-254.

Kamprath, E.H. and Wilson, M.E. 1980. Conventional soil and tissue test for assessing the phosphorus status of soil. In *The Role of Phosphorus in Agriculture* (Eds. F.E. Khasawneh., E.C. Sample, and E.J. Kamprath), ASA-CSSA-SSSA, Madison, Wisconsin, USA, p433-470.

Kanabo, I.A.K. and Gilkes, R.J. 1987a. The role of soil pH in dissolution of phosphate rock fertilizers. *Fertilizer and Research* 12: 165-179.

Kanabo, I.A.K. and Gilkes, R.J. 1987b. The influence of the addition of goethite to soil on the dissolution of North Carolina phosphate rock. *Australian Journal of Soil Research* 25: 313-322.

Kanabo, I.A.K. and Gilkes, R.J. 1988a. The effect of particle size of North Carolina phosphate rock on its dissolution in soil and on levels of bicarbonate-extractable phosphorus. *Fertilizer Research* 15: 137-145.

Kanabo, I.A.K. and Gilkes, R.J. 1988b. The effect of level of phosphate rock application on its dissolution and bicarbonate-extractable phosphorus. *Fertilizer Research* 16: 67-85.

Kanabo, I.A.K. and Gilkes, R.J. 1988c. The effect of moisture regime and incubation period on the dissolution of North Carolina phosphate rock. *Australian Journal of Soil Research* 26: 153-163.

Khasawneh, F.E. and Doll, E.C. 1978. The use of phosphate rock for direct application to soils. *Advances in Agronomy* 30: 159-206.

Kinniburgh, D.G., Syers, J.K. and Jackson, M.L. 1975. Specific adsorption of trace amounts of calcium and strontium by hydrous oxides of iron and aluminium. *Soil Science Society of America Proceedings* 39: 464-470.

Kirk, G.J.D. and Nye, P.H. 1985a. The dissolution and dispersion of dicalcium phosphate dihydrate in soils. I. A predictive model for a planar source. *Journal of Soil Science* 35: 445-459.

Kirk, G.J.D. and Nye, P.H. 1985b. The dissolution and dispersion of dicalcium phosphate dihydrate in soils. II. Experimental evaluation of the model. *Journal of Soil Science* 35: 461-468.

Kirk, G.J.D. and Nye, P.H. 1986a. The dissolution and dispersion of dicalcium phosphate dihydrate in soils. III. A predictive model for regularly distributed particles. *Journal of Soil Science* 37: 511-524.

Kirk, G.J.D. and Nye, P.H. 1986b. The dissolution and dispersion of dicalcium phosphate dihydrate in soils. IV. Experimental evaluation of the model particles. *Journal of Soil Science* 37: 525-524.

Kirk, G.J.D. and Nye, P.H. 1986c. A simple model for predicting the rates of dissolution of sparingly soluble calcium phosphate in soils. I. The basic model. *Journal of Soil Science* 37: 529-540.

Kirk, G.J.D. and Nye, P.H. 1986d. A simple model for predicting the rates of dissolution of sparingly soluble calcium phosphate in soils. II. Application of the model. *Journal of Soil Science.* 37: 541-554.

Kucey, R.M.N and Bole, J.B. 1984. Availability of phosphorus from 17 rock phosphates in moderately and weakly acidic soils as determined by ^{32}P dilution, A and total P uptake methods. *Soil Science* 138: 180-188.

Kumar, P. and Mishra, B. 1986. Dissolution pattern of Indian rock phosphates in acid soils. *Journal of Indian Society of Soil Science* 34: 611-613.

Le Mare, P.H. 1991. Rock phosphates in agriculture. *Experimental Agriculture* 27: 413-422.

Lee, A., Watkinson, J.H., Orbell, G., Bagyaraj, J. and Lauren, D.R. 1987. Factors influencing dissolution of phosphate rock and oxidation of elemental sulphur in some New Zealand soils. *New Zealand Journal of Agricultural Research* 30: 373-385.

Levesque, M. 1969. Characterization of model and soil organic matter-metal phosphate complexes. *Canadian Journal of Soil Science* 49: 365-373.

Leon, L.A., Fenster, W.E. and Hammond, L.L. 1986. Agronomic potential of eleven phosphate rocks from Brazil, Columbia, Peru and Venezuela. *Soil Science Society of America Journal* 50: 798-802.

Li. G.C., Mahler, R.L. and Everson, D.O. 1990. The effect of plant residues and environmental factors on phosphorus availability in soils. *Communications in Soil Science and Plant Analysis* 21: 471-481.

Lindsay, W.L. and Vlek, P.L.G. 1977. Phosphate minerals. In *Minerals in Soil Environments* (Eds. J.B. Dixon and S.B. Weed). Soil Science Society of America, Madison, Wisconsin, p639-672.

Lindsay, W.L., Frazier, A.W. and Stephenson, H.F. 1962. Identification of reactions products from phosphate fertilizes in soils. *Soil Science Society of America Proceedings* 26: 446-452.

McLaughlin, M.J. and Alston, A.M. 1986. The relative contribution of plant residues and fertiliser to the phosphorus nutrition of wheat in a pasture/cereal system. *Australian Journal of Soil Research* 24: 515-26.

McNaughton, K.G., Clothier, B.E. and Kerr. J.P. 1979. Evaporation from land surfaces. In *Physical Hydrology-New Zealand experience* (Eds. D.L. Murray and P. Ackroyd). New Zealand Hydrological Society, wellington, p97-119.

Mackay, A. D. and Wewala, G.S. 1990. Evaluation of partially acidulated phosphate fertilisers and reactive phosphate rock for hill pastures. *Fertilizer Research* 21: 149-156.

MacKay, A. D. and Syers, J.K. 1986. Effect of phosphate, calcium and pH on the dissolution of a phosphate rock in soil. *Fertilizer Research* 10: 175-184

MacKay, A.D., Syers, J.K. and Gregg, P.E.H. 1984a. A glasshouse comparison of six phosphate fertilizers. *New Zealand Journal of Agricultural Research* 12: 131-140.

MacKay, A.D., Gregg, P.E.H. and Syers, J.K. 1984b. Field evaluation of Chatham Rise phosphorite as a phosphatic fertiliser for pasture. *New Zealand Journal of Agricultural Research* 27: 65-82.

MacKay, A.D., Syers, J.K. and Gregg, P.E.H. 1984c. Ability of chemical extraction procedures to assess the agronomic effectiveness of phosphate rock materials. *New Zealand Journal of Agricultural Research* 27: 219-230.

MacKay, A.D., Syers, J.K., Tillman, R. W. and Gregg, P.E.H. 1984d. A comparison of 3 soil testing procedures for estimating the plant-availability of phosphorus in soil receiving either superphosphate of phosphate rock. *New Zealand Journal of Agricultural Research* 27: 231-245.

Mackay, A.D., Syers J.K, Tillman, R.W. and Gregg, P.E.H. 1986. A simple model to describe the dissolution of phosphate rock in soils. *Soil Science Society of America Journal* 50: 291:296.

Martoyo, K. and Suwandi. 1988. Prospects of phosphate rock use for oilpalm cultivation in Indonesia (in Indonesian). In *Prosiding Pertemuan Teknis Pupuk Fosfat Alam* (Eds. M.M. Siahaan., Z. Poeloengan, and A. Hardjono), Balai Penelitian Perkebunan Medan, Indonesia, p56-61.

McClellan, G.H. and Lehr, J.R. 1969. Crystal chemical investigation of natural apatites. *America Mineralogist* 54: 1374-1391.

McClellan, G.H. and Gremillion, L.R. 1980. Evaluation of phosphatic raw materials. In *The Role of Phosphorus in Agriculture* (Eds. F.E. Khasawneh., E.C. Sample, and E.J. Kamprath), ASA-CSSA-SSSA, Madison, Wisconsin, USA, p43-80.

McLaughlin, M.J. and Alston, A.M. 1986. The relative contribution of plant residues and fertiliser to the phosphorus nutrition of wheat in a pasture/cereal system. *Australian Journal of Soil Research* 24: 517-526.

McLaughlin, M.J., Alston, A.M. and Martin, J.K. 1988a. Phosphorus cycling in wheat-pasture rotations. I. The source of phosphorus taken up by wheat. *Australian Journal of Soil Research* 26: 223-231.

McLaughlin, M.J., Alston, A.M. and Martin, J.K. 1988b. Phosphorus cycling in wheat-pasture rotations. II. The role of microbial biomass in phosphorus cycling. *Australian Journal of Soil Research* 26: 333-342.

Menon, R.G., Chien, S.H. and Hammond, L.L. 1989a. Comparison of Bray I and Pi tests for evaluating plant-available phosphorus from soils treated with different partially acidulated phosphate rocks. *Plant and Soils* 114: 211-216.

Menon, R.G., Chien, S.H., Hammond, L.L. and Hanao, J. 1989b. Modified techniques for preparing paper strips for new Pi soil test for phosphorus. *Fertilizer Research* 19: 85-91.

Menon, R.G., Hammond, L.L. and Singh, H.A. 1989c. Determination of plant-available phosphorus by the ion hydroxide-impregnated filter paper (Pi) soil test. *Soil Science Society of America Journal* 52: 110-115.

Munns. D.N. 1978. Legume-rhizobium relation. In *Mineral Nutrition of Legumes in Tropical and Subtropical soils* (Eds. C.S. Andrew and E.J. Kamprath). CSIRO, Melbourne, Australia, p247-263.

Murphy, J. and Riley, J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27: 31-31.

Moersidi, S. and Adiningsih, S.R. 1988. The quality of a range of phosphate rock materials used as direct application fertilizers for annual upland crops (in Indonesian). In *Prosiding Pertemuan Teknis Pupuk Fosfat Alam* (Eds. M.M. Siahaan., Z. Poeloengan and A. Hardjono). Balai Penelitian Perkebunan, Medan, Indonesia, p90-107.

