APPLICATION OF ISOTOPIC DILUTION METHODS TO THE STUDY OF THE DISSOLUTION OF PHOSPHATE FERTILISERS OF DIFFERING SOLUBILITY IN THE SOIL

A thesis

submitted in partial fulfilment

of the requirements for the degree

of

Doctor of Philosophy

in

Lincoln University

New Zealand

by

HONG JIE DI

1991

Abstract of a thesis submitted in partial fulfilment of
the requirements for the degree of Doctor of Philosophy

Application of isotopic dilution methods to the study of the dissolution of phosphate fertilisers of differing solubility in the soil

by

Hong Jie Di

An injection technique, in which undisturbed soil cores are labelled with ^{32}P to study dissolution of phosphate fertilisers in the soil, was evaluated in field and glasshouse trials. When ^{32}P was injected between 0-150 mm depths of the undisturbed soil columns and fertilisers applied at the surface, the amounts of fertiliser P dissolved, as measured by the increases in the exchangeable P pools, were overestimated. Three possible reasons were suggested: (i) the interaction between surface-applied fertiliser, ^{32}P injected through the whole soil column, and the vertical decline in root density, (ii) the decline of specific activity in the exchangeable P pool due to losses of ^{32}P to non-exchangeable P pools and continuous addition of P from fertiliser dissolution, and (iii) non-uniform distribution of ^{32}P vis-a-vis ^{31}P phosphate.

The injection technique may be employed to assess the effectiveness of phosphate fertilisers by introducing a concept, the fertiliser equivalent (FE). The FE is a measure of the amounts of soil exchangeable P that the fertilisers are equivalent to in supplying P to plants, when applied at the specific location. Soluble single superphosphate (SSP) applied at the surface of undisturbed grassland soil cores (Tekapo fine sandy loam), was much more effective than surface-applied unground North Carolina phosphate rock (NCPR) and 30% acidulated NCPR with phosphoric acid (NCPAPR) within the 56 day period of plant growth.

An isotopic dilution method, based on tracer kinetic theory, was developed to study the rates of dissolution (F_{in}) and retention (F_{out}) of phosphate fertilisers in the soil in growth chamber experiments. The estimation of F_{in} and F_{out} required labelling of the soils with carrier-free ^{32}P and determination of the corresponding values of the specific activities of the exchangeable P pools, SA_1 and SA_2, and the sizes of the exchangeable P pools, Q_1 and Q_2, at times t_1 and t_2.

Most of the phosphate in the monocalcium phosphate (MCP) solution entered the exchangeable P pool immediately after addition to the soils (Tekapo fine sandy loam and Craigieburn silt loam), and there was little further phosphate input. With increasing periods of incubation, the phosphate was quickly transformed to less rapidly exchangeable forms. In the soils treated with ground North Carolina phosphate rock (<150 μm, NCPR) or partially acidulated (30%) NCPR with phosphoric acid (NCPAPR), the initial exchangeable P pools were not as large as those in the soils treated with MCP, but were maintained at relatively stable concentrations for extended periods, due to the continuous dissolution of PR materials and to lower rates of P-retention.

An increase in P-retention caused a slight rise in the rate of PR dissolution, but also a rise in the rate of P-retention by the soil. The rate of dissolution was higher at a lower application rate in relative terms, but smaller in absolute terms.

The trends in the changes of plant-available P in the soils, measured by the water extractable P, Bray I P and Olsen P, correspond to those predicted by the F_{in} and F_{out} values. The average rates of dissolution between 1-50 and 50-111 days estimated by the F_{in}, however, were higher than those estimated by extractions with 0.5 M NaOH followed by 1 M HCl, and with 0.5 M $BaCl_2$/TEA. This is partly because the F_{in} values reflect a plant growth effect on PR dissolution.

The relative agronomic effectiveness of NCPR and NCPAPR with respect to MCP was higher after 50 and 111 days of incubation than after 1 day. The F_{in} values were included in all the two-variable models constructed by stepwise regression to describe the relationship between plant P uptake and soil measurements. The amounts of variation in plant P uptake accounted for by the regression model was significantly improved by including F_{in} in the model. This indicates the importance of fertiliser dissolution rates in affecting soil P supply, when phosphate fertilisers differing in solubility are applied.

Keywords: Isotopic dilution; tracer kinetics; ^{32}P; phosphate dissolution; phosphate retention; plant availability; phosphate rock; partially acidulated phosphate rock; monocalcium phosphate; single superphosphate; chemical extraction; plant response; model; field trial; glasshouse trial.

Acknowledgements

First of all, I would like to thank my supervisor, Dr R. Harrison, for his enthusiastic and helpful supervision, and constructive criticism throughout the programme of this study. I would also like to thank Dr A.S. Campbell, my associate supervisor, for his helpful comments on various parts of the study, particularly on the thesis.

I am grateful to the Miss E.L. Hellaby Indigenous Grasslands Research Trust for funding the study. I would like to thank the Chairman of the Trust, Professor G.T.S. Baylis, for his encouragement.

I would like to thank Lincoln University for awarding me the MacMillan Brown Agricultural Research Scholarship 1990.

I would like to extend my thanks to Dr L.M. Condron for his useful advice on various aspects of the project, and to Dr P.J. Tonkin for his expert assistance in selecting the appropriate soils for the study. Constructive suggestions by Professor I.S. Cornforth, Head of the Soil Science Department, Professor R.S. Swift, former Head of the Department, and Professor K.M. Goh are also gratefully acknowledged.

Technical assistance from Rob McPherson, Leanne Hassall, Maureen McCloy, Roger McLenaghen, Huntly Horn, Gaye Ridgen, Norma Grimwood and Lynne Mason is gratefully acknowledged.

I would like to express our gratitude to Dr M.J. Hedley, Soil Science Department of Massey University, for kindly lending the isotope injector, the Animal Science and Plant Science Departments of Lincoln University, and MAFTech Lincoln, for allowing access to their research farm, growth chamber and glasshouse respectively.

Thanks are also extended to Charles Kibii Chepkwony, Tan Ze, Trish Fraser, Chowdhury, Ruth Belton, and Sonia Olykan for their assistance.

I would like to especially thank Henny-Jane Siefkes-Boer for her support and for typing part of the thesis.

I would like to thank all the staff and students of the Soil Science Department and friends at Lincoln University, whose friendship and support have made my study at Lincoln a pleasant one.

Lincoln University

Te Whare Wānaka O Aoraki

Telephone: (03)3252811
Fax: (64)(03)3252944

P.O. Box 84
Lincoln University
Canterbury
New Zealand

15 July, 1991

Declaration of originality

This thesis reports the original work of the author except where otherwise stated.

Di Hong Jie

Hong Jie Di

Lincoln University

Te Whare Wānaka O Aoraki

Telephone: (03)3252811
Fax: (64)(03)3252944

P.O. Box 84
Lincoln University
Canterbury
New Zealand

15 July, 1991

Certificate of supervision

I certify that the work described in this thesis was conducted under my direct supervision.

R. Harrison

Dr R. Harrison

Lecturer

Department of Soil Science

Table of contents

Part two

Assessment of an isotopic injection technique to study dissolution of phosphate fertilisers in the soil

Part three

Development and assessment of an isotopic dilution technique to study the dissolution and retention of phosphate fertilisers in the soil

List of tables

List of figures

Part one

Introduction and literature review

Chapter 1

Introduction

The use of fertilisers containing phosphate rocks (PR's) has become increasingly widespread in recent years (Khasawneh and Doll, 1978; Hagin, 1985; Hammond *et al.*, 1986; Stephen and Condron, 1986; Bolan *et al.*, 1990a). This trend has been encouraged by many factors, of which reducing cost while maintaining production at a satisfactory level is of particular importance. It has been estimated that in New Zealand between 5 and 10% of the total P fertiliser applied annually consists of reactive phosphate rocks, and similar amounts are applied as partially acidulated phosphate rocks (PAPR's) or single superphosphate-reactive phosphate rock mixtures (SSP-RPR's). About 8 million hectares of pastures are potentially suitable for the use of reactive PR's (Bolan *et al.*, 1990a).

The suitability of a rock for direction application as a phosphate fertiliser is determined by the nature and reactivity of the PR and by external edaphic and environmental conditions (Bolan *et al.*, 1990a; Bolland and Gilkes, 1990). For a particular soil-plant system, the agronomic performance of a PR depends primarily on its rate of dissolution when added to the soil. This must be known in order to predict the optimum rate and frequency of application to achieve desired levels of production.

The suitability of phosphate rocks for direct application have been evaluated by measuring their solubility in chemical extractants, such as neutral ammonium citrate, 2% citric acid and 2% formic acid (Chien and Hammond, 1978). The solubility of a PR in an particular extractant depends on the chemical and physical properties of the PR, such as reactivity and particle size. The ability of extraction methods to predict the agronomic effectiveness of PR's is variable and complicated by the presence of impurities or accessory compounds in the rock materials (Mackay *et al.*, 1984; Braithwaite *et al.*, 1989).

Methods used to measure dissolution of phosphate rocks in the soil involve measuring the changes of soil P (ΔP) or Ca (ΔCa) following the addition of a PR (Khasawneh and Doll, 1978; Smyth and Sanchez, 1982; Hughes and Gilkes, 1984; Mackay *et al.*, 1986; Kanabo and Gilkes, 1987a; Bolan and Hedley, 1989). The choice of extractants to study PR dissolution in soil is critical. Acidic or inadequately buffered extractants may dissolve apatite during the extraction process and overestimate the extent of PR dissolution in the soil, particularly when little PR has dissolved (Hughes and Gilkes, 1984). Relatively weak extractants, on the other hand, may underestimate the amount of PR which has dissolved, especially if this is considerable (Bolan and Hedley, 1989). Most of the single extraction methods are designed for incubation studies of PR dissolution. They may not be appropriate under plant growing conditions in the glasshouse or field, because considerable amounts of P or Ca dissolved from the PR might be removed by plant uptake or leaching, or converted to organic forms. Since extraction methods measure PR dissolution on the basis of increases in extractable P or Ca dissolved from PR, the extent of PR dissolution may be underestimated where losses of P or Ca are substantial.

Isotopic tracer methods provide an alternative to chemical extractions. In fact, tracer methods have been regarded as standards in soil fertility studies against which chemical extraction methods are compared (Vose, 1980; Menzel and Smith, 1984). Most of the tracer studies on PR dissolution and availability to plants are based on the A value concept (Fried and Dean, 1952). Application of this concept requires labelling the fertiliser. As it is difficult to label a phosphate rock, the amounts of plant available P supplied by the PR's can be measured in terms of another fertiliser standard which is easier to label (Fried, 1954; Kucey and Bole, 1984). The drawbacks with this approach are that the amounts of plant available P supplied by a PR vary depending on the fertiliser standard and thus do not represent the actual quantities of P dissolved from the PR material.

An alternative to labelling the fertiliser is to label the soil with a carrier-free isotope such as ^{32}P-phosphate. The amount of P dissolved from the PR may then be estimated using the L value concept. The extent of dilution of the added tracer (determined from the specific activity in growing plants) (Larsen, 1952) gives a measure of the amount of phosphate dissolved from the PR. The difficulty with using the L value concept is that a state of isotopic equilibrium is difficult to attain, as the PR continues to dissolve P into the soil for prolonged periods. In addition, whilst phosphate is continuously added to the labile P pool, dissolved P and the tracer may be removed from the P pool by precipitation, sorption, organic immobilisation or plant uptake (Syers and Iskander, 1981). These processes affect the specific activity in the labile P pool and thus the estimation of PR dissolution. Therefore, a new approach is required to assess the effect of these processes and to take them into account when studying the rate of dissolution of PR fertilisers.

Soils may be labelled by mixing with tracer solution, but it is difficult to label an undisturbed natural soil with the existing vegetation intact. A technique of this nature would be useful in studying PR dissolution on natural pastures. An apparatus developed at the Department of Soil Science, Massey University, makes it possible to label natural soil cores without significantly disturbing the soil structure and vegetation (Hedley, 1988, personal communication). Tracer solution is introduced into the soil columns by an injector consisting of 20 syringe needles. However, because of the many variables associated with natural soil-plant systems, particularly in the field, this injection technique needs to be evaluated for the study of the dissolution of phosphate fertilisers in the soil.

The rate of PR dissolution controls the amount of P that may be released into the soil from a PR. However, not all the P dissolved is available to plants, due primarily to processes of soil retention. Strongly P-retentive soils may encourage PR to dissolve, but the released P may not be available for plant uptake (Syers and Mackay, 1986). A method that measures the rates of phosphate retention by the soil as

well as PR dissolution would be very useful in providing information for the understanding of PR dissolution and the availability of dissolved P to plants.

The major objectives of this study were thus:

(1) to assess an isotopic injection technique for studying the dissolution and availability of phosphate fertilisers in undisturbed natural soils,

(2) to develop an isotopic dilution technique, based on tracer kinetic principles, for measuring the rates of PR dissolution and retention in the soil,

(3) to compare the rates of dissolution and the fate of dissolved P from NCPR, NCPR partially (30%) acidulated with phosphoric acid and MCP in two soils of contrasting P retention,

(4) to compare results from the isotopic dilution technique with those derived from chemical extraction methods,

(5) to assess the isotopic dilution technique in terms of its ability to predict plant responses to fertiliser applications.

The thesis has 8 chapters and is divided into 4 parts. The first part consists of an introduction (Chapter 1) and literature review (Chapter 2). The second part describes the assessment of the injection technique in field (Chapter 3) and greenhouse trials (Chapter 4). In part three, an isotopic dilution technique is developed and applied to study the rates of dissolution of PR-containing fertilisers (Chapter 5). The results obtained are then compared with those from chemical extraction methods (Chapter 6). In Chapter 7, the isotopically and chemically derived parameters regarding the dissolution of PR-containing fertilisers are compared in terms of their ability to predict plant responses. The thesis concludes with a brief summary and general conclusions (Chapter 8) in part four.

Chapter 2

Literature review

2.1 Introduction

Phosphorus (P) is essential for plants. Few soils are capable of producing high crop yields without the use of P fertilisers. Much research has been done on reactions of P in soils, its availability to plants and on the type and amount of P fertilisers for specific soil, crop and climatic conditions.

Recently, attention has focused on the use of unacidulated or partially acidulated phosphate rocks as fertilisers. In contrast with acidulated, water-soluble phosphate fertilisers, the effectiveness of phosphate rocks (PR) depends on their ability to dissolve in the soil, thus releasing P in plant-available form. Naturally occurring phosphate rocks vary greatly in the rate at which they dissolve. Soil properties also influence dissolution rates and much recent research has examined techniques for characterising PR's and soils in terms of their ability to supply P for plant growth.

The first part of this review will focus on the forms and transformations of phosphorus in soil-plant systems. This will be followed by a brief discussion on the methods used to measure plant available P in the soil. The third part examines the dissolution characteristics and agronomic effectiveness of phosphate fertilisers and the various influencing factors.

2.2 The roles of phosphorus in plant life

Phosphorus is indispensable for plant growth because of its involvement in physiological and biochemical processes occurring in plants. The concentration of P in most plants ranges from 0.1% to 0.4% (Tisdale *et al.*, 1985). Plants absorb most of their P from the soil in the form of orthophosphate, $H_2PO_4^-$, and to a lesser extent,

HPO_4^{2-}. Other forms of phosphorus, such as pyrophosphates and metaphosphates, are normally hydrolysed to orthophosphates in the soil before they are absorbed by plants.

The importance of phosphorus for plant growth may be seen from its existence in various plant organic compounds which play vital roles in the metabolic or genetic cycles of plant life (Bieleski, 1973). Energy derived from photosynthesis and carbohydrate metabolism is stored and transferred through adenosine di- and triphosphates (ADP and ATP) for subsequent use in growth and reproductive processes. Almost every energy-requiring biological process in plants is driven by the energy released from these compounds. Phosphorus is also an important component of a variety of other compounds, such as nucleic acids, co-enzymes, nucleotides, phosphoproteins and phospholipids. The two nucleic acids, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), are of particular importance because of their involvement in the control of hereditary processes (Bieleski and Ferguson, 1983).

Inadequate P supply has been found to lower the rate of photosynthesis and the activity of various enzymes (Avdeeva and Andreeva, 1974). It has also long been recognised that phosphorus is associated with early maturity of crops, particularly grain crops. A good supply of P improves root growth and strength of cereal straw. An increase in P supply also increases nitrogen fixation by nodulating legumes (Andrew and Robins, 1969; Ozanne, 1980).

2.3 Forms of phosphorus in soils

2.3.1 Introduction

The ultimate source of P in soils is primary apatite contained in the parent rocks. As a consequence of weathering, these primary phosphates dissolve. The phosphate released into solution may subsequently be leached, utilised by plants and micro-organisms to become an integrate part of their organic matter, or be transformed into insoluble or slowly soluble secondary P minerals. The P content of soils varies considerably, depending on the nature of the parent material, degree of weathering, and

extent to which P has been lost through leaching and cropping. Total P in soils is of the order of 200 to 2000 $\mu g\ g^{-1}$ (NZ Soil Bureau Bulletin, 1968). About 20 to 80% of total soil P is in organic forms.

2.3.2 Soil phosphorus in the solution phase

The concentration of P in soil solution ranges from about 0.01 to 1 $\mu g\ mL^{-1}$ (Barber *et al.*, 1963). The phosphate ion can occur in three states of protonation arising from the dissociation of orthophosphoric acid: $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. The concentration of each form depends largely on soil solution pH. In pH ranges usually encountered in most soils (5 to 8), $H_2PO_4^-$ and HPO_4^{2-} are the most abundant ionic species. Concentrations of $H_2PO_4^-$ and HPO_4^{2-} are about equal in solutions of pH 7.2, below this pH, $H_2PO_4^-$ predominates and above it, HPO_4^{2-} becomes the dominant form.

The concentration of P in soil solution is very low in unfertilised soils, often around 0.05 $\mu g\ mL^{-1}$ and seldom exceeds 0.3 $\mu g\ mL^{-1}$ (Fried and Shapiro, 1961; Barber *et al.*, 1963). The concentration of P in soil solution required for maximum plant growth varies between plant species. In a field experiment, for instance, Fox *et al.*, (1974) showed that the P concentrations needed for 95% of maximum yield for head lettuce, sweet potato and corn were 0.4, 0.1 and 0.06 $\mu g\ mL^{-1}$ respectively.

Substantial amounts of organic phosphorus have also been found in soil solution (Fuller and McGeorge, 1951). The concentration of organic P in soil solution may be even higher than that of inorganic P in some soils (Pierre and Parker, 1927), or in some soil horizons (B horizon) (Frossard *et al.*, 1989). Air-drying soil samples tends to increase the proportion of organic P in soil solution (Wild and Oke, 1966).

The nature of organic P in soil solution is unclear. It has been postulated that most is colloidal in nature and is related to microbial cells and cellular debris (Dalal, 1977). The identification of organic P compounds in the soil solution is important for achieving better understanding of the role of organic P in plant P nutrition.

2.3.3 Soil inorganic phosphorus in the solid phase

The solid phase soil inorganic P may be present as sorbed (cf. Section 2.4.3) on the surfaces of soil Fe, Al and Ca compounds (non-occluded), within the matrices of Fe and Al soil components (occluded) or as discrete phase of crystalline phosphate minerals (Syers and Walker, 1969; Williams and Walker, 1969; Ryden *et al.*, 1973).

The separation of inorganic phosphate compounds into calcium, aluminium and iron phosphates is made mainly on the basis of the inorganic P fractionations. A widely used fractionation scheme is that of Chang and Jackson (1957) or its subsequent modifications (Williams *et al.*, 1967; Syers *et al.*, 1972). In the Chang and Jackson procedure the soil sample is extracted sequentially with (i) neutral NH_4F to give aluminium phosphate, (ii) NaOH to provide iron phosphate, (iii) H_2SO_4 to give calcium phosphate, (iv) sodium dithionite buffered with citrate to give occluded iron phosphate, and (v) neutral NH_4F to give occluded aluminium phosphate. The limitations of this fractionation scheme for characterising inorganic P in soils are that: (i) part of the released P may be resorbed from solution by soil components, (ii) intermediate reaction products of applied fertiliser P may persists for extended periods and the behaviour of the products during sequential extraction is unknown, and (iii) the reagents are not completely specific for the fractions that they are claimed to release (Stevenson, 1986).

Other schemes have been developed to fractionate soil P according to its lability or ease of extraction, and thus availability to plants (Stewart *et al.*, 1980; Hedley *et al.*, 1982b, c). Soil samples are sequentially extracted with anion exchange resin, $NaHCO_3$, NaOH and HCl. Both inorganic and organic P are determined in the extracts. Phosphate extracted by resin and $NaHCO_3$ is more readily available to plants than that extracted by NaOH and HCl.

Calcium phosphates are the predominant phosphate compounds in alkaline and neutral soils. They constitute a series of phosphate compounds which vary considerably in solubility. The calcium phosphates most likely to occur in soils in

decreasing order of solubility are: (i) monocalcium phosphate (MCP) [$Ca(H_2PO_4)_2.H_2O$], (ii) dicalcium phosphate dihydrate (DCPD) ($CaHPO_4.2H_2O$) and the unhydrated form (DCP) ($CaHPO_4$), (iii) octacalcium phosphate (OCP) [$Ca_8H_2(PO_4)_6.5H_2O$], (iv) tricalcium phosphate (TCP) [$Ca_3(PO_4)_2$], and (v) hydroxyapatite [$Ca_5(PO_4)_3OH$], fluorapatite [$Ca_5(PO_4)_3F$], and substituted apatites, e.g. carbonate apatite.

Iron and aluminium phosphate compounds are mainly present in acidic soils. Much less is known of the exact composition of these compounds. Part of the Fe and Al phosphates may exist as the minerals strengite ($FePO_4.2H_2O$) and variscite ($AlPO_4.2H_2O$), which are very stable and insoluble. In fertilised soils, a range of transient reaction products between phosphate fertilisers and soil components may exist (cf. Sections 2.4.2, 2.4.3 and 2.6.2).

Availability of the P in these inorganic compounds is largely determined by the solubility of the compounds or the bond energies of the sorbed P, and is influenced by soil factors including pH, concentrations of soluble calcium, iron, aluminium and their containing minerals, organic matter content, and activities of microorganisms.

2.3.4 Soil organic phosphorus in the solid phase

I. Forms and chemical nature

Soils vary greatly in the amounts of organic P they contain. Higher values are expected in peats, uncultivated forest soils and grassland soils. Organic P decreases with depth in a soil profile in much the same way as organic carbon. When soils are initially cultivated, the concentration of organic P usually declines.

Total organic P in soils is generally determined indirectly, either by extraction (Mehta *et al.*, 1954; Anderson, 1960) or by ignition methods (Legg and Black, 1955; Saunders and Williams, 1955). Fractionation schemes have been developed to separate soil organic P according to its stability or ease of extraction by chemical reagents (Stewart *et al.*, 1980; Hedley *et al.*, 1982b, c) (cf. Section 2.3.3).

The chemical nature of soil organic P is complex and a large fraction of it is still not characterised. Existing data show that most of the organic P in soil is associated with the humic and fulvic acid complexes of soil organic matter (Anderson, 1967). Of the specific forms of organic P that have been identified in soils, inositol phosphates are the dominant compounds, accounting for up to 60% of total organic P. Other compounds present in smaller quantities include nucleic acids (5-10%), and other phosphate esters such as phospholipids, sugar phosphates and phosphoproteins (<1-2%) (Anderson, 1967; Cosgrove, 1967; McKercher, 1968).

II. C:N:S:P ratios

The amount of organic P in soils is roughly correlated to that of organic C, N and S. On average, the proportion of C:N:S:P in soil humus is 140:10:1.3:1.3 (Stevenson, 1986). It has been suggested that the organic C, N, S and P contents of a soil are ultimately controlled by the P content of the parent material, and that P availability to organisms ultimately limits organic matter accumulations (Walker and Adams, 1958, 1959; Walker *et al.*, 1959; Walker, 1965; Walker and Syers, 1976).

However, the organic C:P ratio is much more variable than the C:N ratio in soils. Explanations have been postulated for this variable nature. Nitrogen and sulphur occur as structural components of humic and fulvic acids whereas phosphorus may not. Nearly all the organic P can be dispersed from a soil comparatively easily, but a fraction of the C, N and S of the soil organic matter remains undispersed (Russell, 1973). Organic P may be divided into two parts: the P intimately bound to the C, N and S of humus, and a varying part of some independent organic P compounds (Williams and Steinbergs, 1958; Swift and Posner, 1972; Goh and Williams, 1982). McGill and Cole (1981) suggest that organic C, N, S and P are immobilised and mineralised through different mechanisms. Nitrogen and part of sulphur are stabilised together with C and mineralised during oxidation of C by soil organisms. Organic P and S esters are stabilised by their interaction with soil components and mineralised

through enzymatic catalysis. The organic C:P ratio, therefore, depends on the relative rates of these independent processes (cf. Section 2.4.4 for further discussion).

III. Plant availability

The availability of organic P compounds to plants is not well understood. It has been suggested that plants may take up P from inositol hexaphosphate, lecithin, nucleic acids and nucleotides (Rogers *et al.*, 1940; Szember, 1960; Martin and Cartwright, 1971). However, the availability of organic compounds in high P retention soils is drastically reduced, possibly due to sorption of these compounds by soil colloids, and formation of insoluble complexes with Fe and Al (Dalal, 1977). There is insufficient evidence to suggest that plants absorb organic P from soil solution. Pierre and Parker (1927), for instance, found that organic compounds in soil solution were not assimilated by corn, soybean or buckwheat plants, although inorganic P was almost completely absorbed. Organic P in soil solution may be hydrolised by phosphatase enzymes excreted by plant roots or microorganisms to release inorganic P. Existence of such enzymes has been confirmed (Cosgrove, 1970; Martin, 1973; Burns, 1978). Dalal (1977) suggested that the hydrolisable fraction of soluble organic phosphates could be utilised by plants, and that mycorrhizae might augment the role of organic P in plant nutrition by producing dephosphorylating enzymes.

2.4 Transformations of phosphorus in the soil-plant system

2.4.1 Introduction

Plants take up phosphate from soil solution. The concentration of soil solution P is governed by a number of reactions or processes. They may be separated into the following categories: (i) precipitation-dissolution; (ii) sorption-desorption; (iii) immobilisation-decomposition; and (iv) plant uptake-return.

Prior to the discussions of these processes it is necessary to clarify a few concepts that are often confusing. Phosphate retention refers to the removal of

phosphate from soil solution by soil or soil constituents. No particular mechanism is implied in this concept. Phosphate adsorption and phosphate absorption mean the retention of phosphate at soil surfaces and within a solid phase respectively. However, the less specific term sorption is preferred due to the difficulties in practically separating the two processes. Phosphate precipitation refers to the formation of discrete phase phosphate compounds of low solubility. However, the distinction between sorption and precipitation is not always clear. Sorption may occur at the same time as precipitation. Phosphate fixation, as defined by Wild (1950), describes "any change that phosphate undergoes in contact with the soil, which reduces the amount that plant roots can absorb". This term is generally used to collectively describe both sorption and precipitation reactions of phosphorus in the soil.

2.4.2 Precipitation-dissolution reactions

Early work on the chemistry of soil phosphorus led researchers to postulate the formation of phosphate compounds (e.g. Al and Fe phosphates) by precipitation (Cole and Jackson, 1950; Kittrick and Jackson, 1955). When concentrated P solutions were added to soil components, such as Fe and Al oxides, compounds of variscite ($AlPO_4.2H_2O$), barrandite [(Al, Fe) $PO_4.2H_2O$] and strengite ($FePO_4.2H_2O$) were formed. The concentration of solution P in neutral and acid soils was believed to be governed by the solubility equilibria of crystalline P compounds. Strengite and variscite may crystallise slowly from the initial reaction products of short-range order (amorphous) ferric and aluminium phosphates (Lindsay *et al.*, 1962).

In calcareous soils, the soluble phosphate may be initially precipitated as dicalcium phosphate. With time, these phosphate compounds may be transformed to more stable precipitates, e.g. octacalcium phosphate. Eventually, P may be precipitated as the most stable Ca-phosphate minerals, the apatites. Phosphate concentrations in soil solutions equilibrated with apatite under near neutral pH

conditions are extremely low, about 10^{-7} to 10^{-8} mol L^{-1} for hydroxyapatites (Mengel, 1985). The formation of apatite is, therefore, a very strong sink for phosphate.

However, a number of studies, e.g. Wild (1954), Bache (1963), Murrmann and Peech (1969), and Ryden and Pratt (1980) have demonstrated that the solubility of phosphate compounds does not satisfactorily account for the concentration of P observed in soil solutions. Wild (1954), for instance, showed that the concentration of P in soil solution did not correspond to the solubility of several P compounds in the pH range 4.0 to 7.5. Firstly, soil solution P is rarely at equilibrium with the least soluble P compounds, particularly in fertilised systems. Secondly, congruent dissolution of strengite and variscite only occurs under very low pH conditions, below 1.4 and 3.1 respectively (Bache, 1963). The solubility constants of these compounds therefore can not be used to estimate P concentration in most soils. It is generally accepted that precipitation reactions may take place at the vicinity of the water-soluble phosphate fertiliser granules in the soil where the concentration of P is very high and pH very low (cf. Section 2.6.2). In most situations, however, the retention and release of P by soils are best described by models developed on the basis of sorption-desorption reactions.

2.4.3 Sorption-desorption reactions

I. Sorption isotherms

In contrast to the precipitation-dissolution concept which requires that the P concentration in soil solution be controlled by the solubility product of the least soluble P compound with the surface activity remaining unchanged, the sorption-desorption theory assumes that the P concentration in soil solution, to a large extent, determines the amount of P sorbed by soil and soil components, with surface activity changing accordingly.

The amount of phosphate that may be sorbed by a soil is operationally determined by shaking the soil with phosphate solutions for a given period of time. The concentration of phosphate in the solution is then measured and the amount of

phosphate sorbed calculated. Sorption isotherms may be obtained by plotting the amounts of phosphate sorbed against the phosphate concentrations remaining in the solution, and they are often described by mathematical models.

The most commonly used models are the Langmuir equation (e.g. Olsen and Watanabe, 1957; Syers *et al.*, 1973; Holford *et al.*, 1974; Ryden *et al.*, 1977b; Taylor and Ellis, 1978) and the Freundlich equation (e.g. Kurtz *et al.*, 1946; Kuo and Lotse, 1972, 1974; Fitter and Sutton, 1975).

The Freundlich model may be written as follows:

$$x = kc^n \qquad (2.1)$$

where x is the amount of phosphate sorbed, c is the solution P concentration and k and n are constants. If this equation holds, logarithmic plots of x against c should give a straight line. The model implies that energy of phosphate sorption decreases as the amount of sorption increases. This model is a convenient approximation of the isotherms within a limited range of phosphate concentrations, but nonlinearity becomes apparent over larger concentration ranges.

The Langmuir equation has been used more frequently. It was derived for describing the adsorption of gases on to solid surfaces. Assumptions are made that adsorption is restricted to a monolayer and that the energy of adsorption does not change with surface coverage. This implies that the adsorption sites are isolated and uniform, and that adsorbed molecules do not interact with each other (Parfitt, 1978). The Langmuir model may be written in the following linear form:

$$c/x = c/x_m + 1/kx_m \qquad (2.2)$$

where c is solution P concentration, x is the amount of phosphate sorbed, x_m is the sorption maximum and k is a constant related to sorption energy. Plotting of c/x

against c should yield a straight line. The x_m and k values can be obtained from the slope and the intercept.

As is the case with the Freundlich model, the plot of c/x against c does not always conform to a single straight line over extended concentration ranges. This has led some workers to apply two- or three-term Langmuir equations which can be better fitted to experimental data (Muljadi *et al.*, 1966a, 1966b, 1966c; Holford *et al.*, 1974; Ryden *et al.*, 1977a, 1977b, 1977c). The Langmuir equation has been criticised for its failure to take into account the changes in surface charge during sorption (Bowden *et al.*, 1974, 1977; Harter and Baker, 1977; Veith and Sposito, 1977; Barrow, 1978; Parfitt, 1978).

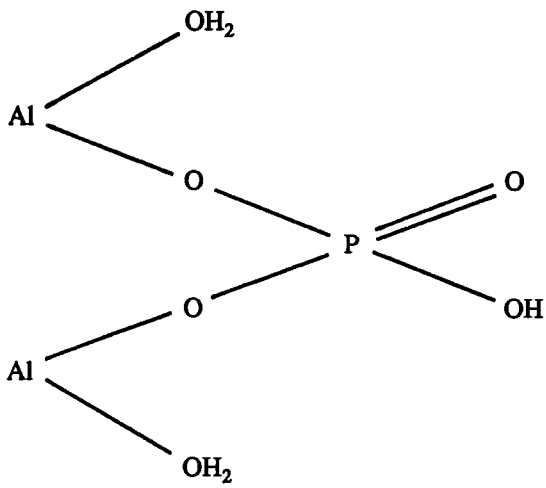
II. Sorption mechanisms by soil components

Phosphate is sorbed on to surfaces of soil components of either constant or of variable charge. The soil components responsible for providing such surfaces involve iron and aluminium oxides, crystalline clay minerals, poorly-ordered aluminosilicate and iron oxide minerals, calcium carbonate and organic matter.

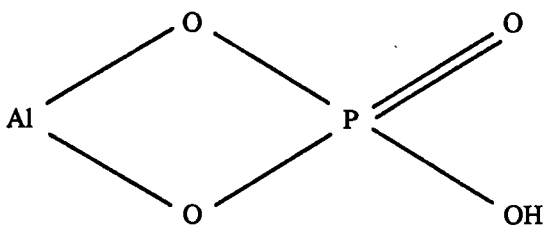
Iron and aluminium oxides Phosphate is specifically sorbed by hydrous iron and aluminium oxides (Hingston *et al.*, 1967, 1968). Phosphate is capable of exchanging with OH_2 and OH on the surfaces of hydrous Fe and Al oxides, and becoming co-ordinated to the metal ion. The net charge on the surface becomes more negative and the solution pH increases as a result of specific sorption.

The reaction sites involved in the exchange on hydrous aluminium oxides may vary with P concentration in the solution (Rajan *et al.*, 1974). At low concentrations, phosphate mainly replaces aquo groups (Al-OH_2); at higher concentrations, more hydroxyl groups (Al-OH) are displaced; at very high concentrations, hydroxyl bridges (Al-OH-Al) are broken and phosphate is sorbed on to the newly-created sites.

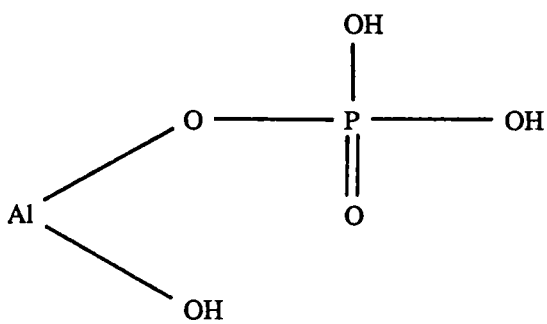
The phosphate sorbed may coordinate with the metal ions in different forms (Muljadi *et al.*, 1966a, 1966b, 1966c; Kyle *et al.*, 1975; Rajan, 1975). White (1980) proposed that any of the following structures were possible for phosphate sorption on Al oxide surfaces:



(Binuclear)



(Bidentate)



(Monodentate)

With regard to the sorption of phosphate with natural goethite, Parfitt (1989) hypothesised that phosphate is strongly and rapidly sorbed on very reactive sites displacing Si, OH and OH_2 groups, forming binuclear complexes. This is followed by weaker ligand exchange on less reactive sites and by phosphate penetration at defect

sites and pores. The extent of these reactions depends on the crystallinity and porosity of the iron oxides.

It is generally believed that phosphate is more strongly bound to hydrous oxides of Al and Fe by the binuclear or bidentate forms than by the monodentate form.

Clay minerals The mechanisms of phosphate sorption by clay minerals are similar to those by hydrous oxides (Muljadi *et al.*, 1966a, 1966b, 1966c; Hingston *et al.*, 1972). Phosphate is sorbed by exchange with Al-OH or Al-OH_2 groups on the edge sites of clay minerals, forming mainly monodentate complexes, though some complexes might be in binuclear form.

Poorly-ordered minerals Poorly-ordered iron and aluminium hydroxides, such as ferrihydrite and proto-imogolite, play important roles in P sorption. According to the hypothesis of Parfitt (1989), reactions of phosphate with imogolite-like structured materials may take place first as a rapid, strong sorption by ligand exchange on the most reactive Al-OH sites, forming either monodentate or binuclear complexes. This is followed by sorption of P on less reactive defect sites. With time or at high concentrations, phosphate reacts with more aluminium, probably located near the defect sites, disrupting the imogolite structure and forming alumino-phosphate precipitates.

The reaction of phosphate with ferrihydrite may take place in a similar sequence as that with natural goethite as discussed before (Parfitt, 1978, 1989).

Calcium carbonate In calcareous soils, calcium carbonate becomes an important component responsible for phosphate sorption. Calcium carbonate occurs in soil primarily as the mineral calcite, although soil calcites tend to be imperfectly crystallised, due to intermittent dissolution, reprecipitation and incorporation of structural impurities.

Studies by Cole *et al.* (1953), Kuo and Lotse (1972), Holford and Mattingly (1975b) and Griffin and Jurinak (1973, 1974) suggest that three steps are involved in the interaction of phosphate with calcite. Phosphate is sorbed at the surface

accompanied by nucleation of poorly crystalline calcium phosphate. This is followed by a slow transformation of the nuclei into crystalline compounds, while a third step involves the growth of crystals. Octacalcium phosphate or dicalcium phosphate may emerge from the crystallisation, but ultimately the most stable mineral, hydroxyapatite, should evolve, although it is an extremely slow process.

Organic matter The role of organic matter in P sorption by soils is controversial. Positive relationships between organic matter content of soils and P sorption have been reported (Sample *et al.*, 1980). Cations such as Al and Fe adsorbed by organic colloids may be capable of sorbing phosphate (Appelt *et al.*, 1975; Bloom, 1981; White and Thomas, 1981). On the other hand, organic matter may complex those cations preventing further reaction with phosphate and thus increasing the P concentration in soil solution. Nagarajah *et al.* (1970) and Holford and Mattingly (1975a) showed that organic acids could compete with phosphate for sorption sites of mineral surfaces, reducing sorption of P by the minerals. Carbon dioxide released from the decomposition of organic matter, which could form carbonic acid in water, could dissolve soil minerals and thus play an important role in increasing the availability of P in soils (Tisdale *et al.*, 1985). On the whole, addition of organic matter to mineral soils would increase availability of soil P.

III. Slow reactions after initial sorption

Phosphate sorption by soils and soil components follows two distinct steps, an initial fast reaction which may be complete in minutes or hours followed by a much slower reaction. The mechanisms of this slow reaction process are still not well understood. It is generally assumed that the rapid reaction between P in solution and soil surfaces involves an adsorption mechanism, while the continuous slow reaction results from a change of P from more loosely bound in the surface to more tightly bound forms. Various mechanisms have been proposed for the exact nature of this change. These include the transformation of sorbed P from a monodentate to a

bidentate form (Kafkafi *et al.*, 1967; Hingston *et al.*, 1974; Munns and Fox, 1976), the diffusive penetration of P sorbed on the surface into soil particles (McLaughlin *et al.*, 1977; Ryden *et al.*, 1977c), and the precipitation of discrete phosphates (Chen *et al.*, 1973; Van Riemsdijk *et al.*, 1975, 1977).

The mechanisms of the slow reaction may vary between different soil components. For example, the slow reaction of P with natural iron oxides may be through penetration of phosphate at defect sites (Ryden *et al.*, 1977c; Parfitt, 1989). The extent of this reaction depends on the degree of crystallinity of the mineral, and this relates to porosity and the degree of substitution of Al for Fe (Berkheiser *et al.*, 1980). Therefore small particles with large surface area, e.g. ferrihydrite, are active in the slow sorption of P, whereas highly crystalline goethite has virtually no slow reaction due to lack of defect sites. Nor would a diffusive penetration reaction occur with imogolite materials since all the Al-OH groups are at the external surface. However, the slow reaction of P with imogolite-like materials may take place through formation of alumino-phosphate precipitates, disrupting the structure and creating new defect sites.

IV. Desorption

When P is removed from the soil solution, there will be a process involving P moving from sorbed to solution form - desorption. However, the sorption process is somewhat "irreversible", or partly reversible, i.e. there exists a hysteresis between sorption and desorption (Kafkafi *et al.*, 1967; Fox and Kamprath, 1970; Syers *et al.*, 1970; Munns and Fox, 1976; Ryden and Syers, 1977). Irreversibility is found to be more apparent as sorption prolongs (Barrow and Shaw, 1975b).

Barrow (1985) suggests that there are two possible interpretations for the hysteresis. One is that desorption is slower than sorption and insufficient time has been allowed to measure desorption, and the other is that the hysteresis is caused by a slower process following the rapid adsorption which converts adsorbed P into a firmly

held form, not in direct equilibrium with solution P. Given sufficient time, probably years, the sorbed P may be reversible, though the rate of desorption may be very slow at the later stages (Barrow, 1980). Since desorption is often measured in the laboratory over a period of hours, it is not surprising that the process is incomplete.