Moersidi, S., Sofyan, A. and Supardi, S. 1982. A study on the use of P and Mg fertilizers in a Sitiung acidic soil (in Indonesian). In *Prosiding Pertemuan Teknis Penelitian Tanah*, No. 3 (Ed. M. Sudjadi). Pusat Penelitian Tanah, Bogor, Indonesia, p151-160.

Naidu, R. and Haynes, R.J. 1991. Chemical and mineralogical properties and soil solution composition of acid soils from the South Pacific Islands. In *Plant-Soil Interaction at Low pH* (Eds. R.J. Wright, V.C. Baligar and R.P. Muurmann). Kluwer Academic Publisher, The Netherlands, p43-53.

Naidu, R., Syers, J.K., Tillman, R.W. and Kirkman, J.H. 1991. Assessment of plant-available phosphate in limed, acid soils using several soil-testing procedures. *Fertilizer Research* 30: 47-53.

Nasution, M.Z., Roshyid-Subandy, A. and Taryo-Adiwiganda, Y. 1986. Effect of P on the growth of several leguminous cover crops (in Indonesian). *Menara Perkebunan* 54(20): 31-34.

Notholt, A.J.G., Sheldon, R.P. and Davidson, D.F. 1989. *Phosphate Deposits of the World* (2). Cambridge University Press, Cambridge, 566p.

Nye, P.H. 1981. Changes of pH across the rhizosphere induced by roots. *Plant and Soil* 61: 7-26.

Nye, P.H. and Tinker, P.B. 1977. *Solute Movent in the Soil-Root System.* Blackwell Scientific Publications, London, 342p.

Nye, P.H. and Ameloko, A.Y. 1987. Predicting the rate of dissolution of lime in soil. *Journal of Soil Science* 38(4): 641-649.

Officer, S.J. 1989. An investigation of the agronomic value of fine grinding and granulating reactive phosphate rocks. MAgrSc thesis, Massey University, Palmerston North, New Zealand.

Official Journal of the European Communities. No. L212/63, Regulation No. 77/535/EEC.

Olsen, S.R., Cole, C.V., Wanatabe, F.S. and Dean, L.A. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circular 939. U.S. Government Printing Office, Washington, DC.

Ottabong, E. 1983. Changes in pH, status of organic carbon, cation exchange capacity and percentage saturation of two acid *Carex* peats incubated without and with lime. *Swedish Journal of Agricultural Research* 13: 107-117.

Oyodole, O.J. 1986. Phosphorus availability in savannah soils of Western Nigeria. *Tropical Agriculture* 63(4): 297-300.

Paauw, W. 1965. Factors controlling the efficiency of rock phosphate for potatoes and rye on humic sandy soils. *Plant and Soil* 22:81-89.

Parfit, R.L. 1978. Anion adsorption by soils and soil materials. *Advances in Agronomy* 30: 1-50.

Payne, D. 1988. The behaviour water in soil. In *Russell's Soil Conditions and Plant Growth* (Ed. A. Wild). John Wiley & Sons, New York, p315-377.

Peaslee, D.E., Anderson. C.A., Burns, G.R. and Black, C.A. 1962. Estimation of relative value of phosphate rock and superphosphate to plants on different soils. *Soil Science Society of America Proceedings* 26: 556-570.

Pek, T.T. 1966. An indigenous phosphate rock as a valuable P source for tree crops (in Indonesian). *Menara Perkebunan* 35(40): 25-28.

Perrot, K.W. and Wise, R.G. 1992. Evaluation of the iron-oxide filter paper (Pi) test for available soil phosphorus with New Zealand soils. Abstracts of Papers on *Efficient Use of Fertilizer and Soil Resources for Tommorow's Agriculture.* NZSSS, Lincoln University, New Zealand.

Phatiratna, L.S.S., de. U.P., Waidyanatha, S. and Perries, O.S. 1987. Effect of leaf litter on direct and indirect mobilization of P from apatite. *Journal of Rubber Research Institute of Sri Lanka* 67: 19-25.

Phatiratna, L.S.S., de. U.P., Waidyanatha, S. and Perries, O.S. 1989. The effect of apatite and elemental sulphur mixtures on growth and P content of *Centrocema pubescens*. *Fertilizer Research* 21: 37-43.

Priestley, C.H.B. and Taylor, R.J. 1972. On the assessment of surface heat flux and evaporation using large-scale parameters. *Monthly Weather Review* 100: 81-92.

Quin, B.F., Dyson, C.B. and Chiao, Y.S. 1987. Agronomic and economic aspects of the use of phosphate rocks for pasture-development of a predictive model. In *The Use of Reactive Phosphate Rocks and Their Derivatives as Fertilisers* (Eds. R.E. White and L.D. Currie). Occasional Report No. 1 , Fertiliser and Lime Research Centre, Massey University, Palmerston North, New Zealand, p147-163.

Rainhorn, T. and Hagin, J. 1978. Reactions of a phosphate rock with soil. In *Seminar of Phosphate Rock for Direct Application.* IFDC, Muscle Shoals, Alabama. USA, p39-45.

Rajan, S.S.S. 1982. Availability to plants of phosphate from "biosuper" and partially acidulated phosphate rock. *New Zealand Journal of Agricultural Research.* 25: 355-361.

Rajan, S.S.S. 1983. Effect of sulphur content of phosphate rock/sulphur granules on the availability of phosphate to plants. *Fertilizer Research* 4: 287-296.

Rajan, S.S.S. and Gilingham, A.G. 1986. Phosphate rocks and phosphate rock/sulphur granules as fertilisers for hill country pasture. *New Zealand Journal of Experimental Agriculture* 14: 313-318.

Rajan, S.S.S. and Watkinson, J.H. 1989. Measurement of rock phosphate dissolution in soil by the inorganic P fractionation method. *Proceedings of the Australian Soil Science Conference*, p113.

Rajan, S.S.S., Fox, R.L., Saunders, W.H.M. and Upsdell, M. 1991a. Influence of pH, time and rate of application on phosphate rock dissolution and availability to pasture. I. Agronomic benefits. *Fertilizer Research* 28: 85-93.

Rajan, S.S.S., Fox, R.L. and Saunders, W.H.M. 1991b. Influence of pH, time and rate of application on phosphate rock dissolution and availability to pasture. II. Soil chemical studies. *Fertilizer Research* 11: 95-101

Ranjan, A.S. and Khotandaraman, G.V. 1986. Influence of organic matter on rock phosphate and its affect on yield and uptake of nutrient by rice. In *Rock phosphate in Agriculture* (Eds. G.V. Khotandaraman, T.S. Manickam and K.M. Natarajan). Tamil Nadu Agricultural University, Coimbatore, India, p161-169.

Resseler, H. and Werner, W. 1989. Preparation and use of ^{33}P labelled carbonate fluorapatite in studies on the effect of phosphate rock containing fertilizers (in German). *Zeithschrift Pflanzenernaehrung und Bodenkunde* 155: 325-332.

Reynolds, B. 1984. A simple method for the extraction of soil solution by high speed centrifugation. *Plant and Soil* 78: 437-440.

Robinson, J.S. and Syers, J.K. 1990. A critical evaluation of the factors influencing the dissolution of Gafsa phosphate rock. *Journal of Soil Science* 41: 597-605.

Robinson, J.S. and Syers, J.K. 1991. Effects of solution calcium and calcium-sink size on dissolution of Gafsa phosphate rock in soils. *Journal of Soil Science.* 42: 389-397.

Saggar, S., Hedley, M.J.H. and White, R.E. 1990. A simplified resin membrane technique for extracting phosphorus from soils. *Fertilizer Research* 24: 173-180.

Saggar, S., Hedley, M.J. and White, R.E. 1991a. An evaluation of a range of soil tests for extracting phosphorus from soils treated with soluble and insoluble P fertilizers. In *Soil and Plant Testing for Nutrient Deficiencies and Toxicities* (Eds. R.E. White and L.D. Currie). Occasional Report No 5, Fertiliser and Lime Research Centre, Massey University, Palmerston North, New Zealand, p72-73.

Saggar, S., Hedley, M.J., White, R.E., Gregg, P.E.H., Perrot, K.W. and Conforth, I.S. 1991b. A glasshouse assessment of the ability of Olsen and Resin P extractions to predict the relative yield of ryegrass in soils fertilized with phosphate rocks. In *Soil and Plant Testing for Nutrient Deficiencies and Toxicities* (Eds. R.E. White and L.D. Currie). Occasional Report No 5, Fertiliser and Lime Research Centre, Massey University, Palmerston North, New Zealand, p149-150.

Sakadevan, K. 1991. Factor influencing the transformation and fate of sulphur and nitrogen in grazed hill country pasture. PhD thesis, Massey University, Palmerston North, New Zealand.

Sample, E.C., Soper, E.J. and Racs, G.J. 1980. Reaction of phosphate fertilizers in soils. In *The Role of Phosphorus in Agriculture* (Eds. F.E. Khasawneh., E.C. Sample, and E.J. Kamprath), ASA-CSSA-SSSA, Madison, Wisconsin, USA, p263-310.

Sanchez, O.A. and Uehara, G. 1980. Management consideration for acid soils with high phosphorus fixation capacity. In *The Role of Phosphorus in Agriculture* (Eds. F.E. Khasawneh., E.C. Sample, and E.J. Kamprath), ASA-CSSA-SSSA, Madison, Wisconsin, USA, p471-524.

Saunders, W.M.H. 1964. Extraction of soil phosphate by anion exchange membrane. *New Zealand Journal of Agricultural Research* 7: 427-431.

Saunders, W.H.M. 1965. Phosphate retention by New Zealand soils and its relationship to free sesquioxides, organic matter and other soil properties. *New Zealand Journal of Agricultural Research* 8: 30-57.

Saunders, W.M.H., Sherell, C.G. and Gravett, I.M. 1987. A new approach to the interpretation of soil tests for phosphate response by grazed pasture. *New Zealand Journal of Agricultural Research* 30: 67-79.

Scotter, D.R., Clothier, B.E. and Turner, M.A. 1979. The soil water balance in a Fragiaqualf and its effect on pasture growth in central New Zealand. *Australian Journal of Agricultural Research* 17: 455-465.

Shamsuddin, J., Che Fauziah, I. and Sharifuddin, H.A.H. 1991. Effects of limestone and gypsum application to a Malaysian Ultisol on soil solution composition and yields of maize and groundnut. In *Plant-Soil Interaction at Low pH* (Eds. R.J. Wright, V.C. Baligar and R.P. Muurmann). Kluwer Academic Publisher, The Netherlands, p501-508.

Sibbessen, E. 1983. Phosphate soil tests and their suitability to assess the phosphate status of soil. *Journal of the Science of Food and Agriculture* 34: 1368-1374.

Sinclair, A.G. and Dyson, C.B. 1988. An interim report on the MAF "National series" forms of phosphate fertiliser trials:herbage dry matter production for growing seasons 1982/83 to 1986/87 inclusive (MAF Tech, Wellington).

Singh, B.B. and Jones, J.P. 1976. Phosphorus sorption and desorption characteristics of soil as affected by organic residues. *Soil Science Society of America Proceedings* 40: 389-394.

Sinha, M. K. 1971. Organo-metallic phosphate. I. Interaction of phosphorus compound with humic substances. *Plant and Soil* 35: 471-484.

Slansky, M. 1986. *Geology of Sedimentary Phosphate.* North Oxford Academic Publisher Ltd, London, 210p.

Smith, G.S., Johnston, C.M. and Conforth, I.S. 1983. Comparison of nutrient solutions for growth of plants in sand culture. *New Phytologist* 91: 337-548.

Smith, J.P. and Lehr, J.R. 1966. An x-ray investigation of carbonate apatites. *Journal of Agriculture and Food Chemistry* 14: 342-349.

Smith, F.W., Ellis, B.G. and Grava. J. 1957. Use of acid-fluoride solutions for the extraction of available phosphorus in calcareous and soils to which rock phosphate has been added. *Soil Science Society of America Proceedings* 21: 400-404.

Smyth, T.J. and Sanchez, P.A. 1982. Phosphate rock dissolution in Cerrado soils as affected by phosphorus sorption capacity. *Soil Science Society of America Journal* 46: 339-345.

Sorn-srivichai, P., Syers, J.K., Tillman., R.W. and Conforth, I.S. 1988. An evaluation of water extraction as a soil-testing procedure for phosphorus. II. Factors affecting the amounts of water-extractable phosphorus in field soils. *Fertilizer and Research* 15: 225-236.

Sparling, G.P., Whole, K.N. and Ramsay, A.J. 1985. Quantifying the contribution from the soil microbial biomass to the extractable P levels of fresh and air-dried soils. *Australian Journal of Soil Research* 23: 613-621.

Sreekantan, L. and Palaniappan, S.P. 1990. Radiotracer studies on P use efficiency in a rice based cropping system. *Journal of Agronomy and Crop Science* 165: 14-18.

Stanford, G. and Dement, J.D. 1957. A method for measuring short-term nutrient absorption by plants. I. Phosphorus. *Soil Science Society of America Journal* 21: 612-617.

Sutopo, G.N. and Kuwatsuka, S. 1990. Concurrent observation of several processes of nitrogen metabolism in soils amended with organic materials. I. Effect of different organic materials on ammonification, nitrification, denitrification, and N_2 fixation under aerobic and anaerobic conditions. *Soil Science and Plant Nutrition* 26(2): 215-224.

Struthers, P.H. and Sieling, D.H. 1950. Effect of organic anions in phosphate precipitation by iron and aluminium as influenced by pH. *Soil Science* 69: 205-213.

Swaby, R.J. 1975. Biosuper-biological superphosphate. In *Sulphur in Australian Agriculture* (Ed. K.D. McLachlan), Sydney University Press, Sydney, p213-220.

Swartzerdruber, D. and Barber, S.H. 1965. Dissolution of limestone particles in soil. *Soil Science* 100: 287-291.

Syers, J.K. and Mackay, A.D. 1986. Reactions of Sechura phosphate rock and single superphosphate in soil. *Soil Science Society of America Journal* 50: 480-485.

Syers, J.K., Smylie, G.W. and Williams, J.D.H. 1972. Calcium fluoride formation during extraction of calcareous soils with fluoride. 1. Implications to inorganic P fractionation schemes. *Soil Science Society of America Proceedings* 36: 20-25.

Syers, J,K., MacKay. A.D., Brown, M.W. and Currie, L.D. 1986. Chemical and physical characteristics of phosphate rock materials of varying reactivity. *Journal of the Science of Food and Agriculture* 37: 1057-1064.

Tabatabai, M.A and Bremner, J.M. 1970. Use of the Leco automatic 70-second carbon analyzer for total carbon analysis of soils. *Soil Science Society of America Proceedings* 34: 608-610.

Terman, G.L., Allen, S.E. and Engelstad, O.P. 1970. Response of paddy rice to rates and sources of applied phosphorus. *Agronomy Journal* 62: 390-394.

Thibaud, M.C., Morel, C. and Fardeau, J.C. 1988. Contribution of phosphorus issued from crop residues to plant nutrition. *Soil Science and Plant Nutrition* 34(4): 481-491.

Thibaud, G.R., Farina, M.P.W., Hughes, J.C. and Johnston, M.A. 1992. The effectiveness of Langebean rock phosphate and superphosphate in two acid, phosphate-deficient soils. *South African Journal of Plant and Soil* 9(1): 19-28.

Till, A.R. and Blair, G.J. 1978. The utilization of grass of sulphur and phosphorus from clover litter. *Australian Journal of Agricultural Research* 29: 235-242.

Trasar-Cepeda, M.C. and Carballas.T. 1991. Liming and the phosphate activity and mineralization of phosphorus in an Andic soil. *Soil Biology and Biochemistry* 23(3): 209-215.

Twine, J.R. and Williams, C.H. 1971. The determination of phosphorus in Kjeldahl digests of plant material by automatic analysis. *Communications in Soil Science and Plant Analysis* 2: 483-489.

Uehara, G. 1978. Mineralogy of the predominant soils in tropical and subtropical regions. In *Mineral Nutrition of Legumes on Tropical and Subtropical soils* (Eds. C.S. Andrew and E.J. Kamprath). CSIRO, Melbourne, Australia, p21-36.

Van Raj, B. and Van Diest. A. 1981. Utilization of phosphate from different sources by six plant species. *Plant and Soil* 51: 577-589.

Wahab, M.H.A. 1978. Rock phosphate sources and their potential as fertilisers in rubber cultivation. *Planters' Bulletin* 157: 147-156.

White, R.E. 1976. Concepts and methods in measurement of isotopically exchangeable phosphate in soils. *Phosphorus in Agriculture* 67: 9-16.

White, R.E. 1980. Retention and release of phosphate by soil and soil constituents. In *Soils and Agriculture* (Ed. P.B. Tinker). Blackwell Scientific Publications, London, p71-114.

White, R.E. and Ayoub, A.T. 1983. Decomposition of plant residues of variable C/P ratio and the effect of soil phosphate availability. *Plant and Soil* 74(2): 163-174.

White, R.E., Hedley, M.J., Bolan, N.S. and Gregg, P.E.H. 1989. Recent developments in the use of phosphate fertilisers on New Zealand pastures. *Journal of the Australian Institute of Agricultural Science* 2(50): 26-32.

Widjaja-Adhi, I.P.G., Sudjadi, M. and Silva, J.A. 1985. An evaluation of residual phosphorus in Paleudults and Eutrostox. *Pemberitaan Penelitian Tanah dan Pupuk* 4: 31-41.

Williams, C.H. 1980. Soil acidification under clover pasture. *Australian Journal of Experimental Agriculture and Animal Husbandry* 20: 561-567.

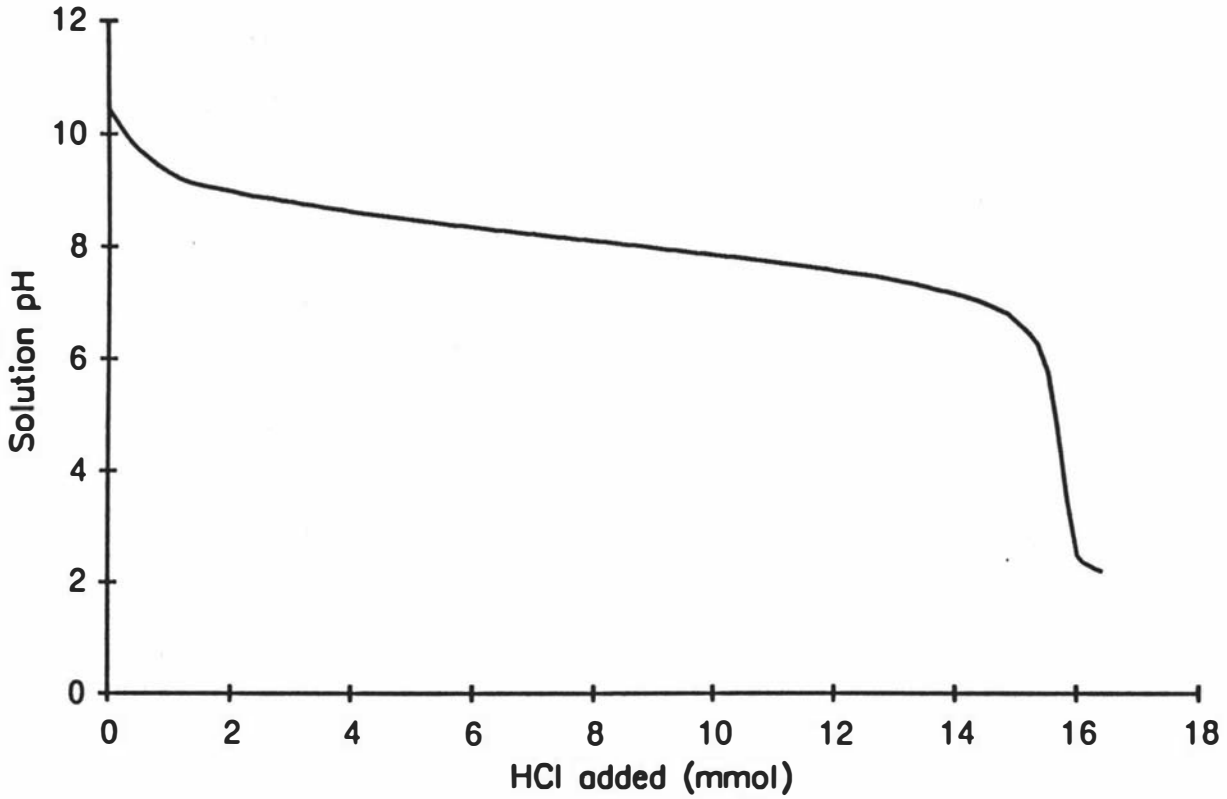
Williams, P.H. and Walker, T.W. 1969. Fractionation of phosphate in a maturity sequence of New Zealand basaltic soil profiles. *Soil Science* 107: 22-30.