The ability of soil to sorb P and the reversibility of the sorbed P is related to the saturation of the sorption complex, that is, the number of sites available for sorption. Desorption becomes easier at higher concentrations because the energy of sorption becomes smaller with increasing surface coverage. White and Taylor (1977) demonstrated that if the soil is pretreated with P solution and stored long enough to eliminate high energy sites and the spatial heterogeneity of P activity on the surfaces, adsorption of P will be reversible at least for small removals of P from the soil solution.

V. Variables affecting sorption-desorption

Sorption and desorption of P by soils are influenced by several factors, some of which including organic matter and P saturation, have been dealt with in the preceding discussions. Other major factors include the nature and amount of soil components, pH, other ions and temperature.

Soil components The nature and amount of soil components affect the sorption-desorption process mainly by controlling the number of sites available to sorb P. The ability of a range of soil components to sorb P at similar solution concentrations are presented in Table 2.1.

The data in Table 2.1 illustrate that poorly-ordered materials (e.g. hydrous ferric oxide gel) have a greater P sorption capacity than do their crystalline counterparts (e.g. goethite), which in turn have a greater capacity than do phyllosilicates (e.g. kaolinite). It should be noted that the amounts of P sorbed by poorly-ordered aluminosilicates vary with Al:Si ratio of the material (Parfitt and Hemni, 1980; Clark and McBride, 1984; Parfitt, 1990), and the ratio for the material

provided is 1.3. It is obvious that iron and aluminium oxides and hydroxides, particularly those poorly-ordered, play significant roles in P retention. Harrison and Swift (1985) studied changes of phosphorus down the profiles of some high country soils in New Zealand and found that phosphorus was predominantly associated with iron oxides and hydrous iron oxides in the soil profiles. The power of P sorption by calcite may also be partially related to hydrous ferric oxide impurities (Holford and Mattingly, 1975b).

Table 2.1 Amounts of P sorbed by several soil components at the equilibrium solution P concentration around 3.1 μg P mL^{-1} (10^{-4} M) (after Syers and Iskandar, 1981).

Component	P sorbed (μg P g^{-1})	P in solution (μg P mL^{-1})	pH of system
Hydrous ferric oxide gel	21700	3.1	5.0
	29700	3.3	7.7
	50000	3.0	5.5
Poorly-ordered aluminosilicates[1]	15500	3.1	5.8
Goethite	5800	2.7	4.2
Gibbsite	7130	3.1	4.0
Kaolinite	465	3.0	5.0
Montmorillonite	110	3.0	6.5
Calcite	60	2.8	9.2

1: Clark and McBride (1984)

pH The effect of pH on P sorption and desorption by soils is of particular interest as soil pH can be manipulated, to some extent, by management measures, such as liming. Literature on the effect of pH on P sorption is conflicting with contrasting results reported (Sanchez and Uehara, 1980; Syers and Iskandar, 1981; Haynes, 1982,

1984). Liming acid soils may increase, decrease or not affect the phosphate that can be extracted from soils (Haynes, 1982). When the pH of an acid soil is increased, the sorption surfaces become more negatively charged resulting in greater electrostatic repulsion and thus a decrease in P sorption. The decrease, however, is relatively slow until pH 7 due to the rapid increase in the concentration of HPO_4^{2-} ions with increasing pH. The increase of HPO_4^{2-} may partially compensate the decrease in electrostatic potential.

On the other hand, liming an acid soil may result in formation by precipitation of new, positively charged hydroxy-Al surfaces which can sorb phosphate. Such hydroxy-Al polymers may form complexes with components of organic matter, or form coatings over the original sorption surfaces of soil colloids. This effect becomes particularly evident in soils containing much exchangeable Al. In such soils, the increase in P retention due to the newly-formed surfaces will outweigh any decrease in P sorption on the original surfaces induced by the pH increase.

Phosphate sorption by limed soils therefore might be increased, decreased or unchanged depending on the relative magnitudes of the two opposing effects: a decrease of P sorption due to the increase of negative charge and the promotion of P sorption as a result of the formation of new hydroxy-Al polymer surfaces (Haynes and Swift, 1985). In general, liming would increase P sorption in soils containing much exchangeable Al, but reduce P sorption if the concentration of exchangeable Al is low (Haynes, 1982).

It should be noted, however, that liming may also increase P availability to plants by stimulating mineralisation of organic matter and by alleviating Al toxicity.

Other ions The species and concentration of cations and anions also affect phosphate sorption by soils and soil components. Increases in concentration of electrolyte cations make the electrostatic potential at the sorption planes less negative and thus increase phosphate sorption and decrease desorption (Ryden and Syers, 1975; Barrow and Shaw, 1979). Divalent cations have a greater power of enhancing P

sorption by soils than monovalent cations. Some cations, such as Ca^{2+}, have a specific affinity for the sorption surfaces and have a particularly strong effect on promoting phosphate sorption (Barrow *et al.*, 1980). The ability of cations in affecting phosphate sorption by soils follows the following order (Parfitt, 1978):

$$Al^{3+} > Ca^{2+} > Mg^{2+} > K^{+} > Na^{+} = NH_4^{+}$$

Both inorganic and organic anions can reduce sorption or increase desorption of P by competing for sorption sites. Nonspecifically sorbed ions such as nitrate and chloride have little effect (Evans and Syers, 1971; Kinjo and Pratt, 1971). For inorganic anions which can be specifically sorbed, such as hydroxyl, sulphate and molybdate, the strength of bonding with the surface metal ion determines their competitive ability of sorption with phosphate. Therefore, the failure of sulphate to form a stronger bond than phosphate at the surface is the reason why sulphate desorbs little phosphate from the surface.

Organic anions such as oxalate and citrate can be specifically sorbed at soil surfaces in a similar manner to phosphate and thus compete with P for sorption sites (Nagarajah *et al.*, 1970). These anions are also capable of dissolving poorly-ordered species such as ferrihydrite and proto-imogolite which sorb large amounts of P. Organic anions capable of forming stable complexes with iron and aluminium of soil components are particularly effective in reducing P sorption by soils. Earl *et al.* (1979) suggested that the contribution of citrate to the reduction of phosphate sorption by soils and iron and aluminium gels was due to the elimination of a large number of sorption sites by the formation of soluble iron and aluminium complexes.

Temperature Temperature can affect phosphate reactions with soils by influencing: (i) the position of the equilibrium between phosphate in solution and adsorbed phosphate, (ii) the rate of transfer from adsorbed to firmly-held, and (iii) the rate of transfer from firmly-held to adsorbed (Barrow, 1979). When the equilibrium

between solution P and sorbed P is disturbed by adding soluble phosphate, a net movement of P from solution to adsorbed and further to firmly-held form is induced, and the slow movement from the adsorbed to the firmly-held form is accelerated by higher temperatures. If the system is disturbed by reducing the concentration of phosphate in solution, a net movement of P in the opposite direction is initiated and this movement is also hastened by increasing temperatures. The forward and backward reactions are neither markedly endothermic nor exothermic. Thus the position of equilibrium between adsorbed and firmly-held is not affected. Nevertheless, temperature does have an effect on the position of the equilibrium between solution phosphate and adsorbed phosphate. Higher temperatures increase the concentration of phosphate in solution which implies that the adsorption process is exothermic. Therefore, if conditions are chosen such that the slow processes have almost completed, increased temperatures, then, should increase the concentration of phosphate in solution.

Greater amounts of P applied in fertilisers are sorbed by soils in warm regions of the world than in more temperate regions, although soils in warm regions also tend to contain higher amounts of hydrous oxides of iron and aluminium.

2.4.4 Immobilisation-decomposition reactions

Parallel to the reactions of precipitation-dissolution and sorption-desorption, phosphate is involved in another cycle - biological immobilisation and mineralisation. Native inorganic phosphorus is transformed into soil organic phosphorus during soil development (Walker and Adams, 1958; Smeck, 1985), while phosphate applied in fertilisers is also incorporated into organic forms (Jackman, 1955; Sadler and Stewart, 1975; Condron and Goh, 1989). This transformation makes added phosphorus temporarily unavailable to plants until it is mineralised.

As the processes of immobilisation and mineralisation occur simultaneously in the soil, the concentration of soluble phosphate in soil solution depends in part on

the magnitude of the two opposing processes. When organic material is added to soils, the magnitude of the two processes depends on the C:P ratio of the organic matter (Stevenson, 1986). In general, if the C:P ratio is 300:1 or more, net immobilisation occurs; if it is 200:1 or less, net mineralisation occurs. The critical level of phosphorus in organic material is, therefore, about 0.2%, below which net immobilisation occurs, and above which net release of P takes place.

Van Diest (1968) suggested that organic P accumulation in soil is the result of an increase in soil microflora following P fertiliser application and an accumulation of crop residues containing a fraction of organic P resistant to rapid hydrolysis. Others (Halstead and McKercher, 1975; Cosgrove, 1977; Dalal, 1977; Anderson, 1980) believe that organic P in soil mainly originates from microbial synthesis rather than from accumulation of plant and animal residues. Another possibility is that organic P compounds could be protected from decomposition by forming complexes with clay minerals and hydrated oxides of iron and aluminium (Anderson *et al.*, 1974).

Mineralisation is largely due to the combined activities of soil microorganisms and free phosphatase enzymes. Mineralisation of organic P can occur as a result of carbon oxidation to provide energy, supplemented by the independent hydrolysis of phosphate esters. The independent process is catalysed by the enzyme, phosphohydrolase, which can be released by microbes and plant roots (McGill and Cole, 1981). Phosphohydrolases are produced in response to need for P and repressed by an adequate supply of P. This independent process is termed biochemical mineralisation in contrast to biological carbon oxidation.

The C:P ratio in soil organic matter (cf. Section 2.3.4) is affected by the relative rates of the biological and biochemical mineralisation. Due to the repression of phosphohydrolase production in soils with high concentrations of available P, organic P tends to accumulate relative to carbon, resulting in a low C:P ratio in the organic matter. Conversely, phosphohydrolase production is induced in soils with low

supplies of available P. The release of P by hydrolysis of phosphate esters results in a high C:P ratio.

Variables that influence mineralisation in the soil include temperature, moisture, aeration, soil pH, addition of fertilisers, cultivation, microorganisms and the presence of plants (Dalal, 1977). In general, favourable conditions for aerobic microorganism activities, such as warm climate, adequate moisture and aeration, and cultivation tend to stimulate organic P mineralisation. Liming of acid soil improves the living environment of microbes, and thus favours mineralisation. Plants deplete available P from the soil, an action which may stimulate excretion of phosphatase, leading to enhanced decomposition of organic P. Application of P fertilisers will generally curb mineralisation and encourage accumulation of organic P (Haynes and Swift, 1988).

2.4.5 Plant uptake and return

I. Soil P supply and plant P uptake

The amount of P available to plants is often associated with the concept of "labile P". Labile P is defined as the fraction of P in the soil that is isotopically exchangeable with ^{32}P within a limited time (Larsen, 1967). The following dynamic system is assumed to exist in the soil:

$$\text{solution P} \Leftrightarrow \text{labile P} \Leftrightarrow \text{nonlabile P}$$

Establishment of the first equilibrium is much faster than that of the second. The concentration of P in solution is often regarded as the intensity factor, whereas the amount of solid phase P that acts as a reserve is regarded as the quantity or capacity factor. When P intensity is decreased by plant uptake, it is quickly replenished by P from the labile pool. Depletion of labile P also induces nonlabile P to become labile,

although at a very slow rate. The methods of determining labile P in the soil will be discussed in Section 2.5.

Three processes are involved in the uptake of P by plants: movement of P from the soil to the root surface, transfer of P from exterior to interior of the root and translocation of P from the root to other parts of the plant. Plant roots absorb ions from the immediate vicinity of the root surfaces. Since they usually have a volume less than 1% of the soil volume, plant roots can only be in direct contact with less than 1% of the available P in the soil. This amount is usually a small proportion of that required for abundant plant growth (Barber et al., 1963). Phosphate needs to be transported from the soil to the root surface for plant absorption.

The two processes responsible for the movement of P from the soil to the root surface are mass flow and diffusion (Barber, 1962). Plant roots absorb water and this generates a convective flow of soil solution toward the roots. Available soil P is thus carried to the roots by this mass flow. When the quantity of P supplied by mass flow and direct interception is inadequate to meet the requirement of the plants, a P concentration gradient is created as a result of the reduction of P concentration at the root surface. Phosphorus in the soil will diffuse toward the roots along this gradient.

The relative importance of these mechanisms in supplying P to plants depends on various factors, such as the size of the root system, the rate of water absorption by the plant and the P concentration in the soil solution. Diffusion is the dominant mechanism governing the supply of P to plant roots, providing 90 to 98% of the P absorbed by plant roots in many soils (Barber *et al.*, 1963; Barber, 1980).

Phosphate diffusion in soils is usually slow, with diffusion coefficients of the order of 10^{-8} to 10^{-11} cm^2 $second^{-1}$. The average distance of diffusion in 4 days ranges from 0.006 cm to 0.08 cm (Barber, 1980). The magnitude is influenced by soil volumetric moisture content, tortuosity, P buffering capacity and temperature.

Phosphate supply to plants is therefore directly controlled by four factors (Larsen, 1967): the intensity factor, the capacity factor, the kinetic factor and the

diffusion factor. The intensity factor is a measure of the concentration of P in soil solution; the capacity factor is the quantity of P in the soil that can rapidly replenish the solution P; the kinetic and diffusion factors refer to the rates of the replenishment processes from the labile P to solution P and from the soil solution in nearby locations to plant roots respectively.

However, the ability of soils to supply P to plants is usually assessed by the intensity and capacity factors. For soils with similar P sorption capacities, phosphate concentration in solution will be in direct relation with the capacity factor. Either the intensity or the capacity factor by itself will be related to plant P uptake. If soils differ considerably in their P sorption capacity, both the intensity and the capacity factor should be taken into consideration when assessing the supplying power of P by soils. In fact, a measure of the intensity and the capacity factor is usually a good indicator for the ability of soil to supply P to plants. Gunary and Sutton (1967) demonstrated that about 80 to 85% of the variation in P uptake from a range of soils could be explained by these two factors.

The concentrations of labile P in unfertilised soils are generally low and inadequate to sustain satisfactory plant growth. Fertilisation is essential for intensive agricultural production. The ability to raise and maintain satisfactory concentrations of plant available P in the soil varies between water-soluble phosphate sources and water-insoluble ones. It would take many more applications of slow-dissolving phosphate fertilisers than fully-soluble fertilisers to bring the soil available P up to a satisfactory concentration (Larsen, 1967). Once a high status of labile P is reached, it would require frequent small applications of water-soluble sources, or less frequent larger additions of slowly-soluble sources to maintain it. The amounts and frequency of slow-dissolving phosphate fertilisers required depend on the dissolution rate of the fertiliser in a specific soil-plant system. It is therefore very important to know the dissolution rates of slow-dissolving phosphate fertilisers for efficient planning of

fertiliser application strategies. The dissolution characteristics of different phosphate fertilisers and their agronomic potentials will be discussed in Sections 2.6, 2.7 and 2.8.

II. Environmental factors and P uptake

The uptake of P by plants is not only controlled by the P supplying power of soils, but also by environmental, plant, microbiological and management factors. Among environmental factors, soil moisture is particularly important as it affects P diffusion in soil solution. When soil moisture decreases, the diffusion path becomes more tortuous. This will result in reduced transportation of P to plant roots.

P uptake by plants generally decreases at low temperatures. This is probably due to decreased rates of root growth, P uptake processes, and decreased concentration of P in soil solution (Barber, 1980).

III. Biological factors and P uptake

The efficiency of P utilisation varies between plant species (Loneragan and Asher, 1967). The possibility of exploiting genotypic differences in utilisation of soil P to improve the efficiency of fertiliser P has attracted greater attention in recent years (Godwin and Wilson, 1976; Nielson and Barber, 1978; Baligar and Barber, 1979; Caradus, 1983; Fageria *et al.*, 1988). Selection of plants with improved efficiency of P utilisation involves finding plants with root systems capable of absorbing more soil P, or plants with root and shoot systems having low metabolic requirements for P.

Plants are capable of altering soil conditions immediately surrounding the root (i.e. in the rhizosphere) which, in turn, may affect P uptake. An imbalance in cation and anion absorption by plant roots results in a pH change at the root surface. When more cations are absorbed than anions, H^+ will be released, and soils near the root surface will become more acid; when more anions are absorbed, then the rhizosphere pH will increase. Since nitrogen is the major nutrient required by non-leguminous plants, the pH in the root-affected soil may be decreased or increased by

supplying plants with NH_4^+-N or NO_3^--N (Riley and Barber, 1969). This change of soil pH, caused by supplying different forms of N, can influence phosphate availability to plants. An investigation by Riley and Barber (1971) showed that, at the same soil pH level, soybeans supplied with NH_4^+-N contained higher levels of P in the shoot than those supplied with NO_3^--N. They attributed this difference to the indirect effect on soil pH by the two forms of N-fertilisers.

Plant roots also give rise to differential microbiological activities in the rhizosphere. In general, the mean population density of microorganisms at the root surface is more than 10 times that in the bulk soil away from the root surface (Tinker, 1980). These microorganisms may be free-living in the rhizosphere or form symbiotic associations with the host plant.

The free-living microorganisms may feed on materials originally present in the soil, or supplied by plant roots, such as soluble exudates, sloughed-off parts of the root cap, root hair residues and abraded epidermal cells. Some microorganisms have the ability to solubilise otherwise insoluble P sources. In fact, almost all soils contain phosphate-solubilising microorganisms (Kucey *et al.*, 1989). Approximately one third of the organisms in the rhizosphere possess P-solubilising abilities (Sperber, 1958; Katznelson and Bose, 1959).

In spite of the large numbers of P-solubilising organisms already present in soils, the population can be further increased by inoculation. The availability of P in soils inoculated with P-solubilising organisms has shown to be increased in a number of studies. Asea *et al.* (1988), for instance, demonstrated that wheat inoculated with *Penicillium bilaji* in greenhouse conditions could take up 18% of its P from sources otherwise unavailable to plants. Kucey (1988) also obtained increased wheat dry matter yield and P uptake as a result of *P. bilaji* inoculation under field and glasshouse conditions.

Different theories about the mechanisms of enhanced P availability by P-solubilising organisms have been suggested. The traditionally-favoured view

(Katznelson and Bose, 1959) has been that the organisms solubilised inorganic forms of P by excreting organic acids to dissolve phosphatic materials directly and/or to chelate cations to release P. Others suggest that the so-called P-solubilising organisms do not release plant-available P directly through solubilisation, rather, they produce substances that can stimulate plant growth (Tinker, 1980).

As regards the role of symbiotic microorganisms, the effects of mycorrhizae on plant P uptake have been studied extensively (Kucey *et al.* 1989; Barea, 1991). Mycorrhizae are a stable symbiotic association of a plant root and a fungus. The most important group is the vesicular-arbuscular (VA) types. They are found in almost all climatic zones and soils with vegetation. Mycorrhizal infection of plant roots are influenced by soil factors such as waterlogging, temperature and, in particular, the supply of P (Tinker, 1980). Generally, increased supply of P, waterlogging and low temperatures lead to lower infection.

Mycorrhizal-infected plants usually grow better than non-infected ones. This is often due to improved efficiency of P utilisation by the infected plants (Tinker, 1980; Kucey *et al.*, 1989). In general, plants infected with mycorrhizae have higher P concentrations and P uptake than non-infected ones.

Mycorrhizae assist plant P uptake probably through a combination of several mechanisms. The suggestion that they may be able to utilise forms of P unavailable to plants is very attractive. However, a number of studies using radioactive labelling techniques have indicated that mycorrhizal and non-mycorrhizal plants basically take up P from the same sources (Sanders and Tinker, 1971; Hayman and Mosse, 1972; Asea *et al.*, 1988; Blal *et al.*, 1990). Mycorrhizae may be unable to use forms of P unavailable to plants, rather, they may utilise the available forms more efficiently. The most favoured mechanism is the extension of the P depletion zone. Mycorrhizal roots are capable of obtaining P from areas far from the root surfaces. The absorption surface area is therefore expanded. This is very important for P uptake because of its low mobility in the soil.

The benefits of mycorrhizal infection in plant P utilisation decreases as soil P concentration increases, due to the negative effect of P on the levels of mycorrhizal infection (Barea, 1991). Greater infections usually occur in low to moderate P-status soils.

IV. Fertiliser placement and P uptake

The amount of fertiliser P that may be absorbed by plants is influenced by the location of fertiliser application in the soil. In cropping systems, P fertilisers may be mixed uniformly with the soil in the plough layer (broadcasting with subsequent incorporation), or localised and mixed with a portion of the plough layer soil (banding near the row when planting). Banding usually results in higher effectiveness per unit of P applied (Engelstad and Terman, 1980), although this effect decreases with increasing soil P status and with increasing application rate (Barber, 1958, 1980). In permanent grasslands, topdressing, i.e. surface broadcasting without subsequent incorporation is usually the method used to apply fertiliser P. Studies have shown that this is a quite satisfactory method for supplying P to grasses or other crops in no-till systems (Engelstad and Terman, 1980).

The effect of fertiliser placement on P uptake is influenced by plant growth stage (Sleight *et al.*, 1984). Increasing the probability of root-fertiliser contact is very important for effective P utilisation by young plants. Fertilisers should be applied close to the seed and thoroughly mixed with the soil into which plant roots would be growing. Eghball and Sander (1989) attributed the poor performance of broadcast P in soils of low P status to the greater distance of fertiliser P from plant roots compared with banded P. This difference, however, diminishes with increasing plant age.

The nature of P fertiliser should also be taken into account. For banding application, P should be mainly in water soluble forms; for low solubility fertilisers, broadcasting is still the favoured method as it accelerates fertiliser dissolution in the soil.

V. Phosphorus returns

Varying amounts of P taken up by plants may be returned to the soil in plant litter or animal dung (Blair *et al.*, 1976). The quantity is dependent on the management practice of the system. Phosphorus may be returned to the available P pool in the soil by leaching or mineralisation of litter and dung materials, or temporarily held up by immobilisation.

In pasture systems with animal grazing, the above-ground P is redistributed and the return of P to the soil is not uniform over the field. The return is expected to be higher on campsites and decreases with increasing slopes (Gillingham *et al.*, 1980). The rate of breakdown of faecal material is influenced by climatic conditions such as rainfall and is more rapid on flat areas than on steep slopes (Rowarth *et al.*, 1985).

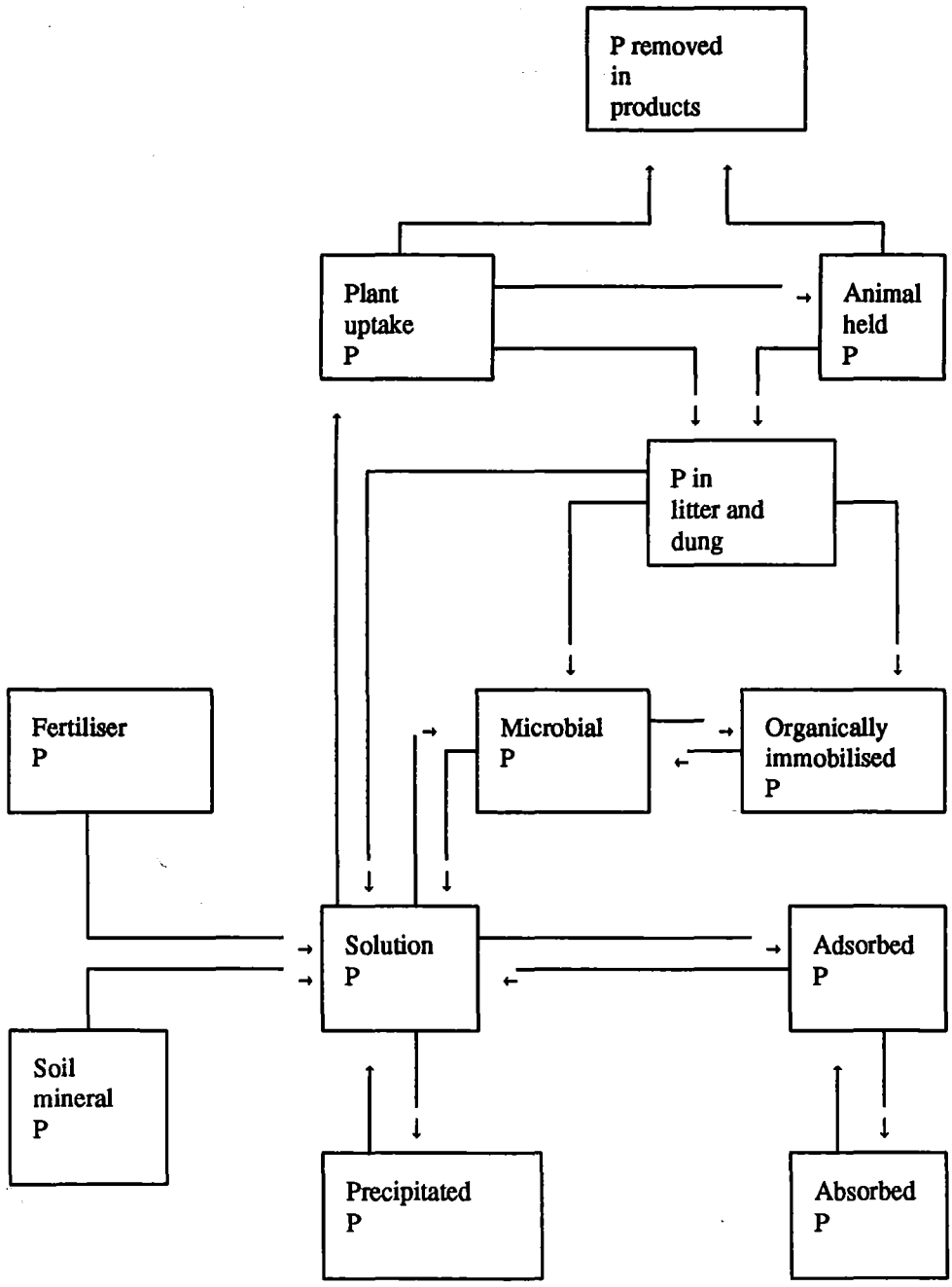
The magnitude of P losses through animal transfer is dependent on the nature of the P fertilisers applied. Studies by Mackay *et al.* (1987) in intensively grazed, steep hill country pasture in New Zealand showed that of the P uptake, the potential losses were twice to three times higher following the application of single superphosphate and triple superphosphate than following the addition of Sechura phosphate rock and Chatham Rise phosphorite. Therefore, when relatively high rates of fertiliser P are topdressed in hill country pasture, considerations should be given to the forms of fertilisers used in order to minimise losses.

2.4.6 The P cycle

In summary, the processes of P transformation in the soil-plant system may be represented by Figure 2.1.

The diagram shows that P in soil solution is in the centre of the interaction between different P pools in the soil-plant system. Phosphate dissolved into the soil solution from either native soil minerals or from added fertilisers may be quickly adsorbed onto soil surfaces, a portion of which may be transformed into firmly-held

Figure 2.1 A simplified schematic illustration of the P cycle in the soil-plant system.



forms with time, or react with soil constituents to be precipitated, especially at high concentrations, or taken up by microbes and plants to become organic P. The P taken by plants and subsequent consumption by animals may be returned to the soil in litter or dung materials; the soluble part can be leached directly into the soil solution P; the insoluble part may be decomposed by microbes to be released into soil solution or to be organically immobilised.

Most of the processes are influenced by different factors, some of which can be controlled by management practice. The purpose of management is to minimise the below-ground conversions of P to less available forms and reduce above-ground losses. One possible choice is to apply slow-dissolving P fertilisers. Discussions on the use of different forms of P fertilisers will be detailed in Sections 2.6, 2.7 and 2.8. To investigate the dissolution characteristics and agronomic effectiveness of fertilisers, it is important that appropriate methods of investigation be adopted.

2.5 Determination of plant available P in soils

2.5.1 Introduction

Soil scientists and agronomists are often confronted with the question of how much fertiliser P is required to meet plant needs. To answer this question requires determination of the concentration of plant available P in the soil. This section examines the methods often used to measure plant available P in soils.

2.5.2 Extraction methods

I. Principles

The immediate source of phosphorus for plants in the soil is largely that provided by the phosphate ions in the soil solution. However, the amount of P that may be taken up by plants is controlled by both the intensity factor (I), that is the concentration of phosphate ions in soil solution, and the quantity or capacity factor (Q), that is the amount of phosphate that can be rapidly released from the soil solid phase

(cf. Section 2.4.5). The relationship between I and Q varies between soils which differ in P sorption capacity. This relationship may be expressed as the phosphate buffering capacity (PBC) (Holford and Mattingly, 1976a, b). PBC is defined as the change in quantity of sorbed P per unit change in concentration of solution P. At equal intensity, plant P uptake is directly proportional to PBC. At equal capacity, plant uptake is inversely proportional to PBC. If soils are similar in P retention capacity, either the intensity or the capacity factor will be related to plant P uptake. If soils differ considerably in P retention capacity, both the intensity and the capacity factors need to be taken into account in assessing plant available P. Assessment of the I-Q relationship requires determination of P sorption isotherms and is not suited for routine testing purposes.

Chemical extractants have therefore been used to test available P in soils (Kamprath and Watson, 1980). The suitability of a test is usually assessed by correlating extractable P with crop growth or responses to fertiliser additions. The concentration of extractable P, above which little or no response to fertiliser, is termed as the critical level. The critical level may vary between different tests, plants and soils. A good extraction test should take into account I-Q interactions in different soils which differ considerably in P retention. As the relative importance of I and Q in supplying P to plants varies with soil PBC, a extraction test must balance the effect of increasing importance of I in soils of low PBC and the increasing importance of Q in soils of high PBC.

The commonly used soil test methods are summarised in Table 2.2. Other methods not listed in the table include the use of anion exchange resins (Amer *et al.*, 1955; Cooke and Hislop, 1963; Sibbesen, 1977; Saggar *et al.*, 1990), and filter paper strips impregnated with iron hydroxide (Menon *et al.*, 1989).

Table 2.2 Commonly used extraction methods for testing plant available P in the soil.

Soil test	Extractant	Soil: solution ratio	Shaking time	Reference
Water	Distilled water	1:10	5 minutes	Olsen and Sommers (1982)
		1:60	1 hour	Van Der Paauw (1971)
Bray I	0.03 N NH_4F + 0.025 N HCl	1:7	1 minute	Bray and Kurtz (1945)
Lactate	0.02 M Calcium lactate + 0.01 M HCl	1:50	1.5 hours	Holford *et al.* (1985)
Truog	0.001 M H_2SO_4 buffered at pH 3 with $(NH_4)_2SO_4$	1:200	30 minutes	Truog (1930)
Olsen	0.5 M $NaHCO_3$, pH 8.5	1:20	30 minutes	Olsen *et al.* (1954)
Colwell	0.5 M $NaHCO_3$, pH 8.5	1:100	16 hours	Colwell (1963)

The chemical nature of P extracted by an extractant varies between soils and depends on the mechanism of extraction. The water extraction measures the P soluble in water. It provides a measure of soil P immediately available to plants.

Extractants using dilute concentrations of strong acids (e.g. Truog P) act mainly through the solvent process of the acid, which greatly accelerate the solubility of all Ca-P compounds. They also attack Al-P and Fe-P, though at slower rates.

Bray I and lactate extractants extract P from the soil through the solvent action of acid plus the complexing mechanism of fluoride or lactate ions. Lactate ions can also replace phosphate from sorption surfaces. Fluoride ions are particularly effective in complexing soluble Ca, releasing P from the more soluble Ca-P

compounds such as $CaHPO_4$. Fluoride ions also complex Al strongly and release phosphate bound to Al compounds (Thomas and Peaslee, 1973).

Two mechanisms are probably involved in the extraction of P by bicarbonate: hydrolysis of Al and to some extent Fe cations releasing P bound by Al and Fe compounds, and precipitation of Ca as $CaCO_3$, releasing P from the more soluble Ca bound P. Bicarbonate ions, however, do not attack basic Ca-P such as hydroxyapatite, and Al-P and Fe-P covered by oxide coatings (Thomas and Peaslee, 1973).

Anion exchange resin acts like plant roots to remove P from soil solution, inducing more P to be released from soil surfaces. Resin-extractable P therefore is not just a measure of the solution P, but also takes into account soil P buffering power.

II. Applications

Kamprath and Watson (1980) reviewed a number of studies correlating the amounts of P extracted with plant yields, P uptake, or plant P concentration. In general, the Olsen and Bray I tests (Table 2.2) are the most satisfactory methods across a wide range of soil conditions, though the Bray I method might perform poorly in certain calcareous soils (Thomas and Peaslee, 1973; Holford and Crocker, 1988). The anion-exchange resin method is also generally correlated with plant response (Sibbesen, 1983), but the time and techniques required for the method have prevented its adoption to routine laboratory use. A simplified resin membrane technique has thus been advanced by Saggar *et al.* (1990). The amount of P extracted by this new technique is slightly less than, but closely correlated with, that extracted by the traditional method (Sibbesen, 1977). The water extraction method is satisfactory over a wide range of soils, but liable to seasonal fluctuations (Sorn-Srivichai *et al.*, 1988).

The relationships between soil tests and plant responses are influenced by plant species and by the type of fertilisers applied to soils. Bolland *et al.* (1988a) evaluated the predictive capacity of the Colwell, Olsen and Bray I soil tests in some

Western Australian soils which received superphosphate and rock phosphate. The three tests were equally predictive of plant yield, but separate calibrations were required for different fertilisers, different plant species and for different years. The validity of using acid-containing extractants such as that of Bray I on soils treated with PR has been questioned on the premise that the acid could dissolve some residual rock P (Chien, 1978; Cope and Evans, 1985).

The suitability of an extractant to determine soil P status also depends on soil properties. Among the more satisfactory extractants, the Bray I test is probably more suitable for moderately to highly weathered soils with low to medium CEC, but is unsuitable for soils having free $CaCO_3$, high CEC and high base saturation (Thomas and Peaslee, 1973). The Olsen test is more effective than the Bray I and other acid reagents for soils with medium to high CEC, high degrees of base saturation and the presence of considerable amounts of $CaCO_3$.

2.5.3 Isotopic dilution methods

I. Principles

The measurement of labile P (isotopically exchangeable P) using isotopes involves the equilibration of phosphate ions labelled with ^{32}P with soil and subsequently sampling the specific activity ($^{32}P/^{31}P$) in the equilibrated system.

If an aliquot containing labelled phosphate is introduced into a soil system, the labelled phosphate will exchange with and be diluted by the isotopically distinguishable, but otherwise identical form of phosphate in the soil. The ratio of the two isotopic forms (specific activity) in any sample taken from the system after equilibration will reflect the relative amounts of the two isotopes. The isotope dilution principle assumes that all the isotope label added to the system remains in isotopic equilibrium and that the final specific activity is uniform in the equilibrated exchangeable system.

The initial specific activity (SA_i) of the labelled phosphate added to the soil is defined as:

$$SA_i = q_0/m_1 \qquad (2.3)$$

where q_0 is the radioisotope activity (Bq) introduced to the system and m_1 the mass (μg) of the labelled phosphate. After the labelled P is mixed uniformly with the non-labelled exchangeable P (m_2) in the soil, its initial specific activity is diluted to SA_f:

$$SA_f = q_0/(m_1 + m_2) \qquad (2.4)$$

The amount of the isotopically exchangeable P in the soil (m_2) can be calculated from the following equation derived by combining equations 2.3 and 2.4:

$$m_2 = m_1 (SA_i/SA_f - 1) \qquad (2.5)$$

If carrier-free or high specific activity isotope is used, the mass, m_1, becomes negligible, and m_2 can be estimated from equation 2.4 as:

$$m_2 = q_0/SA_f \qquad (2.6)$$

The merits of the isotopic dilution approach are that alterations of the existing soil conditions are minimal, and that complete isolation or extraction of the compound in question is not necessary; only a portion of the system needs to be sampled and analysed.

II. Applications

The measurement of exchangeable P in soil by isotopic dilution may be achieved by shaking the soil as a suspension (distilled water or dilute carrier-phosphate solution) labelled with ^{32}P and sampling the specific activity of the solution after equilibration (McAuliffe *et al.*, 1948; Russell *et al.*, 1954; Jose and Krishnamoorthy, 1972). The exchangeable P so measured is often referred to as the "E" value. Fried (1964) defined the E value of a soil as "the amount of phosphorus on the surface of the soil and in the soil solution that is exchangeable with the orthophosphate ion added in solution, as measured in the laboratory".

Kinetic studies of the isotope exchange of phosphate between soil surface and the soil solution (McAuliffe *et al.*, 1948; Wiklander, 1950; Russell *et al.*, 1954) showed that the exchange could usually be resolved into two processes: a fast one which may be completed in a few hours and a slow one which continues over a period of many days. McAuliffe *et al.* (1948) showed that the ratio of ^{32}P on soil surfaces to ^{32}P in solution changed at first logarithmatically with respect to time and later (after 20 hours) linearly. They assumed that the readily exchangeable P of soil corresponded to that fraction of P which underwent exchange reactions for which the ratio of the ^{32}P-surface to ^{32}P-solution changed logarithmatically with time. The period of equilibration required for estimating the readily exchangeable P in soil, therefore, should be determined as that required for the completion of the logarithmatical reaction. In practice, however, the distinction between fast and slow reactions is not always obvious. The time of equilibration adopted by different workers vary greatly, from minutes to days, depending on the specific soil and suspension conditions in each experiment (Fried, 1964; Jose and Krishnamoorthy, 1972). The amount of exchangeable P measured will vary, depending on the period of isotopic equilibration.

Increasing the soil to solution ratio decreases the amount of exchangeable P estimated, although this effect diminishes with longer equilibration times. Addition of carrier-phosphate to the equilibrating solution may also affect estimation of the exchangeable P after very short periods of equilibration.

Larsen (1952) suggested that when a labelled phosphate fertiliser was added to a soil, and plants grown, the amount of exchangeable P in the soil could be estimated by sampling specific activity in the plant materials. This measurement is often regarded as the "L" value. Fried (1964) defined the L value as "the amount of phosphorus in the soil and in the soil solution that is exchangeable with orthophosphate ions added to the soil measured by a plant growing in the system". The L value concept requires the attainment of isotopic equilibrium at which the specific activity is used to derive the L value (Larsen, 1967). However, equilibrium often can not be achieved within a reasonable period of time, particularly in fertilised soils. The value calculated using specific activity before equilibrium will still provide a measure of soil exchangeable P.

Another concept often related to the isotopic dilution methods is called the "A" value (Fried and Dean, 1952). A definition of the A value was given by Fried (1964) as "the amount of available nutrient in a particular source measured in terms of a fertiliser standard and based on the assumed definition that if a plant is confronted by two sources of a nutrient, it will take up nutrient from each of these sources in direct proportion to the amounts available". It can be calculated from the following equation:

$$A = B(1 - y)/y \qquad (2.7)$$

where B is the amount of fertiliser nutrient (standard) applied, and y is the proportion of nutrient in the plant derived from the standard, which is calculated from the following formula:

$$y = SA_{plant}/SA_{fertiliser} \quad (2.8)$$

where SA_{plant} is the specific activity of plant and $SA_{fertiliser}$ is the specific activity of labelled standard nutrient. The A value can be derived by combining and rearranging equations 2.7 and 2.8:

$$A = B\ (SA_{fertiliser}/SA_{plant} - 1) \quad (2.9)$$

Equation 2.9 has exactly the same form as equation 2.5 from which the E or L values are calculated (E or L = m_2 in equation 2.5).

The use of an isotope is not an essential part of the A value concept. If a linear relationship is found between the amount of nutrient taken up by plant and the amount present in the soil, then, the amount of nutrient taken up by plant from the standard can be obtained by deducting the value for a control treatment from that obtained with added standard. It should be borne in mind, however, that such a linear relationship does not always hold.

Since the A value is essentially a measure of the amount of available nutrient in the soil compared with a standard fertiliser, its measurement is likely to be influenced by factors such as crop species, stage of plant growth, types of fertiliser, and quantity and method of application (Fried and Dean, 1952; Raju, 1988).

The objective of the A concept is to measure the availability of a soil nutrient relative to a standard fertiliser, whereas that of the E and L concepts is to determine the total quantity of readily available soil P. The ideal conditions for an A value determination require that the fertiliser and soil interaction should be minimal, whereas maximum mixing and interaction is required for the determination of E and L values.

Although both the E and the L values measure soil exchangeable P, identical values are not expected for a given soil, since the isotopic exchange occurs in two different environments. The E value is measured in soil suspension, whereas the L

value under conditions of plant growth at a soil moisture level below field capacity. Dalal and Hallsworth (1977) showed that the E values measured either by carrier-free or with carrier methods were comparable to L values in low P-fixing soils, but much higher in high P-fixing soils. They confirmed their earlier reports (Dalal and Hallsworth, 1976) that the L value gave a better estimate of available P than the E value across a wide range of soils. The L values were significantly correlated with exchangeable Ca, Mg soil pH, organic C, and oxalate and dithionite extractable Fe, all of which influence the P availability in the soils.