Williams, P.H., Syers, J.K. and Walker, T.W. 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jacksons' procedure. *Soil Science Society of America Proceedings* 31: 736-739.

Wilson, M.A. and Ellis, B.G. 1984. Influence of calcium solution activity and surface area on the solubility of selected rock phosphates. *Soil Science* 138: 354-358.

Wolf, A.M., Baker, D.E. and Pionkee, H.B. 1986. The measurement of labile phosphorus by the isotopic and anion resin method. *Soil Science* 141(10): 60-70.

Wright, R.J., Baligar, V.C. and Belesky. D.P. 1992. Dissolution of phosphate rock in soils of the Appalachian region. *Soil Science* 153(1): 25-36.



Appendix 3.1 Titration curve for 100 ml portion of 0.5 M NaCl/TEA mixture against 1 M HCl.

Appendix 5.1

```
CLOSE
'       THE CUBIC MODEL (RAJAN AND WATKINSON, 1986)
'       USED TO SIMULATE THE DISSOLUTION RATE CONSTANT OF
'       PHOSPHATE ROCK (PR) USING LEAST SQUARE ITERATION
'       PROCEDURE
'QuickBASIC  Program Title: CUBIC.BAS

'Units and Symbols:
'         Rate = mg/mm2
'           dR = mm/day
'            p = particle density (mg/mm3)
'           No = # particles
'            z = # samplings
'            m = # size fractions
'            D = diameter, mm
'            R = radius, mm
'            A = area, mm2
'            V = volume, mm3
'        Mpart = Mass per particle, mg
'            S = days
'           Th = predicted PR remaining (%)
'           Ob = observed PR remaining (%)

CLS
'Initial Section
'INPUT "Enter PR dissolution inputfile : ", inputfile$
INPUT "Enter output filename : ", outputfile$
'OPEN inputfile$ FOR INPUT AS #1
OPEN outputfile$ FOR OUTPUT AS #2
INPUT "Enter # samplings : ", z
INPUT "Enter # size fractions : ", m
pi = 3.14159: p = 2.75: Rate = 6: dRmax(1) = 6 / 1000: L = 0
Obm = 0: Obs = 0: Smdiffs = 0: mdiffs = 0: mdiff = 0: IN = .2: h = 0
DIM S(z), Ob(z), Th(z), SS(z)
DIM D(m), R(m), A(m), V(m), Mpart(m), Mtot(m), No(m), TotalA(m), percent(m)
FOR n = 1 TO z
   INPUT "Day No. and % PR Remaining : ", S(n), Ob(n)
   'INPUT #1, S(n), Ob(n)
   Obs = Obs + Ob(n)
NEXT
Obm = Obs / z

FOR n = 1 TO z
   mdiff = Ob(n) - Obm
   mdiffs = mdiff * mdiff
   Smdiffs = Smdiffs + mdiffs
NEXT
```

```
FOR n = 1 TO m
  PRINT "enter diameter & percent "; n
  INPUT "diameter (mm) "; D(n)
  INPUT "percent "; percent(n)
NEXT

1850 h = 1: L = L + 1
FOR n = 1 TO m
  R(n) = D(n) / 2
  A(n) = 4 * pi * R(n) ^ 2
  V(n) = 4 / 3 * pi * R(n) ^ 3
  Mparticle(n) = p * V(n)
  Mtot(n) = Rate * percent(n) / 100
  No(n) = Mtot(n) / Mparticle(n)
NEXT
'PRINT "InputFile : "; inputfile$
'PRINT "OutputFile : ";
'Dynamic Section
FOR day = 1 TO S(z)
  TotMnet = 0: TotMoxid = 0
  FOR n = 1 TO m
    dR(n) = dRmax(L)
    R(n) = R(n) - dR(n)
    IF R(n) < 0 THEN R(n) = 0
    Mnet(n) = 4 / 3 * pi * (R(n) ^ 3) * p * No(n)
    Moxid(n) = Mtot(n) - Mnet(n)
    TotMnet = TotMnet + Mnet(n)
    TotMoxid = TotMoxid + Moxid(n)
    PerMnet = TotMnet / Rate * 100
    PerMoxid = TotMoxid / Rate * 100
  NEXT

  IF INT(day) = INT(S(h)) THEN
    Th(h) = PerMnet
    h = h + 1
    IF h > z THEN h = h - 1
  END IF
NEXT

'Calculates 3 Residual Sum of Squares on First Cycle
'2 Calculation on Subsequent Cycle from 3(2) estimates of dRmax(L)
 P = 0
 FOR i = 1 TO z
   Diff = Th(i) - Ob(i)
   diffs = Diff * Diff
   S = S + diffs
 NEXT
SS(L) = S
IF L = 3 THEN 3000
```

```
2800 dRmax(L + 1) = dRmax(1) * (1 + IN)
    IN = -IN
    GOTO 1850

'Choosing the Smallest Residual Sum of Squares and Best dRmax Estimate
'If Best dRmax is the Previous Value (ie. SS(1) is selected) then
'Line 3035 Reduces Change in dRmax(1)
3000  IF SS(1) < SS(2) AND SS(1) < SS(3) THEN
       IN = IN * .5: GOTO 3800
      END IF
      IF SS(2) < SS(3) THEN
       SS(1) = SS(2)
       dRmax(1) = dRmax(2)
      ELSE
       SS(1) = SS(3)
       dRmax(1) = dRmax(3)
      END IF
3800  L = 1
      IF ABS(IN) < .01 THEN
       GOTO 4000
      ELSE
       GOTO 2800
      END IF

4000  CLS
      'PRINT "Input Filename: "; inputfile$
      PRINT ; "dRmax = ";
      PRINT USING "####.##"; dRmax(1) * p * 100000
      PRINT "Day  Predict%  Observed% "

      FOR n = 1 TO z
       PRINT USING "###"; S(n),
       PRINT USING "   ###.## "; Th(n), Ob(n)
      NEXT
      PRINT : PRINT "R sq.= ";
      PRINT USING "#.##"; (1 - SS(1) / Smdiffs)
      PRINT #2, "Input Filename : ", inputfile$
      PRINT #2, "dRmax = ";
      PRINT #2, USING "####.##"; dRmax(1) * p * 100000
      PRINT #2, "Day  Predict%  Observed% "

      FOR n = 1 TO z
       PRINT #2, USING "###"; P(n),
       PRINT #2, USING "   ###.## "; Th(n), Ob(n)
      NEXT

      PRINT #2, : PRINT #2, "R sq.= ";
      PRINT #2, USING "#.##"; (1 - SS(1) / Smdiffs)
CLOSE : END
```

Appendix 5.2

```
1       REM MODIFIED VERSION OF KIRK AND NYE'S MODEL TO
2       REM SIMULATE THE DISSOLUTION OF NCPR AND MPR UNDER
        REM LABORATORY CONDITIONS.

3       REM FOLLOW 4, 5 & 6 TO RUN THIS PROGRAMME
4       REM UNLOAD "PRDISS.BAS" & LOAD "DATA.1" TO ENTER THE
        REM INPUT VALUES & SAVE
5       REM UNLOAD "DATA.1" & LOAD "OUTPUT.1" TO CLEAR THE
        REM PREVIOUS OUTPUT & SAVE.
6       REM UNLOAD "OUTPUT.1" & LOAD "PRDISS.BAS" & RUN

7       PRINT : PRINT "KIRK AND NYE MODELLING IS RUNNING - KEEP"
        PRINT : PRINT "AWAY"
8       PRINT
9       PRINT
11      PRINT : PRINT "HAVE YOU CHECKED YOUR INPUT FILE -"
        PRINT : PRINT "INPUT.1"
12      PRINT
14      PRINT
15      PRINT : PRINT "HAVE YOU CREATED AN OUTPUT FILE -"
        PRINT : PRINT "OUTPUT.1"

20    DIM Label$(200)

32    OPEN "a:output.1" FOR APPEND AS #2
34    OPEN "a:data.1" FOR INPUT AS #1
35    PRINT #2,
36    INPUT #1, Ai, W, L, F, Pd, Ci, pHi, CL, Fai, Fb, bHsi
38    ON ERROR GOTO 3515

41      REM Ai = INITIAL RADIUS OF PR PARTICLES (Dm)
42      REM W  = PR ADDED (Kg/M^3)
43      REM L  = VOLUMETRIC WATER CONTENT - THETA
44      REM F  = TORTUCITY FACTOR
45      REM Pd = BULK DENSITY OF DRY SOIL (Kg/M^3)
46      REM Ci = INITIAL CON. OF H2PO4 IN SOLN. (Mol/L)
47      REM pHi= INITIAL pH OF SOIL
48      REM Cl = INITIAL CON. OF ANIONS IN SOIL SOLN. (Mol/L)
49      REM Fai= "a" COEFF. FOR FREUNDLICH P SORPTION (Mol/Kg)
50      REM Fb = "b" COEFF. FOR FREUNDLICH (EXPONENTIAL COEFF)
51      REM bHsI= pH BUFFER CAPACITY

100     D1 = 8.9E-08: REM D1 - Diffusion coeff in liquid for H2PO4-
102     D2 = 8.4E-07: REM D2 - Diffusion coeff in liquid for H30+
104     D3 = 1.08E-11: REM D3 - Diffusion coeff in liquid for HCO3-

120     KF = 1.45E-10: REM KF-Sol prod for CaF2 (KCaF2)
```

```
122   KH = 8.17E-11: REM KH - 1st diss const H2CO3 * solubility of CO2 *
      Press CO2
124   KH2 = 3.78E-21: REM KH2 - Product of above * 2nd dissociation constant
126   K2 = 6.12E-08: REM K2 - Second dissoc const of phosporic acid

140   Pi = 3.14159: REM Pi
142   T = 86400!: REM T - No of seconds in one day
144   Nn = 10: REM Nn - No of days in reporting unit
146   P = 8640: REM P - Time for each step in sec - note Nn*T/P must be an
      integer

310   Pcv = 13.56: REM 15.5 for MPR. Pcv - Mol of P per L of calcium phosphate
320   pKs = 16.4: REM 12.9 for NCPR. pKs - pK in eqn (20) or (24) of part 1
330   nP = 4.8: REM 5.2 for MPR. nP - Coefficient np in same equations
340   nC = 8.8: REM 8.66 for MPR. nC - Coefficient nC in same equations
350   nH = 12: REM nH - Coefficient nH in same equations
360   Lv = 0.5: REM Lv - Root density "Lv"
370   a = 0.2: REM A - Root radius "ar"
380   Fx = 0: REM Fx - Flux of acid across root surface "F"

500   Rk = 4 * Pi * Pcv / 3
510   Mo = Rk * Ai ^ 3
520   No = W / (31 * Mo)
530   R = (3 / (4 * Pi * No)) ^ (1 / 3)
540   Ans = Ai
550   X = 1 / (SQR(Pi * Lv))
560   Rt = Lv / (LOG(X / (1.65 * a))) / No
570   Ra = 2 * Pi * a * Fx * Lv / No
580   Fa = Fai * Pd
590   bHs = bHsi * Pd
600   pHs = pHi + .05
610   Hs = 10 ^ (-pHs)
620   pHr = pHi
630   Hr = 10 ^ (-pHr)
640   Cas = .5 * CL
650   Car = Cas
660   Cs = 10 ^(-((nH*pHs+nC*(LOG(Cas)/2.3026)-pKs))/nP)
670   Cr = Ci
680   Cav = Cr
690   Hcs = KH / Hs
700   Hcr = KH / Hr
710   P2s = K2 * Cs / Hs
715   P2r = K2 * Cr / Hr

716   Tt = 0
717   Mb = 0
718   Mp = 0
719   Pu = 0
```

```
720   PRINT #2, "FOR THE INPUT VALUES"
722   PRINT #2, USING "\  \"; "Ai"; "W"; "L"; "F"; "Pd"; "Ci"; "pHi";
723   PRINT #2, USING "\  \"; "Cl"; "Fai"; "Fb"; "bHsi"
724   PRINT #2, Ai; W; L; F; Pd; Ci; pHi; CL; Fai; Fb; bHsi
725   PRINT #2,
726   PRINT #2, "OUTPUT VALUES"
728   PRINT #2, "TIME  RADIUS  P UPTAKE  OH NEUT.  P DISSOLVED"
729   PRINT #2, "(DAYS)  (MM)      (%)       (%)         (%)"

7201  PRINT "FOR THE INPUT VALUES"
7221  PRINT USING "\  \"; "Ai"; "W"; "L"; "F"; "Pd"; "Ci";
7231  PRINT USING "\  \"; "pHi'; "Cl"; "Fai"; "Fb"; "bHsi"
7241  PRINT Ai; W; L; F; Pd; Ci; pHi; CL; Fai; Fb; bHsi
7251  PRINT
7261  PRINT "OUTPUT VALUES"
7281  PRINT " TIME   RADIUS  P UPTAKE  OH NEUT.  PDISSOLVED"
7291  PRINT " (DAYS)  (MM)     (%)       (%)         (%)"

730   REM START OF TIME LOOPS

750   REM CALCULATE P BUF CAP & P & BASE DIF COEF AS IN EQ 10,9
      & 14 OF PART 1
770   Bp = Fa * (Cs ^ Fb - Cr ^ Fb) / (Cs - Cr)
780   Dp = D1 * L * F / Bp
790   dB=L*F/(bHs*(pHr-pHs))*(D2*(Hs-Hr)-D1*(P2s-P2r)-D3*(Hcs- Hcr))

800   REM CALCULATE SPREAD OF BASE AND P - 4th PAGE, PART 1

830   IF rB < R THEN rB = Ans + SQR(Pi * dB * Tt)
850   IF Rp < R THEN Rp = Ans + SQR(Pi * Dp * Tt)

851   REM BEGIN SEQUENCE OF REPEATED ETIMATES OF pHs
853   Difference = 1: Icount = 1
854   WHILE ABS(Difference) > .001

860   REM CALCULATE THE AMOUNT OF BASE DISSOLVED IN dt - EQN
      4a in Part 1
870   dmb=bHs*(pHs-pHr)*4*Pi*Ans*rB/(rB-Ans)*dB*P

880   REM REVISE DMB FOR ACID/BASE RELEASE FROM ROOTS-EQn 7
      Ptl
890   dmb = dmb + Ra * P

900   REM CALCULATE CONCS AND ACT COEETS AT R=S - EQNS 5a, 5b,
      & 5c, Pt 1

905   Cs = Cr + (dmb * nP / (nH * P * 2 * Pi * D1 * L * F) - Rt * Cav) / (2 *
      Ans * Rp / (Rp - Ans))
910   Cas = .5 * (Cs + Hcs + 2 * P2s + CL + 2 * Co + Fs - Hs)
```

```
915   Ins = SQR(2 * (Cas + P2s + Co) + .5 * (Cs + Hcs + Hs + CL + Fs))
920   Acs = -.524 * (Ins / (1 + Ins) - .3 * Ins ^ 2)
925   pHsEst = (pKs - nC * (LOG(Cas) / 2.3026 + 4 * Acs) - nP * (LOG(Cs) /
      2.3026 + Acs)) / nH
930   Difference = pHs - pHsEst


935   REM ON FIRST CYCLE RE-USE THIS EST OF pHs BY TAKING MEAN
940   IF Icount = 1 OR ABS(Difference) > 10 THEN
941   REM  note made 0.5 instead of 0.3
945   PrepHs = pHs
950   pHs = (PrepHs + pHsEst) / 2

951   ELSE

952   REM ON OTHER CYCLES USE NEWTON RAPHSON EXTRAPOLATION
      TO EST pHs
953   Slope = (Difference - PreDiff) / (pHs - PrepHs)
954   Intercept = Difference - Slope * pHs
955   PrepHs = pHs
956   pHs = -Intercept / Slope
957   END IF
961   PreDiff = Difference
962   IF Icount > 30 THEN
963   PRINT "NOT CONVERGING"
964   PRINT "VALUES OF pHs & DIFFERENCE ARE ", PrepHs, pHs,
      Difference
965   STOP
966   END IF

967   Icount = Icount + 1

970   Hs = 10 ^ (-pHs)
980   Hcs = KH * 10 ^ (-2 * Acs) / Hs
990   P2s = K2 * 10 ^ (-4 * Acs) * Cs / Hs
1000  Fs = SQR(KF * 10 ^ (-6 * Acs) / Cas)
1010  Co = KH2 * 10 ^ (-6 * Acs) / (Hs ^ 2)

1020 WEND
1030 REM END OF EST OF pHs

1050 Mb = Mb + dmb
1060 IF rB > R THEN

1070 REM CALCULATE AVERAGE pH AND pH AT r=R

1080  pHav=pHi+(Mb-Ra*Tt)*3/(4*Pi*(R^3-Ans^3)*bHs)
1090  pHr = pHav * (1 + Ans / (2 * R)) - pHs * Ans / (2 * R)
1100  Hr = 10 ^ (-pHr)
```

```
1110  END IF

1120 REM CALCULATE AMOUNT OF P DISSOLVED IN dt - Eqn (4), Pt 1

1230 Dmp=P*4*Pi*D1*L*F*(Cs-Cr)*Ans*R/(Rp-Ans)

1240 REM REVISE Dmp FOR P TAKEN UP BY ROOTS - Eqn (5), Pt 2

1250 Dmp = Dmp + P * 2 * Pi * D1 * L * F * Rt * Cav
1260 Mp = Mp + Dmp
1270 Pu = Pu + (2 * Pi * D1 * L * F * Rt * Cav * P)

1280   REM CALCULATE AVERAGE P CONC AND CONC AT r=R - Eqn (6)
       and (6c), Ptl

1290   Cav = ((Mp - Pu) * 3 / (4 * Pi * (R ^ 3 - Ans ^ 3) * Fa)
       + Ci ^ Fb) ^ (1 / Fb)
1300   IF Rp >= R THEN Cr = Cav * (1 + Ans / (2 * R)) - Cs * Ans / (2 * R)
1310   IF Cr < Ci THEN Cr = Ci

1320   IF Cs = Cr THEN
1321   PRINT "SOLUTION STOPPED AT ###.### "; N; "  DAYS"
1325   GOSUB 3400
1326   END
1327   END IF

1330   IF rB >= R OR Rp >= R THEN

1340   REM CALCULATE OTHER CONCENTRATIONS AT r=R

1350   Car = .5 * (Cr + Hcr + 2 * P2r + CL - Hr)
1360   Ins = SQR(2 * (Car + P2r) + .5 * (Cr + Hcr + Hr + CL))
1370   Acr = -.524 * (Ins / (1 + Ins) - .3 * Ins ^ 2)
1380   Hcr = KH * 10 ^ (-2 * Acr) / Hr
1390   P2r = K2 * 10 ^ (-4 * Acr) * Cr / Hr
1400   END IF


1410 REM CALCULATE NEW PARTICLE RADIUS- Eqn (15), Pt 1

1420 Ans = ((Mo - Mp) / Rk) ^ (1 / 3)
1430 N = Tt / T
1440 IF N <> Nn GOTO 740
1490 GOSUB 3400: REM Print!
1500 IF Mp >= Mo * .99 THEN STOP
1510   IF Nn = 360 THEN 3510
1520 Nn = Nn + 10

1530 REM RETURN FOR NEXT TIME LOOP
```

```
1540 GOTO 740

3000   RETURN

3400   REM PRINT SUBROUTINE
3410   Pup = Pu / Mo * 100
3420   Hop = Ra * Tt / (Mo * nH / nP) * 100
3430   Pm = Mp / Mo * 100!
3450   PRINT #2, USING " ####          #.#####     "; N, Ans * 100;
3460 PRINT #2, USING "    ###.###  "; Pup, Hop, Pm

34501 PRINT USING " ####          #.#####     "; N, Ans * 100;
34601 PRINT USING "    ###.###  "; Pup, Hop, Pm

3500 RETURN
3510 IF EOF(1) THEN
3515 END
3520 CLOSE #1
3525 CLOSE #2
3530 ELSE GOTO 35
3540 END IF
3550 RETURN
```