2.6 Water-soluble phosphate fertilisers

2.6.1 Introduction

The most commonly used water-soluble phosphate fertilisers are single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). The discussion in this section focuses on the first two for comparison with phosphate rocks and partially acidulated phosphate rocks.

Single superphosphate is manufactured by reacting sulphuric acid with rock phosphate. It is essentially a mixture of monocalcium phosphate (MCP) and gypsum. It contains about 9% P, of which about 90% is water-soluble. It also contains about 8-10% sulphur as calcium sulphate, which is an important source of S in S-deficient soils. Single superphosphate is a good source of fertiliser P for plants, but high transport costs and its low P content have led to increasing use of more concentrated fertilisers such as TSP.

Triple superphosphate is manufactured by treating rock phosphate with phosphoric acid. It contains about 20% P, of which 95-98% is water-soluble. It is essentially composed of MCP. It has a low S content.

2.6.2 Dissolution in soils

When water-soluble phosphate fertilisers are applied to soils, a sequence of reactions occur between the fertilisers and the soil constituents. The following discussion is focused on the behaviour of MCP, the major component of both SSP and TSP, in soils.

The reactions that occur in vicinity of the fertiliser granules were studied in great detail by Tennessee Valley Authority (TVA) workers and the findings were reported by Huffman (1962). The dissolution of water-soluble P fertilisers in the soil is fairly rapid even under low soil moisture conditions. The solutions formed surrounding the fertiliser granules are essentially saturated with respect to the fertiliser salts. The composition of the solution leaving the fertiliser granules is very close to that of the metastable triple-point solution (MTPS) formed by the incongruent dissolution of MCP in a pure system: it has a pH of 1-1.5 and P and Ca concentrations of 4.0-4.5 M and 1.3-1.4 M respectively (Lindsay *et al.*, 1962). The osmotic potential established between the concentrated fertiliser solution and the surrounding soil water draws water to move towards the concentrated zone, while the concentrated solution diffuses into the surrounding soil. The concentrated solution is maintained at near saturation under the processes of the inward flow of water and the outward flow of solution as long as any of the original fertiliser salt remains present (Sample *et al.*, 1980). As the fertiliser granules dissolve, a portion of the phosphate is deposited *in situ* mainly in the form of dicalcium phosphate (DCP).

When the concentrated solution leaves the granule site and moves into the surrounding soil, it dissolves Ca, Fe, Al, Mn and other soil constituents from soil minerals. The concentrations of some of these cations in the outmoving solution could be several thousand times that normally encountered in soil solutions (Huffman, 1962). As a consequence, a considerable amount of P is precipitated by these cations. The initial precipitates in alkaline or calcareous soils are most likely to be dominated by dicalcium phosphate dihydrate (DCPD). In more acid soils, in addition to the

formation of DCPD, precipitation of Fe and Al containing phosphate compounds [e.g. $H_8K(Fe, Al)_3(PO_4)_6.6H_2O$] and poorly-ordered Fe and Al phosphates also occur. These initial products are moderately available to plants. Although some of these initial precipitates may persist for considerable periods, most of the compounds are metastable and with time will convert to more stable and less soluble forms. In calcareous and neutral soils, the MCP may change along the following sequence (Lehr and Brown, 1958):

MCP → DCPD → OCP (octacalcium phosphate) → hydroxyapatite

In acid soils the initial reaction products of Fe, Al and Ca compounds are thought to change to variscite- and strengite-like crystalline compounds (Sample *et al.*, 1980). The availability of P in these products is much less than that of the initial products (Lindsay and Taylor, 1960).

Away from the fertiliser granules, as the concentrated solution moves through the soil, progressively becoming more dilute due to precipitation and contact with soil moisture, the separate-phase precipitation processes gradually diminish and are replaced by sorption processes. Sample *et al.* (1980) attempted to estimate the maximum possible contribution of sorption reactions to total P retention by soil at different distances from the fertiliser granule. For one soil, sorption could account for about 60% of total P retained at a distance of 15 mm; for another soil, less than 1% and 16% of P retained could be accounted for by sorption adjacent to the granule and at 10 mm distance, respectively.

Since considerable amounts of P from water-soluble fertilisers are precipitated or sorbed by soil components, its availability to plants is more or less dependent on the solubility of the reaction products. Although the initial products are of some value to plants, the ability of the end products to supply P to plants is very limited. It is generally believed that phosphate retained by soil through adsorption is

more available to plants than through precipitation (Rajan, 1976). Precipitation occurs mainly as a result of the high acidity and high P concentration in the solution diffusing out of the fertiliser granule (cf. Section 2.4.2). It is therefore possible to limit precipitation reactions by using low solubility fertilisers which will generate lower acidity and lower concentrations of P in the soil solution.

2.7 Phosphate rocks

2.7.1 Introduction

There has been an increasing trend in the use of phosphate rock (PR) for direct application as a source of fertiliser P. The major rationale for this practice includes: (i) the prices of the traditionally manufactured water-soluble P fertilisers such as SSP have dramatically increased, (ii) high analysis fertilisers are preferred to reduce transport and application costs per unit of fertiliser P, (iii) in some regions of the world, particularly in the tropics where plant growth is limited by a variety of environmental and edaphic conditions, the use of indigenous PR's is more economical than water-soluble fertilisers, (iv) in well-established agricultural systems where the soil P status has been raised to considerable levels, large inputs of fertiliser P are not required for agricultural production at a maintenance level, (v) a considerable amount of water-soluble fertiliser P is converted to unavailable forms when applied to soils, and this can be reduced by using slow-dissolving fertilisers, and (vi) alternative processing techniques are required, as some PR's are not suitable for the processing procedures to manufacture water-soluble fertilisers.

The suitability of a PR for direct application and its agronomic effectiveness depend both on the inherent nature of the PR and the external environmental conditions.

2.7.2 Mineralogy

Extensive discussions on PR mineralogy are given by Khasawneh and Doll (1978) and McClellan and Gremillion (1980).

PR's may be separated into three basic groups on the basis of their composition. They are, in the order of increasing economic significance, Fe-Al phosphates, Ca-Fe-Al phosphates and Ca phosphates. The most common Fe-Al phosphates are wavellite [$Al_3(PO_4)_2(OH)_3.5H_2O$], variscite ($AlPO_4.2H_2O$) and strengite ($FePO_4.2H_2O$). The major minerals in the second group include crandallite [$CaAl_3(PO_4)_2(OH)_5.H_2O$] and millisite [$(Na, K)CaAl_6(PO_4)_4(OH)_9.3H_2O$]. The PR's in these two groups are generally unsuitable for sulphuric or phosphoric acid acidulation, and can only be treated with nitric acid or by heating before application. The third group comprises the apatite minerals. They occur in all geological settings, igneous, metamorphic and sedimentary, with sedimentary apatites being the major source of commercial fertiliser phosphate.

Sedimentary apatites vary widely in their chemical composition. Extensive chemical characterisation of a large number of PR's by the TVA workers showed that isomorphous substitution is common in the basic fluorapatite [$Ca_{10}(PO_4)_6F_2$] structure. Significant amounts of Ca^{2+} are substituted for mainly by Mg^{2+} and Na^+ ions. As much as 25% of phosphate may be substituted for by carbonate and/or fluoride, and the fluoride ion may be substituted for by OH^- and Cl^- ions. Because of these substitutions, natural sedimentary apatites are represented by the following average formula (Khasawneh and Doll, 1978):

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{2+y}$$

The substitutions are generally limited to the extent that x/(6 - x) is less than or nearly equal to 0.3 and y is equal to 0.4x. The relationship between a, b and x are as follows:

$$a(Na) = 1.327x/(6 - x) \quad (2.10)$$

$$b(Mg) = 0.515x/(6 - x) \quad (2.11)$$

This series of substituted apatites are known as carbonate apatite or francolite.

The substitution of carbonate for phosphate has profound impact on the crystal structure, physical and chemical stability of the apatites. It influences the a and c dimensions of the crystal structure, reducing the crystal size and increasing the specific surface area. Phosphate rocks with considerable carbonate substitution are more reactive than those without substitution. The magnitude of the substitution may be estimated on the basis of the observed crystal a dimension by X-ray diffraction (XRD) using the following relationship (Lehr and McClellan, 1972):

$$a(XRD)\ (Å) = 9.374 - [0.204x/(6-x)] \quad (2.12)$$

PR's are often accompanied by accessory minerals which impose marked influence on the PR solubility (cf. Section 2.7.4, II). The major accessory minerals include silica, silicates, carbonates, iron and aluminium oxides and hydroxides, and evaporate minerals (McClellan and Gremillion, 1980). Considerable amounts of these accessory minerals can be removed through beneficiation processes, but substantial quantities remain in commercial PR's.

2.7.3 Dissolution in soils

I. Determination of dissolution

Extraction methods The extent of PR dissolution in soil is often determined by estimating the changes of soil P (ΔP), or Ca (ΔCa) in various extractions after a PR has been applied. The commonly used methods to follow changes of soil P include the conventional Bray I, Olsen and anion exchange resin methods (cf. Section

2.5) and a more recently developed 0.5 M NaOH extraction method (Khasawneh and Doll, 1978; Smyth and Sanchez, 1982; Hughes and Gilkes, 1984; Mackay and Syers, 1986; Mackay *et al.*, 1986; Syers and Mackay, 1986; Kanabo and Gilkes, 1987a, b; Bolan and Hedley, 1989, 1990). The changes of exchangeable Ca are usually measured by extractions using 0.5 M barium chloride ($BaCl_2$) buffered at pH 8.1 with triethanolamine (TEA) ($BaCl_2$/TEA), 1 M ammonium acetate at pH 7.0 (1 M NH_4OAc) or with 1 M KCl (Smyth and Sanchez, 1982; Hughes and Gilkes, 1984; Kanabo and Gilkes, 1987a, b; Bolan and Hedley, 1989).

The ability of these extractants to estimate PR dissolution and predict plant response is variable. Khasawneh and Doll (1978) examined studies up to the 1970's and suggest that there is generally a good relationship between plant response and Bray I extractable P from PR-treated soils. Olsen P is also correlated with plant P uptake from PR sources (Bolan and Hedley, 1990).

Mackay *et al.* (1986) suggest that any increase in the 0.5 M NaOH extractable P in a soil to which a PR is added should provide a good estimate of the amount of PR dissolved. However, acidic or inadequately buffered extractants may induce dissolution of apatite and could lead to overestimation of PR dissolution when only a small proportion of the applied PR is dissolved (Hughes and Gilkes, 1984). A study by Bolan and Hedley (1989) showed that most of the extractants currently used for determining PR dissolution in soils tend to remove varying amounts of undissolved PR during the extraction process. However, extractants, such as 0.5 M $NaHCO_3$ and 1 M NH_4OAc, although extracting certain amounts of undissolved P and Ca, still underestimate the extent of PR dissolution when the concentrations of dissolved P and Ca are high. The 0.5 M NaOH and 0.5 M $BaCl_2$/TEA extractants are better under laboratory incubation conditions. These extractants, however, might not be suitable in glasshouse or field conditions where the P and Ca from PR dissolution are removed by plant uptake or leaching. In such cases, it is more appropriate to use 1 M HCl

extraction, following the extraction with either 0.5 M NaOH or 0.5 M $BaCl_2$/TEA, to estimate the amount of undissolved PR residue (cf. Section 6.2 for further discussion).

Isotopic dilution methods The isotopic dilution principles described in Section 2.5.3 have also been employed to measure the dissolution and availability of PR fertilisers. Most of the applications involve the use of the A value concept of Fried and Dean (1952). Fried (1954) extended the A value concept and developed a technique to measure the availability of phosphate rocks by assuming that the A values are quantitative measures that can be added or subtracted. The technique uses a labelled fertiliser standard to determine the A values of the soil alone and the soil plus PR materials. Subtracting the A value of the soil alone from that of soil plus PR yield the amount of available P from the PR measured in terms of the fertiliser standard. The same technique was used by Kucey and Bole (1984) to study the dissolution of 17 PR's. The A values measured were highly correlated with dry matter yield for one soil but less so with another. The drawback of this technique is that the amount of plant available phosphate released from the dissolution of a PR varies depending on the fertiliser standard used in each experiment.

The difficulty with applying the L value concept to measure PR dissolution is that the isotopic equilibrium defined in the concept can not be attained, as the PR releases P into the soil slowly to dilute the isotopic tracer over a long period. At the same time, increasing amounts of tracer may be removed by soil retention. These simultaneous processes of input and removal to and from the exchangeable P pool may have erratic effects on the estimation of the L value.

There is a general lack of determination of the kinetics of PR dissolution and subsequent fixation by soils, particularly under the influence of growing plants. Measurements of this nature are fundamental to determining the suitability of a PR for direct application and the rate and frequency of applications to maintain satisfactory productions.

II. Dissolution mechanisms

In neutral and calcareous soils, soil P tends to precipitate out principally as hydroxyapatite and possibly to a lesser extent fluorapatite. The chances of dissolution of directly applied apatites in these soils are thus slight. In acid soils, on the other hand, the lowest free energy form of soil P is not apatite, but Al and Fe phosphates. Thus, apatite will dissociate upon contact with acidic soil, and eventually transform to increasingly stable phases of soil P.

The congruent dissolution of apatite in soil solution, using fluorapatite as an example, may be represented in general by the following formula (Hammond *et al.*, 1986):

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

Lesser amounts of Mg^{2+}, Na^+, CO_3^{2-} and OH^- will also dissociate from the apatites with isomorphous substitutions. The fluoride ion released will be precipitated by calcium. The dissolution of PR in soil solution would be favoured by low soil pH, low exchangeable Ca and solution P concentrations.

For many years, soil acidity has been considered the most important agent responsible for inducing dissolution of PR materials in soil (Peaslee *et al.*, 1962). The dissolution process of PR in soil could be regarded as a simple chemical reaction between apatite and hydrogen ions supplied by soil constituents (Kanabo and Gilkes, 1987a). It is the supply of protons which is controlled by both the soil pH and the titratable acidity of the soil that determines the extent of the PR dissolution in soils.

The concentration of exchangeable Ca in the soil is also an important factor that controls PR dissolution (Mackay and Syers, 1986; Mackay *et al.*, 1986; Robinson and Syers, 1990). Mackay and Syers (1986) showed that the extent of PR dissolution is influenced more by the concentration of exchangeable Ca than by the concentration of P in the soil. This may be related to the fact that the concentration of Ca in the soil

solution is generally several orders of magnitude higher than that of P. The use of reactive PR thus is not just restricted to soils of relatively low P status. "Reactive PR materials may have a role as a maintenance P fertiliser for soils of moderate and high P status, provided other soil factors, which also affect the dissolution and availability of P in a soil to which a PR has been added, are favourable" (Mackay and Syers, 1986).

The role of soil P-retention capacity in PR dissolution has also been studied (Chu *et al.*, 1962; Chien *et al.*, 1980; Smyth and Sanchez, 1982; Syers and Mackay, 1986). PR dissolution generally increases with an increase in P sorption capacity. The increased dissolution is probably due to the effective removal of phosphate ions from the solution. However, the increased dissolution of PR, as a result of high P-retention, does not necessarily imply increased plant available P in these soils. Smyth and Sanchez (1982) and Syers and Mackay (1986) found that Olsen, resin or Bray I extractable P in PR treated soils decreased with increasing soil P retention. This aspect will be further pursued in the next section (cf. Section 2.7.4).

The dissolution of PR in the soil is also controlled by the intrinsic nature of PR's, in particular, the degree of carbonate substitution for phosphate. Chien and Black (1976), for instance, demonstrated that the solubility product of carbonate apatites (K_{CA}) generally increased with an increase in the number of moles of carbonate per mole of apatite. The impact of PR solubility or reactivity on the agronomic performance will be examined in Section 2.7.4 along with other factors.

2.7.4 Variables affecting agronomic effectiveness

I. Introduction

Numerous glasshouse and field trials have been conducted world wide to evaluate the agronomic performance of PR's. The results, however, are somewhat equivocal. Studies on the use of PR's indigenous to the tropics were reviewed by Hammond *et al.* (1986). Both positive and negative comparisons were reported in terms of P uptake or dry matter production between unacidulated PR's and completely

water-soluble phosphate fertilisers. They suggested that finely-ground PR alone was unlikely to be as consistent as processed P fertilisers in satisfying P requirements for high levels of plant production over a wide range of soil and environmental conditions. Where favourable comparisons of PR's over SSP or TSP were obtained, the PR's used were usually the highly reactive types, or factors other than available P were limiting plant growth.

Davies (1984) summarised findings from a series of trials carried out in England and Wales, mostly on permanent grassland. Ground Gafsa rock was found to be about 50% as effective as superphosphate in the year of application, but more responsive in the following two years.

Experience in Australia was discussed by Bolland *et al.* (1988b) and Bolland and Gilkes (1990). They indicated that PR fertilisers were not effective substitutes for water-soluble fertilisers for most agricultural systems in Australia. Relative to freshly applied superphosphate, rock phosphates were found to be low in effectiveness both in the year of application and in subsequent years. This contrasts with studies in New Zealand (Syers and Gregg, 1981; Rajan *et al.*, 1987; Gregg *et al.*, 1988) which have shown that reactive PR can be effective alternatives to superphosphates for a range of acidic grassland soils. The contrasting results obtained between New Zealand and Australia are due to differences in the reactivity of the PR's used, and environmental conditions, such as soil acidity and moisture content, which affect PR dissolution in soils (Bolland and Gilkes, 1990; Bolan *et al.*, 1990a).

These reports clearly show that the agronomic effectiveness of PR's is not consistent with respect to water soluble P fertilisers. The role of a PR as a phosphate fertiliser depends on its inherent reactivity and the environmental conditions.

II. Chemical and physical nature of PR's

PR's differ in their ability to supply P to plants, not only because they differ in P content per unit weight of rock, because they have fundamental chemical and

mineralogical differences. It has been noted previously (cf. Section 2.7.3, II) that the solubility product of francolite varies with the degree of carbonate substitution in the apatite structure. Moreover, isomorphous substitution of CO_3^{2-} for PO_4^{3-} leads to smaller crystallite sizes and increases specific surface area, favouring dissolution in the soil (cf. Section 2.7.2).

Chemical extractions and XRD have been used to assess the suitability of individual PR's for direct application. Extractions have been used more widely than XRD because of the formers' simple nature. The most commonly used extractants are neutral ammonium citrate (NAC), 2% citric acid (2%CA) and 2% formic acid (2%FA). Based on the solubility in these extractants, PR's may be classified as 'reactive' or 'unreactive'. In New Zealand, the division between reactive and unreactive PR's is made at 30% of the P in the rock (as received state) being soluble in 2%CA. Amongst the PR's used in New Zealand and Australia, Sechura (from Peru), North Carolina (USA), Gafsa (Tunisia), Chatham Rise (NZ) and Arad (Israel) are the most reactive ones, whereas Nauru, Christmas Island and Duchess (Australia) PR's are the unreactive ones (Bolan *et al.*, 1990a).

The ability of extraction methods to predict the agronomic effectiveness of PR's is variable and influenced by impurity or accessory components of the rocks (Caro and Hill, 1956; Chien and Hammond, 1978; Mackay *et al.*, 1984). In general, the 2%FA, NAC (second extraction) and ammonium citrate (pH 3.0) methods are better indicators for agronomic performance of PR's than 2%CA, NAC (first extraction) and the absolute citrate solubility (ACS) methods (Chien and Hammond, 1978; Mackay *et al.*, 1984). The ACS concept was introduced by Lehr and McClellan (1972) as the ratio of citrate-soluble (NAC) P_2O_5 to the theoretical P_2O_5 content determined by XRD.

The solubility of PR's in chemical extractants is influenced by accessory minerals such as calcite, dolomite and Fe and Al compounds (Chien and Hammond, 1978; Khasawneh and Doll, 1978; Mackay *et al.*, 1984). All the potential impurity

elements could affect the solubility of PR's through mechanisms such as common ion effects, complexation, acid-base reactions and reduction (Braithwaite *et al.*, 1989). The solid to solvent, and P to solvent ratios also affect the PR solubility. Suggestions have been made to reduce the influence of accessary minerals by discarding the first extraction and analysing the second extraction (Chien and Hammond, 1978), or by adopting a sequential extraction procedure (sum of 2 to 4 extractions) (Mackay *et al.*, 1984). These methods, however, may not be suited for routine tests because of increased time and expenses.

In addition to the chemical reactivity, particle size also affects the solubility of PR's. PR dissolution and availability to plants increase with increasing fineness of grinding up to about 150 μm. Further reduction in particle size below 150 μm does not significantly improve the effectiveness (Khasawneh and Doll, 1978). The effect of particle size reduction on the performance of PR's may be governed by the net effect of increased rate and extent of PR dissolution against increased fixation of dissolved P, as a result of increased PR-soil contact. The 150 μm size division might correspond to a point at which the increase in dissolution balanced by increase in P fixation (Kanabo and Gilkes, 1988a).

The particle size effect is complicated by application rates. The improved performance of PR from fine grinding diminishes as the rate of application reaches very high levels (Hammond *et al.*, 1986; Kanabo and Gilkes, 1988a).

Fine grinding of PR gives rise to handling problems because of dustiness and material losses. Attempts have been made to granulate finely-ground PR with materials such as KCl or urea. It is generally noted, however, that granulation to considerable sizes reduces the agronomic effectiveness (Davies, 1984; Hammond *et al.*, 1986). A compromise has been sought to granulate finely-ground PR to granules big enough to stop the dust problem, but sufficiently small to avoid significant losses in effectiveness (Hammond *et al.*, 1986).

III. Soil factors

It has been established (cf. Section 2.7.3, II) that dissolution of PR in soils is favoured by high acidity, low concentrations of P and Ca and high P-retention. Bolan *et al.* (1990a) suggested that for effective performance, reactive PR's should be applied to soils with pH (H_2O) values no more than 6.0. Increased dissolution, however, does not necessarily imply improved availability to plants. Although increasing plant responses to PR's due to lower soil pH have been reported (Khasawneh and Doll, 1978; Kucey and Bole, 1984), the negative effect of excessive soil acidity on P availability and plant growth may counteract the positive value of increased PR dissolution (Kanabo and Gilkes, 1987b; Bolan and Hedley, 1990). Similarly, although PR dissolution increases with increasing soil P retention capacity, the concentration of plant available P decreases (Smyth and Sanchez, 1982; Syers and Mackay, 1986; Kanabo and Gilkes, 1987b). Both PR and superphosphates decline in effectiveness as the soil P-retention increases, but PR tends to decline more rapidly. The reduced effectiveness of PR on high P-retention soils may be related to decreased root development in the early stages of plant growth (Hammond *et al.*, 1986).

Dissolution and availability of PR may be enhanced by soil organic matter (Khasawneh and Doll, 1978). Upon hydrolysis, organic matter produces anions such as citrate or oxalate which can chelate Ca^{2+} ions to lower the Ca activity in soil solution, and this, in turn, promotes PR dissolution.

Soil texture is another factor known to affect PR dissolution. PR dissolution increases with increasing content of fine particles in the soil. This is possibly due to a combination of greater P and soil Ca sorption and greater pH buffering capacity of the fine-grained soil components (Kanabo and Gilkes, 1988b).

PR's seem to perform better under moist conditions than under dry conditions. Plant responses to PR's are more erratic in dry environments, and are expected to improve with increasing rainfall. This is because PR dissolution increases with increasing soil moisture content (Kanabo and Gilkes, 1988c). The increased

dissolution in moister soils result from enhanced transfer of the dissolved products away from the rock particles. Bolan *et al.* (1990a) suggested that reactive PR's should be mainly applied to areas with evenly distributed annual rainfall of at least 800 mm.

IV. Plant and microbial factors

Plants differ in their ability to utilise P from PR sources in the soil. For instance, PR is most available to buckwheat, more available to legumes, alfalfa, crotalaria and ladino clover than to grasses, ryegrass, millet and oats (Fried, 1953). The ability of a plant to utilise P from a PR is mainly related to the nutrient uptake pattern of the plant (Johnston and Olsen, 1972; Van Ray and Van Diest, 1979; Hedley *et al.*, 1982a, 1982b; Grinsted *et al.*, 1982; Bekele *et al.*, 1983). On an equivalence basis, imbalances in cation and anion uptake will alter the acidity of the root environment. If excess cation over anion uptake occurs (alkaline uptake pattern), for maintenance of electroneutrality, plants excrete H^+, decreasing pH in the root environment, and thus enchancing solubilisation of PR material. If excess anion over cation uptake occurs (acidic uptake pattern), OH^- is excreted by plant roots, increasing pH in the root environment. This will lessen the chances of PR dissolution. As nitrogen is the major nutrient required by non-leguminous plants, the nutrient uptake pattern may change, depending on the form of N (NO_3^- or NH_4^+) taken up.

Cereals absorb more anions than cations when N is taken up as NO_3^-. This increases pH in the root environment and reduces PR dissolution. Buckwheat has a highly alkaline uptake pattern of nutrients even when N is absorbed as NO_3^-. This exerts a strongly acidifying effect on the soil environment, thus promoting the dissolution of PR's. In addition, buckwheat has a high Ca uptake. This will bring about a shift in mass-action equilibria toward PR dissolution. Legumes, when using symbiotically-fixed N_2, have a strongly alkaline uptake pattern, thus enhancing soil acidity and PR dissolution.

An area drawing considerable attention in recent years is that of microbially-enhanced utilisation of P from PR by plants. The general mechanisms with regard to the improved power of plants to absorb P from soil as a result of microbial inoculation has been discussed previously (cf. Section 2.4.5, III). They include direct acidulation of insoluble P by organic acids produced by organisms, stimulated plant growth by microbially-derived enzymes, or the extension of plant depleting zone. All these processes tend to provide favourable conditions for PR dissolution and plant uptake. Recent studies by Salih *et al.* (1989) and Kucey and Leggett (1989) all demonstrated that inoculation of P-solubilising fungi of *Penicillium* sp. could significantly increase the availability of P in soils treated with PR's.

Microorganisms are also employed to produce a fertiliser known as "Biosuper" to assist dissolution of PR in the soil. Biosuper is prepared by granulating PR and elemental S with the bacteria *Thiobacillus* sp. (Swaby, 1975). The theory is that S in the granule would be oxidised to sulphuric acid by the organisms present and that the acid would then dissolve the rock *in situ*. Several studies (Rajan and Edge, 1980; Rajan, 1982; Pathiratna *et al.*, 1989) have shown that biosuper is an effective fertiliser for providing P to plants. The performance, however, is not consistent and is dependent on environmental conditions (Kucey *et al.*, 1989). Not only is the activity of the added bacteria sensitive to environmental conditions, but the acidulation of PR by the acid produced is also affected by soil properties. More studies need to be undertaken to characterise the conditions favourable for the agronomic performance of the PR-S-bacteria mixture fertiliser.

V. Management factors

The availability of PR to plants is influenced by the methods and rates of application and the accompanying fertilisers, particularly the form of N fertilisers. The influence of application method has been discussed in Section 2.4.5, IV. As regards the influence of application rate, the extent of PR dissolution and relative effectiveness

generally decrease with increasing application rate (Hughes and Gilkes, 1986a, b; Kanabo and Gilkes, 1987b, 1988a; Bolland and Barrow, 1988; Bolland *et al.*, 1989).

With regard to the effect of N fertiliser form on the PR dissolution and subsequent availability to plants, plant yield and P uptake from soil and from PR are increased by the application of N fertilisers in the following order (Apthorp *et al.*, 1987):

ammonium sulphate > sulphurised urea > ammonium nitrate > urea > potassium nitrate

The increase of plant P uptake is related to decreases in soil pH. The acid may be generated by nitrification or S oxidation of the fertiliser materials. An earlier study by Bekele *et al.* (1983) suggested that the effectiveness of PR may be improved by supplying N to plants as NH_4^+ rather than as NO_3^-. PR dissolution was increased by the acidifying effect resulting from the alkaline uptake pattern (uptake of NH_4^+ rather NO_3^-). It seems possible, therefore, that the efficiency of P utilisation from PR by plants can be improved by choosing the right form of N fertiliser.

2.8 Partially acidulated phosphate rocks

2.8.1 Introduction

Rather than completely acidulating PR's with mineral acids, such as sulphuric or phosphoric acid as is the case for the production of superphosphates, partially acidulated phosphate rocks (PAPR) are produced by acidulating PR's with less acid than that required for complete acidulation. The percentage acidulation refers to the proportion of acid used to prepare PAPR relative to the quantity of acid that would have been required for full acidulation of the PR. A PAPR fertiliser thus contains part of the P in water-soluble form (MCP) and part in water-insoluble forms, mainly unreacted rock. Compared with SSP, it has the merits of lower production

costs and higher P analysis, and in addition the quality of the acid and rocks used for production may be lowered (Chien and Hammond, 1988).

Alternatively, PAPR's may be prepared by mixing different proportions of superphosphates and reactive PR's. In New Zealand, the fertilisers produced by this method are referred to as SSP-RPR mixtures or "Longlife". The following discussions are based on directly acidulated PAPR's unless otherwise specified.

2.8.2 Dissolution in soils

Upon incorporation into the soil, the soluble part of a PAPR undergoes similar reactions to a superphosphate granule (cf. Section 2.6.2). However, the phosphoric acid in a PAPR granule formed from the incongruent dissolution of MCP may be dissipated on the PR residue rather than move outwards dissolving soil minerals (McLean and Wheeler, 1964). Consequently, part of the phosphoric acid would be neutralised by the PR. This not only reduces the magnitude of fixation reaction between water-soluble P and the soil components, but also results in more P to be released into the available P pool.

Mokwunye and Chien (1980) conducted an experiment on an acid soil using partially acidulated North Carolina phosphate rock (NCPAPR) and observed that the concentration of water-extractable P was higher in soils treated with NCPAPR than in those treated with superphosphate. The results suggested that the presence of PR in PAPR slowed the process of fixation of water-soluble P. Similarly, Logan and McLean (1977) found that more phosphate diffused out into the surrounding soil from 20% PAPR than from totally acidulated phosphate granules.

The occurrence of the interaction between unacidulated PR and phosphoric acid as a result of MCP hydrolysis has been noted by others (Rajan, 1985; McSweeney and Charleston, 1985; Harrison and Hedley, 1987; Junge and Werner, 1989). However, these workers suggest that the interaction is small and that its effect on the agronomic effectiveness of PAPR's may be limited. In an incubation study using 30%

PAPR labelled with ^{32}P, Harrison and Hedley (1987) noted a small increase in isotopically exchangeable P during the incubation. The increase, however, apparently ceased after 6 hours. The solution pH fell in the first 6 hours after PAPR application, but rose subsequently. The pH changes were believed to correspond to the production of phosphoric acid as a result of MCP hydrolysis and subsequent neutralisation by unreacted PR materials. They suggested, however, that the scale of the interaction was generally small and that the agronomic effectiveness of PAPR, in a short term, would mainly rely on the water-soluble fraction, while that in a long term would depend on the ability of the PR component to supply P to plants.

Dissolution of the PR fraction of PAPR in the soil follows principles similar to those discussed in a previous section (cf. Section 2.7.3, II), i.e. the rate and extent of dissolution are controlled by the PR reactivity, soil acidity, calcium and phosphate status, and other related conditions. The dissolution of the MCP fraction of PAPR following addition to the soil increases the solution concentration of P in the close proximity of the fertiliser granule. This may retard dissolution of the PR residue. However, the concentration of P in soil solution is likely to be reduced as a result of diffusion, fixation and plant uptake (Stephen and Condron, 1986).

2.8.3 Variables affecting agronomic effectiveness

I. Introduction

A number of glasshouse or field trials conducted world wide tend to suggest that PAPR's compare favourably with the superphosphates in supplying P to plants (e.g. McLean and Wheeler, 1964; McLean *et al.*, 1965; Mclean and Balam, 1967; McLean and Logan, 1970; Rajan, 1982, 1985, 1986, 1987; Rajan and Quin, 1985; Hagin, 1985; Hammond *et al.*, 1986; Chien *et al.*, 1987; Chien and Hammond, 1988, 1989; Bolan *et al.*, 1990b). Most of the studies were conducted on acidic soils with PAPR's of 20 to 50% acidulation. The effective performance of PAPR is attributed to two mechanisms: the interaction of PR residue and H_3PO_4 derived from MCP

hydrolysis, and the initial stimulation of plant growth for establishment by the water-soluble P, which encourages further exploration of P from the PR residues.

While these mechanisms may explain the performance of PAPR on acidic soils, they are inadequate to explain the comparable effectiveness of PAPR with respect to superphosphates on calcareous soils (Garbouchev, 1981; Hagin and Katz, 1985). For example, Hagin and Katz (1985) in glasshouse and field trials noted that in terms of dry matter yield and P uptake of clover, alfalfa, millet or maize, the fertilisers containing about 50% P as PR (Arad) and the rest as TSP were as good sources of P to plants as superphosphate on calcareous and slightly alkaline soils. DCP is the major reaction product of the MCP in the granules of both TSP and PAPR fertilisers incubated with calcareous soils. Bolan *et al.* (1990b) speculated that the DCP particles formed with PAPR in calcareous soils might be smaller than those formed with TSP, and the P in finer DCP particles would be more readily available to plants than in coarser particles (Kirk and Nye, 1986).

However, reports on the agronomic performance of PAPR's in the literature are not always positive. Terman *et al.* (1964), Terman and Allen (1967), Hammond *et al.* (1980) and Stephen (1985), for example, showed that PAPR's were inferior to superphosphates in plant production. Davies (1984) noted that a PAPR with 50% of its P water-soluble was only about 60-79% as effective as superphosphate in the first year, but 89-115% in the second year.

The agronomic performance of PAPR depends on a number of variables including the degree of acidulation, type of PR and acid used for acidulation and the properties of soils to which the PAPR is applied (Stephen and Condron, 1986; Bolan *et al.*, 1990b).

II. The nature and properties of PAPR's

The degree of acidulation is an important parameter that influences the agronomic effectiveness of PAPR's, particularly for PR's of relatively low reactivity

(Friesen *et al.*, 1987). It governs the ratio of water-soluble P to the insoluble P in the fertiliser, and determines the amount of P readily available to stimulate the early growth of plants. As the cost of PAPR increases with increasing degrees of acidulation, PR's should be acidulated to the lowest level that could meet a desired agronomic performance.

The quality of the PR used for acidulation, such as reactivity and impurities, also influence the concentration of water-soluble P in PAPR and its agronomic performance. This is particularly true if H_2SO_4 is used for acidulation as the soluble P is contributed solely by the PR. The reactivity of the PR will logically influence the ability of the unacidulated fraction of PAPR to supply P to plants. Moreover, PAPR's made from PR's with much free carbonate, such as Chatham Rise phosphate rock, will have less water-soluble P than a PR without much free carbonate, such as NCPR. This is because the acid is preferentially consumed by the free $CaCO_3$, resulting in an under-acidulation of the PR (Bolan *et al.*, 1990b). The water-soluble P content in PAPR's also decreases with increasing levels of Fe and Al oxides in the PR's used, and the agronomic effectiveness drops accordingly (Hammond *et al.*, 1989). This is attributed to a reversion reaction which changed the water-soluble P to citrate-soluble or even citrate-insoluble forms.

The solubility of the PR residues of PAPR are generally reduced compared with that of the original PR (Charleston *et al.*, 1989; Junge and Werner, 1989; Resseler and Werner, 1989; Bolan *et al.*, 1990b). The agronomic effectiveness of the residual PR is also lower than the original PR. This is probably caused mainly by preferential dissolution, i.e. the more soluble fraction of the PR is preferentially dissolved and a less reactive part left in the residue (Bolan *et al.*, 1990b), although formation of low solubility coatings enriched in Fe and Al or F has also been proposed (Resseler and Werner, 1989).

Acid type, and quality (if H_3PO_4 is used) also influence the concentration of soluble P in the PAPR products (Bolan *et al.*, 1990b). PAPR produced by phosphoric

acid has a higher P analysis than that of sulphuric acid for the same nominal acidulation. Commercial grade H_3PO_4, however, often contains impurities. Production of PAPR with such acid will result in reduced acidulation of the PR.

In the production of SSP-RPR mixtures, the interaction between the newly added RPR with the SSP component deserves attention. It has been observed that residual acid preferentially acidulates the added reactive PR at the expense of the less reactive PR used for the SSP production (Bolan *et al.*, 1987, 1990b). This preferential acidulation is probably due to the higher reactivity of the RPR compound than the unreactive PR. The result of this interaction is that the unreactive PR is under-acidulated and left in the fertiliser product. This is an undisirable consequence as the unreactive PR left in the mixture has a lower agronomic value than a reactive PR. The highest agronomic value occurs when the amount of unreactive PR residue in the SSP-RPR mixture is at a minimum. The amount of unreactive PR residue left in a SSP-RPR mixture depends on the type of PR used for SSP, the type of RPR and the time of RPR addition to SSP (Bolan *et al.*, 1987; Hedley *et al.*, 1988; Bolan *et al.*, 1990b).

III. Soil factors

One of the soil properties reported to affect the agronomic performance of PAPR with respect to SSP or TSP is soil P fixing capacity. In relative terms, PAPR's seem to perform well in high P retention soils with respect to superphosphates (McLean and Wheeler, 1964; McLean *et al.*, 1965; McLean and Balam, 1967; McLean and Logan, 1970; Chien and Hammond, 1989). The good performance of PAPR may be due to less sorption of phosphate from the PAPR granule by Fe and Al containing minerals than from superphosphates. In low P-retention soils, this advantage that PAPR has over superphosphates may become less obvious as P-retention is significantly reduced with both fertilisers. In addition, the increased concentration of P in soil solution due to MCP dissolution in the vicinity of PAPR granules may retard effective dissolution of PR residue. However, the relative

performance of PAPR with respect to superphosphates also depends on other factors, such as the period of soil-fertiliser contact, soil pH and P status, and the nature and property of the PAPR. A conclusion can not be drawn with regard to the relative performance of PAPR against superphosphates simply on the basis of the soil P-retention. The likely effects by the period of soil-fertiliser contact, soil pH and P status on PAPR dissolution and thus agronomic effectiveness have been speculated upon by Stephen and Condron (1986). Few studies, however, have been reported investigating the manner and magnitude of these effects.

2.9 Summary

Phosphorus is an essential element for plant growth. It occurs in a number of organic compounds which are involved in vital physiological and biochemical processes in the plant. Plants take up P from the soil mainly in the form of orthophosphate ions, $H_2PO_4^-$ and, to a lesser extent, HPO_4^{2-}.

Phosphorus occurs in both inorganic and organic forms in the soil. The inorganic phosphate compounds of calcium, aluminium and iron are generally low in solubility and their ability to supply P to plants is limited. The organic P compounds in the soil are mainly of microbial origin. They are generally of minor importance as sources of P for higher plants before decomposition. The concentration of plant-available phosphate ions in the soil solution is very low in most unfertilised soils, and fertilisation is essential for satisfactory agricultural production.

The concentration of plant-available P in the soil is governed by a combination of at least four processes: (i) precipitation-dissolution; (ii) sorption-desorption; (iii) immobilisation-decomposition and (iv) plant uptake-return.

Phosphate dissolved into the soil solution from either native soil minerals or added fertilisers may be precipitated by soil Ca, Al and Fe constituents. The stable compounds in acidic soils are Al and Fe phosphates, whereas those in alkaline soils are Ca phosphates. The plant availability of P in these compounds is drastically reduced.

Their dissolution is controlled by the solubility product principle. Precipitation of P mainly occurs at the contact of concentrated P solutions with soil constituents, such as at the vicinity of a water-soluble fertiliser granule.

Phosphate in soil solution may also be adsorbed on to soil surfaces, and subsequently absorbed by soil particles where it becomes less easily exchangeable. The phosphate ions may be sorbed by ligand exchange with the aquo or hydroxyl groups forming monodentate, bidentate or binuclear bridges with the metal ions on the surfaces. The soil components responsible for providing the sorption surfaces include iron and aluminium oxides, crystalline clay minerals, poorly-ordered minerals, calcium carbonate, and possibly organic matter. The short-range order materials are particularly powerful in retaining P from the soil solution. Sorption is the main process responsible for P retention under most soil conditions away from the water-soluble fertiliser granules.

The sorbed phosphate may be only partly reversible and the desorption processes may take place at much slower rates than the sorption processes.

The concentration of phosphate in the soil solution may be reduced by microbial fixation which converts P into organic forms temporarily unavailable to plants. The organically-immobilised P may be released back into the soil solution by mineralisation. The mineralisation processes probably result from a combination of activities of microorganisms and free enzymes.

The ability of a soil to supply P to plants is directly controlled by at least four factors. They are the intensity, capacity, kinetic and diffusion factors. The uptake of P by plants is influenced by environmental, plant, microbial and management factors.

The phosphorus taken up by plants and consumed subsequently by animals may be removed from the soil-plant system in the form of agricultural products, or returned to the soil in the forms of plant litter and animal dung. The return is usually not uniform over the field due to animal transfers. The potential losses of P is heavier

with water-soluble P fertilisers than with phosphate rocks, particularly in steep country areas.

The use of totally water-soluble Ca-phosphate fertilisers usually results in considerable fixation of P by precipitation due to the very strong acid and high concentrations of phosphate in the soil solutions surrounding the fertiliser granules. This together with the high cost of production and low analysis of SSP have led to the application of increasing amounts of slowly-soluble P fertilisers.