Appendix 5.3 Correlation coefficients (r) relating chemical properties of soils.

Soil properties	pH_{H2O}	Org.C	Exch. Ca	CEC	Ca sat.	P retn.
pH_{H2O}	-					
Organic C (%)	0.28	-				
Exchangable Ca (cmol (+) kg^{-1})	0.63	0.24	-			
CEC (cmol (+) kg^{-1})	0.47	0.72	0.78	-		
Ca saturation. (%)	0.57	-0.41	-0.70	0.11	-	
P retention (%)	0.16	0.97**	0.19	0.72	-0.47	-
Titratable acidity (cmol (+) kg^{-1})	0.21	0.97**	0.25	0.67	-0.34	0.96**

**Indicates significance at P<0.01.

Appendix 8.1 Layout of (a) Sembawa and (b) Serong field trials.

(a) Sembawa

Section B#	Section A##			
				3 m
Control	T_1P_2	T_1P_4	T_1P_3	T_1P_1 2 m
TSP_{40}	T_3P_4	T_3P_2	T_3P_1	T_3P_3
TSP_{60}	T_4P_4	T_4P_3	T_4P_1	T_4P_2
Control	T_2P_2	T_2P_1	Control	Control
TSP_{120}	Control	Control	T_2P_2	T_2P_1
TSP_{160}	T_1P_3	T_1P_4	T_1P_1	T_1P_2
TSP_{240}	T_4P_4	T_4P_3	T_4P_1	T_4P_2
Control	T_3P_3	T_3P_1	T_3P_2	T_3P_4
Control	T_3P_4	T_3P_3	T_3P_2	T_1P_1
$NCPR_{40}$	T_1P_1	T_1P_4	T_1P_3	T_1P_2
$NCPR_{160}$	T_4P_3	T_4P_2	T_4P_1	T_4P_4
Control	T_2P_2	T_2P_1	Control	Control
Control	Control	Control	T_2P_2	T_2P_1
$NCPR_{320}$	T_3P_3	T_3P_4	T_3P_1	T_3P_2
$NCPR_{560}$	T_4P_2	T_4P_1	T_4P_3	T_4P_2
Control	T_1P_4	T_1P_2	T_1P_1	T_1P_4

Figures in Section B denote form and rate (kg ha^{-1}) of P fertilizer applied at T_1.
##Figures in Section A denote application time and form of P fertilizer.

Application times and forms of P fertilizer in Section A.

Application time (MAT)*	P fertilizer form	Crop**
1. T_1:0	1. P_1: TSP	1. *Calopogonium caeruleum* (Calopogonium)
2. T_2:6	2. P_2: NCPR	
3. T_3:12	3. P_3: PPR	
4. T_4:18	4. P_4: MPR	2. Maize

* MAT: Months after transplanting Calopogonium seedlings.
**Calopogonium was grown during the first 18 months before sowing maize.

Appendix 8.1 (contd)

(b) Serong*

Section B	Section A			
				3 m
Control	T_1P_2	T_1P_4	T_1P_3	T_1P_1 2 m
TSP_{40}	T_3P_4	T_3P_2	T_3P_1	T_3P_3
TSP_{60}	T_4P_4	T_4P_3	T_4P_1	T_4P_2
TSP_{120}	T_2P_2	T_2P_1	T_2P_2	T_2P_1
TSP_{160}	T_1P_3	T_1P_4	T_1P_1	T_1P_2
TSP_{240}	T_4P_4	T_4P_3	T_4P_1	T_4P_2
Control	T_3P_3	T_3P_1	T_3P_2	T_3P_4
Control	T_3P_4	T_3P_3	T_3P_2	T_1P_1
$NCPR_{40}$	T_1P_1	T_1P_4	T_1P_3	T_1P_2
$NCPR_{160}$	T_4P_3	T_4P_2	T_4P_1	T_4P_4
Control	T_2P_2	T_2P_1	T_2P_2	T_2P_1
$NCPR_{320}$	T_3P_3	T_3P_4	T_3P_1	T_3P_2
$NCPR_{560}$	T_4P_2	T_4P_1	T_4P_3	T_4P_2
Control	T_1P_4	T_1P_2	T_1P_1	T_1P_4

*Figures in each plot are explained in Appendix 8.1a.

Appendix 8.2 Time and rate of N, P and S fertilizer application during maize growth at Sembawa and Serong field trials.

Field Site	Form of fertilizer	Amounts of fertilizer applied (kg ha^{-1})			
		Incorporated into seedbed*	2 WAE**	4 WAE	6 WAE
Sembawa	Urea	19.1	52.7	152.2	86.7
	KCl	95.2	95.2	142.8	142.8
	Ammonium sulphate	8.3	12.5	29.2	16.7
Serong	Urea	19.1	173.8	391.5	174.0
	KCl	238.1	238.1	333.3	333.3
	Ammonium sulphate	8.3	33.3	75.0	33.3

* All plots received Boron (5 kg B ha^{-1}).
**WAE=weeks after emergence.

Appendix 9.1

```
1     REM Modified version of Kirk and Nye's model to simulate
2     REM the dissolution of NCPR and MPR under field
      REM conditions. A water balance submodel is added to
      REM estimate soil volumetric water content in the top
      REM 100 mm during the experimental period.
      REM Species of crop used:  Calopogonium caeruleum.

3     REM FOLLOW 4, 5 & 6 TO RUN THIS PROGRAMME
4     REM UNLOAD "PRDISS.BAS" & LOAD "DATA.1" TO ENTER THE
      REM INPUT VALUES & SAVE
5     REM UNLOAD "DATA.1" & LOAD "OUTPUT.1" TO CLEAR THE
      REM PREVIOUS OUTPUT & SAVE.
6     REM UNLOAD "OUTPUT.1" & LOAD "PRDISS.BAS" & RUN

7     PRINT : PRINT "KIRK AND NYE MODELLING IS RUNNING - KEEP AWAY"
8     PRINT
9     PRINT
11    PRINT : PRINT "HAVE YOU CHECKED YOUR INPUT FILE - INPUT.1"
12    PRINT
14    PRINT
15    PRINT : PRINT "HAVE YOU CREATED AN OUTPUT FILE - OUTPUT.1"

20    DIM Label$(200)

32    OPEN "a:output.1" FOR APPEND AS #2
34    OPEN "a:data.1" FOR INPUT AS #1
35    PRINT #2,
36    INPUT #1, Ai, W, L, F, Pd, Ci, pHi, CL, Fai, Fb, bHsi
38    ON ERROR GOTO 3515
        REM "LAYER MODEL BASED ON 0-10cm,10-20cm,20-30cm AND
        30-55CM REM DEPTHS ON A DAILY BASIS OVER A PERIOD OF TIME.
        POTENTIAL ET IS REM CALCULATED USING THE PRIESTLY AND TAYLOR
        APPROACH FROM MAX AND MIN TEMP AND SUNSHINE HOURS"
        DIM Drn(5), SW(5), rain(5), ETs(5), Root(5), MaxSW(5), z(5)

        Ll = -3.08: REM Li-Latitude of the field site
        Pi = 3.141592654#
        Ll = Ll * Pi / 180
        'INTERACTIVE OPTION SWITCHED OFF
        'INPUT "ENTER METEOROLOGICAL DATA : ", filename$
        OPEN "a:clida.2" FOR INPUT AS #3
        'ENTER ROOT DENSITY PROFILE AND SOIL MOISTURE CHARACTERISTICS
        'INPUT "ENTER OUTPUTFILE NAME :", outputfile$
        'FOR n = 1 TO 4
        'PRINT "Layer "; n
        'INPUT "Enter depth interval (in mm) "; Z(n)
        'INPUT "Enter root density (in percent) ", Root(n)
```

```
'INPUT "Enter the max. soil water this layer can hold (in
'mm) "; MaxSW(n)
'INPUT "Enter the initial soil water in this layer (mm) ";
 SW(n)
'NEXT

Root(1) = 60: REM Root in the first layer is considered
'Root(2) = 20
'Root(3) = 15
'Root(4) = 5
MaxSW(1) = 30:REM mm of water in 100 mm at field capacity
'MaxSW(2) = 33
'MaxSW(3) = 33
'MaxSW(4) = 95
SW(1) = 28.9
'SW(2) = 33
'SW(3) = 33
'SW(4) = 95
 z(1) = 100: REM Depth of the fertilized zone is
'z(2) = 100" REM assumed to be 100 mm
'z(3) = 100
'z(4) = 250


41    REM Ai = INITIAL RADIUS OF PR PARTICLES (Dm)
42    REM W  = PR ADDED (Kg/M^3)
43    REM L  = VOLUMETRIC WATER CONTENT - THETA
44    REM F  = TORTUCITY FACTOR
45    REM Pd = BULK DENSITY OF DRY SOIL (Kg/M^3)
46    REM Ci = INITIAL CON. OF H2PO4 IN SOLN. (Mol/L)
47    REM pHi= INITIAL pH OF SOIL
48    REM Cl = INITIAL CON. OF ANIONS IN SOIL SOLN. (Mol/L)
49    REM Fai= "a" COEFF. FOR FREUNDLICH P SORPTION (Mol/Kg)
50    REM Fb = "b" COEFF. FOR FREUNDLICH (EXPONENTIAL COEFF)
51    REM bHsI= pH BUFFER CAPACITY

100   D1 = 8.9E-08: REM D1 - Diffusion coeff in liquid for H2PO4-
102   D2 = 8.4E-07: REM D2 - Diffusion coeff in liquid for H30+
104   D3 = 1.08E-11: REM D3 - Diffusion coeff in liquid for HCO3-

120   KF = 1.45E-10: REM KF-Sol prod for CaF2 (KCaF2)
122   KH = 8.17E-11: REM KH - 1st diss const H2CO3 * solub of CO2 * Press CO2
124   KH2 = 3.78E-21: REM KH2 - Product of above * 2nd dissociation constant
126   K2 = 6.12E-08: REM K2 - Second dissoc const of phosporic acid

140   Pi = 3.14159: REM Pi
142   T = 86400!: REM T - No of seconds in one day
144   Nn = 10: REM Nn - No of days in reporting unit
146   P = 8640: REM P - Time for each step in sec - note Nn*T/P must be an integer
```

```
310   Pcv = 13.56: REM 15.5 for MPR. Pcv - Mol of P per L of calcium phosphate
320   pKs = 16.4: REM 12.9 for NCPR. pKs - pK in eqn (20) or (24) of pt 1
330   nP = 4.8: REM 5.2 for MPR. nP - Coefficient np in same equations
340   nC = 8.8: REM 8.66 for MPR. nC - Coefficient nC in same equations
350   nH = 12: REM nH - Coefficient nH in same equations
360   Lv = 52: REM Lv - Root density "Lv"
370   a = .002: REM A - Root radius "ar"
380   Fx = 3E-12: REM Fx - Flux of acid across root surface "F"

500   Rk = 4 * Pi * Pcv / 3
510   Mo = Rk * Ai ^ 3
520   No = W / (31 * Mo)
530   R = (3 / (4 * Pi * No)) ^ (1 / 3)
540   Ans = Ai
550   X = 1 / (SQR(Pi * Lv))
560   Rt = Lv / (LOG(X / (1.65 * a))) / No
570   Ra = 2 * Pi * a * Fx * Lv / No
580   Fa = Fai * Pd
590   bHs = bHsi * Pd
600   pHs = pHi + .05
610   Hs = 10 ^ (-pHs)
620   pHr = pHi
630   Hr = 10 ^ (-pHr)
640   Cas = .5 * CL
650   Car = Cas
660   Cs = 10 ^(-((nH*pHs+nC*(LOG(Cas)/2.3026)-pKs))/nP)
670   Cr = Ci
680   Cav = Cr
690   Hcs = KH / Hs
700   Hcr = KH / Hr
710   P2s = K2 * Cs / Hs
715   P2r = K2 * Cr / Hr

716   Tt = 0
717   Mb = 0
718   Mp = 0
719   Pu = 0

720   PRINT #2, "FOR THE INPUT VALUES"
722   PRINT #2, USING "\  \"; "Ai"; "W"; "L"; "F"; "Pd"; "Ci"; "pHi";
723   PRINT #2, USING "\  \"; "Cl"; "Fai"; "Fb"; "bHsi"
724   PRINT #2, Ai; W; L; F; Pd; Ci; pHi; CL; Fai; Fb; bHsi
725   PRINT #2,
726   PRINT #2, "OUTPUT VALUES"
728   PRINT #2, "TIME  RADIUS  P UPTAKE  OH NEUT.  P DISSOLVED"
729   PRINT #2, "(DAYS)  (MM)     (%)       (%)        (%)"

7201  PRINT "FOR THE INPUT VALUES"
7221  PRINT USING "\ \"; "Ai"; "W"; "L"; "F"; "Pd"; "Ci";
```