The dissolution of PR's in the soil is favoured by conditions of high acidity, low exchangeable Ca, low P status, high P-retention, fine soil texture and high soil moisture. The agronomic effectiveness is inconsistent compared with that of superphosphates, and is dependent on the internal reactivity of the PR and the external environment. In general, a highly reactive PR may compare favourably with superphosphates in terms of plant production if other conditions are also suitable. The effectiveness increases with increasing fine-grinding above the size of 150 μm. Plants differ in their ability to utilise P from PR sources mainly due to the differences in their nutritional patterns. Plants infected with appropriate strains of microorganisms can utilise P from PR's more efficiently than non-infected ones. The main disadvantage of the PR fertiliser is its failure to stimulate plant growth at the early stages.

The agronomic effectiveness of PAPR's generally improves compared with that of PR's. It is often comparable with that of superphosphates over a wide range of conditions. PAPR supplies a portion of P in readily-available form to stimulate early plant growth, and the rest in a form with residual value. The solubility and availability of PAPR's depend on the quality of the PR and acid used for production, degree of acidulation and environment.

The ability of chemical extraction methods to determine the concentration of plant-available P in the soil is variable. No one single reagent can be used universally for different soils and soils treated with different types of fertilisers. The ability of chemical extraction methods to determine PR dissolution in soils is limited. Acidic or

inadequately buffered reagents may induce apatite dissolution during the extraction process. Most of the single extraction methods may be inappropriate under glasshouse or field conditions where considerable amounts of P or Ca dissolved from the PR might be removed by plant uptake or leaching.

The use of isotopic tracer methods to determine plant available P in the soil is usually based on three concepts: the E, L and A values. The advantage of the isotopic dilution methods compared with chemical extractions is that the disturbance of the soil conditions is kept to a minimum. The ability of the E value to represent soil P status is limited. The determination of the amounts of plant available P dissolved from PR fertilisers has usually been based on the A value concept. The limitation of this approach is that the amount of plant available P released from a PR varies depending on the fertiliser standard employed in the experiment. The difficulty with applying the L value concept to measure PR dissolution is that the isotopic equilibrium can not be attained due to the slow PR dissolution.

There is little information on the rates of dissolution of PR-containing fertilisers in soil and the subsequent fixation by the soil under plant-growing conditions. Knowledge of this kind is particularly important for determining the suitability, rate and frequency of application, of a specific fertiliser for a soil-plant system. There is need for the development of appropriate methodologies by which to derive such information.

Part two

Assessment of an isotopic injection technique to study dissolution of phosphate fertilisers in the soil

Chapter 3

Application of an isotopic injection technique to study dissolution of phosphate fertilisers in field trials

3.1 Introduction

This part of the study assesses an isotopic dilution technique for studying the dissolution of phosphate fertilisers in undisturbed soils. Isotopic tracer solution is injected into soil cores without significantly damaging the natural soil structure and vegetation. The potential and limitations of the technique are investigated in both field and greenhouse trials. Chapter 3 describes the conduct of the field trial and discusses the results obtained.

3.2 Theory

Undisturbed soil cores, confined in metal cylinders, are labelled by an injector with 20 syringe needles (cf. Section 3.3.1). The tracer solution is distributed in 20 vertical columns within the cylinders. When a dose of carrier-free ^{32}P-orthophosphate is injected into the soil, it is mixed and diluted by the isotopically distinguishable, but otherwise identical forms of phosphate in the exchangeable P pool. The extent of this dilution, which will be greater in fertilised than in non-fertilised soil, depends on the quantity of P released from the fertiliser (Figure 3.1). As plants will take up P with a $^{32}P/^{31}P$ ratio identical to that of the readily exchangeable P pool (Larsen, 1952), the size of the exchangeable P pool can be calculated from the specific activity ($^{32}P/^{31}P$) in plant material. If the activity of carrier-free tracer initially injected into the system is q_0, and the specific activity of plant material is SA, then the quantity of the readily exchangeable P pool, Q, can be determined from the following equation:

$$Q = q_0/SA \qquad (3.1)$$

The difference in the Q values between fertilised and non-fertilised treatments may be taken as P dissolved from the fertiliser.

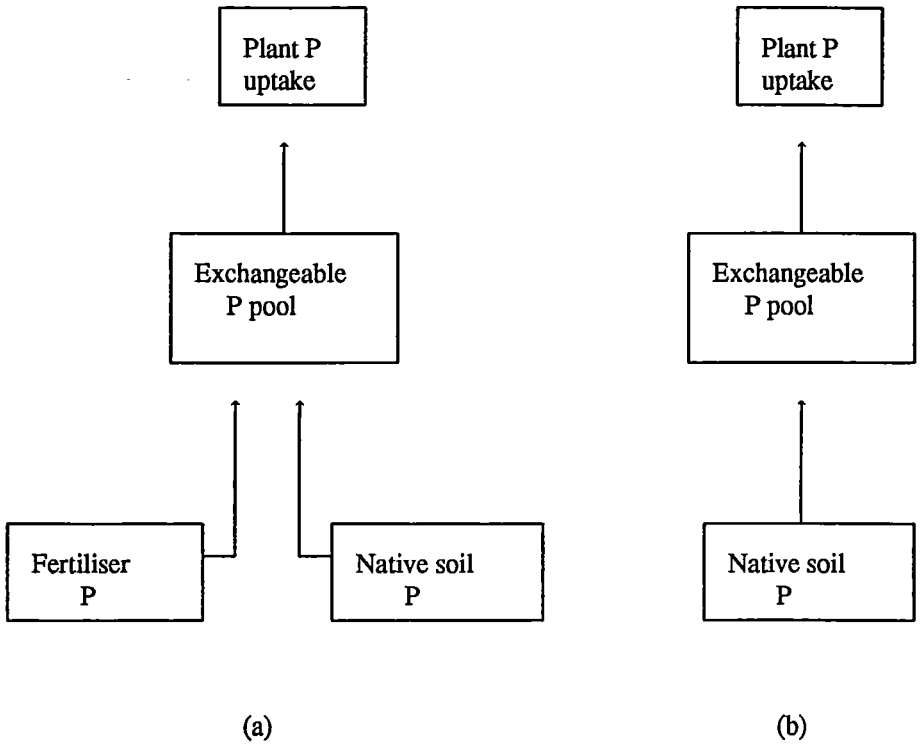


Figure 3.1 Simplified conceptual models used as the theoretical basis for the isotopic dilution experiment: (a) fertilised treatment, (b) non-fertilised treatment.

The readily exchangeable P pool (Q value in Equation 3.1) is similar to the A value (Fried and Dean, 1952) and the L value (Larsen, 1952) (cf. Section 2.5.3) in that plants are used to sample the specific activity in the soil medium. However, it differs from the A value where plant available P in soil is measured in terms of a fertiliser standard. It also differs from the L value in that the attainment of isotopic equilibrium, as defined in the L value, is not required. The results derived show that the exchangeable P pool should be calculated using the instantaneous specific activity immediately after labelling. The exchangeable P pool therefore refers to the fraction of

phosphate in soil solution and on soil surfaces that undergoes rapid exchange with ^{32}P-phosphate immediately after the introduction of the isotope tracer into the system.

Assumptions are made that the isotope label introduced into the soil remains in the exchangeable P pool and that the specific activity is uniform in the equilibrated system. However, these assumptions may not hold. Firstly, the ^{32}P label introduced in the exchangeable P pool may be converted to less rapidly exchangeable forms with increasing periods after injection. At the same time, phosphate may continue to dissolve and thus increase the exchangeable P pool. Such processes will decrease the specific activity in the soil exchangeable P pool and thus in the plants, and affect the estimation of the P pool. Secondly, since the ^{32}P label is injected into separate columns in undisturbed soil cores, it is unlikely that the specific activity will be uniform in the exchangeable P pool throughout the soil medium. It is necessary therefore to assume that plant roots essentially exploit the whole potentially exchangeable P pool, and sample ^{32}P and ^{31}P in proportion to the amounts of the two isotopes in the exchangeable P pool of the whole soil medium.

The validity of these assumptions are investigated. Variables that are related to these assumptions are examined in view of their possible effects on the specific activity in the exchangeable P pool as sampled by plants. These variables include spatial distributions of ^{32}P, soil and fertiliser P and plant root systems, and conversion of ^{32}P to less rapidly exchangeable forms.

As the objective of this study was to assess the injection technique, water-soluble fertilisers, single superphosphate (SSP) and monocalcium phosphate (MCP), instead of slowly-soluble ones were used for the experiment. This was to establish the relationship between the amount of water-soluble fertiliser P applied to soils and the amount of P released into the soil exchangeable P pool from the fertiliser, as measured by the injection technique. Upon contact with the soil, these fertilisers dissolve rapidly releasing P into the plant available P pool (Huffman, 1962; Sample *et al.*, 1980) (cf. Section 2.6.2). About 20 to 30% of the P applied might precipitate as DCP at the site

of fertiliser granules as MCP (a major component of SSP) dissolves in the soil (Lehr *et al.*, 1959; Brown and Lehr, 1959). A fraction of the dissolved phosphate might be sorbed by soil components near the fertiliser granules. The freshly sorbed phosphate would be isotopically exchangeable, with the rate of exchange decreasing with increasing period of soil-fertiliser contact (Barrow and Shaw, 1975a). The amount of exchangeable P from fertiliser dissolution is thus expected to be less than that applied, depending on the period of soil-fertiliser contact before labelling.

3.3 Materials and methods

3.3.1 Layout of the experiment

The study was carried out on a research farm of Lincoln University, New Zealand. The soil type is Templeton fine sandy loam on sand (Udic Ustochrept, coarse loamy, mixed, mesic) developed mainly on fine greywacke alluvium laid down by flood waters from overflow channels of the Waimakariri River (Cox, 1978; Di and Kemp, 1989). The soil of the surface horizon (0-150 mm) has an organic carbon content of 2.8% and an average Olsen P (Olsen *et al.*, 1954) of 21 μg P g^{-1} soil. The pH (H_2O) is 5.7 and the P retention capacity (Blakemore *et al.*, 1987) is 30%. The area has been under continuous pasture (dominantly perennial ryegrass) since 1981. The mean annual temperature and rainfall in the region are about 11 °C and 650 mm respectively (Ryan, 1987).

The experiment consisted of eight treatments, each having four replicates (Table 3.1). These were randomly allocated to 32 3m x 3m field plots. SSP (9.5% P) was applied at four different rates, 0, 30, 60 and 100 kg P ha^{-1}, while MCP was applied at 60 kg P ha^{-1}. These rates are in the range usually applied to New Zealand pastures. The fertiliser for each plot was thoroughly mixed with 1 kg of prewashed fine sand, and then evenly spread onto the soil surface by hand. An effort was made to ensure uniform distribution of the fertilisers across each plot by repeatedly spreading fractions of the mixture four times. The application was made after the existing vegetation was

mowed 10 mm above the ground and removed. Visible sheep dung material was also cleared.

Table 3.1 Treatments of the experiment designed to assess the isotopic injection technique in the field.

Treatment No.	Fertiliser applied	Application rate (kg P ha^{-1})	^{32}P injection depth (mm)
1	None	0	0-150
2	SSP	30	0-150
3	SSP	60	0-150
4	SSP	100	0-150
5	MCP	60	0-150
6	SSP	100	0-50
7	SSP	100	50-100
8	SSP	100	100-150

The ^{32}P tracer solution was injected into a small volume of soil within each plot, which was confined by a metal cylinder of 150 mm in diameter and 250 mm height. The injection was made in different depth increments, 0-50, 50-100, 100-150, and 0-150 mm to investigate possible effects that the zonal distribution of ^{32}P might have on the estimation of fertiliser dissolution.

A solution containing 2.88 MBq of ^{32}P-orthophosphate carrier-free solution was injected into each of the soil cores. This was done one week after the application of the fertilisers, and after the grass within each core was again cut 10 mm above the ground and removed.

The injection of ^{32}P solution was performed using an apparatus (Figure 3.2) containing 20 syringe needles linked to a common reservoir. The needles are evenly arranged and fixed on a metal plate of 150 mm in diameter. Holes are first made in the soil cylinder, into which ^{32}P is to be injected, by a separate set of needles fixed on a common plate in the same pattern as that of the syringe needles. The alignment of the needles when positioned on top of a soil core is controlled by a common basal support. The tracer solution is drawn into the syringe needles from the reservoir as the needles reach the bottom of the injection zone, and injected into the soil from an opening on the side of each needle tip as the needles are gradually withdrawn from the soil. The solution emerging from the opening of the needle tip is intercepted and absorbed by the surrounding soil as the needles are raised, preventing any solution from dropping to the bottom of the hole (Hedley, 1988, personal communication). The ^{32}P solution is therefore distributed in 20 vertical columns within the soil.

3.3.2 Sampling and analytical procedures

The fertilisers were applied on 15 December, 1988. The plots were sprinkle-irrigated, to about 70% of soil field capacity, weekly during the experiment. Plant samples were taken 14 and 63 days after injection of the ^{32}P tracer, by hand cutting the grass 10 mm above the ground from the area confined by the metal cylinder. The samples were dried for three days at 80 °C in an oven and then ground. Duplicate subsamples (about 0.1000 g) were digested on a heating block using nitric/perchloric acids for the determination of activity and total P concentration.

After the second cut the soil cores were removed and the field-moist soil used for analyses. The soil columns were forced out of the metal cylinders and the section with injected ^{32}P was isolated and thoroughly mixed. Duplicate subsamples were then taken for extractions by 0.5 M $NaHCO_3$ (1:20 soil:solution ratio, 30 minutes shaking; Olsen *et al.*, 1954) and 0.5 M H_2SO_4 (1:30 soil:solution ratio, 16 hours

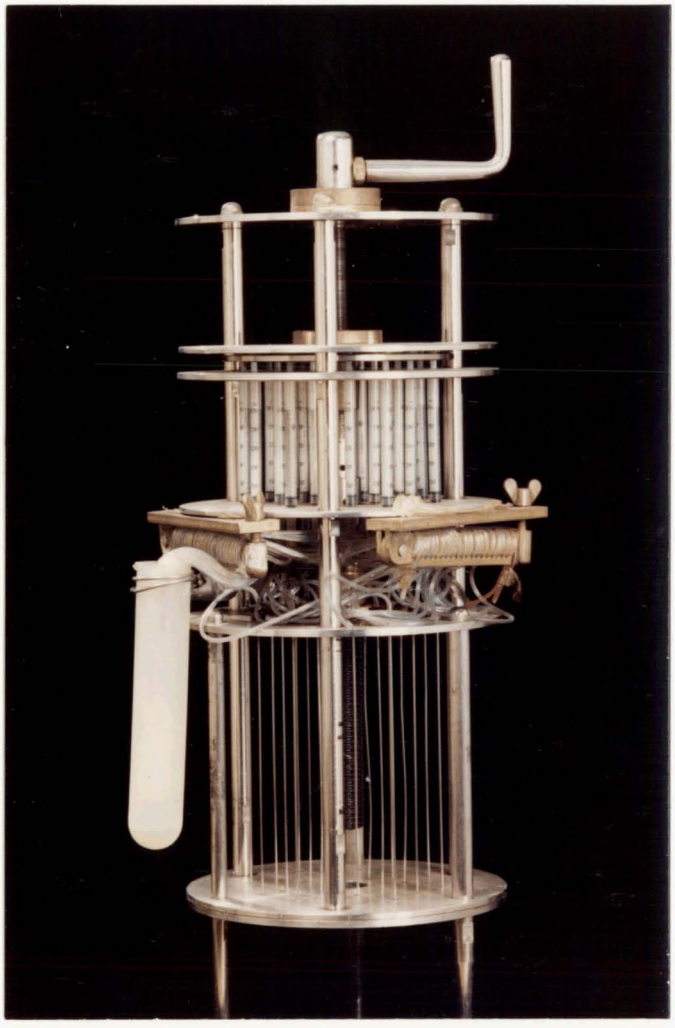


Figure 3.2 Photograph of the isotopic injector used to inject ^{32}P solution into undisturbed soil cores.

shaking; Saunders and Williams, 1955), and for digestion by perchloric acid (Olsen and Sommers, 1982), to recover the ^{32}P injected into the soil.

A 15 mL plant digest or soil extracts solution was taken in a glass scintillation vial for Cerenkov counting on a LKB 1219 RackBeta spectral liquid scintillation counter.

Cerenkov radiation consists of a continuous spectrum of wavelengths concentrated mainly in the UV region, extending to the visible part of the spectrum. Photons produced when charged particles travel through a transparent medium, result from a coherent disturbance of adjacent molecules of the medium by the travelling charged particles. Although Cerenkov radiation is not derived from the scintillation phenomenon, Cerenkov photons can be detected and counted by a conventional liquid scintillation counter when produced at a significant level. This radioassay may be carried out in water or another transparent liquid without using scintillation fluors or chemical reagents. The samples are not contaminated and may be used for subsequent chemical analyses.

The production of Cerenkov radiation requires that the energy of electrons (or beta particles) be above a threshold value, 0.263 MeV if water is the transparent medium (L'Annunziata, 1984). The energy of β^- radiation from ^{32}P is 1.71 MeV, and therefore can be conveniently adopted for Cerenkov counting.

Cerenkov counting is free of chemical quenching because Cerenkov photons arise from physical disturbance of solvent molecules rather than from chemical fluorescence which is the case for liquid scintillation phenomenon. However, colour quenching can be significant and needs to be corrected. A standard quench correction curve showing the relationship between counting efficiency and sample spectral quenching parameter (SQP) was generated using a series of standards containing the same activity (37 kBq) and incremental amounts of yellow 0.01% CrO_3 solution (Figure 3.3). The SQP (unitless) is a number which describes the features of pulse height distribution of the sample spectrum (L'Annunziata, 1984). Analysis and

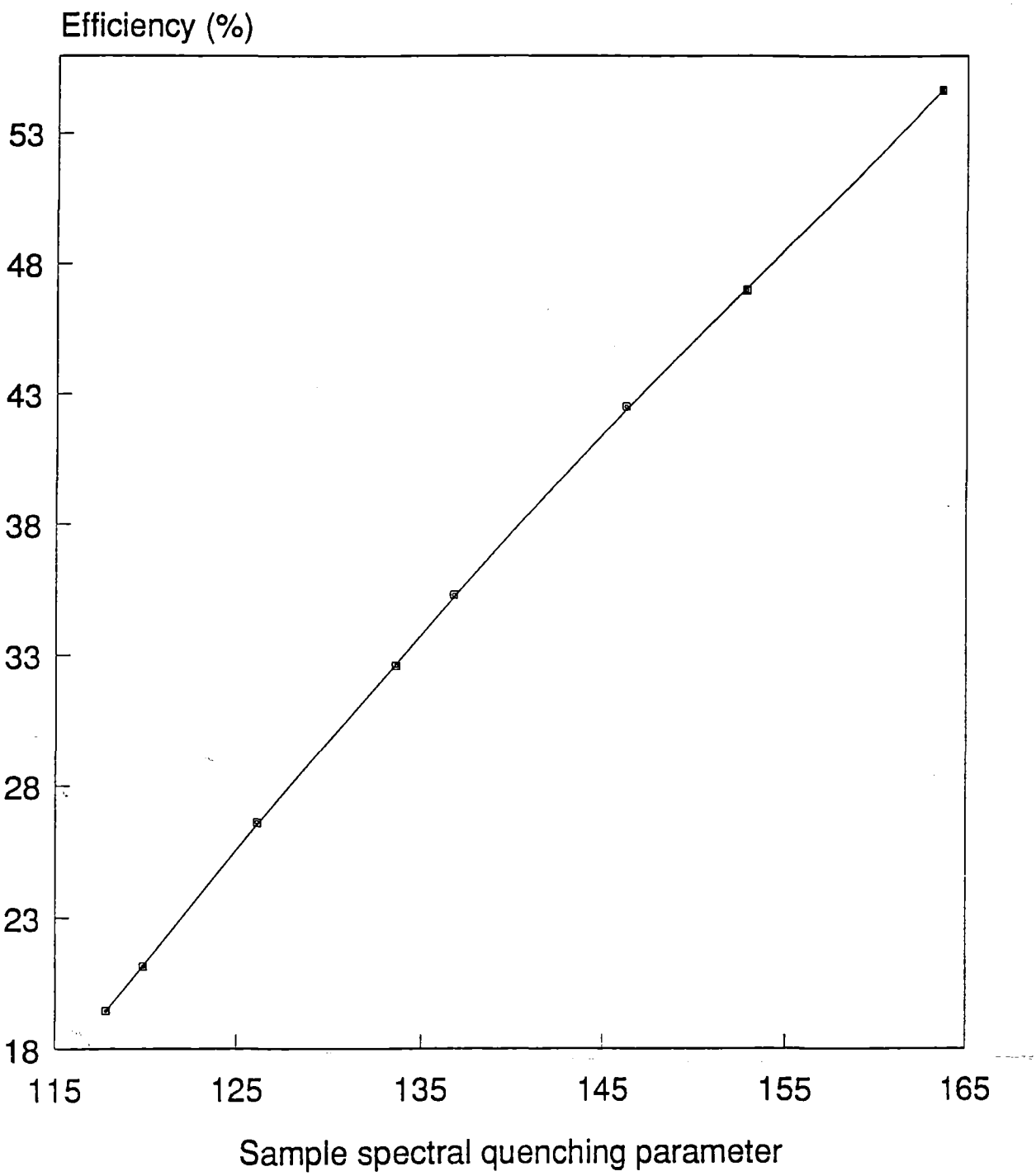


Figure 3.3 Standard curve for colour quenching correction in Cerenkov counting.

quantification of the pulse height are based on the total stored spectrum. The standard curve was generated by a smoothing spline method which fits a continuous curve through all the standard points using a third degree polynomial function. The counting efficiency of each sample was read from the relationship (Figure 3.3) according to the SQP values of each particular sample.

Each sample was counted for a period of 10 minutes. The percentage error of counting was generally less than 1%. The activity of each sample was corrected to the same zero reference time and the background value provided by a blank subtracted.

The concentration of phosphate in the plant digest and the perchloric acid soil digest was determined on an autoanalyzer using the vanadomolybdate yellow method (Olsen and Sommers, 1982) whilst that in the 0.5 M $NaHCO_3$ and 0.5 M H_2SO_4 extracts was determined using the molybdate blue method (Murphy and Riley, 1962).

3.3.3 Safety precautions

Appropriate safety precautions for use of radioactive materials were taken. The field area used for the experiment was fenced, and warning signs erected. A 6.5 mm thick Perspex glass sheet which adequately absorbs energetic beta radiation such as that from ^{32}P was used for shielding in most operations. Laboratory coat, rubber and disposable gloves were worn. Dilution of the stock radioisotope solution was done in a designated radioactive fume cupboard with Perspex shield. Grinding of plant materials was carried out in a fume cupboard and a face mask was worn in addition to the protective clothing mentioned above. Radioactive solutions, soil and plant materials contained in glass bottles or double thick-walled plastic bags were transported in sealed plastic buckets. Radioactive wastes were disposed at a designated dump for radioactive materials. Contaminated glassware and equipment were stored in a safe place until the activity decayed to insignificant levels. A film badge was constantly

worn, replaced and monitored regularly. Working areas were frequently checked using a portable Geiger-Muller counter.

3.4 Results and discussion

3.4.1 Specific activity in the plant

Plant specific activities from the two individual cuts and the two cuts bulked together are illustrated in Figure 3.4. Three features are prominent in this figure.

(i) When the same amount of ^{32}P tracer is injected to the same depths (0-150 mm in Treatments 1-5), the specific activity in the plant decreased with increasing fertiliser application rate. This decrease is due to the different degrees of dilution of the isotopic tracer by phosphate dissolved from the fertilisers.

(ii) The specific activity of the plant materials varies with the location of ^{32}P injected (Treatments 6-8). When injected closer to the surface, more ^{32}P was taken up, resulting in higher specific activities in the plants. This variation is most likely related to vertical changes in plant root density as roots in permanent grasslands are more concentrated towards the surface than lower in the profile. This also complicates changes in plant specific activity between the two cuts. When injected between 0-50 mm depths (Treatment 6), a large amount of ^{32}P was taken up immediately after injection, but when injected between 100-150 mm (Treatment 8), plant specific activity had not reached the maximum at the first cut. This was probably due to the relatively slow uptake of ^{32}P by a small population of plant roots in this deeper zone.

(iii) The specific activity dropped from the first cut (14 days after the injection of ^{32}P) to the second (63 days after the injection) when ^{32}P was injected to the same soil zones (Treatments 1-5). There are several possible reasons for this. The isotopic exchange process in soils is concerned with surfaces which may show considerable variation in the sorption energy for phosphate ions (Jose and Krishnamoorthy, 1972; Mattingly, 1975). This would result in different rates for exchange reactions. Studies by McAuliffe *et al.* (1948), Wiklander (1950) and Russell

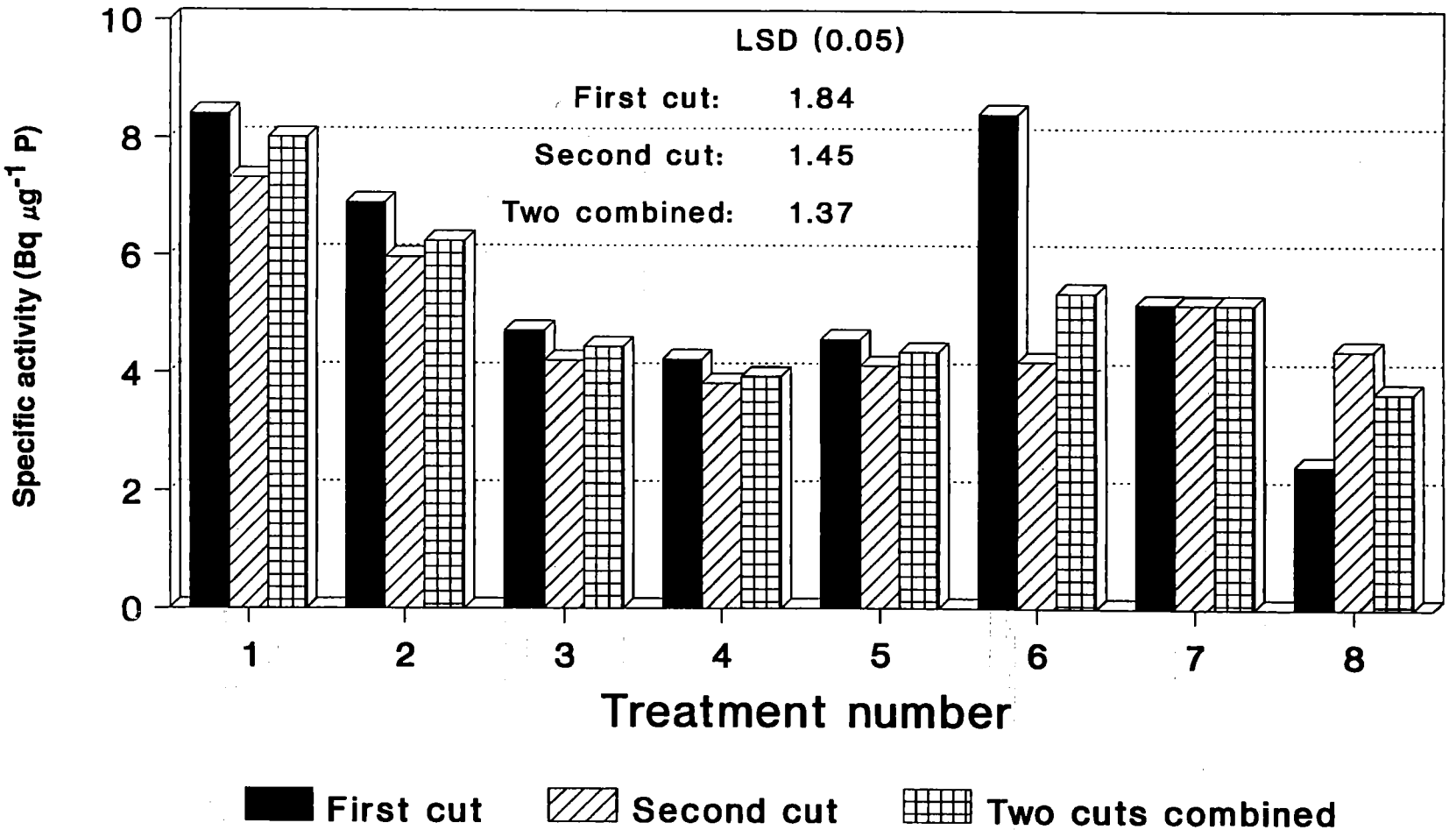


Figure 3.4 Changes of plant specific activity with rate of fertiliser application, time, and location of ^{32}P injected. The treatment numbers refer to those in Table 3.1.

et al. (1954) indicate that the exchange reaction can usually be resolved into two processes: a fast one which is completed in hours and a slow one which may require many days. Consequently, when the ^{32}P tracer was injected into the soil, it would be diluted quickly by phosphate in the soil solution and by the most readily exchangeable fraction of phosphate on the soil surfaces. This rapid process is followed by slow exchange reactions which continue to dilute the tracer and thus reduce the specific activity for prolonged periods.

In addition, continuous release of phosphate from the fertiliser granules or from soil sources (dissolution of inorganic P compounds or mineralisation of organic matter) continues to lower the specific activity in the exchangeable P pool. This reduction in specific activity is enhanced by the removal of ^{32}P as a result of soil retention and plant uptake. The removal processes (sorption, precipitation and organic immobilisation) (cf. Sections 2.4.2, 2.4.3 and 2.4.4) themselves do not influence the specific activity as ^{32}P and ^{31}P would be lost in proportion. However, they do contribute to the reduction of specific activity as continued input of newly released phosphate to the soil solution dilutes a decreasing fraction of ^{32}P initially injected into the soil. This aspect is further investigated in a greenhouse trial and detailed discussions are documented in the next chapter (cf. Section 4.3.1).

The extent of ^{32}P retention by the soil may be appreciated by examining the recovery of ^{32}P from the soil by chemical extractions (Table 3.2). Although most of the injected ^{32}P in Treatments 1-5 was recovered by the perchloric acid digestion, only a small fraction remained extractable by the 0.5 M $NaHCO_3$ solution. This indicates that the ^{32}P injected has undergone changes in the soil which reduced its extractability by $NaHCO_3$. The greater recovery in the 0.5 M H_2SO_4 extraction indicates that the tracer remained predominantly in inorganic forms. The 0.5 M H_2SO_4 extractant would also extract some ^{32}P in organic forms which were also counted by the Cerenkov counting. It was found that about 15% of the total P extracted by 0.5 M H_2SO_4 was organic P (McLaughlin *et al.*, 1988). The percentages of ^{32}P recovered by this reagent

are, therefore, slightly higher than if only inorganic ^{32}P was counted. In Treatments 6-8, where the ^{32}P tracer was injected to 0-50, 50-100 and 100-150 mm depths respectively, the lower recovery rate was believed to be due to losses of ^{32}P into neighbouring soil zones, and contamination of the samples analysed by the unlabelled neighbouring soil when the labelled soil zones were separated from the unlabelled ones.

Table 3.2 Recovery of ^{32}P from the soil by chemical extractions. The treatment numbers refer to those in Table 3.1.

Extractants	Rates of recovery (%)							
	Treatment No.							
	1	2	3	4	5	6	7	8
0.5 M $NaHCO_3$	28	29	25	27	29	18	17	15
0.5 M H_2SO_4	90	85	87	92	94	56	49	47
70% $HClO_4$	94	102	104	96	109	64	70	60

3.4.2 Readily exchangeable P pools

The readily exchangeable P pools, calculated on the basis of the plant specific activities (bulked together from the two cuts of each treatment) and the amount of ^{32}P injected, are presented in Figure 3.5.

The plant response to the fertilisers applied, as measured by the dry matter yield and total P uptake (data not presented), is not significantly different between the treatments because of the high level of plant available P already in the soil (cf. Section 3.3.1). The calculated readily exchangeable P pools for Treatments 1 to 5, however,

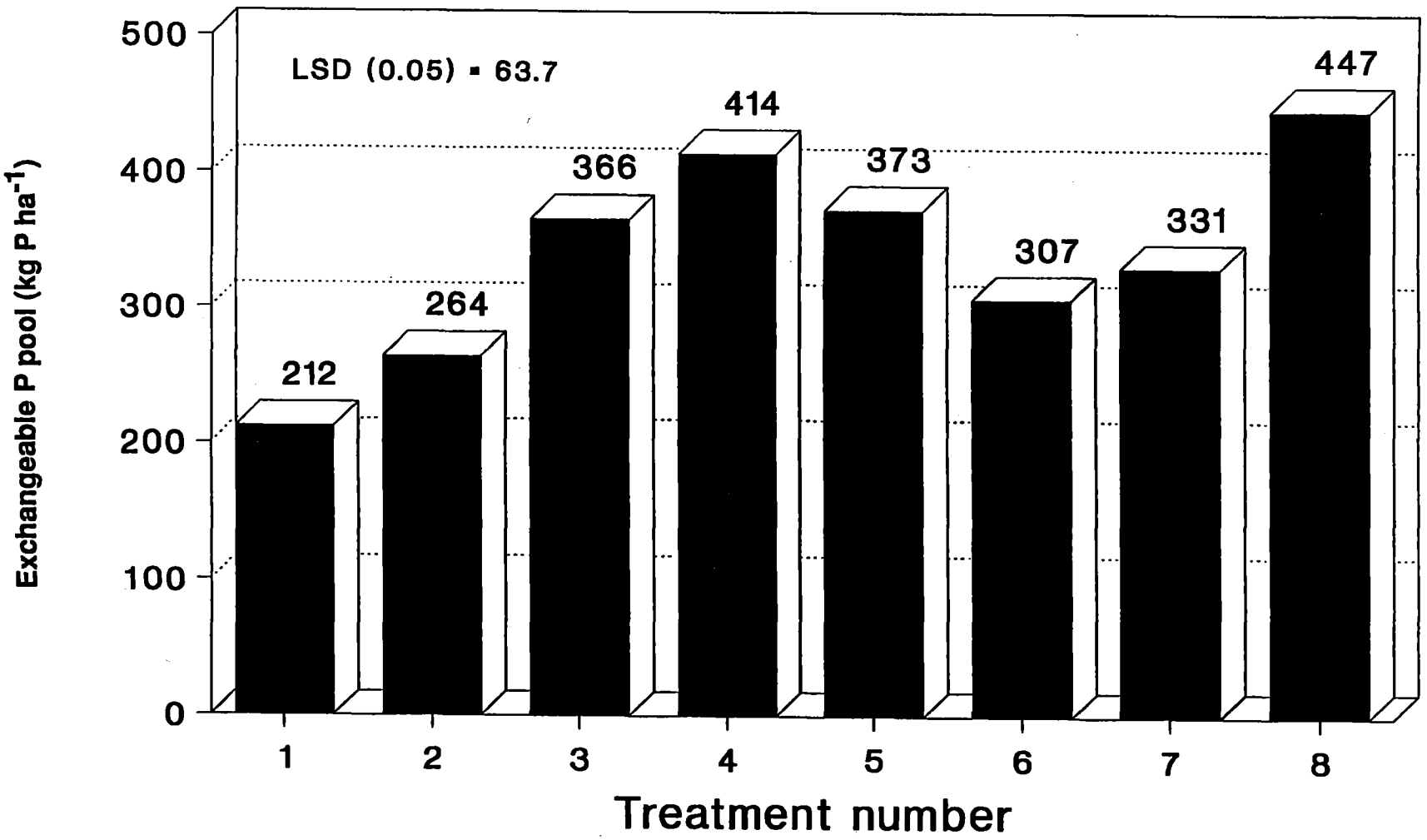


Figure 3.5 Readily exchangeable P pools calculated on the basis of the plant specific activities from the two cuts combined together and the total ^{32}P injected. The treatment numbers correspond to those in Table 3.1.

clearly differentiate the different amounts of applied fertiliser between treatments. This suggests that the application of the isotopic dilution technique to study fertiliser dissolution is not restricted to conditions of low soil P status and clear plant responses in dry matter production or total P uptake. This is particularly important as the soil phosphate status on many established farms, operating at maintenance levels, has accumulated to considerable concentrations, and plant responses to fertiliser applications may not be significant. Since the isotopic dilution principle is based on the ratio of two isotopically distinguishable but otherwise identical forms of phosphate isotopes, its use is not influenced by the absolute quantity of phosphate taken up by plants.

The difference in the size of the readily exchangeable P pool between fertilised treatments (Treatments 2-5) and the control (Treatment 1) is considerably larger than the total amounts of P applied for each treatment. A regression between the readily exchangeable P pools (REPP) and the total amounts of P applied (TPA) shows the following relationship:

$$REPP = 213 + 2.12TPA \text{ (kg P ha}^{-1}\text{)} \quad (3.2)$$

$$(R^2 = 96\%)$$

This indicates that the estimated readily exchangeable P pools contributed by the fertilisers are about twice the size of the total amounts of P applied. Thus, the amounts of P released from the fertilisers are considerably overestimated. Although the water-soluble fertilisers applied would dissolve rapidly upon contact with the soil, it is unlikely that all the soluble fertiliser phosphate would add to the exchangeable P pool immediately, as precipitation of phosphate (e.g. formation of DCP) might occur at the site of phosphate granules during hydrolysis of MCP. The amounts of phosphate released into the exchangeable P pool from fertiliser dissolution should therefore be less than, or at maximum, equal to the application rates.

This overestimation may be caused by one or more of the following mechanisms.

(i) Removal of ^{32}P tracer from the exchangeable P pool and the release of phosphate into the P pool continue to lower the specific activity causing the estimated P pools to rise. The assumption that ^{32}P tracer remains in the exchangeable P pool may not hold (cf. Sections 3.2. and 3.4.1).

(ii) Plants not only take up ^{32}P and ^{31}P from the soil zone (0-150 mm in Treatments 1-5) where the ^{32}P was injected, but also from the soil below this depth where ^{32}P was absent. This latter uptake of ^{31}P-phosphate was not accompanied by that of ^{32}P. This additional amount of ^{31}P-phosphate would further dilute the isotopic tracer in the plants, lowering the specific activity and increasing the estimated P pool.

(iii) Theoretically, both the isotopic tracer and the plant available phosphate in the soil must have an equal chance of being taken up by plants if the specific activity in the plant is to reflect the size of the plant available P pool. It is assumed that plants essentially sample the two isotopes in proportion to the amounts of the two isotopes in the exchangeable P pool of the whole soil medium (cf. Section 3.2). If the injected ^{32}P is not uniformly mixed with the phosphate in the soil, it might be disadvantaged in terms of the chances of being absorbed by the plants. Since the ^{32}P labels are distributed in 20 vertical columns, the chances of their diffusing to or being intercepted by plant roots might be smaller than phosphate distributed throughout the soil medium.

(iv) Root density declines with soil depths in permanent grasslands. Plants absorb more nutrients from soil closer to the surface than deeper in the profile. Since all the fertilisers were applied at the surface and ^{32}P injected to certain depths, plants will take up more fertiliser P located at the surface than ^{32}P at depth. The ratio of the two isotopes in plants (specific activity) is thus not proportional to the quantities of the two isotopes in the exchangeable P pool of the whole soil volume, but depends on the zonal location of ^{32}P vis-a-vis fertiliser P. Since more fertiliser was taken up than ^{32}P tracer for equal amounts of the two sources, the specific activity in plants is lower than

the ratio of the two isotopes in the soil. The exchangeable P pool estimated on the basis of this specific activity would thus be overestimated.

The values presented in Figure 3.5 are means of four replicates. Considerable variation occurs between the replicates of each treatment. The coefficient of variation (C.V.) ranges from 2% to 29%. This reflects the generally high variability in natural soils under field conditions. The fact the ^{32}P was injected into separate columns in the soil might also contribute, to some extent, to the variation, because the chances of ^{32}P in these columns being absorbed by plant roots might vary between the replicates.

3.5 Summary and conclusions

The specific activity in the exchangeable P pool, as sampled by plants, declines with time. This decline probably results from two mechanisms: (i) the slow exchange processes following the initial fast exchange reaction, and (ii) the continued release of P from the fertilisers applied or from the native sources in the soil and removal of ^{32}P (together with ^{31}P) by soil retention and plant uptake. Further investigations are required to verify these hypotheses.

The specific activity in the plants depends on the location of the ^{32}P injected. The lower in the soil profile the ^{32}P is injected, the lower the plant specific activity. This is probably due to the vertical decline of root density in the soil profile.

The size of the readily exchangeable P pools contributed by fertiliser dissolution is overestimated. The overestimation may arise from at least four possible mechanisms which tend to lower the specific activity and increase the P pools estimated:

(i) continuous release of P into the exchangeable P pool and removal of ^{32}P from the P pool;

(ii) phosphate uptake from the soil below the ^{32}P-injected soil zones;

(iii) non-uniform distribution of ^{32}P with respect to ^{31}P in the soil in terms of the chances of being taken up by plants; and

(iv) the relative zonal locations of injected ^{32}P and surface applied fertilisers with respect to a declining plant root distribution pattern.

These mechanisms, however, are speculative. The magnitude of the influence, if any, from each of the four mechanisms is unknown. More detailed studies are required under more controlled conditions with one factor being varied at a time. Results from a greenhouse trial investigating these factors are presented in Chapter 4.

Chapter 4

Application of the isotopic injection technique to study dissolution of phosphate fertilisers in greenhouse trials

4.1 Introduction

The results from the field trial (Chapter 3) indicated that the amounts of P dissolved from the fertilisers into the soil were considerably overestimated by the isotopic injection technique. This overestimation was probably due to the joint effects of at least four mechanisms: (i) temporal changes of specific activity in the readily exchangeable P pool of the soil, (ii) uptake of phosphate by plants from depths below which ^{32}P was injected, (iii) non-uniform distribution of ^{32}P with respect to ^{31}P in the soil in terms of their chances of being taken up by plants, and (iv) effects arising from the combination of surface-applied fertilisers and injected ^{32}P against the vertical decline in root density. Because results from field trials are very variable, a greenhouse trial was conducted to identify the influence of the individual mechanisms and to investigate the magnitude of the effect from each mechanism on the quantification of phosphate fertiliser dissolution. The temporal changes of specific activity in the exchangeable P pool were investigated in detail by monitoring the specific activity in the soil P pools measured by chemical extractions and in the plant. Uptake of phosphate from lower horizons was eliminated completely in the greenhouse trial by labelling the whole volume of the soil columns. The effect of the distribution of ^{32}P against ^{31}P was examined by varying the intensity of ^{32}P injection in the soil and by completely mixing the isotope tracer with the soil as an alternative to injection. The fourth mechanism was studied by using both natural soil cores with fertilisers applied at the surface and repacked soil cores with fertilisers completely mixed throughout the soil.

It was hoped that this trial would not only answer the questions raised from the field trial reported in Chapter 3, but also pave the way for the development of a technique that could be used to measure the rate of phosphate dissolution and subsequent retention by the soil.

4.2 Materials and methods

A total of 9 treatments were laid out (Table 4.1). Treatments 1-3 were set up to study the temporal changes of specific activity in the soil P pools by destructively sampling the soil cores at different intervals after labelling. Comparisons between Treatment 3 (^{32}P injected once) and Treatment 4 (^{32}P injected four times), and between Treatment 8 (^{32}P injected once) and Treatment 9 (^{32}P mixed) would indicate the effect of distribution of ^{32}P with respect to ^{31}P. Results from Treatment 3 (undisturbed soil cores with natural root structure, fertiliser applied at the surface) and Treatment 8 (repacked soil cores, fertiliser mixed with the soil) would show the influence due to the spatial distributions of fertiliser P, ^{32}P and plant root systems. The inclusion of Treatment 7 was to investigate possible effects of soil properties, particularly organic matter content, on the changes of specific activity in soil P pools, and that of Treatments 5 and 6 to measure the amounts of P released from PR-containing fertilisers.

Two soils were used in the experiment, the Tekapo fine sandy loam (Typic Dystrochrept, coarse loamy, mixed, mesic) and the Onepunga sandy loam (Typic Dystrochrept, coarse loamy, siliceous, mesic) (Tonkin, 1990, personal communication). The Tekapo soil samples were taken from the eastern hill country near Lake Coleridge of central Canterbury, South Island. The soil was developed on greywacke loess overlying coarse and stony glacial till with undulating topography. The mean annual temperature in the region is about 10 °C and the mean annual rainfall about 840 mm. The native vegetation, mainly fescue tussock, has been replaced with a

mixture of improved pastures dominated by ryegrass, and the area has been used for animal grazing.

Table 4.1 Description of the treatments for the greenhouse trial to assess the variables which influence the estimation of fertiliser dissolution in the soil by the isotopic injection technique.

Treat. No.	Soil No.	Nature of soil core	Fert. applied	Appl. location	Appl. rate (kg P ha^{-1})	Method of labelling	Number of replicates
1	I	Undisturbed	None	--	0	Inject x 1	16
2	I	Undisturbed	SSP	S	30	Inject x 1	16
3	I	Undisturbed	SSP	S	60	Inject x 1	16
4	I	Undisturbed	SSP	S	60	Inject x 4	4
5	I	Undisturbed	NCPAPR	S	60	Inject x 1	4
6	I	Undisturbed	NCPR	S	60	Inject x 1	4
7	II	Undisturbed	SSP	S	60	Inject x 1	4
8	I	Mixed	SSP	M	60	Inject x 1	4
9	I	Mixed	SSP	M	60	Mixing	4

I: Tekapo fine sandy loam.
II: Onepunga sandy loam.
S: Applied at the surface.
M: Mixed with the soil.

The Onepunga soil is situated in north Canterbury. It was developed on rolling lands from siliceous sandstones and siltstones. The mean annual temperature in the region is about 11 °C and the mean annual rainfall about 700 mm. The existing vegetation is mainly ryegrass with a mixture of other pastures and the area has been used for sheep grazing. The key properties of the two soils in the surface horizon (0-150 mm) are summarised in Table 4.2.

Table 4.2 Major properties of the two soils in the surface horizon used for the greenhouse trial to assess the isotopic injection technique to study dissolution of phosphate fertilisers.

Soil type	Organic carbon (%)	pH (H_2O)	Olsen P ($\mu g\ P\ g^{-1}$)	P-retention (%)	Exch. Ca (NH_4OAc) ($eq\ kg^{-1}$)	CEC ($eq\ kg^{-1}$)
Tekapo	4.3	5.5	10.8	30	0.053	0.15
Onepunga	3.2	5.4	7.2	19	0.013	0.088

The Tekapo soil was used for most of the treatments (Treatments 1-6 and 8-9) designed to investigate variables such as the intensity of ^{32}P injection and the distribution of ^{32}P and phosphate fertilisers in the soil.

Undisturbed cylindrical soil cores of 150 mm in diameter and 160 mm in height were used for Treatments 1 to 7. They were obtained from the field by forcing galvanised metal cylinders (165 mm long) vertically into the ground, leaving 5 mm of the cylinder protruding above the soil surface, and then digging them out. The 5 mm protrusion was designed to prevent overflow when the pots were subsequently fertilised and irrigated. Each soil core was put in a thick-walled plastic bag and placed in a shallow plastic bucket in a greenhouse. The existing vegetation (a mixture of pastures dominated by ryegrass) was cut 10 mm above the soil surface, but otherwise kept intact as the test plant.

To investigate the effect that root distribution might have on the uptake of ^{32}P and ^{31}P from the soil, the natural plant root structures were disturbed in Treatments 8 and 9. The soil samples were mixed and repacked into the metal cylinders when moist, leaving 5 mm of cylinder protrusion. After being fertilised and labelled with ^{32}P, the soils were revegetated using a method which is described below.

Three commercial phosphate fertilisers were applied in the trial, a single superphosphate (SSP), a granular (2-3 mm diameter) 30% phosphoric acid acidulated

North Carolina phosphate rock (NCPAPR) and an unground North Carolina phosphate rock (NCPR). The major properties of the three fertilisers are described in Table 4.3. The difference in the amount of sulphur contained in the fertilisers applied to different treatments was adjusted using calcium sulphate.

Table 4.3 Properties of the phosphate fertilisers applied in the greenhouse trial to assess the isotopic injection technique.

Fertiliser	Total P (%)	Water soluble P (%)	2% citric acid soluble P (%)	2% formic acid soluble P (%)	Total S (%)
SSP	9.5	8.7	9.0	9.0	12.0
NCPAPR	17.2	7.2	10.0	9.8	----
NCPR	13.2	----	4.2	7.8	----

The fertiliser application rate was calculated on an area basis and is in the range usually applied on New Zealand pastures. For the undisturbed soil cores (Treatments 1-7), the fertilisers were uniformly applied on to the soil surface by repeatedly spreading the appropriate amounts of fertilisers weighed out and mixed with fine sand. For Treatments 8 and 9, where soils were disturbed, the fertilisers were completely mixed with the soils of each individual pot. The mixing was carried out by shaking the fertilisers with the soils in plastic buckets on an end-over-end shaker for 20 minutes.

A total of 2.747 MBq of carrier-free ^{32}P-orthophosphate was introduced into each pot. In Treatments 1, 2, 3, 5, 6, 7, and 8, the radioactive solution was injected once into each individual soil core between 0 to 150 mm depths using the injector described in Chapter 3. This left 10 mm of soil at the bottom of each pot unlabelled to prevent the tracer being injected or washed down to the very bottom of the soil cores. In Treatment 4, a diluted radioactive solution was injected four times into each core by rotating the injector to a different position for each injection. This was to investigate

the effect of the intensity of ^{32}P injection (or the uniformity of ^{32}P distribution in the soil core) on the specific activity in the plants. For the same objective, the isotope solution was completely mixed with the soil in Treatment 9. The mixing was carried out by shaking the soil samples of each individual pot with the appropriate volume of isotope solution on an end-over-end shaker for 20 minutes.

Whilst the existing natural plants on the undisturbed soil cores (Treatments 1-7) were used as test plants, the repacked soil cores (Treatments 8 and 9) were revegetated using a method similar to that of Stanford and Dement (1957). This involved growing grass seedlings on Perlite, a natural volcanic glass material in a "double pot" and then transferring the seedlings on to the soil cores. The procedures involved are as follows.

A baseless plastic pot (150 mm diameter x 80 mm height), with a sheet of synthetic curtain material underneath and having a knitted mesh of about 2 mm square apertures, was placed inside another identical complete pot. Perlite material (15 g) was weighed into each double pot and about 100 ryegrass seeds applied uniformly on to the surface. The seeds were covered with 6 g of Perlite. The pot was wetted up by slowly spraying with 50 ml of P-free nutrient solution containing N (NH_4NO_3), K (KCl), Ca ($CaSO_4.2H_2O$), Mg ($MgSO_4.7H_2O$), Zn ($ZnSO_4.7H_2O$), Cu ($CuSO_4.5H_2O$), Fe ($FeSO_4.7H_2O$), Mn ($MnSO_4.4H_2O$), B (H_2BO_3) and Mo [$(NH_4)_6Mo_7.4H_2O$] (Middleton and Toxopeus, 1973), and 50 ml of distilled water, and then placed randomly in a growth chamber at 15-25 °C with 16 hours of lighting daily. The Perlite was kept moist by spraying daily with 50 ml of distilled water until seeds had germinated. Ten ml of 100 μg P ml^{-1} phosphate solution were added to each pot. The plants were grown for two weeks by adding 50 ml of P-free nutrient solution twice a week. A mat of roots emerged at the bottom of each pot at the end of the two-week period. The grass was cut above the first tiller and discarded. The double pots were separated by rotating and removing the bottom pot from the rest. The "baseless" pot containing the

Perlite and plants with the meshed sheet underneath was then placed on to the column containing soils already fertilised and labelled with ^{32}P.

This double pot method has the advantage that it essentially shortens the period of experimentation involving the use of radioactive materials, by establishing the grass seedlings before labelling the soils. The seedlings grown on the Perlite are P deficient and thus are expected to respond quickly when transferred to the soil cores. This is particularly important in experiments involving the use of ^{32}P which has a relatively short half-life of only 14.3 days.

Treatments 1 to 3 had 16 replicates, four of which were for plant sampling and the rest for destructive sampling for soil analyses. The other treatments were all replicated four times. The pots were placed in the greenhouse in a completely random manner.

The soil moisture was adjusted to about 70% field capacity weekly and each pot received 50 ml of P-free nutrient solution fortnightly (Middleton and Toxopeus, 1973). Plants were cut 10 mm above the soil surface at two weekly intervals. The samples were dried in an oven at 80 °C for three days before being ground. Duplicate subsamples of about 0.1000 g were digested on a heating block by nitric/perchloric acids for radioassay and determination of total P.

Soil samples from Treatments 1 to 3 were taken by destructively sampling 3 pots from each treatment at 3 days and subsequently at two weekly intervals after labelling. The soil from each pot was thoroughly mixed while still moist and duplicate subsamples were then taken for extractions by water (Olsen and Sommers, 1982), 0.03 M NH_4F + 0.025 M HCl (Bray and Kurtz, 1945), 0.5 M $NaHCO_3$ (Olsen *et al.*, 1954), and 0.5 M H_2SO_4 (for both non-ignited soils and for soils ignited for 60 minutes at 550 °C) (Saunders and Williams, 1955). The Bray and Kurtz test is usually referred to as the Bray I P test and the 0.5 M $NaHCO_3$ as the Olsen P test. The differences in the 0.5 M H_2SO_4 extractable P between the ignited and non-ignited samples indicate the

amount of total organic P. The extractions were made at 20 °C. Other conditions under which the extractions were made are described in Table 4.4.

Table 4.4 Conditions for the extraction of soil samples.

Soil test	Soil:solution ratio	Shaking time
water	1:10	5 minutes
Bray I	3:20	1 minute
Olsen	1:20	30 minutes
0.5 M H_2SO_4	1:30	16 hours

The solution and the soil residue were separated by centrifugation at 10,000 rpm for 10 minutes on a Sorvall RC-5B centrifuge using a SS-34 Rotor. Radioassay of ^{32}P in the solutions was performed using the method of Cerenkov counting described in Chapter 3. The concentration of P in the plant digest was determined on an autoanalyzer by the vanadomolybdate yellow method (Olsen and Sommers, 1982) whilst that in the other soil extracts by the molybdate blue method (Murphy and Riley, 1962).

Similar safety precautions to those described in Chapter 3 were observed in all operations involving the use of radioactive ^{32}P materials in this experiment.

4.3 Results and discussion

4.3.1 Changes of specific activity in soil P pools

The changes of specific activity in the water, Bray I, Olsen, 0.5 M H_2SO_4 extractable and organic P pools are shown in Figure 4.1. The water extractable P measures the concentration of P in the soil solution, the immediate source for plant uptake; the Bray I and Olsen extractable P pools estimate the immediate phosphate

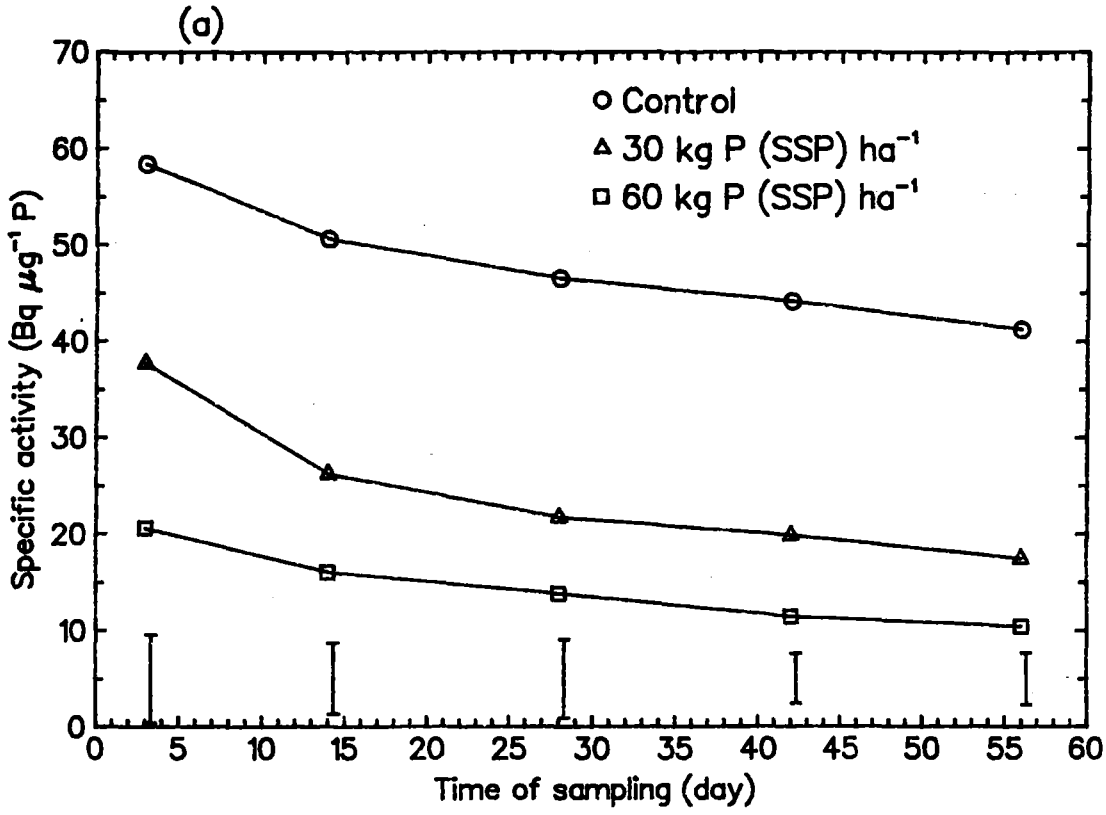
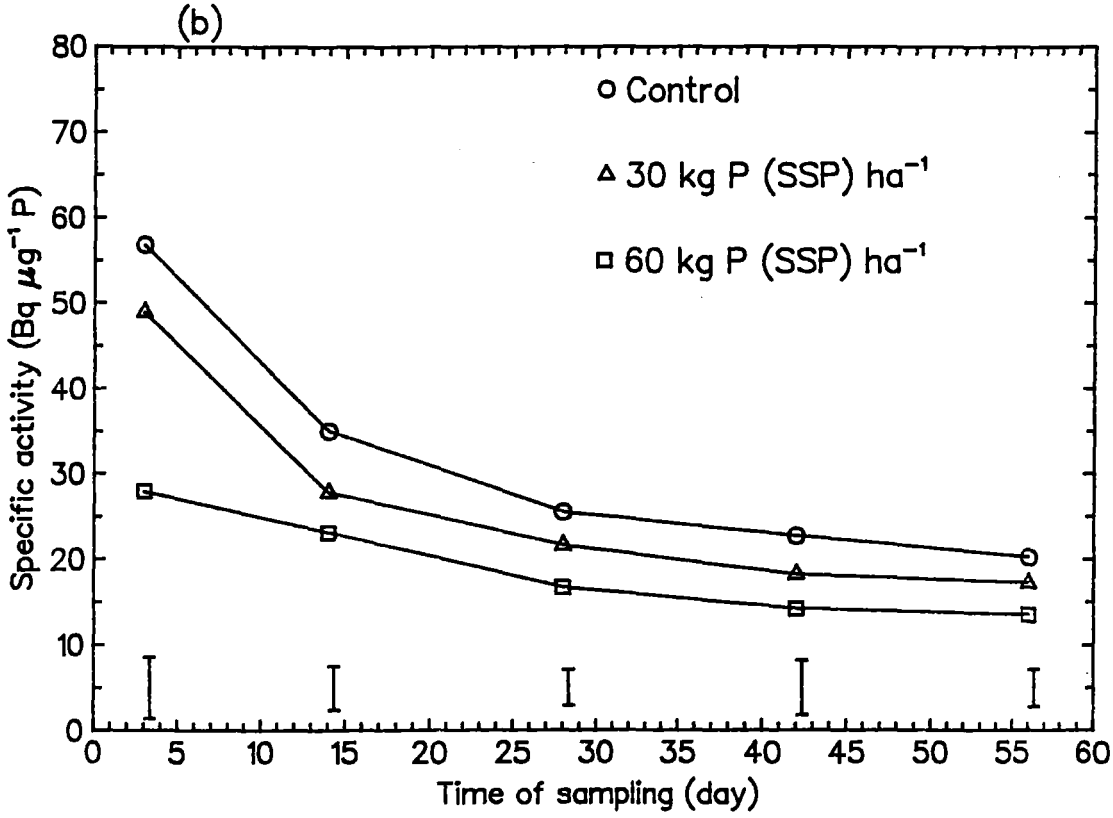
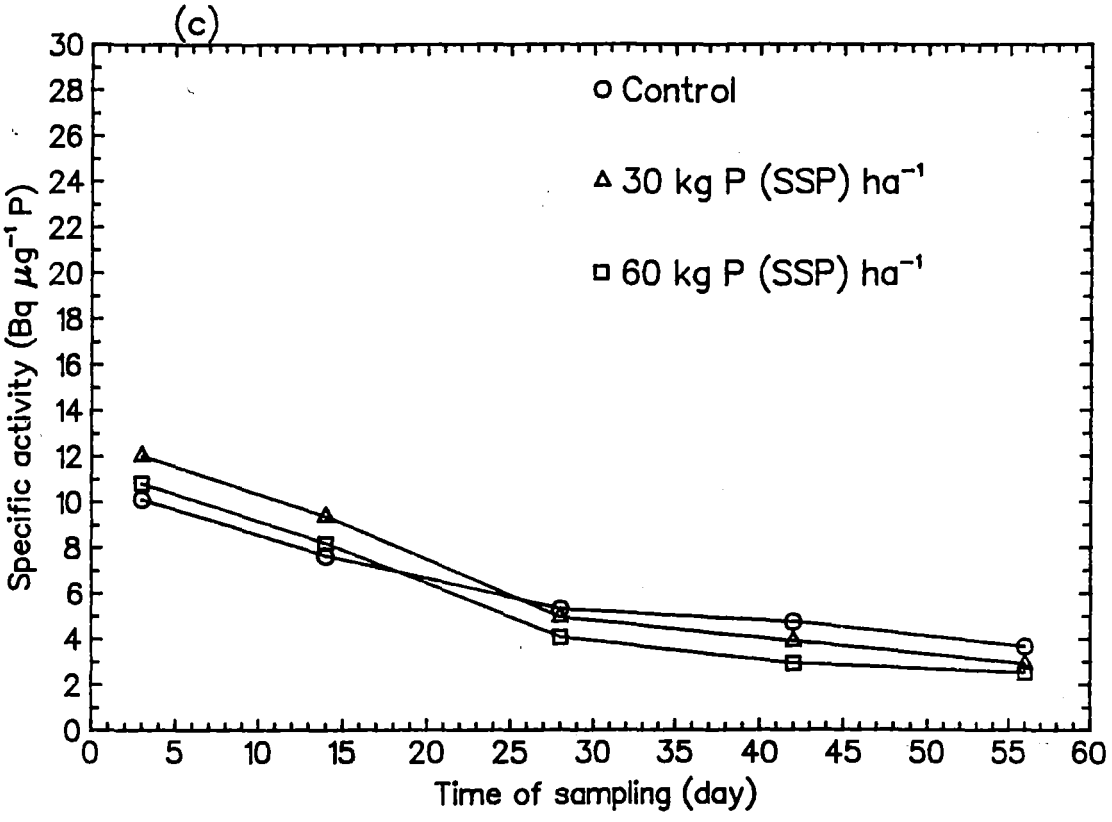
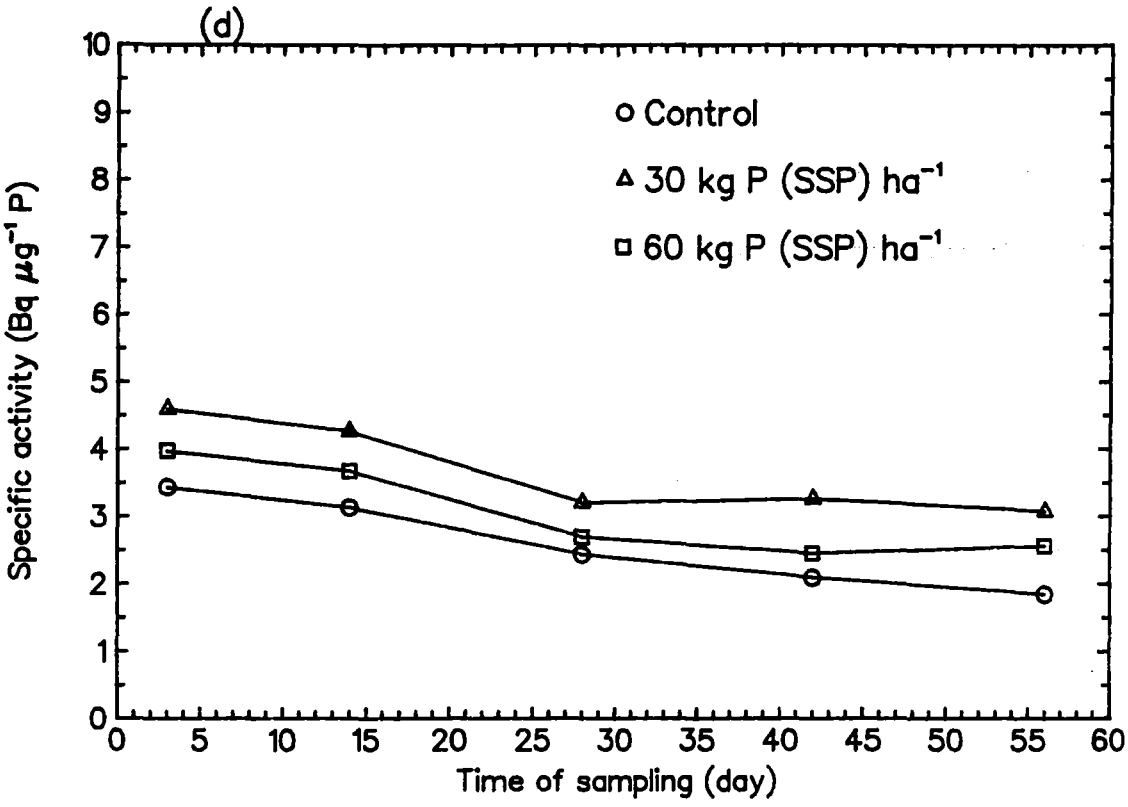
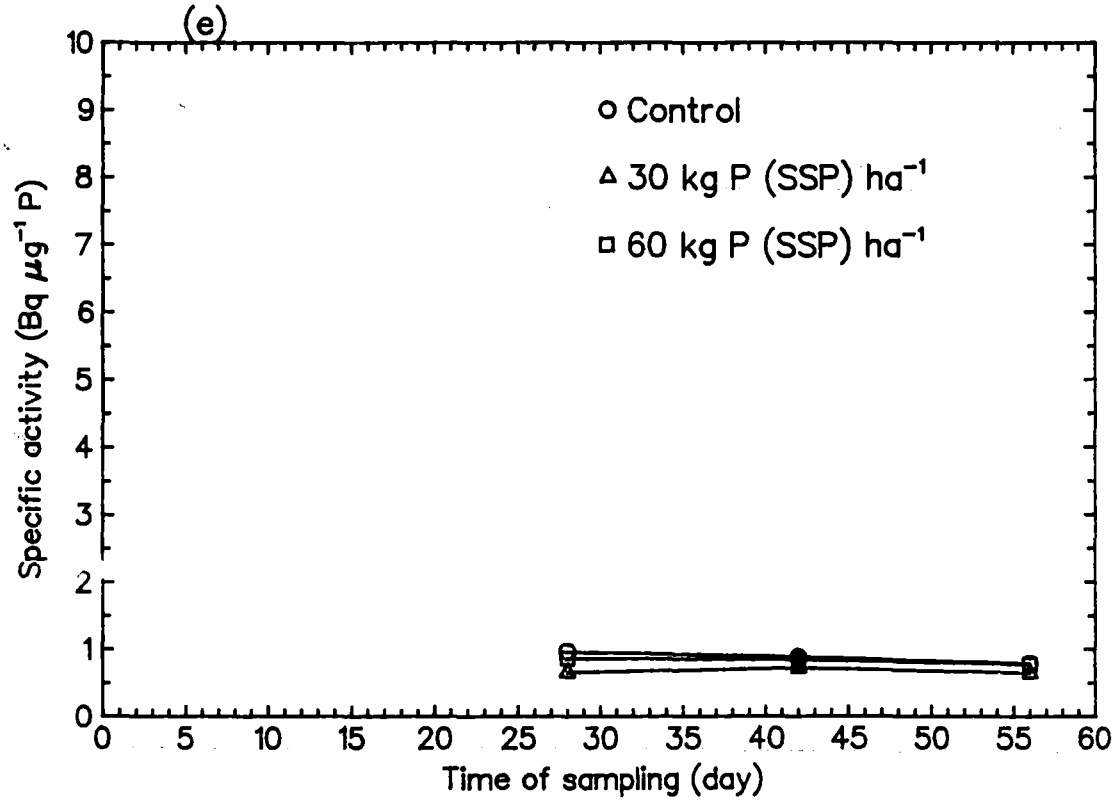


Figure 4.1 Changes of specific activity with time in (a) water extractable P pool, (b) Bray I P pool, (c) Olsen P pool, (d) inorganic P pool (0.5 M H_2SO_4), and (e) organic P pool. The vertical bars indicate LSD (0.05) where significant differences occur.


(b)
Control
30 kg P (SSP) ha^{-1}
60 kg P (SSP) ha^{-1}
Specific activity (Bq μg^{-1} P)
Time of sampling (day)
0
10
20
30
40
50
60
70
80
0
5
10
15
20
25
30
35
40
45
50
55
60


(c)
Control
30 kg P (SSP) ha^{-1}
60 kg P (SSP) ha^{-1}
Specific activity (Bq μg^{-1} P)
Time of sampling (day)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0
5
10
15
20
25
30
35
40
45
50
55
60


(d)
Control
30 kg P (SSP) ha^{-1}
60 kg P (SSP) ha^{-1}
Specific activity (Bq μg^{-1} P)
Time of sampling (day)
0
1
2
3
4
5
6
7
8
9
10
0
5
10
15
20
25
30
35
40
45
50
55
60


(e)
Control
30 kg P (SSP) ha^{-1}
60 kg P (SSP) ha^{-1}
Specific activity (Bq μg^{-1} P)
Time of sampling (day)
0
1
2
3
4
5
6
7
8
9
10
0
5
10
15
20
25
30
35
40
45
50
55
60

reserves, i.e. the amount of phosphate that can be readily released from the soil solid phase to soil solution (cf. Sections 2.4.5 and 2.5). Although the nature and size of these P pools are not exactly the same as the isotopically measured rapidly exchangeable P pool, the general trend of specific activity measured in these extractable P pools may be related to or indicative of that in the rapidly exchangeable P pool. The following discussions, therefore, are conducted in general terms, assuming that the temporal trend of specific activity in the rapidly exchangeable P pool is analogous to that revealed by the three soil analyses. Mechanisms responsible for the changes of specific activity in the exchangeable P pool (rather than in the individual extractable P pools) are proposed.

The specific activity in the exchangeable P pool, as indicated by that in the water, Bray I and Olsen extractable P pools (Figures 4.1 a, b and c), decreased with time after labelling. The decline is probably due to the following processes: (i) the release of phosphate into the exchangeable P pool, (ii) prolonged exchange of ^{32}P into less rapidly exchangeable sites, and (iii) removal of ^{32}P from the exchangeable P pool.

Dissolution of phosphate fertilisers will be a major process releasing P into the exchangeable P pool. The rate of release is dependent on the solubility and quantity of the fertilisers applied. Although SSP is expected to dissolve rapidly upon contact with the soil, reducing the specific activity immediately after labelling, some P would continue to be released from fertiliser residues and reaction products (e.g. DCP) formed during hydrolysis of the fertiliser (Huffman, 1962) (cf. Section 2.6.2).

Other processes that release phosphate into the exchangeable P pool include mineralisation of organic P (cf. Section 2.4.4) and desorption of sorbed P (cf. Section 2.4.3, IV). The rate and amount of P released through mineralisation can not be calculated from these results. With respect to desorption, as the concentration of P in the soil solution was lowered by plant uptake, phosphate held at less exchangeable sites might be drawn into the rapidly exchangeable P pool. The extent of this process depends on the concentration of P in the soil solution and the amount of P taken up by

plants. It was unlikely to have occurred to any significant extent in the fertilised treatments, as the high concentration of P in the soil solution would favour sorption rather than desorption. It might occur, however, in the unfertilised control treatment.

Isotopic exchange involves the displacement of phosphate ions on soil surfaces by ^{32}P-phosphate ions. As phosphate sorbed on to soil surfaces varies in bonding energy, the rate of isotope exchange might also be expected to vary (Jose and Krishnamoorthy, 1972). Upon labelling the soils, the ^{32}P tracer will equilibrate first with the most rapidly exchangeable fractions of P in the soil, a fast process that would be completed in hours, and then with the less rapidly exchangeable fractions, a slow process that might last for many days (McAuliffe *et al.*, 1948; Wiklander, 1950; Russell *et al.*, 1954). The effect of this prolonged exchange process is to reduce the specific activity in the exchangeable P pool.

In addition it is necessary to consider losses of ^{32}P from the exchangeable P pool. Processes that remove ^{32}P from the exchangeable P pool include sorption and precipitation, organic immobilisation and plant uptake. These processes, by themselves, do not reduce the specific activity in the exchangeable P pool, as ^{32}P and ^{31}P are removed together in proportion. They do however interact with the release of phosphate into the exchangeable P pool and the on-going exchange of ^{32}P into the less rapidly exchangeable sites, to reduce the specific activity below that which would pertain in the absence of such losses of ^{32}P from the exchangeable P pool. Thus, newly-released P, from either fertiliser dissolution or mineralisation, would dilute decreasing amounts of ^{32}P left in the exchangeable P pool, reducing the specific activity below that for systems where ^{32}P remained entirely in the exchangeable P pool.

Of these processes, sorption is probably the dominant one accounting for a major part of the ^{31}P and ^{32}P retained by the soil (Sample *et al.*, 1980; Syers and Iskander, 1981). Phosphate is sorbed on to the surfaces of soil components, such as iron and aluminium oxides, crystalline clay minerals and poorly-ordered minerals, replacing mainly the aquo or hydroxyl groups (Parfitt, 1978) (cf. Section 2.4.3). Like

isotopic exchange, the sorption process follows two steps, a fast step which is essentially completed in a few hours, and a subsequent slow process which may continue for many days. The slow sorption process may result as more loosely bound P on soil surfaces becomes more tightly bound. The mechanisms proposed include the change of sorbed P from a monodentate to a bidentate form, the diffusive penetration of P sorbed on the surface into soil particles and the precipitation of discrete phosphates (cf. Section 2.4.3). With increasing periods of soil-fertiliser-^{32}P contact, increasing amounts of ^{32}P and phosphate are therefore transformed to less rapidly exchangeable forms. The measurement of specific activity began three days after labelling. Recorded changes of specific activity in the exchangeable P pool, contributed by removals of ^{32}P and ^{31}P by sorption, would be dominated by the second slow process, as the fast steps would have been completed before the first samples were taken. Removal of ^{32}P and ^{31}P from the exchangeable P pool by precipitation would occur mainly in the fertilised treatments where the concentration of P in the soil solution was raised (Sample *et al.*, 1980) (cf. Section 2.6.2). It was unlikely to have occurred to any significant extent in the unfertilised control where the P concentration in the soil solution remained low. The removal of ^{32}P and ^{31}P through organic immobilisation may be appreciated by examining the changes of specific activity in the inorganic (0.5 $\underline{M}$ H_2SO_4 extractable P) and organic P pools. Figures 4.1 d and e suggest that the specific activity did not change significantly in the two P pools during the periods that the measurements were made. This agrees with findings by Friesen and Blair (1988) and McLaughlin *et al.* (1988) who also demonstrated that the amount of tracer incorporated into the organic forms reached relatively stable levels shortly after labelling. The transformation of ^{32}P from inorganic to organic forms, therefore, occurred at the very beginning of the experiment, perhaps within hours of labelling. The temporal changes of this process were not recorded as measurement in the inorganic and organic P pools did not begin until 3 and 28 days respectively after labelling. The rapid incorporation of the tracer from inorganic to organic forms may

be due to sorption of ^{32}P by organic compounds and/or through microbial immobilisation (Friesen and Blair, 1988).

The changes of specific activity in the exchangeable P pool are therefore governed by the inputs of phosphate to the P pool and removals of ^{32}P from the P pool. Fertiliser dissolution is likely to be the dominant process releasing P into the exchangeable P pool, and soil retention the major process responsible for the removal of ^{32}P and phosphate from the P pool. The continuing slow isotopic exchange process complicates the picture somewhat, since the effect is to slowly increase the size of the exchangeable P pool in a different manner to that of the other inputs. Estimation of fertiliser dissolution and retention (Chapter 5) requires that the exchangeable P pool only be influenced by these processes, i.e. all inputs to the exchangeable P pool should be of ^{31}P only, and all outputs should be of ^{31}P and ^{32}P in the ratio of the specific activity. However, it is possible to consider the slow isotopic exchange process in these terms. This process can be thought of as the result of a retention process involving ^{31}P and ^{32}P in the ratio of the specific activity, together with a compensating input of ^{31}P alone. Thus the rates of inputs and outputs may be estimated by monitoring the temporal changes of specific activity and the sizes of the exchangeable P pools. These rates would reflect the rates of fertiliser dissolution and subsequent retention by the soil with an addition component representing the slow isotopic exchange process. This forms the basis for the development of a technique to study the rates of phosphate dissolution and retention in the soil. The theory and applications of the technique are detailed in Chapter 5.

The specific activity in the water extractable P pool (Figure 4.1 a) and Bray I extractable P pool (Figure 4.1 b) was significantly reduced by the addition of the phosphate fertiliser. The difference in the Olsen extractable P pool between the three treatments (Figure 4.1 c), however, was not obvious. In addition, the specific activity generally decreases from the water to Bray I and to Olsen P pools. These variations may be related to the nature of the extractants and the period of the extraction. Firstly,

the three extractants may preferentially extract phosphate associated with different soil constituents (Thomas and Peaslee, 1973) (cf. Section 2.5.2). Water is a very mild extractant and extracts the very labile fraction of phosphate in the soil. The Bray I reagent (0.03 M NH_4F + 0.025 M HCl) is a stronger extractant than water, and is probably more effective in extracting the more soluble Ca and Al phosphates. The Olsen reagent (0.5 M $NaHCO_3$) is effective in hydrolysing Al, and to some extent, Fe cations, releasing phosphate bound by Al and possibly Fe compounds. More importantly, unlike the water and Bray I extractions which require only 5 minutes and 1 minute shaking respectively, the Olsen P extraction requires 30 minutes of shaking. New sorption surfaces may be created and resorption (or redistribution) of ^{32}P and ^{31}P may take place during the relatively long extraction. This is probably the main reason for the irregular patterns of the specific activity values in the Olsen P pools between the three treatments.

4.3.2 Changes of specific activity in the plant

Figure 4.2 illustrates the changes of specific activity in the plant materials with increasing periods of plant growth. A general pattern that may be abstracted from these curves is that the specific activity in the plants increased first, then remained relatively constant before starting to decrease. This contrasts with the changing patterns of specific activity in the soil exchangeable P pools which declined continuously with time after labelling (cf. Figure 4.1).