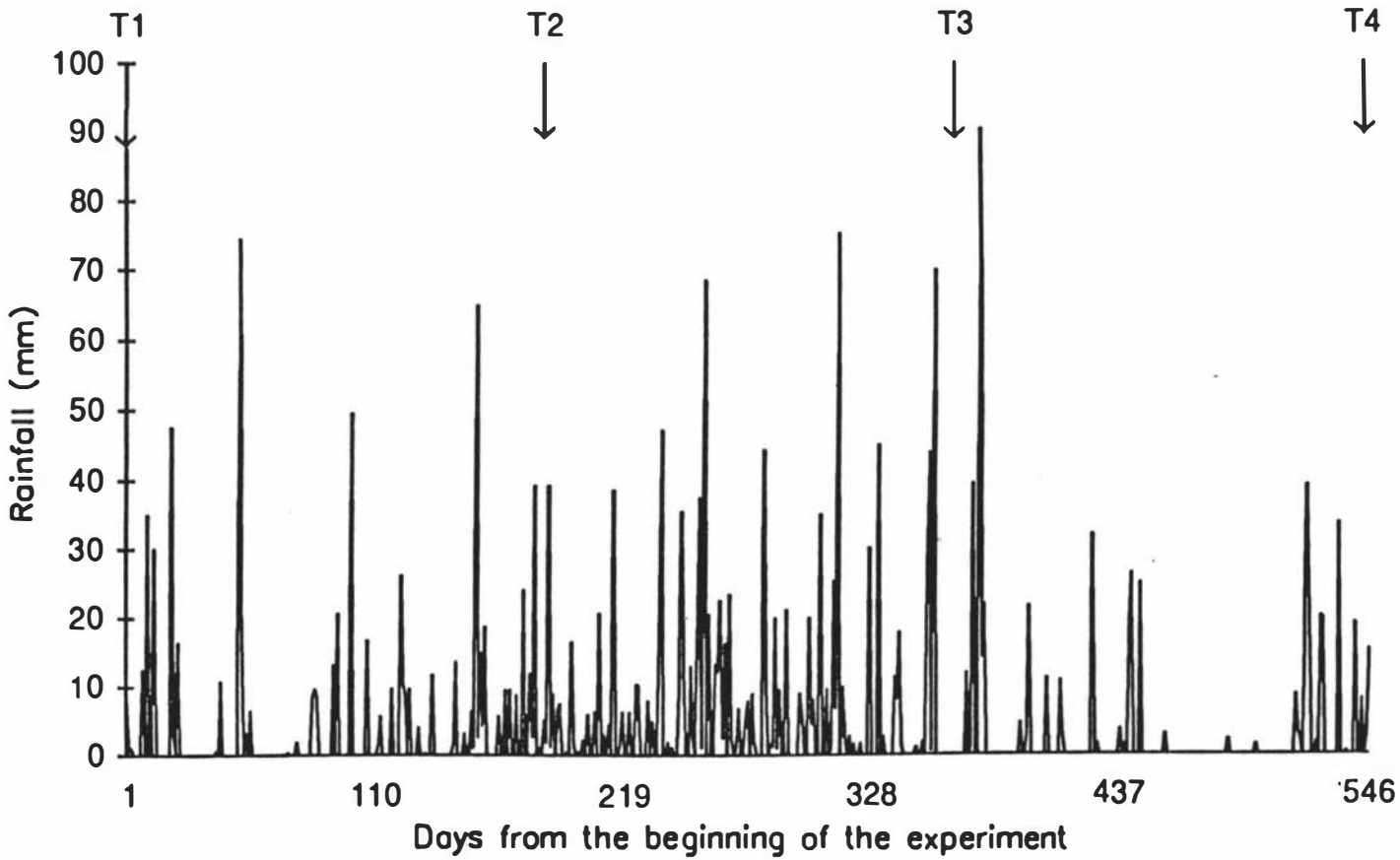
```
7231  PRINT USING "\ \"; "pHi'; "Cl"; "Fai"; "Fb"; "bHsi"
7241  PRINT Ai; W; L; F; Pd; Ci; pHi; CL; Fai; Fb; bHsi
7251  PRINT
7261  PRINT "OUTPUT VALUES"
7281  PRINT " TIME   RADIUS  P UPTAKE  OH NEUT.  PDISSOLVED"
7291  PRINT " (DAYS)  (MM)    (%)       (%)        (%)"

730   REM START OF TIME LOOPS

740   Tt = Tt + P
      IF Tt / T = INT(Tt / T) THEN
      INPUT #3, M, rain, TMAX, TMIN, G

'CALCULATE D--ANGLE OF DECLINATION
D = (23.5 * SIN(.986 * (M - 79) * Pi / 180)) * Pi / 180
'CALCULATE H--HALF DAY LENGTH (H=90 AT EQUINOX)
a = -TAN(Ll) * TAN(D)
h = (Pi / 2) - ATN(a / SQR(1 - (a) ^ 2))
'CALCULATE N--MAX NO. OF HR MEASUREABLE W/ SUNSHINE HR 'RECORDER
N = (h * 180 / Pi) / 7.5 - .5
'CALCULATE R0--EXTRA-TERRESTRIAL SOLAR RAD NORMAL TO EARTH
'SURFACE
c = 1 + .0334 * SIN(.986 * (M - 274) * Pi / 180)
R0 = 3.85 * 10 ^ 7 * (h * SIN(Ll) * SIN(D) + COS(Ll) * COS(D) * SIN(h)) * c
'CALCULATE RS--INCOMING SOLAR RADIATION AT SURFACE (J/M^2)
a = .28: b = .51
RS = R0 * (a + b * G / N)
'CALCULATE RN--NET RADIATION
Rn = .62 * RS - 1.47 * 10 ^ 6
'CALCULATE TAV--AVERAGE AIR TEMP (C)
Tav = (TMAX + TMIN) / 2
'CALCULATE s--RATIO OF DENSITIES OF WATER VAPOR & DRY AIR
S = .403 + .0165 * Tav - .00012 * (Tav ^ 2)
'CALCULATE ETw--PRIESTLY & TAYLOR ESTIMATE OF EVAPORATION
'(POTENTIAL ET)
ETw = (1.26 * S * Rn / (2.45 * 10 ^ 9)) * 1000

'CALCULATE SOIL WATER BALANCE, DRAINAGE AND LEACHING FOR THE FOUR
LAYERS


FOR   N = 1 TO 1: REM Only 1 layer is considered
      IF SW(N) >= 1.3*MaxSW(N)/2 THEN ETs(N)=ETw*Root(N)/100 ELSE ETs(N)=
      Root(N) * .01 * ETw * (SW(N) - .3 * MaxSW(N)) / (.35 * MaxSW(N))
IF SW(N) <= .3 * MaxSW(N) THEN ETs(N) = 0
      rain(1) = rain
      Drn(N) = 0
      SW(N) = SW(N) + rain(N) - ETs(N)
      IF SW(N) > MaxSW(N) THEN
```

```
        Drn(N) = SW(N) - MaxSW(N)
        SW(N) = MaxSW(N)
        rain(N + 1) = Drn(N)
        dailydrn = Drn(4)
        END IF
        NEXT
        L = SW(1) / z(1): REM L (theta) is estimated from the
        first layer only
        F = L ^ (1.49) * Pd
        END IF
750     REM CALCULATE P BUF CAP & P & BASE DIF COEF AS IN EQ 10,9
        REM & 14 OF PART 1
770     Bp = Fa * (Cs ^ Fb - Cr ^ Fb) / (Cs - Cr)
780     Dp = D1 * L * F / Bp
790     dB=L*F/(bHs*(pHr-pHs))*(D2*(Hs-Hr)-D1*(P2s-P2r)-D3*(Hcs- Hcr))

800   REM CALCULATE SPREAD OF BASE AND P - 4th PAGE, PART 1

830   IF rB < R THEN rB = Ans + SQR(Pi * dB * Tt)
850   IF Rp < R THEN Rp = Ans + SQR(Pi * Dp * Tt)

851   REM BEGIN SEQUENCE OF REPEATED ETIMATES OF pHs
853   Difference = 1: Icount = 1
854   WHILE ABS(Difference) > .001

860     REM CALCULATE THE AMOUNT OF BASE DISSOLVED IN dt - EQN 4a Part
        1
870     dmb=bHs*(pHs-pHr)*4*Pi*Ans*rB/(rB-Ans)*dB*P

880     REM REVISE DMB FOR ACID/BASE RELEASE FROM ROOTS-EQn 7 Pt1
890     dmb = dmb + Ra * P

900     REM CALCULATE CONCS AND ACT COEETS AT R=S - EQNS 5a, 5b, & 5c, Pt
        1

905     Cs = Cr + (dmb * nP / (nH * P * 2 * Pi * D1 * L * F) - Rt * Cav) / (2 * Ans * Rp
        / (Rp - Ans))
910     Cas = .5 * (Cs + Hcs + 2 * P2s + CL + 2 * Co + Fs - Hs)
915     Ins = SQR(2 * (Cas + P2s + Co) + .5 * (Cs + Hcs + Hs + CL + Fs))
920     Acs = -.524 * (Ins / (1 + Ins) - .3 * Ins ^ 2)
925     pHsEst = (pKs - nC * (LOG(Cas) / 2.3026 + 4 * Acs) - nP * (LOG(Cs) / 2.3026 +
        Acs)) / nH
930     Difference = pHs - pHsEst

935 REM ON FIRST CYCLE RE-USE THIS EST OF pHs BY TAKING MEAN
940 IF Icount = 1 OR ABS(Difference) > 10 THEN
941 REM  note made 0.5 instead of 0.3
945 PrepHs = pHs
```

```
950 pHs = (PrepHs + pHsEst) / 2

951 ELSE

952   REM ON OTHER CYCLES USE NEWTON RAPHSON EXTRAPOLATION TO
      ESTIMATE pHs
953   Slope = (Difference - PreDiff) / (pHs - PrepHs)
954   Intercept = Difference - Slope * pHs
955   PrepHs = pHs
956   pHs = -Intercept / Slope
957   END IF
961   PreDiff = Difference
962   IF Icount > 30 THEN
963   PRINT "NOT CONVERGING"
964   PRINT "VALUES OF pHs & DIFFERENCE ARE ", PrepHs, pHs,
    Difference
965   STOP
966   END IF

967   Icount = Icount + 1

970   Hs = 10 ^ (-pHs)
980   Hcs = KH * 10 ^ (-2 * Acs) / Hs
990   P2s = K2 * 10 ^ (-4 * Acs) * Cs / Hs
1000  Fs = SQR(KF * 10 ^ (-6 * Acs) / Cas)
1010  Co = KH2 * 10 ^ (-6 * Acs) / (Hs ^ 2)

1020 WEND
1030 REM END OF EST OF pHs

1050 Mb = Mb + dmb
1060 IF rB > R THEN

1070 REM CALCULATE AVERAGE pH AND pH AT r=R

1080  pHav=pHi+(Mb-Ra*Tt)*3/(4*Pi*(R^3-Ans^3)*bHs)
1090  pHr = pHav * (1 + Ans / (2 * R)) - pHs * Ans / (2 * R)
1100  Hr = 10 ^ (-pHr)
1110  END IF

1120 REM CALCULATE AMOUNT OF P DISSOLVED IN dt - Eqn (4), Pt 1

1230 Dmp=P*4*Pi*D1*L*F*(Cs-Cr)*Ans*R/(Rp-Ans)

1240 REM REVISE Dmp FOR P TAKEN UP BY ROOTS - Eqn (5), Pt 2

1250 Dmp = Dmp + P * 2 * Pi * D1 * L * F * Rt * Cav
1260 Mp = Mp + Dmp
1270 Pu = Pu + (2 * Pi * D1 * L * F * Rt * Cav * P)
```

```
1280  REM CALCULATE AVERAGE P CONC AND CONC AT r=R - Eqn (6) and (6c),
      Pt1

1290  Cav = ((Mp - Pu) * 3 / (4 * Pi * (R ^ 3 - Ans ^ 3) * Fa)
      + Ci ^ Fb) ^ (1 / Fb)
1300  IF Rp >= R THEN Cr = Cav * (1 + Ans / (2 * R)) - Cs * Ans / (2 * R)
1310  IF Cr < Ci THEN Cr = Ci

1320  IF Cs = Cr THEN
1321  PRINT "SOLUTION STOPPED AT ###.### "; N; "  DAYS"
1325  GOSUB 3400
1326  END
1327  END IF

1330  IF rB >= R OR Rp >= R THEN

1340  REM CALCULATE OTHER CONCENTRATIONS AT r=R

1350  Car = .5 * (Cr + Hcr + 2 * P2r + CL - Hr)
1360  Ins = SQR(2 * (Car + P2r) + .5 * (Cr + Hcr + Hr + CL))
1370  Acr = -.524 * (Ins / (1 + Ins) - .3 * Ins ^ 2)
1380  Hcr = KH * 10 ^ (-2 * Acr) / Hr
1390  P2r = K2 * 10 ^ (-4 * Acr) * Cr / Hr
1400  END IF


1410 REM CALCULATE NEW PARTICLE RADIUS- Eqn (15), Pt 1

1420 Ans = ((Mo - Mp) / Rk) ^ (1 / 3)
1430 N = Tt / T
1440 IF N <> Nn GOTO 740
1490 GOSUB 3400: REM Print!
1500 IF Mp >= Mo * .99 THEN STOP
1510 IF Nn = 360 THEN 3510
1520 Nn = Nn + 10

1530 REM RETURN FOR NEXT TIME LOOP

1540 GOTO 740

3000  RETURN

3400 REM PRINT SUBROUTINE
3410 Pup = Pu / Mo * 100
3420 Hop = Ra * Tt / (Mo * nH / nP) * 100
3430 Pm = Mp / Mo * 100!
3450   PRINT #2, USING " ####          #.######     "; N, Ans * 100;
3460 PRINT #2, USING "     ###.###   "; Pup, Hop, Pm
```

```
34501 PRINT USING " ####         #.#####     "; N, Ans * 100;
34601 PRINT USING "    ###.###  "; Pup, Hop, Pm

3500 RETURN
3510 IF EOF(1) THEN
3515 END
3520 CLOSE #1
3525 CLOSE #2
3530 ELSE GOTO 35
3540 END IF
3550 RETURN
```



Appendix 9.2 Amounts of daily rainfall during the experimental period from May 1989 (T_1) to November 1990 (T_4).