The increase-plateau-decrease pattern of specific activity in the plant compared to the decline in the soil exchangeable P pool is mainly due to the influence of the original plant P content (Figure 4.3). Curve (a) in Figure 4.3 was generated on the basis of the specific activity changes in the water extractable P pool in Treatment 3, while curve (b) was modeled on the assumption that 75% of the plant material was removed by each individual cut. Plants take up P from soil solution P, which makes up part of the rapidly exchangeable P pool. The specific activity in the plants should in

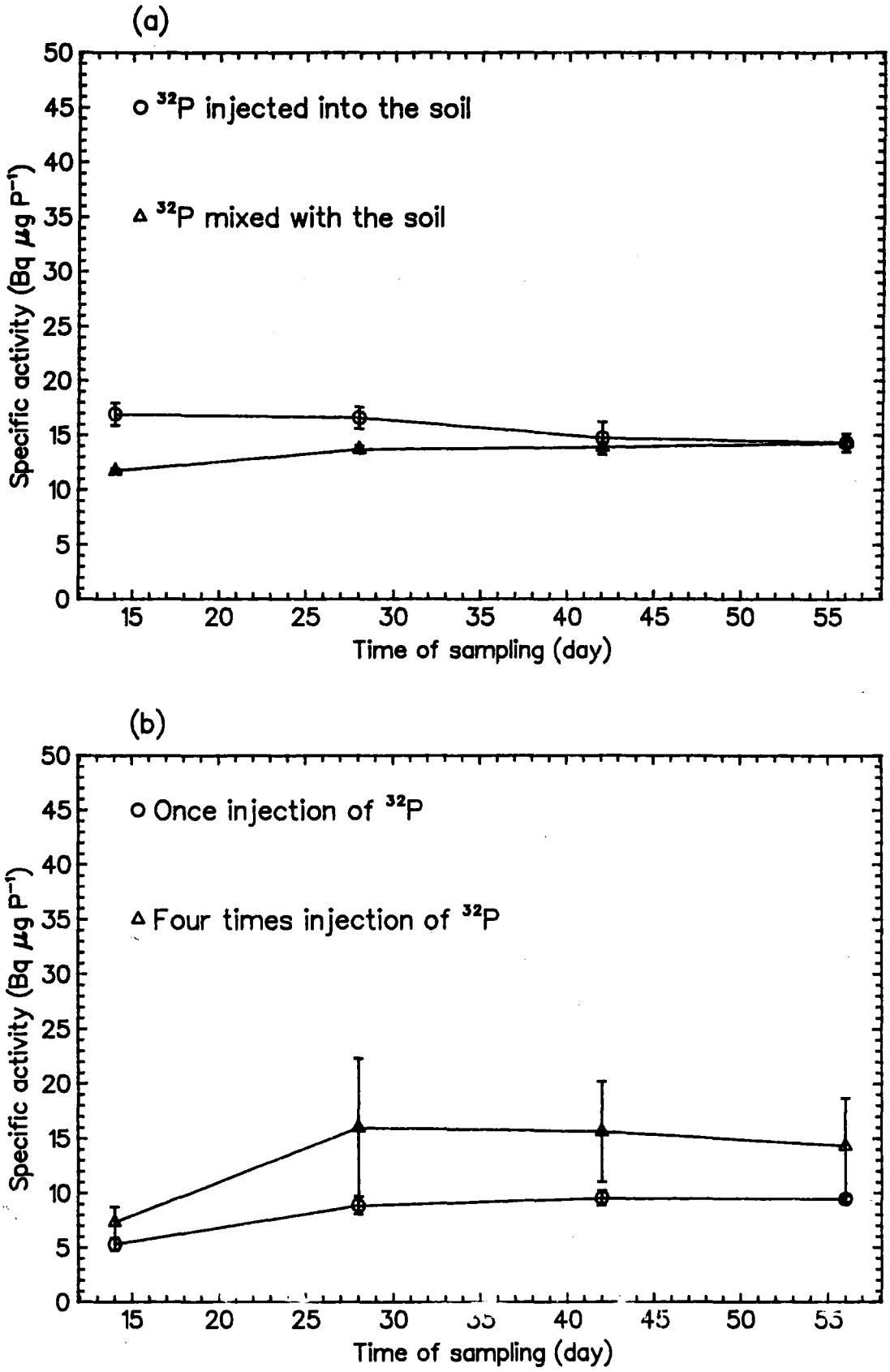
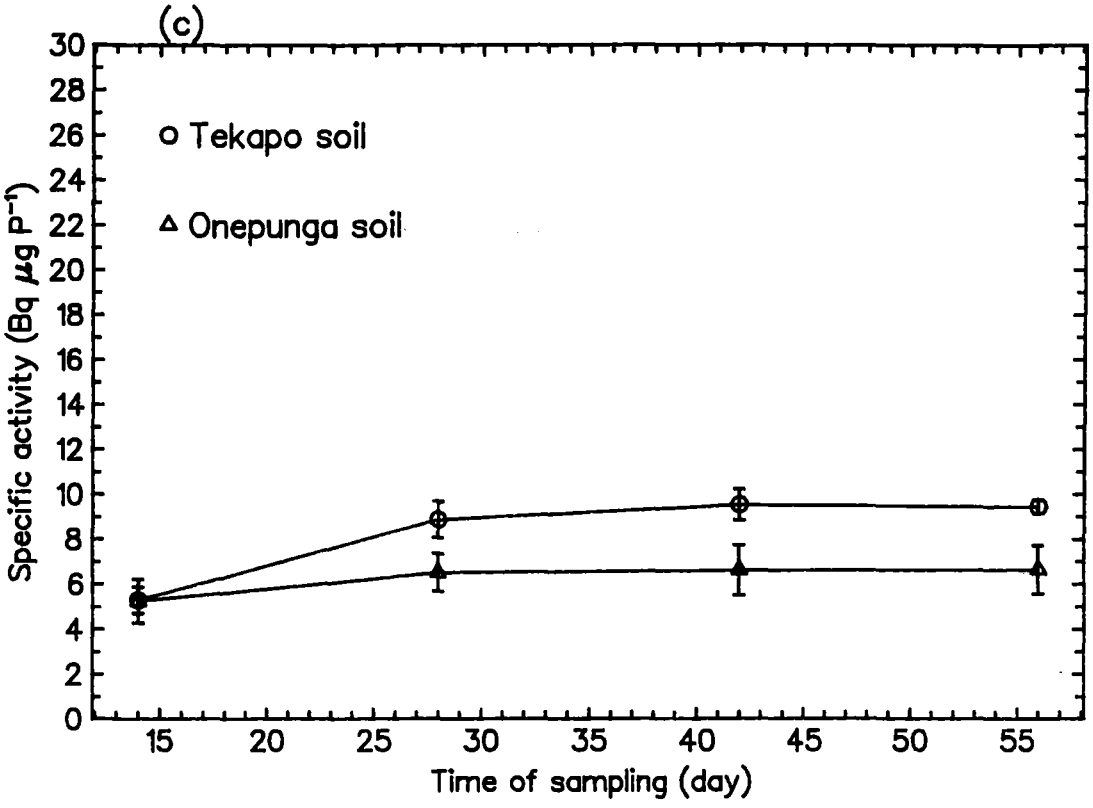
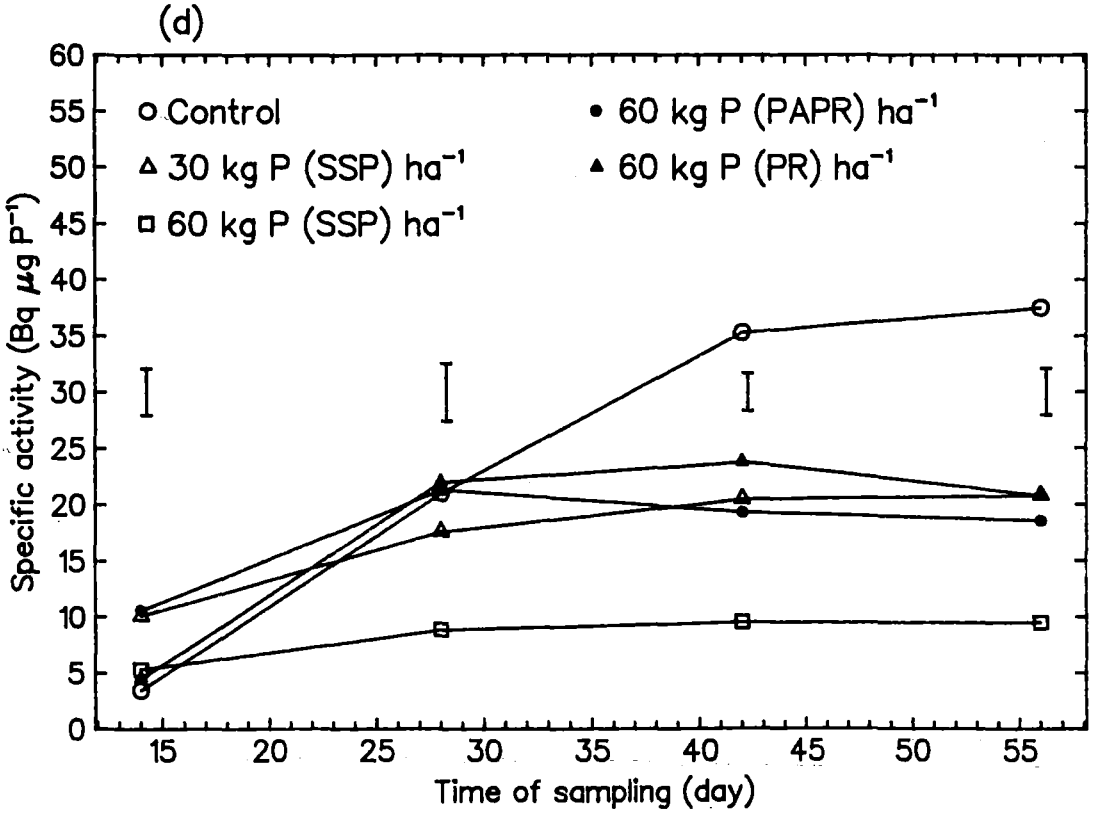


Figure 4.2 Changes of plant specific activity with time influenced by (a) injection and mixing of ^{32}P, (b) number of ^{32}P injections, (c) soil types, and (d) fertiliser types. The vertical bars represent standard errors of the mean in (a), (b) and (c), and LSD (0.05) in (d).


(c)
Tekapo soil
Onepunga soil
Specific activity (Bq μg P⁻¹)
Time of sampling (day)


(d)
Control
30 kg P (SSP) ha⁻¹
60 kg P (SSP) ha⁻¹
60 kg P (PAPR) ha⁻¹
60 kg P (PR) ha⁻¹
Specific activity (Bq μg P⁻¹)
Time of sampling (day)

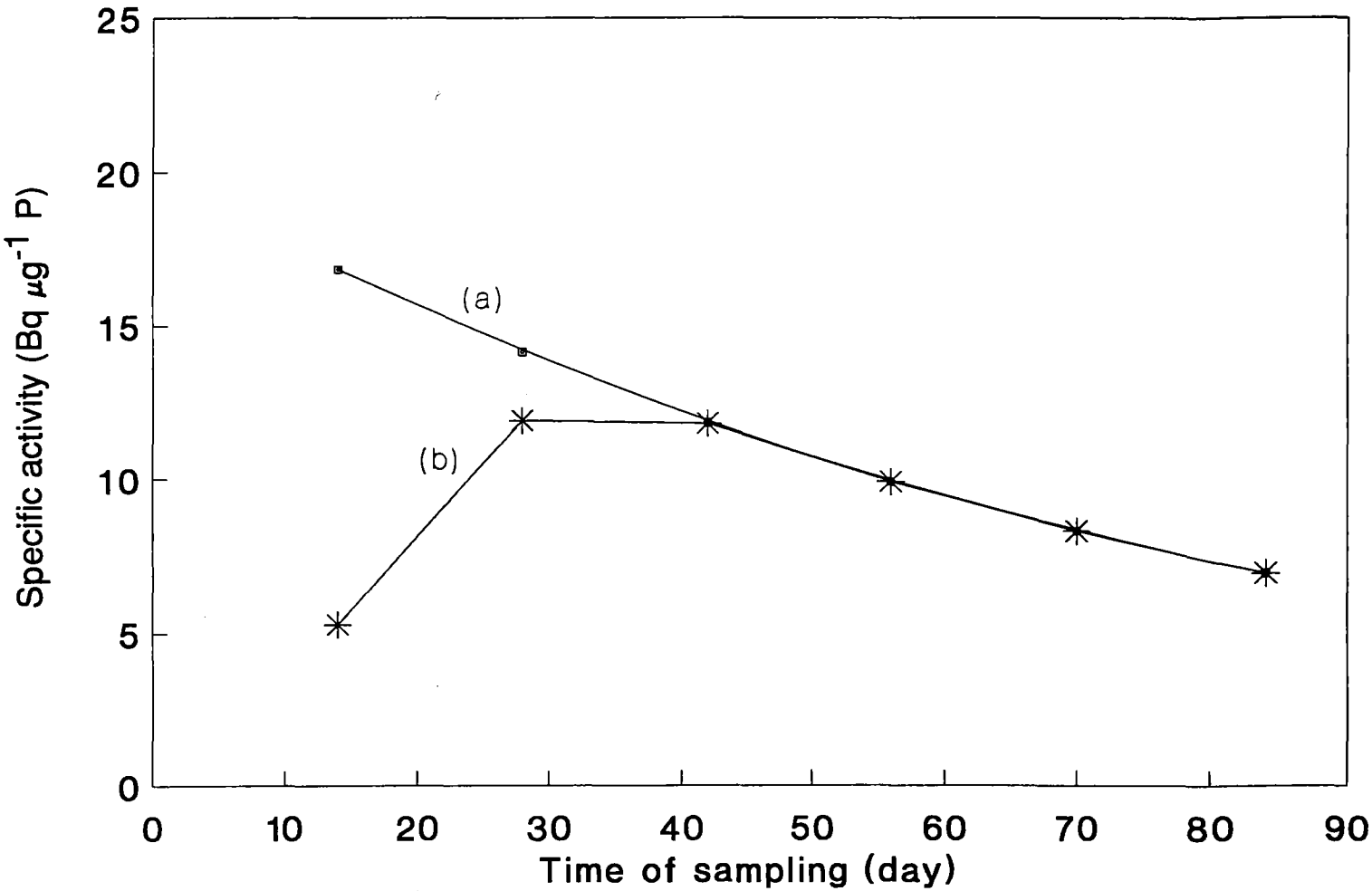


Figure 4.3 Diagrammatic illustration of the influence of the original plant P content on the temporal changes of specific activity in the plant: (a) specific activity in the soil exchangeable P pool; (b) specific activity in the plant influenced by the original plant P content.

theory reflect that in the rapidly exchangeable P pool, as the plants simply sample the soil in a ratio of $^{32}P/^{31}P$ identical to that in the exchangeable P pool. However, the specific activity was further reduced inside the plants by their original plant P (curve b). With increasing numbers of harvests, this effect diminishes to insignificant levels and the plant specific activity then follows that of the soil exchangeable P pool.

The two curves, after the disappearance of the initial plant P effect, may or may not perfectly superimpose, depending on the rate of the specific activity decline in the exchangeable P pool, the rate of plant growth and the frequency of harvests. This is because the specific activity in the plant material of every individual cut is influenced by both the changes of specific activity in the exchangeable P pool during the periods between the previous and the present harvests of plants, and the specific activity in the plant material remaining after the previous cut. The specific activity in the left-over plant material (or carry-over plant material) reflects the changes of specific activity in the exchangeable P pool before the previous harvest rather than that between the previous and the present harvests. The position of curve (b) therefore depends on the relative proportions contributed by each source. In any case, curve (b) is closely associated with curve (a).

The magnitude of this initial internal dilution effect depends on the amount of P present in the original plant material relative to the amount of P taken up by plants from the soil. The influence is greater when the original plant P content is higher and the amount of P taken up by plant from the soil is lower and vice versa. Moreover, the faster the plants grow, the higher the proportion of the original plant P removed by each harvest, and the sooner the effect diminishes. The exact temporal variation pattern of specific activity in the plant material is therefore influenced by the rate of plant growth. An effective way of removing the plant P content effect would be to encourage fast plant growth with frequent harvests. The consequent influence on the estimation of readily exchangeable P pools is discussed in the next section (cf. Section 4.3.3).

The ratio of ^{32}P:^{31}P sampled by plant from the exchangeable P pool of the soil is influenced by the spatial distribution of the two isotopes in the soil column. In principle, when the exchangeable P pool is uniformly labelled with ^{32}P throughout the whole soil medium, a small sample taken from any part of the soil column will be representative of the whole. Therefore, the specific activity sampled by a single root would indicate the ratio of ^{32}P:^{31}P in the exchangeable P pool of the whole soil column. If the exchangeable P pool is not uniformly labelled, the whole soil column needs to be uniformly sampled to reveal the ratio of the two isotopes in the exchangeable P pool. A small sample taken from different parts of the soil column may or may not be representative of the whole soil. The plant specific activity is the ratio of the sum of ^{32}P to the sum of ^{31}P drawn from limited parts of the soil column by plant roots. The plant specific activity depends on the chances of the two isotopes being absorbed by plant roots, which in turn depend on the spatial distributions of the two isotopes and plant roots in the soil. In effect, the injection technique produces narrow columns of soil with high specific activity which are surrounded by soil with zero specific activity. Provided the plant root system samples this system in a representative manner, the plant specific activity should represent the average specific activity of the exchangeable P pool in the soil. However, the plant specific activity would be higher if ^{32}P is advantaged over ^{31}P in being absorbed by plant roots and vice versa.

Figure 4.2 a compares the changes of specific activity in the plant, as influenced by the way the ^{32}P was introduced into the soil, i.e. injection compared with mixing (Treatment 8 compared with Treatment 9). The fertilisers were uniformly mixed with the soils in both treatments. The plant specific activity did not follow exactly the same trend in the two treatments. It was initially higher in the ^{32}P injected soil than in the mixed soil. The difference, however, narrowed progressively with time. The initial higher specific activity in the ^{32}P-injected treatment might have resulted from possible preferential proliferation of plant roots along the injection holes where the ^{32}P was concentrated, immediately after the grass seedlings were transferred

to the top of the soil cores. The injected ^{32}P in this case had a greater chance of being taken up by plants than the phosphate uniformly mixed in the bulk of the soil where plant roots had not yet reached extensively. With time plant roots would reach increasing volumes of the soil and take up increasing proportions of P distributed away from the injection holes. Eventually, when extensive root systems are established in the bulk of the soil, specific activity for the two treatments reached similar values. This result suggests that extensive plant root systems are able to representatively sample the injected soil.

The influence of ^{32}P distribution on the plant specific activity in soils where extensive root systems have established was investigated by comparing injecting ^{32}P tracer four times with a single injection. The results are shown in Figure 4.2 b. The mean values of the plant specific activity are generally higher in the four-times injected treatment than in the single injection. This is most likely due to an increased chance of ^{32}P being taken up by plants in the four-times injection treatment. When ^{32}P was distributed to a few isolated columns in the soil (e.g. single injection), some relatively concentrated ^{32}P spots might not be reached within a limited period of experiment. Plant roots however could always reach phosphate distributed throughout the exchangeable P pool of the soil. This would result in a lower plant specific activity. In a situation where the whole soil column is not uniformly sampled, i.e. small samples are drawn from several locations by plant roots, the more closely associated the ^{32}P distribution is with phosphate in the whole soil medium, the more likely the two isotopes would be sampled in proportion to their amounts in the soil. Therefore, when ^{32}P was more extensively distributed in the soil medium (e.g. injected four times), greater proportions of plant roots would absorb phosphate together with ^{32}P, contributing to a relatively higher plant specific activity. However, the specific activity values in the multiple-injection treatment are much more variable than in the single-injection treatment. This probably resulted from increased disturbance of the natural

soil structure and possible overlapping among the injection holes in the four-time injection treatment.

The results obtained from experiments involving established root systems and those involving transferred pots are therefore at variance. The specific activity in the plants is influenced by the distribution of ^{32}P with respect to ^{31}P in the soil, which in turn is influenced by the method of labelling. The once-injected ^{32}P may be advantaged in being taken up by plants over ^{31}P distributed in the bulk of the soil when plants are at the early establishing stage due to preferential growth of plant roots along the injection holes, but disadvantaged in established systems where the chances of ^{32}P located in isolated spots being reached by plant roots may be smaller than those of phosphate distributed throughout the system.

Treatment 7 was set up to check whether soil organic matter content affects changes of specific activity in the exchangeable P pool as sampled by plants. Figure 4.2 c shows that similar patterns occurred in both soils. The difference in organic matter content did not seem to have significantly altered the changing patterns of specific activity in the exchangeable P pool. This might indicate that the recycling of organically held ^{32}P through mineralisation was an insignificant factor in influencing the changes of specific activity in the exchangeable P pool. However, more studies are required before firm conclusions could be made.

The specific activity in the plant is influenced by the solubility and quantity of the fertilisers applied. Figure 4.2 d shows that the specific activity in the soil exchangeable P pool was significantly reduced by phosphates dissolved from all three fertilisers. The specific activity in the 60 kg P (SSP) ha^{-1} treatment is clearly lower than that in the 30 kg P (SSP) ha^{-1}, which is in turn significantly lower than that in the control treatment. The dissolution of PR and PAPR materials produced specific activity levels similar to those in the soils treated with SSP at half the rate. It is interesting to note that 60 kg P ha^{-1} in the PAPR treatment contains a similar amount of

water soluble P to 30 kg P ha^{-1} in the SSP treatment (Table 4.3), and that the specific activity of plant material from these treatments is also similar.

4.3.3 Readily exchangeable P pools

The sizes of the readily exchangeable P pools in the Tekapo soil treatments with a single injection or mixing of ^{32}P are illustrated in Figure 4.4. Treatment 4 which yielded highly variable results from four ^{32}P-injections and Treatment 7 which used the Onepunga soil are not included in the figure. The sizes of the P pools are calculated using Equation 3.1 (cf. Section 3.2) on the basis of the total amount of tracer injected (or mixed) and the plant specific activity after the disappearance of the dilution effect by the original plant P.

A comparison between the exchangeable P pools of Treatments 1, 2 and 3 reveals that the differences are considerably larger than the application rates [30 kg P (SSP) ha^{-1} and 60 kg P (SSP) ha^{-1} for Treatments 2 and 3 respectively]. This is similar to the results obtained from the field trial using the same technique (cf. Section 3.4.2). As suggested in Section 3.4.2, the amounts of phosphate dissolved into the exchangeable P pool should, at maximum, not exceed the application rates. This suggests that the amounts of P contributed to the exchangeable P pool by fertiliser dissolution are overestimated.

However, the differences in the exchangeable P pools of Treatments 8 and 9, both fertilised with 60 kg P (SSP) ha^{-1}, from the control treatment are only slightly greater than the application rates. Therefore, the amounts of P dissolved from the fertilisers in Treatments 8 and 9 are not overestimated to the same extent as those in Treatments 2 and 3.

The differences in conditions between Treatment 3 and Treatments 8 and 9 were that in Treatment 3 the fertiliser was applied to the surface of the soil cores with the natural root systems undisturbed, whilst in Treatments 8 and 9 the natural root structure was completely destroyed and the fertilisers uniformly mixed with the soils.

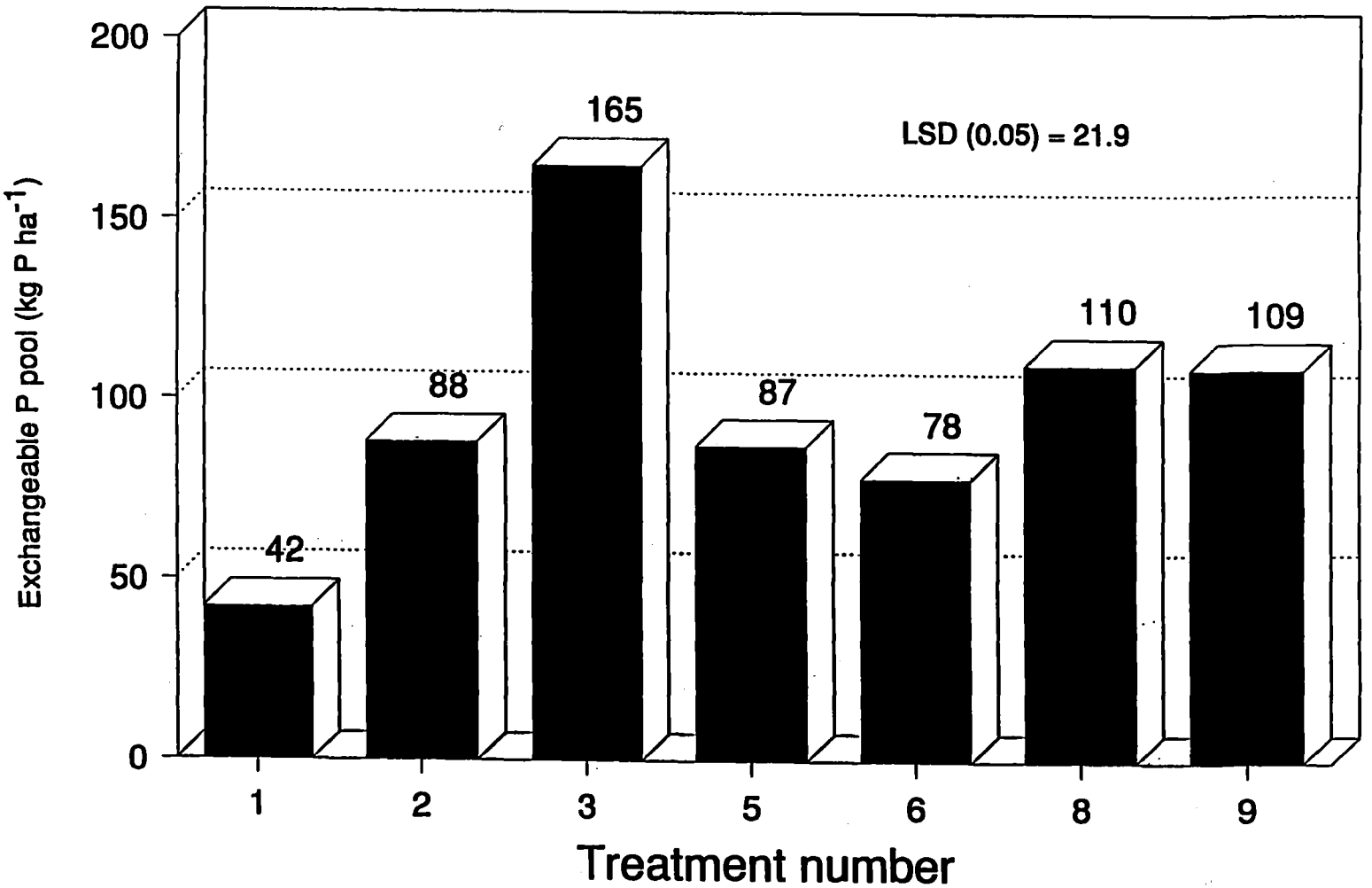


Figure 4.4 Exchangeable P pools estimated in the soils of different treatments. The treatment numbers refer to those in Table 4.1.

A large proportion of the overestimation of exchangeable P pools in Treatment 3 (and Treatment 2) is therefore attributable to the effect arising from the combination of surface application of the fertilisers and the natural root distribution patterns. Indeed, the root density of established natural grassland decreases markedly with depth. Surface-applied fertiliser P thus had a greater chance of being taken up by plants than soil P and ^{32}P tracer at depth. The specific activity in the plant material, therefore, was not proportional to the ratio of ^{32}P over ^{31}P in the exchangeable P pool of the whole soil column (150 mm in depth). Rather, it was heavily weighted by that in the thin layer of soil at the very top of the soil core, where a small fraction of the ^{32}P injected into the whole soil column was diluted by a large amount of P dissolved from the fertilisers plus the soil P present locally in that layer. This would result in a much lower value of specific activity in the plant than the actual ratio of $^{32}P/^{31}P$ in the exchangeable P pool of the whole soil volume. The exchangeable P pools calculated using the total amount of ^{32}P injected and the plant specific activity in the fertilised treatments were consequently overestimated. The overestimation, however, would be negligible in the control treatment which received no fertilisers and where the natural gradient of P concentration in the exchangeable P pool of the top 150 mm soil profile is expected to be small.

The degree of mycorrhizal infection between the natural vegetation in Treatment 3 and the newly-established vegetation in Treatments 8 and 9 might also be different. This might result in differences in the actual amount of P taken up by plants, but not in the plant specific activity and thus the estimated exchangeable P pools. Mycorrhizal and non-mycorrhizal plants basically absorb P from the same available sources (Kucey *et al.*, 1989). Mycorrhizae could assist plants to utilise the available P more efficiently by extending the depletion zones, but could not utilise forms of phosphate unavailable to plants.

The exchangeable P pools calculated for Treatments 5 and 6 where PAPR and PR were applied must also have been overestimated to varying extents, depending

on the amount of P released from each fertiliser. The higher the gradient of P concentration was between the surface soil and the soil below, the greater the overestimation would be.

The decline of specific activity in the exchangeable P pool as shown by the soil analyses (cf. Section 4.3.1) also contributed to the overestimation of the P pool sizes. Part of the decline in specific activity is due to the removal of ^{32}P from the rapidly exchangeable P pool. This invalidates the assumption supporting Equation 3.1 that the isotope label introduced into the soil remains in the exchangeable P pool. The calculation of the size of the readily exchangeable P pool can only be made using the specific activity in the exchangeable P pool sampled immediately after labelling, when all the tracer is in the exchangeable P pool. The calculation of the exchangeable P pool using specific activity values at a later time and the total activity of ^{32}P introduced into the system at the beginning will result in overestimation. The plant specific activity at the quasi-plateau level, after the disappearance of the original plant P effect (Figure 4.3), was in fact considerably lower than that immediately after labelling. The exchangeable P pools estimated on the basis of plant specific activities at this point are therefore exaggerated. The exaggeration would be greater in the fertilised treatments than in the control because of greater phosphate input to the exchangeable P pool from the fertilisers. This is probably the main reason for the overestimation in Treatments 8 and 9.

Part of the overestimation in the treatments using natural soil cores with established plants may be contributed by effects arising from the spatial distribution of ^{32}P with respect to ^{31}P. The ^{32}P introduced into discrete columns of the soil by a single injection might be disadvantaged with respect to ^{31}P distributed in the bulk of the soil medium in terms of being absorbed by plants. This produces an effect as if less ^{32}P was introduced into the system, lowering the plant specific activity and exaggerating the size of the exchangeable P pool. The mean specific activity values in the four-time

injection treatment (Treatment 4) were indeed higher than those in the single-injection treatment (Treatment 3) (cf. Figure 4.2 b).

The overestimation of the amount of P dissolved from the fertilisers in established grassland was therefore caused by at least three mechanisms: (i) the interaction between surface-applied fertilisers, ^{32}P injected through the whole soil column, and the vertical decline in plant root density (Type I), (ii) the decline of specific activity in the exchangeable P pool relating to the losses of ^{32}P (Type II), and (iii) the disadvantaged distribution of ^{32}P with respect to ^{31}P in terms of the chances of being taken up by plants (Type III). The occurrence of Types I and III overestimation could be avoided by completely mixing the fertiliser and tracer with the soil. The magnitude of type II overestimation could be reduced by using the plant specific activity at the earliest possible time after labelling without the original plant P dilution effect to calculate the P pool sizes. This can be achieved by encouraging fast plant growth to remove the original plant P as soon as possible, or to run the experiment long enough to obtain a specific activity time curve after the disappearance of the original plant P dilution effect which would allow the specific activity immediately after labelling to be extrapolated. The extrapolation is usually performed on a semi-log linear basis (Shipley and Clark, 1972). Detailed discussions with respect to the application of this technique are provided in Chapter 5.

The reliability of the injection technique to study the dissolution of phosphate fertilisers in the soils may be further assessed by the amount of variability associated with the estimates. Table 4.5 presents the coefficients of variation (C.V.) associated with the sizes of the exchangeable P pools estimated.

The variability in each treatment depends mainly on three factors: the manner in which the soil was labelled, the method of fertiliser application, and the soil (undisturbed vs mixed) and plant (established vs establishing) conditions. The variability in Treatments 2-7, where the fertilisers were applied to the surface of undisturbed soil cores, is considerably higher than in the control without fertilisers and

in Treatment 8 where the fertiliser was mixed with the soil. The high variation in Treatments 2-7 again relates to the combination of surface-applied fertilisers and the plant root distribution in undisturbed soil cores. The rate of vertical decline in root density was likely to vary among individual pots. The magnitude of overestimation of the amount of P supplied by the fertilisers would vary accordingly. The greater the difference between the root density at surface and that at depth, the larger the overestimation would be. The sizes of the exchangeable P pools calculated would therefore vary depending on the extent of overestimation occurred in each individual pot. The considerably lower variation in Treatment 8 than in Treatments 2-7 implies that the variation was significantly reduced by mixing the fertilisers with the soil.

Table 4.5 Coefficients of variation (C.V.) associated with the estimated exchangeable P pool values. The treatment numbers correspond to those in Table 4.1.

Treatment No.	1	2	3	4	5	6	7	8	9
C.V. (%)	5	21	19	35	23	23	24	12	6

The particularly high variability associated with Treatment 4 (four-time injection) suggests that the multiple-injection technique is not a reliable approach to increasing the uniformity of ^{32}P distribution in the soil. This is probably due to the physical disturbance of the soil cores brought about by the repeated injections. The C.V. values in Treatments 8 and 9 suggest that complete mixing of the tracer with the soil introduces slightly less variation than injection. The slightly higher variation in Treatment 8 is probably due to a less uniform distribution of ^{32}P injected into the soil. Complete mixing of the fertilisers and tracer with the soil is therefore the most reliable method to produce consistent results.

4.3.4 The fertilising equivalent values

The Type I mechanism responsible for the overestimation of the sizes of exchangeable P pools in natural grassland soils in fact indicates that the availability of phosphate fertilisers to plants varies depending on the location of application. Because of the vertical decline of root density, the phosphate dissolved from the fertilisers applied at the surface is more available to plants than phosphate of the same chemical form located at greater depth. The fertilising effect of one unit of chemically available P at the surface is therefore equivalent to that of more than one unit of phosphate of the same chemical form located at depth. The isotopic injection technique described in this chapter can be conveniently used to assess the availability of different fertilisers as influenced by application locations, and soil and plant conditions by introducing a new concept - fertilising equivalent (FE).

In the FE concept, the exchangeable P uniformly distributed in a specific layer of soil (0 - 150 mm in this experiment) is taken as a standard and labelled with ^{32}P by injection. The effectiveness of phosphate fertilisers applied at the surface is compared with the effectiveness of this exchangeable P standard. If the plant specific activity (without the influence of the original plant P) of the fertilised treatments is SA_{s+f} and that of the control is SA_s, the proportion of P derived from the soil exchangeable P pool (rather than from the fertiliser P) in the plants of the fertilised treatments (Z) can be calculated using Equation 4.1:

$$Z = SA_{s+f}/SA_s \qquad (4.1)$$

The size of the exchangeable P pool (Q_s) uniformly distributed in the soil can be estimated using Equation 4.2 on the basis of the amount of ^{32}P introduced (q_0) and the plant specific activity in the control:

$$Q_s = q_0/SA_s \qquad (4.2)$$

As this value may vary depending on how the soil is labelled and with plant root distribution patterns, the treatments to be compared should therefore have the same method of labelling and similar plant root systems. The effectiveness of the fertilisers can then be evaluated using Equation 4.3 in terms of the amounts of soil exchangeable P that the fertilisers are equivalent to:

$$FE = Q_s[(1-Z)/Z] \qquad (4.3)$$

The FE value is therefore not the absolute amount of P dissolved from the fertilisers, but the equivalent amount measured in terms of the soil exchangeable P standard. The FE values could be larger, equal to or smaller than the fertiliser application rate, depending on the solubility of the fertiliser, the location of application and plant root distributions. The higher the values are, the more advantageous the fertilisers are over the soil exchangeable P in terms of supplying P to the plants.

Equation 4.3 has an identical form with the equation by Fried and Dean (1952) for calculating the "A" value (cf. Equation 2.7 of Section 2.5.3). Conceptually, the equation to calculate the FE values is in fact the inverse of that to calculate the A value. The A value is a measure of the amount of available P in the soil compared with a fertiliser standard. Its measurement usually involves the use of a labelled fertiliser, whereas the FE value provides a measure of the amount of available fertiliser P in terms of the soil exchangeable P standard. Its measurement requires the labelling of the soil. In comparison to the A value concept, the FE value concept has the advantage that the labelling of the fertilisers, which is difficult for certain fertilisers (e.g. PR's) required for the measurement of the A value, is not necessary in the measurement of the FE values.

The FE values of different fertilisers applied at the surface for the compatible treatments (Tekapo soil, single injection of ^{32}P, natural soil) are summarised in Table 4.6.

Table 4.6 The fertilising equivalents of different fertilisers applied at the surface of established grassland. The treatment numbers correspond to those in Table 4.1.

Treatment No.	1	2	3	5	6
Application rate (kg P ha^{-1})	0	30(SSP)	60(SSP)	60(PAPR)	60(PR)
FE values (kg P ha^{-1})	0	46	120	35	24

Single superphosphate, when applied at the surface of undisturbed soil cores (Treatments 2 and 3), is equivalent to much higher amounts of soil exchangeable P uniformly distributed in the soil column. This is because plants take up more P from the surface than from lower down as a result of a vertical decline in root density. This superiority, per unit P applied, seems to have increased with application rates, with FE values increasing 2.6 times when the application rate is doubled. The FE values for the PAPR (Treatment 5) and PR (Treatment 6) applied at the surface, however, are substantially lower than those of their water soluble fertiliser counterparts. The effectiveness of the surface-applied PR-containing fertilisers may be limited over the period of the experiment, because the rate of dissolution of PR is much less than that of water soluble fertilisers. These results are consistent with the cumulative plant P uptake data from these treatments through the 56 day period of plant growth (Figure 4.5). The figure clearly shows that the PAPR and PR applied at the soil surface are not as effective as SSP in supplying P to plants over the period of the experiment.

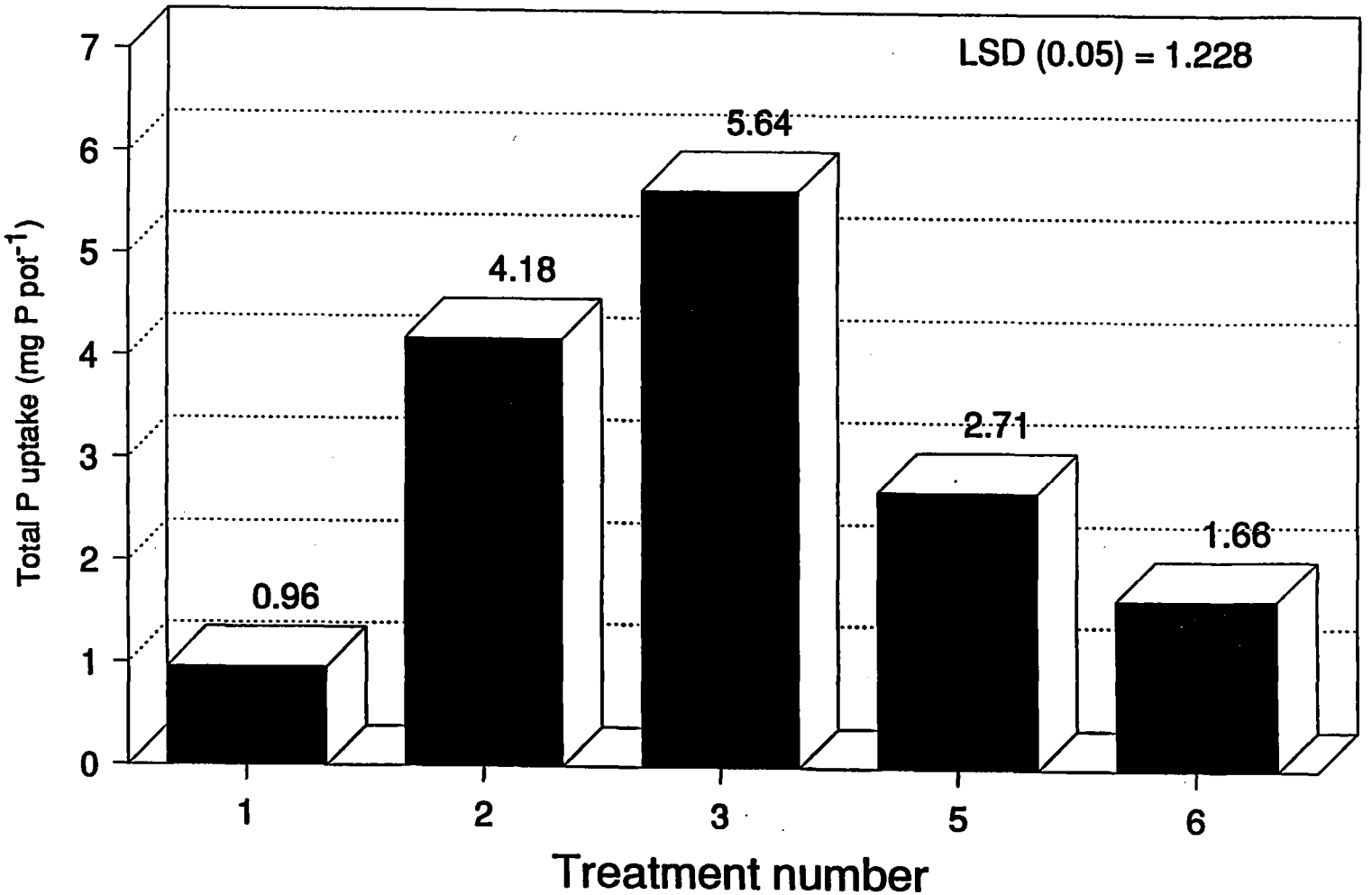


Figure 4.5 Total plant P uptake through the 56 day period of plant growth. The treatment numbers refer to those in Table 4.1.

The results, however, might be different if the fertilisers are uniformly mixed with the soils and/or given longer periods of plant growth.

4.4 Summary and conclusions

Specific activity in the soil exchangeable P pool declines with time mainly because of the continuous release of P from fertiliser dissolution, continued exchange of ^{32}P at less rapidly exchangeable sites, and removal of ^{32}P from the exchangeable P pool. In contrast, the specific activity in the plant follows an increase-plateau-decrease pattern, mainly due to the initial dilution effect of the original plant P content.

The amount of P dissolved from the fertilisers applied at the surface of natural soil is overestimated by at least three mechanisms: Type I overestimation, arising from the combination of surface-applied fertilisers, ^{32}P injected through the whole soil columns, and vertical decline in root density, Type II overestimation, arising from the decline of specific activity in the exchangeable P pool related to losses of ^{32}P from the exchangeable P pool, and Type III overestimation, arising from the non-uniform distribution of ^{32}P against ^{31}P in terms of the chances of being taken up by plants. The Type I and III overestimation may be avoided by mixing the fertilisers and the tracer with the whole volume of soil experimented with, whilst the type II may be reduced by using as early as practically possible a plant specific activity without the initial effect of the original plant P to calculate the exchangeable P pool.

Multiple injections produce particularly variable results. A large amount of variation also arises because of differing plant root distribution patterns combined with the surface-applied fertilisers. The variability is minimised if the fertilisers and the tracer are thoroughly mixed with the whole volume of soil in each pot.

The introduction of the fertilising equivalent (FE) concept enables the isotopic injection technique to be adopted to study the effectiveness of different fertilisers. The FE value is a measure of the amount of P dissolved from the fertilisers in terms of the soil exchangeable P. The results derived from the trial indicate that

when applied at the surface of established grassland soil cores, the water soluble fertiliser, SSP, is much more effective than the surface-applied PAPR and PR fertilisers within the period of experiment. The limited effectiveness of PAPR and PR was presumably due to inadequate time of contact between fertilisers and soil which is prerequisite for dissolution of PR materials.

Part three

Development and assessment of an isotopic dilution technique to study the dissolution and retention of phosphate fertilisers in the soil

Chapter 5

Development and application of an isotopic dilution technique to study the kinetics of phosphate fertiliser dissolution and retention in soils

5.1 Introduction

Chapters 5, 6 and 7 present the studies assessing an isotopic dilution technique used to study the kinetics of phosphate fertiliser dissolution and retention in soils. The technique was developed from the studies reported in Chapters 3 and 4. It involves the determination of temporal changes of the soil exchangeable P pool and the specific activity in the P pool following application of a fertiliser and labelling of the soil. Because of the many variables associated with the use of undisturbed soils, which affect the determination of specific activity in the exchangeable P pool sampled by plants and the estimation of the sizes of the P pool (cf. Chapters 3 and 4), the isotopic tracer and the fertilisers used in this experiment were completely mixed with the soils. This minimises effects from variables other than the ones under investigation. This chapter describes the conceptual models and their applications to studying dissolution and retention of different types of phosphate fertilisers applied to soils and discusses the results obtained. Emphasis in the discussions is on the applications of the methods developed. In Chapter 6, the results from this kinetic study are compared with those derived from chemical extractions. In Chapter 7, the kinetic along with the chemical parameters obtained are assessed in terms of their agronomic significance, i.e. their capability to account for the variations of plant responses to phosphate supplies.

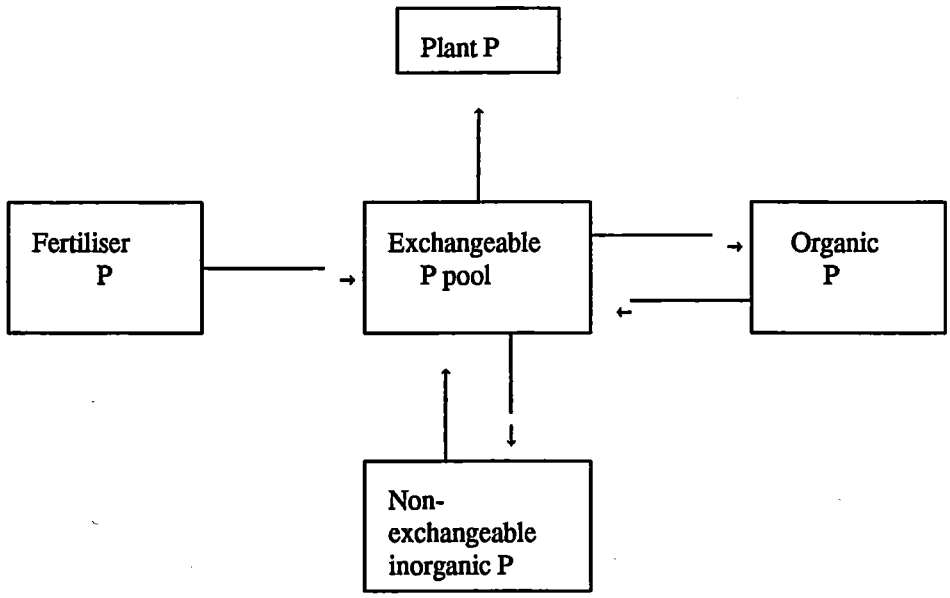
5.2 Theory and applications

5.2.1 Theory

The theoretical models used in the present study are developed on the basis of kinetic principles described in detail by Shipley and Clark (1972).

The dynamics of P transformations in the soil - plant system may be simplified into Figure 5.1.

Figure 5.1 A simplified conceptual model showing the dynamics of phosphate in the soil - plant system.



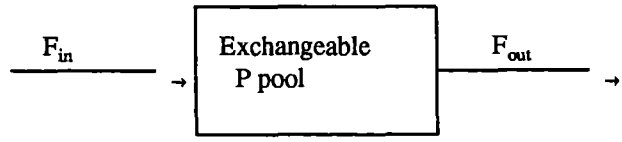
The exchangeable P pool in the above model refers to inorganic P in soil solution and that fraction on soil surfaces that undergoes rapid exchange with ^{32}P-phosphate introduced into the system. The size of this exchangeable P pool is determined using the specific activity in the P pool, as sampled by plants, immediately after labelling of the soil. With increasing time after labelling, specific activity declines due to releases of P and removal of ^{32}P from the rapidly exchangeable P pool, and the on-going exchange processes of ^{32}P with P at the less rapidly exchangeable sites (cf. Section 4.3.1). Thus, exchangeable P pools calculated using specific activity

values sampled at later stages overestimate the P that undergoes rapid exchange with ^{32}P (cf. Section 4.3.3). The exchangeable P pool therefore has an operational boundary separating the rapidly exchangeable from the slowly exchangeable or non-exchangeable phosphates.

Figure 5.1 shows that there are on-going processes adding phosphate to or removing phosphate from the exchangeable P pool. In fertilised soils, possible inflow processes which add P to the exchangeable P pool include dissolution of fertilisers and native soil inorganic P compounds, desorption, and decomposition of organic P. The on-going slow isotopic exchange processes (cf. Section 4.3.1) after labelling can also be considered to have the net effect of adding phosphate to and thus increasing the size of the exchangeable P pool. Possible outflows which remove P from the exchangeable P pool include P sorption and precipitation by soil components, organic immobilisation and plant uptake (cf. Sections 2.4 and 4.3.1). The size of the exchangeable P pool is controlled by the sum of these gains and losses. The sum of the inflows is probably dominated by dissolution of fertilisers, whilst that of the outflows by sorption and possibly precipitation. The rates of fertiliser dissolution and P retention may thus be characterised by quantifying the rates of P inflow to and outflow from the exchangeable P pool.

In developing a working model to quantify the rates of inflow and outflow of P to and from the exchangeable P pool, the model illustrated in Figure 5.1 is simplified into a single compartment model (Figure 5.2).

Figure 5.2 A simplified conceptual model illustrating the inflow and outflow of P to and from the exchangeable P pool.



The F_{in} in Figure 5.2 represents the sum of inflows, whilst the F_{out} represents the sum of outflows. If $F_{in} = F_{out}$, the size of the soil exchangeable P pool will not change with time. As F_{in} does not always equal F_{out}, the size of the exchangeable P pool may increase or decrease with time depending on the relative magnitude of the two processes.

If a single dose of carrier-free ^{32}P with the total activity of q_0 is introduced into the soil, the ^{32}P will undergo rapid exchange with P in soil solution and on soil surfaces. This will generate an instantaneous specific activity (SA) in the exchangeable P pool. The size of the rapidly exchangeable P pool (Q) can be calculated on the basis of this initial specific activity using Equation 5.1:

$$Q = q_0/SA \qquad (5.1)$$

The effect of F_{in} is to increase the size of the exchangeable P pool and further dilute the ^{32}P tracer and thus reduce the specific activity, whilst that of F_{out} is to reduce the size of the exchangeable P pool by removing ^{31}P and ^{32}P in proportion to the ratio of the two isotopes in the P pool. The rate of change with time of the specific activity in the exchangeable P pool is related to the size of the P pool and the rates of inflow and outflow. F_{in} and F_{out} values therefore may be estimated according to the changes of the exchangeable P pool sizes and the specific activity values in the P pool.

If q and Q denote the quantity of tracer (^{32}P) and ^{31}P-phosphate respectively in the exchangeable P pool, and if $F_{in} = F_{out}$, and both are constant (stationary through a specified period of time), then the changing rate of tracer quantity in the P pool follows Equation 5.2,

$$q = q_0 \cdot e^{-kt} \qquad (5.2)$$

and the specific activity (SA) follows Equation 5.3,

$$SA = SA_0 \cdot e^{-kt} \qquad (5.3)$$

where q_0 and SA_0 are the quantity of tracer and specific activity at the time of ^{32}P addition, e is the base of the natural logarithm, k is a rate constant and t is time. If a series of measurements of the specific activity in the exchangeable P pool is made at various intervals after labelling, the semilog plot of specific activity against time will provide a straight line with slope k. The rate of inflow and outflow can then be calculated using the following equation:

$$F_{in} = F_{out} = kQ \qquad (5.4)$$

If F_{in} and F_{out} are constant but unequal following the introduction of a single dose of ^{32}P tracer, the changing rate of tracer quantity in the P pool is

$$dq/dt = -F_{out} \cdot SA(t) \qquad (5.5)$$

where SA(t) is specific activity as a function of time. Equation 5.5 implies that the loss of ^{32}P together with ^{31}P due to F_{out} is in proportion to the ratio of the two isotopes in the P pool. The change in quantity of the ^{31}P-phosphate is

$$dQ/dt = F_{in} - F_{out} \qquad (5.6)$$

Equation 5.6 shows that an incremental or decremental change in Q in unit time is provided by the difference between the two constant rates of inflow and outflow in the same units of time. At any given point of time after labelling, the quantity of ^{32}P remaining in the exchangeable P pool is given by the following equation,

$$q(t) = Q(t) \cdot SA(t) \qquad (5.7)$$

or expressed in its derivative form:

$$dq/dt = Q(t) \cdot dSA/dt + SA(t) \cdot dQ/dt \qquad (5.8)$$

Rearranging Equations 5.5, 5.6 and 5.8 yields:

$$F_{in} = -Q(t) \cdot (dSA/dt)/SA(t) \qquad (5.9)$$

Integration of Equation 5.9 allows calculation of F_{in}:

$$F_{in} = [(Q_1-Q_2) \cdot \ln(SA_1/SA_2)]/[(t_2-t_1)\ln(Q_1/Q_2)] \qquad (5.10)$$

where Q_1, Q_2 and SA_1, SA_2 are the quantities of P and values of the specific activities in the exchangeable P pool, respectively, at any two points of time t_1 and t_2, after labelling. F_{out} can then be obtained from Equation 5.6 which may be rearranged as follows:

$$F_{out} = F_{in} - (dQ/dt) = F_{in} - (Q_2-Q_1)/(t_2-t_1) \qquad (5.11)$$

It is assumed in the treatments of the above equations that the rates of inflow and outflow remain constant through a specified period of time. If F_{in} and F_{out} are not constant, in addition to being unequal, i.e. if they vary as a function of time (F_{in} and F_{out} now become $F_{in}(t)$ and $F_{out}(t)$), Equation 5.9 is then only applicable for a short time interval, Δt. An approximation of $F_{in}(t)$ is possible if curves for Q and SA versus time are separated into sufficiently short segments. The equivalent slope, dSA/dt, in

Equation 5.9 is assumed to be that of the straight line between SA_1 and SA_2 at times t_1 and t_2. Q(t) and SA(t) are taken as the midpoint in time between t_1 and t_2:

$$F_{in}(t) = -[(Q_1+Q_2)/2] \cdot [(SA_2-SA_1)/(t_2-t_1)]/[(SA_1+SA_2)/2] \qquad (5.12)$$

$F_{out}(t)$ can then be estimated using Equation 5.11.

5.2.2 Application

Assuming that F_{in} and F_{out} are unequal but constant through a specified period, calculations using Equations 5.10 and 5.11 require values of SA_1 and SA_2, specific activities of the exchangeable P pools at times t_1 and t_2 for a given labelling operation, and Q_1 and Q_2, the respective sizes of the exchangeable P pools at the two times. Values of SA_1 and SA_2 may be obtained by using plants to sample the exchangeable P pool over time, after labelling. Corresponding values of Q_1 and Q_2 must be obtained on the basis of instantaneous specific activities sampled immediately after labelling.

As it takes a finite length of time to produce enough plant sample for analysis and as the specific activity in the plant is initially affected by the original plant P content (cf. Sections 4.3.2 and 5.4.1), it is not possible to measure directly specific activity values of exchangeable P pools immediately after labelling. The instantaneous specific activity values immediately after labelling were therefore estimated by means of a semi-logarithmic-linear extrapolation method, as shown in Figure 5.3, using specific activity-time curves (SA-t curves). The SA-t curves were obtained using growing plants to sample specific activity in the exchangeable P pool by harvesting the plant material over an extended period after labelling. Thus, SA_1 (the instantaneous specific activity value immediately after labelling) and SA_2 (the specific activity of the exchangeable P pool at some later time) were accessible from this procedure.

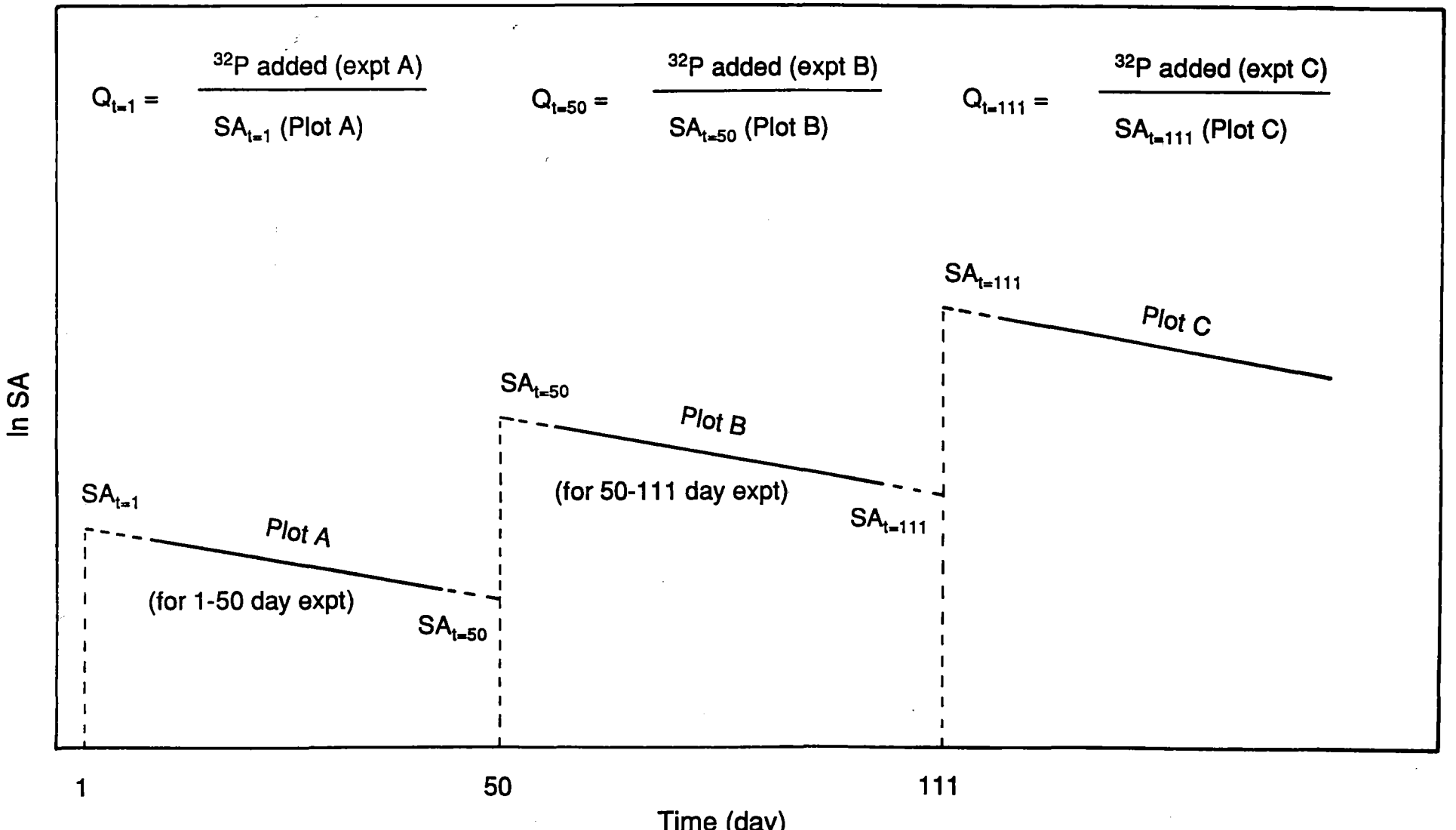


Figure 5.3 Diagrammatic illustration of the estimation of the parameters, specific activity and exchangeable P pools for the calculation of F_{in} and F_{out} values.

However, although SA_1 can be used in conjunction with q_0 to calculate Q_1 (cf. Equation 5.1), specific activity values sampled at later times after labelling can not be used to directly calculate Q values at these times. The determination of the Q value at a later time (corresponding to SA_2) requires the conduct of a second SA-t experiment. The Q_2 value can then be extrapolated from this curve. Thus, changes in F_{in} and F_{out} can be followed, in time, by carrying out a series of experiments, each providing an SA-t curve.

A succession of three labelling experiments (referred to as Experiments A, B and C respectively) were conducted after the fertilisers were incubated with the soils for 1, 50 and 111 days. Each of the three SA-t curves obtained was extrapolated back to the time of labelling, using the declining fragment of the curves that was free from any initial plant P content influence (i.e. the last four points of each curve in Figures 5.4A, 5.4B and 5.4C), to derive the values of $SA_{t=1}$, $SA_{t=50}$ and $SA_{t=111}$ (cf. Appendix for the equations fitted). The instantaneous exchangeable P pools, $Q_{t=1}$, $Q_{t=50}$ and $Q_{t=111}$ were subsequently calculated on the basis of the total ^{32}P added in each experiment and the respective extrapolated SA values (Figure 5.3).

Since the sizes of exchangeable P pools were only obtained for three points in time which are separated for sufficient periods, the average values of F_{in} and F_{out} were estimated for the two periods of 1-50 and 50-111 days, assuming that the rates of inflow and outflow are unequal but constant within each period. For the period of 1-50 days, $Q_{t=1}$ from Plot A and $Q_{t=50}$ from Plot B were taken as Q_1 and Q_2 respectively in Equations 5.10 and 5.11, and $SA_{t=1}$ and $SA_{t=50}$ both from Plot A were taken as SA_1 and SA_2 respectively. For the period of 50-111 days, $Q_{t=50}$ from Plot B and $Q_{t=111}$ from Plot C were used as Q_1 and Q_2 respectively, and $SA_{t=50}$ and $SA_{t=111}$ from Plot B as SA_1 and SA_2 respectively (Figure 5.3). Since the three experiments did not overlap in time, Plots A and B were also extrapolated forward to the beginning of the next succeeding curve where the Q values are known to derive $SA_{t=50}$ for Plot A and $SA_{t=111}$ for Plot B.

5.3 Materials and methods

A succession of three labelling experiments referred to as Experiments A, B and C were conducted after the fertilisers were incubated with the soils for 1, 50 and 111 days. Each of the three experiments comprised 10 treatments (Table 5.1).

Table 5.1 Description of the treatments to study the dissolution and retention of phosphate fertilisers in soils using the isotopic dilution technique.

Treatment No.	Soil No.[1]	Dry weight of soil (g pot^{-1})	Fertiliser applied	Application rate (μg P g^{-1} soil)	Number of replicates[2]
1	I	200	None	0	12
2	I	200	MCP (solution)	75	12
3	I	200	MCP (solution)	150	12
4	I	200	NCPAPR	150	12
5	I	200	NCPR	150	12
6	I	200	NCPR	750	12
7	II	200	None	0	12
8	II	200	MCP (solution)	150	12
9	II	200	NCPAPR	150	12
10	II	200	NCPR	750	12

[1] I: Tekapo fine sandy loam; II: Craigieburn silt loam.

[2] Four replicates were used in each of the three experiments.

Two soils were used: the Tekapo fine sandy loam, the soil used in the greenhouse trial described in Chapter 4 (cf. Section 4.2); and the Craigieburn silt loam (Typic Dystrochrept, fine loamy, mixed, mesic) (Tonkin, 1990, personal communication). The Craigieburn soil samples were taken from the same region as the Tekapo soil (near Lake Coleridge in central Canterbury, South Island). The soil is developed on greywacke loess and alluvium over gravels on gently-sloped fans. The vegetation was mainly fescue tussock with patches of brown top. It differs from the Tekapo soil in its higher P-retention capacity (Table 5.2). Treatments 1 to 6 were conducted on the Tekapo soil; Treatments 7, 8, 9 and 10 are repeats of Treatments 1, 3, 4 and 6 respectively on the Craigieburn soil.

Table 5.2 Major properties of the two soils in the surface horizon used to study the dissolution and retention of phosphate fertilisers using the isotopic dilution technique.

Soil type	Organic C (%)	pH(H_2O)	Olsen P ($\mu g\ P\ g^{-1}$ soil)	P-retention (%)	Exch. Ca (NH_4OAc) ($eq\ kg^{-1}$)	CEC ($eq\ kg^{-1}$)
Tekapo	4.3	5.5	10.8	30	0.053	0.15
Craigieburn	5.4	5.7	7.7	49	0.036	0.17

Soil samples from the surface horizons (0 - 150 mm) were thoroughly mixed and passed through a 5 mm sieve. A 200.00 g oven-dry-equivalent soil sample was weighed out for each individual pot (80 mm diameter x 50 mm height).

Three fertilisers were applied in the experiment: MCP in solution form, 30% phosphoric acid acidulated NCPAPR granules (2-3 mm diameter) crushed into debris, and NCPR ground and passed through a 150 μm sieve. The properties of these are summarised in Table 5.3.

Table 5.3 Properties of the phosphate fertilisers used for the kinetic studies of dissolution and retention in soils.

Fertiliser type	Total P (%)	Water soluble P (%)	2% citric acid soluble P (%)	2% formic acid soluble P (%)
MCP		Applied as a solution		
NCPAPR	17.2	7.2	10.0	9.8
NCPR (<150 μm)	13.2	---	5.4	9.6

The MCP solution was applied at two rates to the Tekapo soil to check the relationship between the amount of water soluble P added to the soil and the sizes of the exchangeable P pools measured by the labelling technique. The NCPR was also applied at two rates to investigate the extents and rates of dissolution and retention and agronomic effectiveness as influenced by the rate of application. The appropriate amounts of fertilisers weighed out or pipetted (as applicable) were thoroughly mixed with each individual 200.00 g soil sample by shaking in plastic containers on an end-over-end shaker for 20 minutes.

Each treatment was replicated four times and a total of 12 pots were set up for the three successional experiments.

The fertilisers were incubated with the soil at a constant temperature of 20 °C and 35% (w/w) moisture content. After the samples were incubated for 1, 50 and 111 days, four pots from each treatment were taken for the isotopic labelling experimentation. Labelling of the samples was achieved by shaking 5 ml of solution containing about 185 kBq carrier-free ^{32}P with the soil plus fertiliser materials in sealed plastic containers on an end-over-end shaker for 20 minutes. The labelled samples were repacked into plastic pots of 80 mm diameter x 50 mm height and revegetated with ryegrass. The revegetation method was the same double pot approach as

described in the previous chapter (cf. Section 4.2). The only alteration was that smaller pots (80 mm diameter x 50 mm height) were used.

The labelled and revegetated pots were randomly placed in a growth chamber at 15 - 25 °C temperature and 16 hours of daily lighting. Soil moisture was adjusted to 70% water holding capacity twice a week and each pot received 50 ml of the P-free nutrient solution weekly (cf. Section 4.2). The grass was cut at about weekly intervals by hand using scissors. A total of six cuts were made from each of the three successive experiments. The whole sample from each pot was analysed for specific activity. The procedures of sample processing, digestion and radioassay have been described above (cf. Section 3.3.2), and the concentration of P in the plant digest was determined manually on a colourimetric spectrophotometer using the vanodomolybdate yellow method (Olsen and Sommers, 1982).

The safety precautions described in Section 3.3.3 were observed throughout the course of the operations involving the use of radioactive ^{32}P.

5.4 Results and discussion

5.4.1 Temporal changes of specific activity in the exchangeable P pools

The changes of specific activity in the exchangeable P pools as sampled by plants obtained from the three experiments (Experiments A, B and C) after the fertilisers were incubated with the soils for 1, 50 and 111 days are shown in Figures 5.4A, 5.4B and 5.4C. The values from the first harvest of each experiment are not included in the figures because they are heavily influenced by the P contained in the original grass seedlings. The first points illustrated in the graphs are therefore from the second harvest, which may also bear varying degrees of influence from the initial P content in most of the treatments. The points that are not significantly affected by the P content of the initial grass seedlings and thus reflect the changes of specific activity in the soil exchangeable P pools are those from the last four samplings of the fertilised treatments in each experiment, and these are the points that are used for the

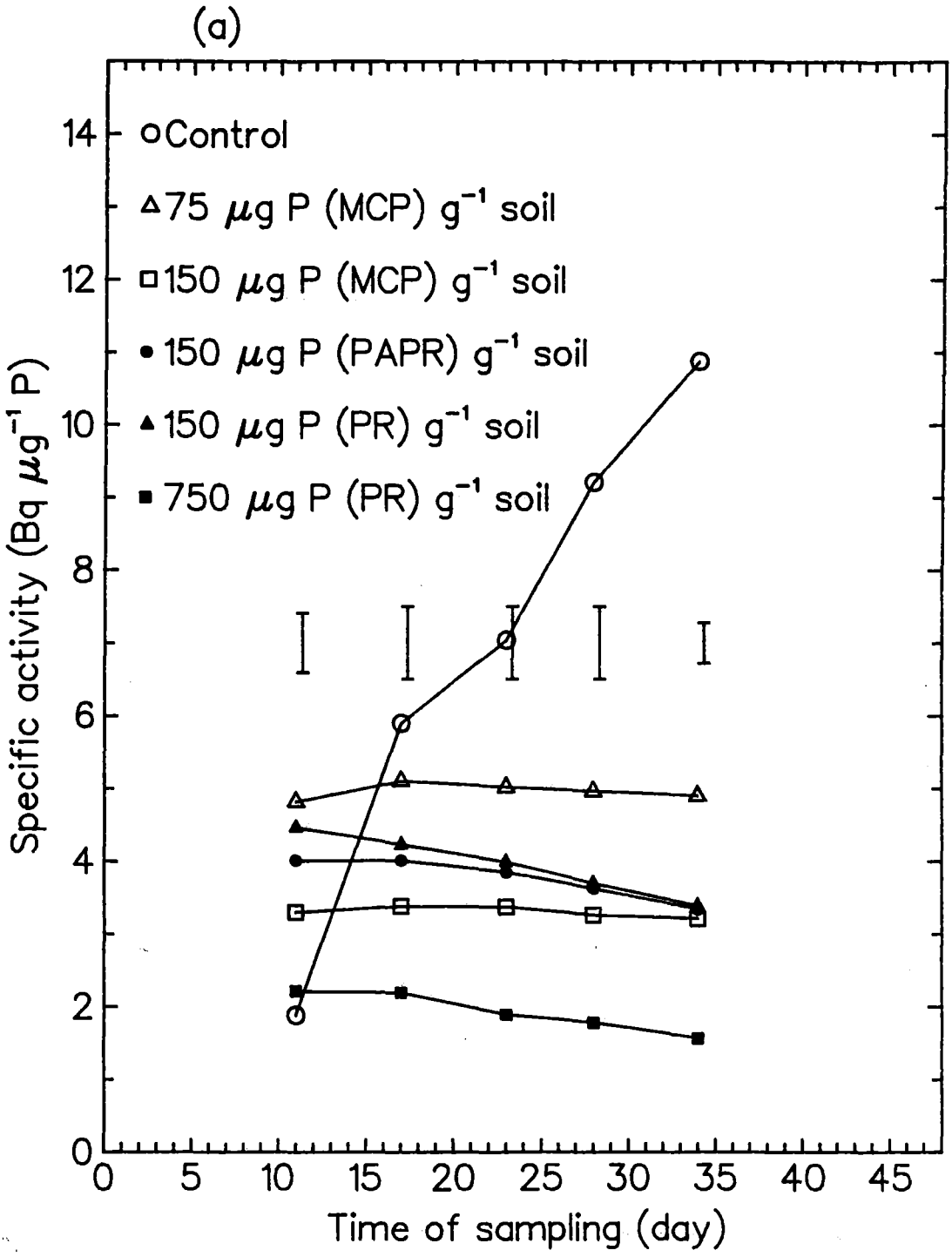
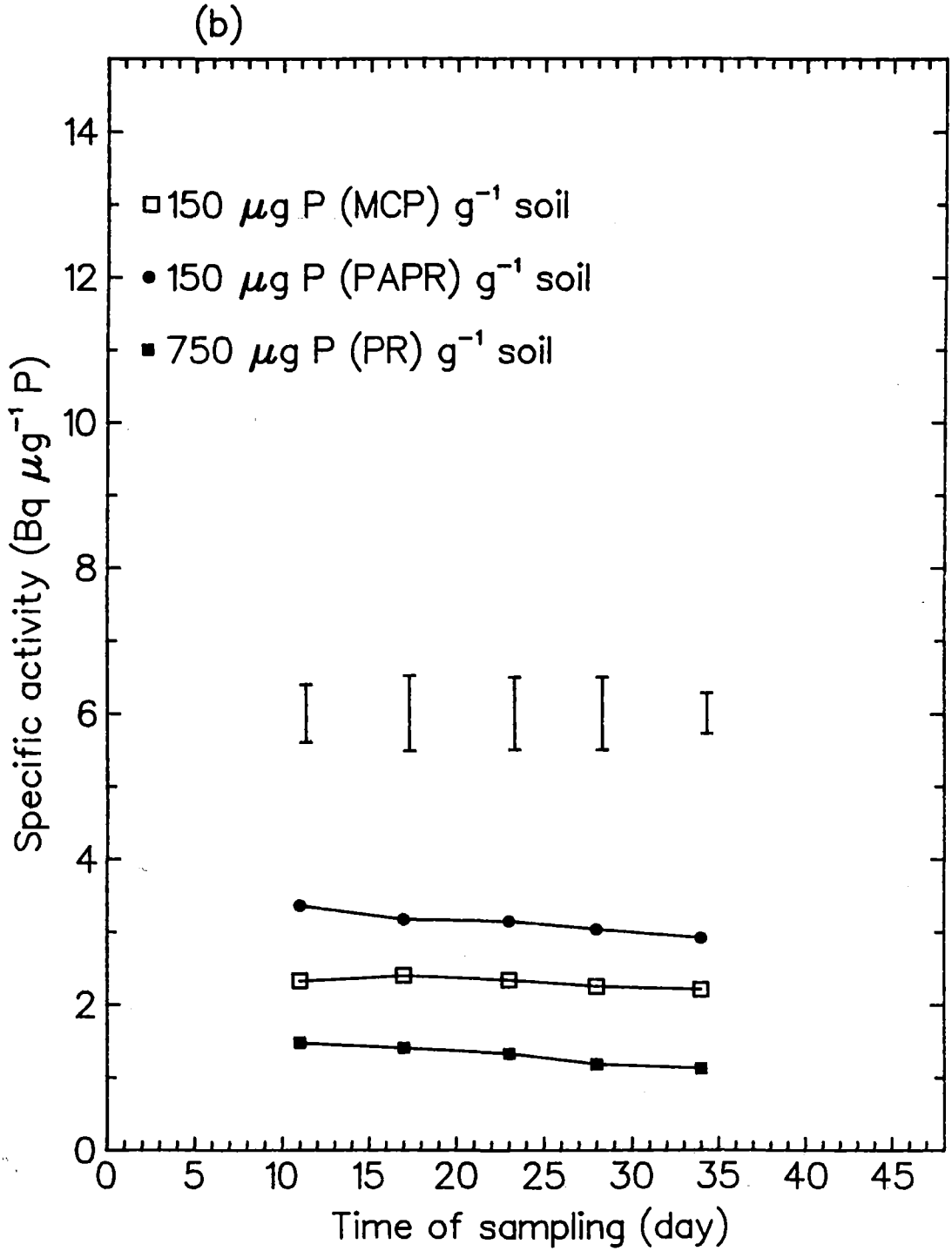


Figure 5.4A Changes of specific activity in the soil exchangeable P pools as sampled by plants through a period of 34 days after one day of incubation (Experiment A): (a) Tekapo soil; (b) Craigieburn soil.

The vertical bars represent LSD (0.05).


(b)
150 μg P (MCP) g⁻¹ soil
150 μg P (PAPR) g⁻¹ soil
750 μg P (PR) g⁻¹ soil
Specific activity (Bq μg⁻¹ P)
Time of sampling (day)
0
2
4
6
8
10
12
14
0
5
10
15
20
25
30
35
40
45

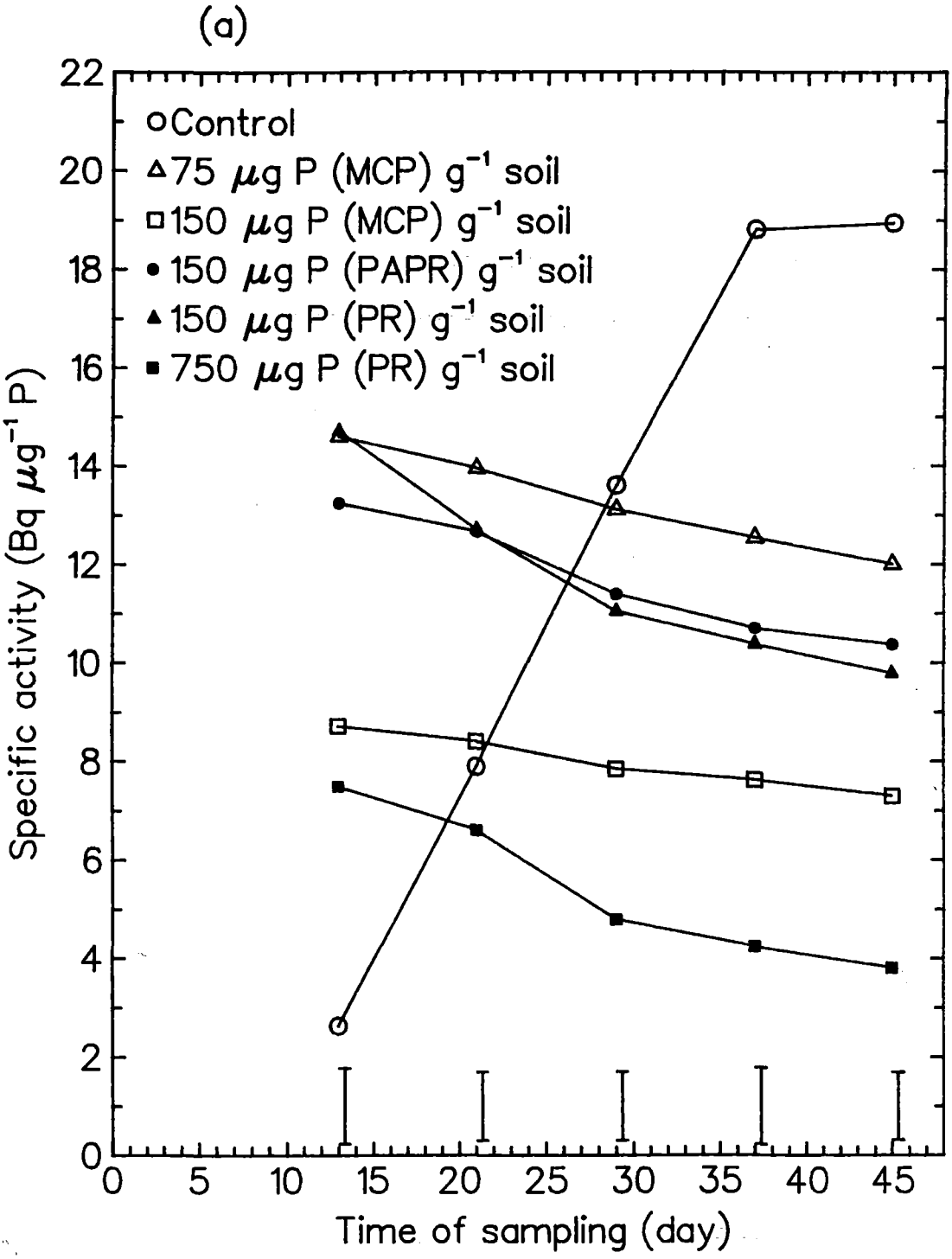
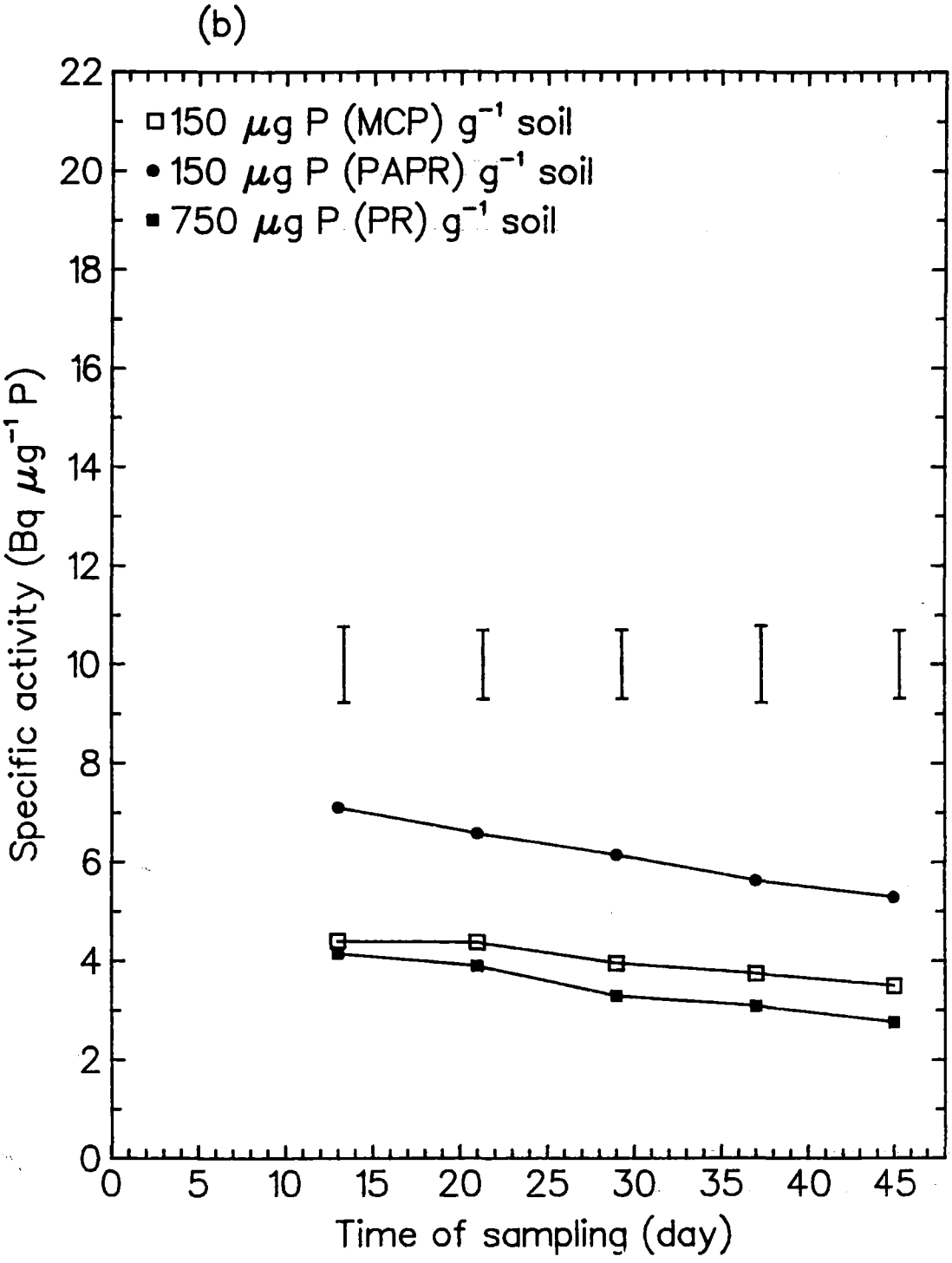


Figure 5.4B Changes of specific activity in the soil exchangeable P pools as sampled by plants through a period of 45 days after 50 days of incubation (Experiment B): (a) Tekapo soil; (b) Craigieburn soil.

The vertical bars indicate LSD (0.05).


(b)
□150 μg P (MCP) g⁻¹ soil
• 150 μg P (PAPR) g⁻¹ soil
■ 750 μg P (PR) g⁻¹ soil
Specific activity (Bq μg⁻¹ P)
Time of sampling (day)
0
2
4
6
8
10
12
14
16
18
20
22
0
5
10
15
20
25
30
35
40
45

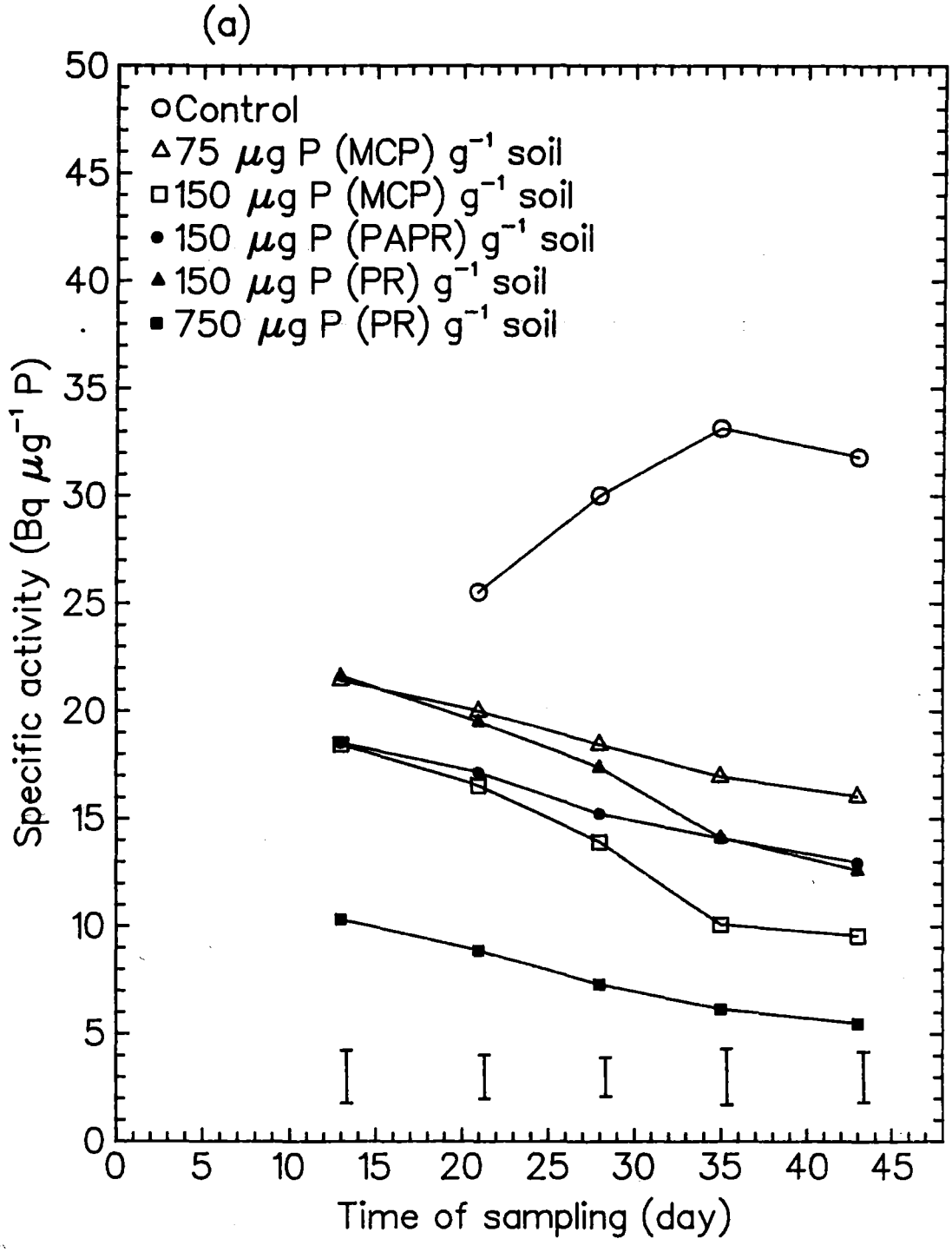
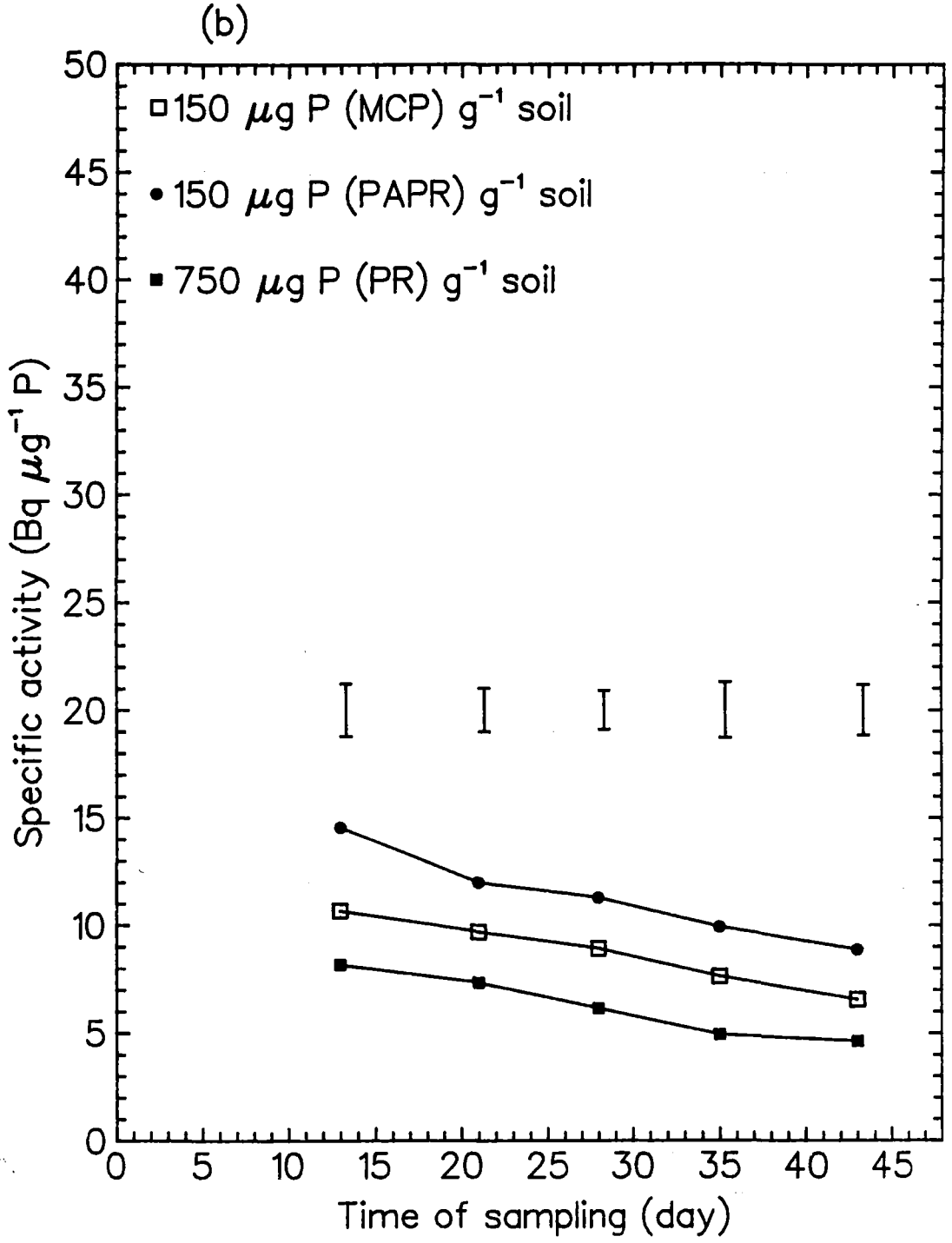


Figure 5.4C Changes of specific activity in the soil exchangeable P pools as sampled by plants through a period of 43 days after 111 days of incubation (Experiment C): (a) Tekapo soil; (b) Craigieburn soil.

The vertical bars indicate LSD (0.05).


(b)
□150 μg P (MCP) g⁻¹ soil
• 150 μg P (PAPR) g⁻¹ soil
■ 750 μg P (PR) g⁻¹ soil
Specific activity (Bq μg⁻¹ P)
Time of sampling (day)
0
5
10
15
20
25
30
35
40
45
50

extrapolation of SA_1 and SA_2 required to calculate F_{in} and F_{out} as discussed in the previous section (Section 5.2.2).

In the control treatment of the Tekapo soil, the effect of the initial plant P content on the specific activity persisted in all the samplings of Experiments A and B, and only vanished in the last two samplings of Experiment C. It was considered that this is due to the very low level of plant available P in the soil which limits sufficient plant growth to remove the effect. In fact, the growth rate of plant in the control of the Craigieburn soil (Treatment 7) was so low that only one or two harvests could be made in each experiment. The specific activity curves therefore could not be shown in the figures.

A general pattern shown in these figures, particularly in Figures 5.4A and 5.4B is that the rate of decline of specific activity in the exchangeable P pools of the soils treated with different fertilisers followed the sequence: NCPR > NCPAPR > MCP. This reflects the high inflow of P dissolving from the apatite of the PR material which continued to dilute the declining amounts of ^{32}P left in the exchangeable P pool. In the MCP (solution) treated soils, the added phosphate was mostly mixed with the ^{32}P immediately after labelling. The specific activity therefore reached a relatively stable value instantly. The small decline probably resulted from the input of P from the reaction products of the fertiliser with soil components and from native soil P sources, both inorganic and organic, and from prolonged isotopic exchange at less rapidly exchangeable sites. The difference in the changing pattern of specific activity between the soil treated with different fertilisers became less obvious in Experiment C after 111 days of incubation. With increasing periods of incubation, considerable amounts of P have been dissolved from the PR materials. The rate of P input to the exchangeable P pool from dissolution of PR materials would have decreased to lower values. The exact nature of the dynamics of P in the soils which received different fertilisers will be discussed in detail in the next section (Section 5.4.2).

5.4.2 Kinetics of dissolution and retention of phosphate fertilisers

The kinetics of phosphate dissolution from the fertilisers and retention by soils is assessed in two ways: the changes of the exchangeable P pools with increasing periods of incubation and the rates of inflow and outflow which are responsible for the P pool changes.

I. Changes of the exchangeable P pools

The exchangeable P pools, $Q_{t=1}$, $Q_{t=50}$ and $Q_{t=111}$, corresponding to 1, 50 and 111 days of incubation are summarised in Table 5.4. The size of the exchangeable P pool for the control of the Craigieburn soil was not determined due to the lack of data from the SA-t curve.

The $Q_{t=1}$ values in the MCP (solution) fertilised treatments of the Tekapo soil indicate that the amounts of exchangeable P contributed by the fertiliser are slightly smaller than the rates of application (70.8 and 126.3 compared with 75 and 150 μg P g^{-1} soil respectively). This is not necessarily due to any erratic mechanisms of underestimation in the MCP-treated soils. Rather, it may imply that a portion of the phosphate applied in solution form had reacted with soil constituents and been transformed to less rapidly exchangeable forms after just one day of incubation. The exchangeable P pool decreased sharply with increasing periods of incubation and was approximately halved after 111 days. In contrast to the sharp decrease in MCP-treated soils, the exchangeable P pools in the PR and PAPR treated soils after 50 and 111 days of incubation remained generally stable. Although the $Q_{t=50}$ values in the MCP-treated soils were higher than those in the PR and PAPR treated soils at the same application rate, they settled to very similar values after 111 days of incubation. This contrasting pattern is due to differences in dissolution and retention characteristics between the totally water-soluble and slowly soluble fertilisers which are discussed below in terms of F_{in} and F_{out}.

Table 5.4 Sizes of the exchangeable P pools as influenced by the periods of incubation.

Treatment	Exchangeable P pools (μg P g^{-1} soil)		
	$Q_{t=1}$	$Q_{t=50}$	$Q_{t=111}$
Tekapo soil:			
Control	45.8 (1.9)[1]	45.8 (1.9)	45.8 (1.9)
75 μg P(MCP) g^{-1}	116.6 (0.7)	82.0 (2.6)	65.4 (5.9)
150 μg P(MCP) g^{-1}	172.1 (5.0)	143.5 (2.1)	71.6 (5.2)
150 μg P(PAPR) g^{-1}	136.8 (14.5)	87.1 (1.5)	73.7 (5.4)
150 μg P(PR) g^{-1}	116.7 (1.1)	76.5 (3.9)	66.3 (2.5)
750 μg P(PR) g^{-1}	206.0 (5.8)	128.6 (10.3)	116.7 (9.4)
Craigieburn soil:			
Control	n.d.	n.d.	n.d.
150 μg P(MCP) g^{-1}	236.3 (6.1)	253.8 (8.2)	117.9 (2.2)
150 μg P(PAPR) g^{-1}	173.9 (9.0)	160.3 (19.9)	91.8 (4.1)
750 μg P(PR) g^{-1}	345.7 (16.0)	243.9 (7.2)	148.4 (9.1)

1: The figures in the brackets are standard errors of the mean.

It should be noted that $Q_{t=1}$ values from the PR-treated soils are likely to be overestimated due to the violation of the assumption that F_{in} and F_{out} remain stable through the period of the measurement (cf. Section 5.2.1). As soon as the PR was added to the soils, it would dissolve quickly due to the favourable conditions (e.g. low concentrations of phosphate and Ca in the soil solution, low soil pH). The SA-t curve would decline initially at a much greater rate than at later stages when the system was more stable with respect to the rate of dissolution (Figure 5.5). The SA-t curve therefore did not follow a single log-linear relationship through the entire period of the

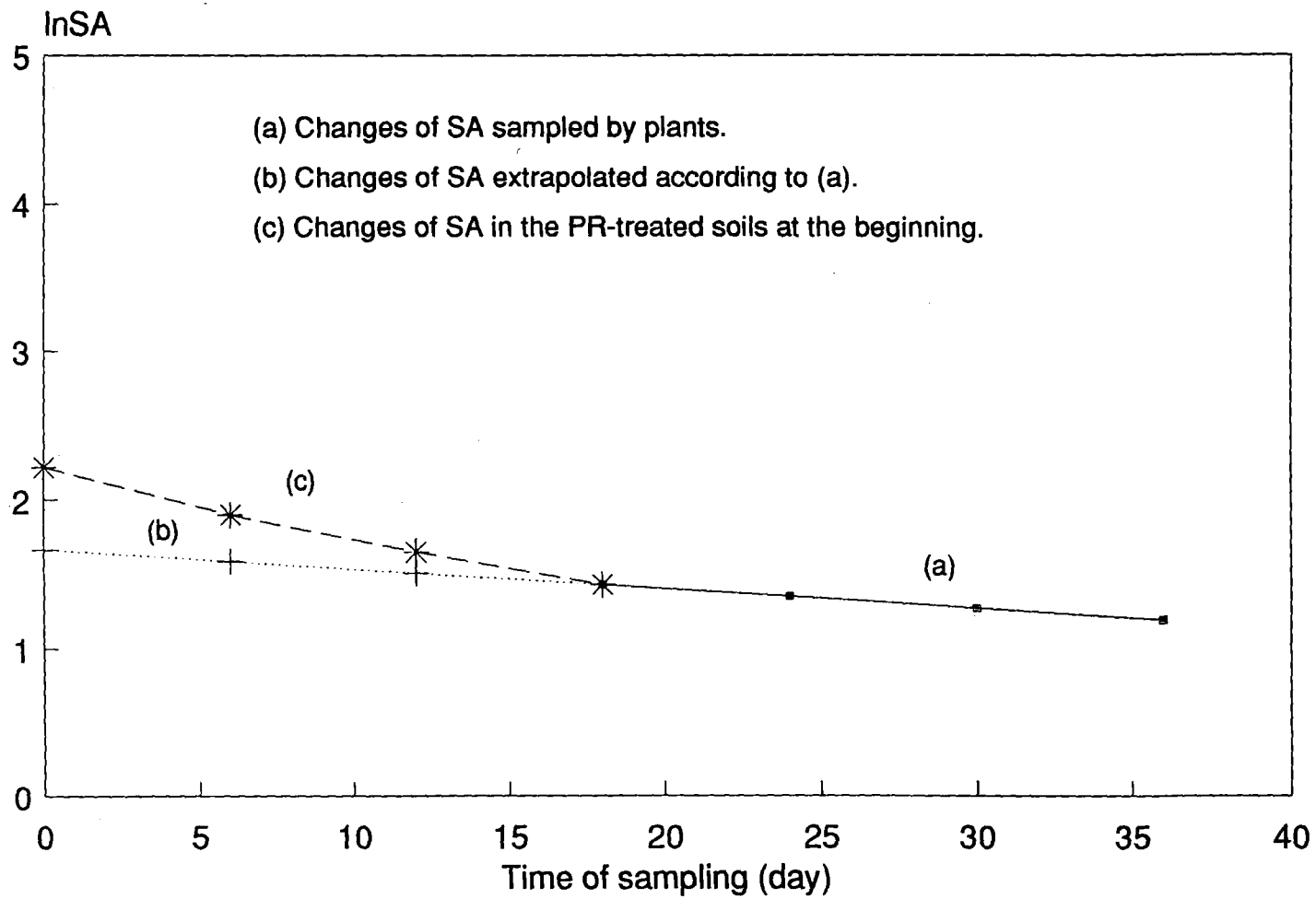


Figure 5.5 Diagrammatic illustration of the underestimation of the instantaneous SA ($SA_{t=1}$) and overestimation of the exchangeable P pool ($Q_{t=1}$) in the PR-treated soils after one day of incubation.

labelling experiment. Unfortunately, the SA-t curve in the early stages were difficult to obtain. The extrapolation back to the time of labelling (Line b) on the basis of the later segment of the SA-t curves (Line a) would underestimate $SA_{t=1}$ (lower than that estimated by Line c) and thus overestimate the $Q_{t=1}$ values, although the degree of overestimation was eased by the extrapolation. The overestimation of $Q_{t=1}$ would lead to underestimation of F_{in} and overestimation of F_{out} between the period of 1 to 50 days. However, this does not invalidate the F_{in} and F_{out} greatly as the F_{in} and F_{out} are average values through a period of 50 days, whereas the $Q_{t=1}$ is an instantaneous result at a particularly unstable point. This effect may also apply, to a lesser extent, to the PAPR-treated soils. It would be negligible, however, in the MCP-treated soil. The MCP was applied in solution and the P applied would enter the exchangeable P pool instantly. The subsequent F_{in} would be very small and the specific activity in the exchangeable P pool would not be expected to change sharply (cf. Figure 5.4). The overestimation would not occur significantly for $Q_{t=50}$ and $Q_{t=111}$. With increasing periods of soil-fertiliser contact, a relatively stable dissolution system was developed in the soil. The rate of dissolution would not change as fast as at the very beginning of the incubation. The F_{in} and F_{out} values between 50 and 111 days therefore bear no effects from the overestimation. As our interest with PR-containing fertilisers lies mainly in the long term effectiveness of these fertilisers, the discussions which follow will centre on the relatively long term F_{in} and F_{out} values.

II. Rates of inflow and outflow

The rates of inflow (F_{in}) and outflow (F_{out}) which govern the sizes of the exchangeable P pools in the soils are summarised in Table 5.5.

Table 5.5 The rates of inflow and outflow of phosphate to and from the exchangeable P pools.

Treatment	Rates of inflow and outflow (μg P g^{-1} soil $\cdot$ day^{-1})			
	F_{in} (1 to 50 days)	F_{out} (1 to 50 days)	F_{in} (50 to 111 days)	F_{out} (50 to 111 days)
Tekapo soil:				
Control	0.102 (0.004)[1]	0.102 (0.004)	0.102 (0.004)	0.102 (0.004)
75 μg P (MCP) g^{-1}	0.239 (0.001)	0.944 (0.005)	0.398 (0.012)	0.671 (0.021)
150 μg P (MCP) g^{-1}	0.535 (0.016)	1.119 (0.033)	0.429 (0.006)	1.608 (0.023)
150 μg P (PAPR) g^{-1}	0.906 (0.096)	1.920 (0.203)	0.659 (0.011)	0.878 (0.015)
150 μg P (PR) g^{-1}	1.265 (0.012)	2.083 (0.019)	0.905 (0.046)	1.072 (0.054)
750 μg P (PR) g^{-1}	3.169 (0.089)	4.749 (0.134)	2.757 (0.464)	2.953 (0.497)
Craigieburn soil:				
Control	n.d.	n.d.	n.d	n.d.
150 μg P (MCP) g^{-1}	1.270 (0.033)	0.913 (0.024)	1.309 (0.042)	3.538 (0.114)
150 μg P (PAPR) g^{-1}	0.969 (0.050)	1.586 (0.082)	1.097 (0.136)	2.221 (0.276)
750 μg P (PR) g^{-1}	4.080 (0.188)	7.590 (0.351)	2.908 (0.086)	4.473 (0.132)

1: The figures in brackets are standard errors of the mean.

The small rates of inflow and outflow in the Tekapo soil control probably resemble those occurring naturally in the soils with growing plants without contributions by fertilisers. The inflow processes would include desorption or dissolution of native inorganic soil P and mineralisation of organic P (cf. Section 2.4).

However, F_{in} will also include a term resulting from on-going slow isotopic exchange processes. It has been assumed in the development of equations for F_{in} and F_{out} that ^{32}P may only leave the exchangeable P pool together with ^{31}P in a ratio given by the specific activity. In reality, on-going slow isotopic exchange processes result in a reduction in specific activity, i.e. a reduction of ^{32}P in the exchangeable P pool without a corresponding reduction of ^{31}P. This process is considered as a ^{32}P and ^{31}P removal from the exchangeable P pool in a ratio given by the specific activity with a compensating inflow of ^{31}P by the model developed above (Section 5.2.1). The outflows consist of the reverse processes of the first three inflows plus plant uptake.

In the Tekapo soil, since the MCP was applied in solution form, most of the phosphate would be expected to enter the exchangeable P pool immediately upon addition to the soil. Further supplies of phosphate to the exchangeable P pools were therefore small (Table 5.5). In addition to those processes discussed for the control treatment, the small inputs also include phosphate sorbed on soil surfaces prior to the time of labelling entering the exchangeable P pools. The rates of outflow were markedly larger than those of inflow. The high rates of outflow indicate the significant removal of phosphate from the exchangeable P pool by soil retention. This was due to the very high concentration of P in the soil solution following the addition of the MCP solution, and may represent a change in the nature of bonding between phosphate ions and soil particles, from more loosely bound to more tightly bound forms. The net effect of these two unequal processes was a sharp decline in exchangeable P pools with increasing periods of incubation (cf. Table 5.4). The use of water soluble phosphate fertilisers therefore results in sharp rises in soil exchangeable P pools immediately following applications and sharp falls with increasing periods of contact with the soil.

In contrast, F_{in} in the PR- and PAPR-treated Tekapo soils was maintained at significantly greater values than that in the MCP-treated soil at the same rate of application. The F_{in} between the three fertilisers follow the order: PR > PAPR > MCP. F_{out} in the soils treated with PR and PAPR between 50 to 111 days was considerably

smaller than that in the soils treated with MCP at the same rate. The smaller F_{out} values, which indicate lower rates of P retention, is due to the gradual dissolution of PR and PAPR, which does not produce very high concentrations of P in soil solution. The continued input of P from PR dissolution at relatively high rates and removal of P at relatively low rates would therefore maintain the exchangeable P pool at relatively stable values for extended periods (Table 5.4).

The P-retention capacity influenced the rates of PR dissolution in the two soils. Assuming that the F_{in} and F_{out} values are similar between the controls of the two soils, the rates of PR and PAPR dissolution were in general slightly greater in the higher P-retention Craigieburn soil than in the Tekapo soil, but the rates of removal from the exchangeable P pool were also higher in the Craigieburn soil with increasing time of soil-fertiliser contact (Table 5.5). The greater rate of dissolution is due to the effective removal of phosphate ions from the soil solution by soil retention (Chu *et al.*, 1962; Smyth and Sanchez, 1982), i.e. the greater F_{in} is due to the effect from a greater F_{out}. Upon addition to a relatively high P-retention soil, the PR material would dissolve rapidly, raising the size of the exchangeable P pool. With time, however, the dissolved P was retained by the soil. The greater F_{out} than F_{in} would therefore result in rapid decreases in the exchangeable P pool (Table 5.4). It should be noted that the concentration of exchangeable Ca in the Craigieburn soil is slightly lower than that in the Tekapo soil (Table 5.2). This also favours greater PR dissolution in the Craigieburn soil (Mackay *et al.*, 1986). However, the magnitude of this effect is likely to be limited, because the difference in exchangeable Ca between the two soils is small.

A comparison of the results between the treatments of 150 μg P (PR) g^{-1} and 750 μg P (PR) g^{-1} in the Tekapo soil (Table 5.5) indicates that although the rate of PR dissolution applied at a lower rate was smaller in absolute terms, it is greater in relative terms than when applied at a higher rate. This agrees with results obtained from chemical extraction methods reported in the literature (e.g. Hughes and Gilkes, 1986a, b; Kanabo and Gilkes, 1987b, 1988a) that the extent of PR dissolution decreases with

increasing application rates. More complete dissolution of PR applied at the lower rate is probably due to greater mean distances between particles and less chance of overlap of zones of H^+ depletion and dissolution product accumulation.

In general, the isotopic dilution technique developed in this study is successful in revealing the kinetics of phosphate in the soils. The method not only measures the sizes of the exchangeable P pools at a point of time, but also the rates of input (fertiliser dissolution) and output (phosphate retention) to and from the P pools which essentially control the sizes of the exchangeable P pools. The most important attribute of this technique is that, unlike other chemical extraction soil testing methods (cf. Section 2.5.2) which extract a small volume of soil under artificially imposed conditions which are drastically different from those of growing plants, it measures the dynamics of phosphate under growing plants using comparatively large volumes of soil. Plants were used to sample the ratio of ^{32}P:^{31}P in the rapidly exchangeable P pool of the soil. Results obtained in this manner would be expected to reflect the conditions of growing plants better than those obtained by chemical extraction methods.

5.5 Summary and conclusions

The kinetic parameters of dissolution and retention of phosphate fertilisers applied to soils are clearly revealed by the methods developed in this study. In general, the results demonstrate that most of the phosphate applied in water soluble form (MCP solution) enters the exchangeable P pool immediately after being added to the soil. The rate of any further supply is small. If not utilised by plants, the phosphate will be quickly transformed to less rapidly exchangeable forms with increasing periods of contact with the soils. The imbalanced rates of inflow and outflow result in a rapid decline in the exchangeable P pool. Thus, the use of water soluble phosphate fertilisers would result in sharp rises in the soil exchangeable P pool immediately after applications and sharp falls afterwards. In the soils treated with PR or PAPR fertilisers (NCPR and NCPAPR), although the exchangeable P pools are initially smaller than

those in the MCP-treated soils, they are maintained at relatively stable sizes for prolonged periods by the continuous dissolution of PR materials. The rates of phosphate retention by the soil are smaller than those in the soils that receive MCP. The application of PR-containing fertilisers would therefore not only maintain the exchangeable P pool in the soil at relatively stable sizes but also reduce the amounts of P being transformed to less rapidly exchangeable forms.

An increase in soil P-retention increases both the rate of fertiliser dissolution and the rate of phosphate retention by the soil. The PR dissolves faster relatively at a lower application rate, although slower in absolute terms.

The most important advantage of this isotopic dilution technique over other chemical extraction methods is that it measures the rates of phosphate retention as well as dissolution under conditions of growing plants using comparatively large volumes of soil. It provides quantitative information for understanding of the dynamics of different types of phosphate fertilisers applied to soils.

Chapter 6

Comparison of isotopically measured kinetic parameters with those derived by chemical extraction methods

6.1 Introduction

Parallel to the isotopic labelling experiment described in Chapter 5, an incubation study encompassing the same treatments as those in the labelling experiment was carried out. The extent of fertiliser dissolution was measured by following the changes of P or Ca extractable by chemical extractants from soils to which different fertilisers had been added. The objective was to assess the dissolution characteristics of different types of phosphate fertilisers applied to soils and to compare the results derived from the extraction methods with those from the isotopic labelling experiment. As no one single extraction is adequate to reveal the extent of dissolution of PR-containing fertilisers in the soil (cf. Section 2.7.3), separate samples were therefore extracted with water, 0.03 M NH_4F + 0.025 M HCl (Bray I P) and 0.5 M $NaHCO_3$ (Olsen P) to investigate the amounts of plant-available P in soil solution and the immediate reserves contributed by the dissolution of fertilisers. Extractions were also made with 0.5 M NaOH followed by 1 M HCl, and with 0.5 M $BaCl_2$/TEA (pH=8.1) to estimate the total amounts of fertiliser transformed from apatite to other inorganic forms in the soil.

This chapter reports the results from this incubation experiment and compares them with those from the kinetic study reported in Chapter 5. The relationships between these chemical indices and plant responses will be examined in Chapter 7.

6.2 Materials and methods

The same treatments using the same soils and fertilisers as those in the kinetic experiment described in Chapter 5 (cf. Section 5.3) were laid out for the incubation experiment. The fertilisers were incubated with the soils under the same conditions as those for the labelling study (20 °C constant temperature and 35% (w/w) soil moisture content). The procedures involved in setting up the incubation have been described in Chapter 5 (cf. Section 5.3).

After 1 day, 8, 24, 51, and 111 days of incubation, the soils were subsampled for extractions. The samples were air-dried, and passed through a 2 mm sieve for the water extractable, Bray I and Olsen P analyses and for the 0.5 M $BaCl_2$/TEA extractable Ca analysis. The samples for the 0.5 M NaOH followed by 1 M HCl extractions were ground to pass a 0.25 mm sieve.

The procedures involved in the extractions of water extractable P (Olsen and Sommers, 1982), Bray I P (Bray and Kurtz, 1945) and Olsen P (Olsen *et al.*, 1954) have been summarised in Chapter 4 (cf. Section 4.2). These extractions were not intended to measure the total amount of fertiliser P dissolved, but to estimate the amount of plant-available P provided by the fertilisers.

The fractionation of soil inorganic P with extractions by 0.5 M NaOH followed by 1 M HCl was based on studies by Rajan (1983), Mackay *et al.* (1986) and Bolan and Hedley (1989). Mackay *et al.* (1986) suggested that extraction with dilute NaOH would remove non-occluded Al-P and Fe-P from a soil but would not dissolve to any significant extent the minerals of the apatite group, and that the increase in the 0.5 M NaOH extractable inorganic P in a soil to which a PR was added should provide a good estimate of the amount of P dissolved from the PR. However, this method alone is unlikely to be accurate under conditions where there is active net mineralisation or immobilisation of soil P, or considerable losses of P by plant uptake or leaching. Bolan and Hedley (1989) therefore recommended the inclusion of a 1 M

HCl extraction following the extraction with 0.5 M NaOH to determine the amount of apatite P remaining undissolved in the soil.

In this experiment, the soil samples (<0.25 mm) were shaken on an end-over-end shaker with 0.5 M NaOH solution at the soil:solution ratio of 1:100 for 16 hours. After centrifugation (cf. Section 4.2), the supernatant was analysed for inorganic P. The soil residue was shaken with 1 M HCl at the soil:solution ratio of 1:50 for 2 hours. Following centrifugation, the supernatant was analysed for the amount of acid soluble apatite P remaining in the soil.

Mackay *et al.* (1986) suggested that a pretreatment with 1 M NaCl prior to the extraction with 0.5 M NaOH should be carried out to prevent the occurrence of $Ca(OH)_2$ precipitation and sorption of inorganic P onto it during the extraction (Syers *et al.*, 1972). Bolan and Hedley (1989), however, observed no such effect on acid soils and suggested that, because of the generally low levels of extractable Ca, the pre-extraction with 1 M NaCl is not necessary for the measurement of PR dissolution by 0.5 M NaOH method on acid soils. In fact, Hughes and Gilkes (1984) and Bolan and Hedley (1989) observed that the pH of this un-buffered 1 M NaCl solution was lowered by the soil exchangeable acidity and dissolution of PR was induced by this low pH solution. The pre-treatment with 1 M NaCl was therefore not included in this experiment. Because of the small amount of sample (0.300 g) used for extraction, a second treatment with 1 M NaCl solution prior to extraction with 1 M HCl was also omitted to minimise possible soil losses associated with the washing operations. This may bring about some carry-over of P to the 1 M HCl extraction, although the quantity is likely to be small.

The concentration of P in the extracts was determined manually on a colourimetric spectrophotometer according to the method of Murphy and Riley (1962).

The approach based on the measurement in the change of Ca (ΔCa) to determine the extent of PR dissolution in the soil assumes that PR dissolves congruently in the soil. The use of inadequately buffered extractants, such as KCl,

NaCl, or NH_4Cl, tends to induce PR dissolution due to the depression of pH in the solutions by the exchangeable acidity (Hughes and Gilkes, 1984). Monovalent salts also fail to attain complete extraction when the levels of Ca dissolved from the PR are high. The extent of PR dissolution may be grossly overestimated when the concentration of dissolved Ca is low and underestimated when the concentration of dissolved Ca is high. Hughes and Gilkes (1984) and Bolan and Hedley (1989) thus recommended the use of 0.5 M $BaCl_2$ buffered at pH 8.1 with triethanolamine ($BaCl_2$/TEA) to extract the dissolved Ca.

The soil samples in the experiment were shaken on an end-over-end shaker with 0.5 M $BaCl_2$/TEA (pH=8.1) at the soil:solution ratio of 1:10 for one hour. After centrifugation (cf. Section 4.2), the supernatant was mixed with diluent solution containing strontium ($SrCl_2 \cdot 6H_2O$) (Blakemore *et al.*, 1987) to eliminate possible phosphate interference. The concentration of Ca in the solution was determined on an atomic absorption spectrophotometer.

Duplicate extractions were carried out on all samples and results reported in subsequent sections are the mean values.

6.3 Results and discussion

6.3.1 Water extractable P, Bray I P and Olsen P

The changes of water extractable P, Bray I P and Olsen P with increasing periods of incubation in the soils which received different types of phosphate fertilisers are illustrated in Figures 6.1, 6.2 and 6.3 respectively. Figure 6.1 shows that the concentration of P in the water extract was increased considerably by the dissolution of the PR materials after one day of incubation. This clearly shows the reactive nature of the ground (<150 μm) North Carolina phosphate rock. The concentration of the water extractable P in the NCPR treated Tekapo soil (Figure 6.1 a) remained generally stable through the period of 111 days of incubation. This pattern sharply contrasts with that in the MCP (solution) fertilised soils whose water extractable P dropped rapidly with

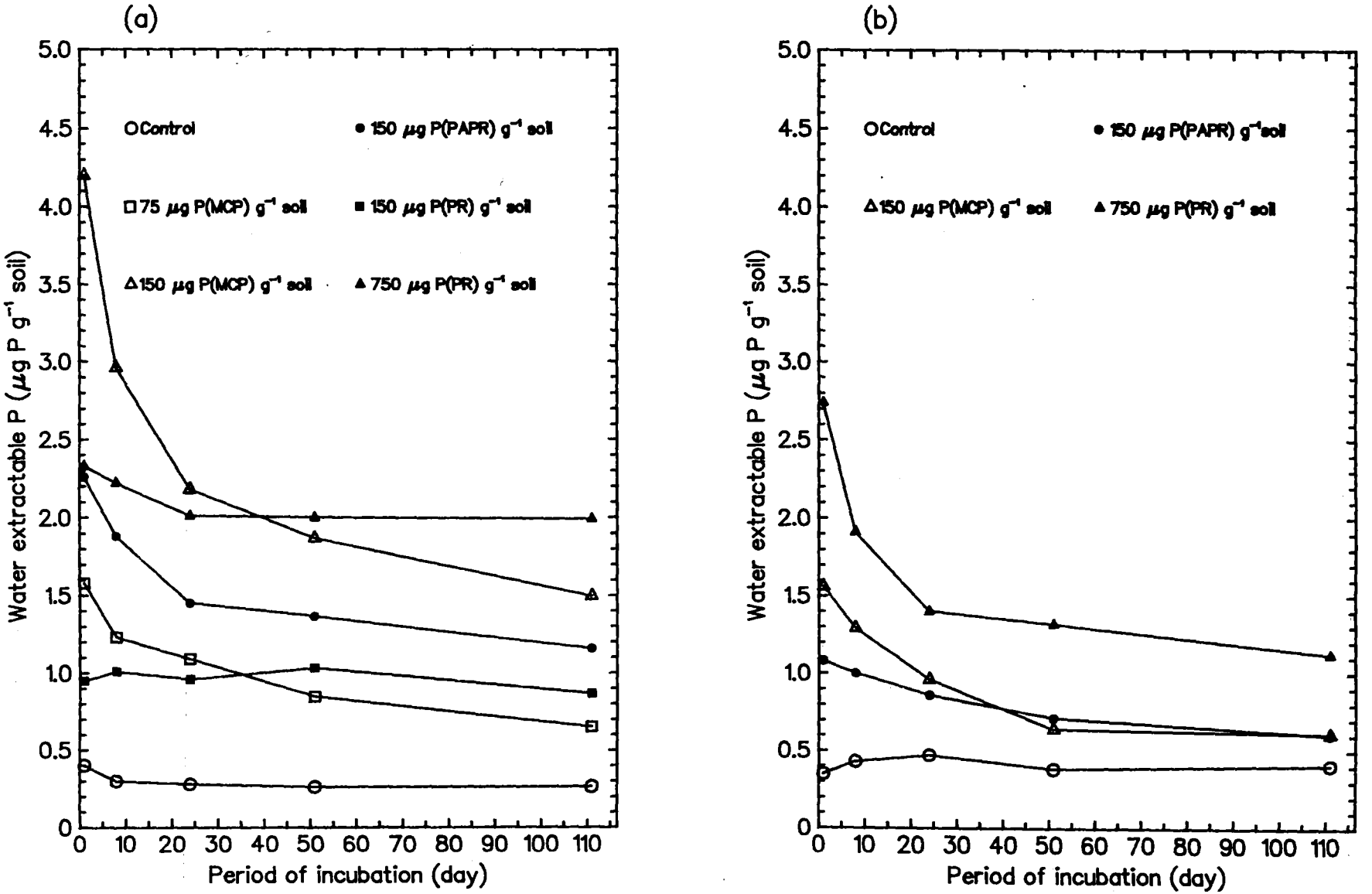


Figure 6.1 Changes of water extractable P with period of incubation: (a) Tekapo soil; (b) Craigieburn soil.

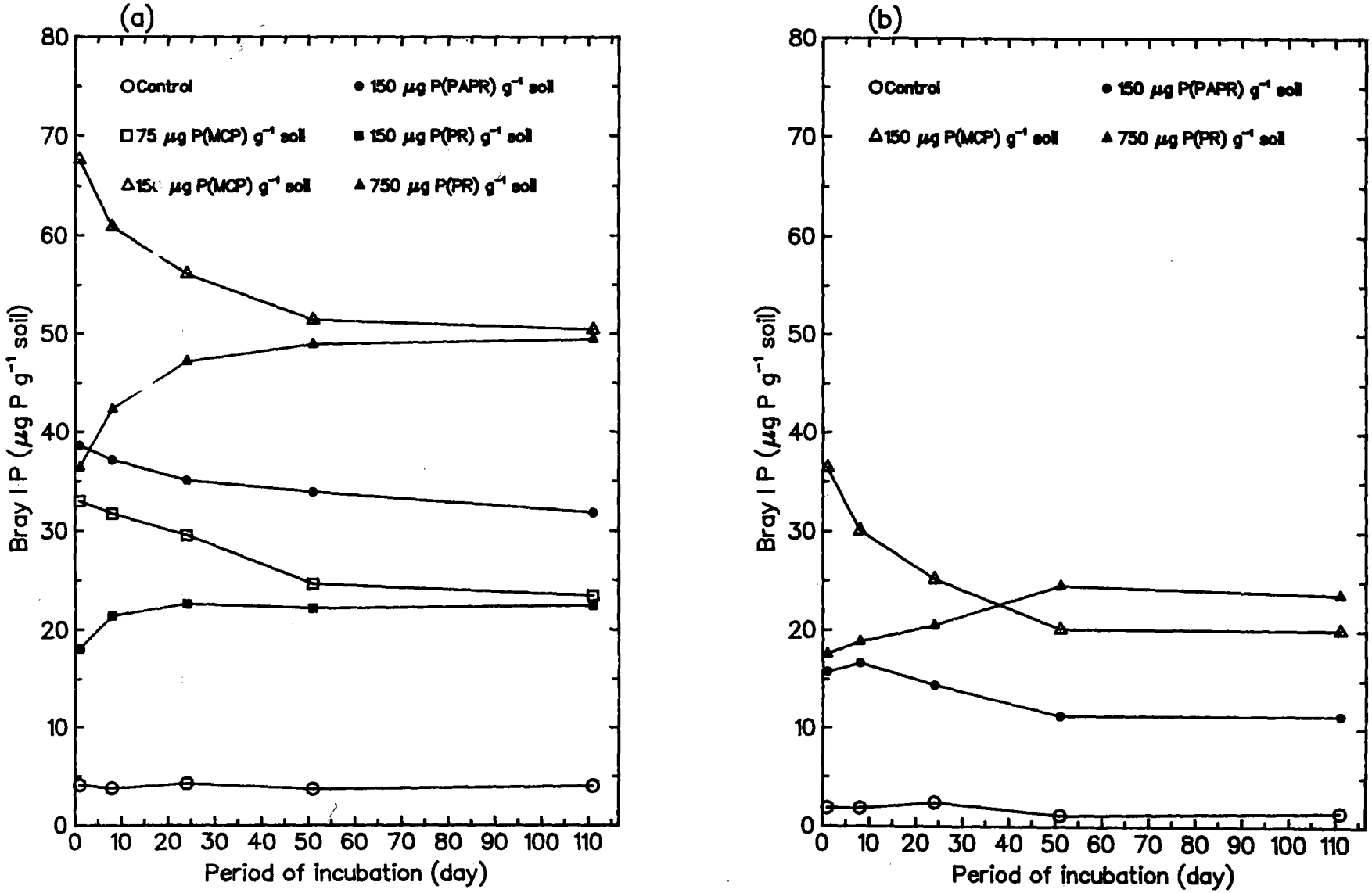


Figure 6.2 Changes of Bray I P with period of incubation: (a) Tekapo soil; (b) Craigieburn soil.

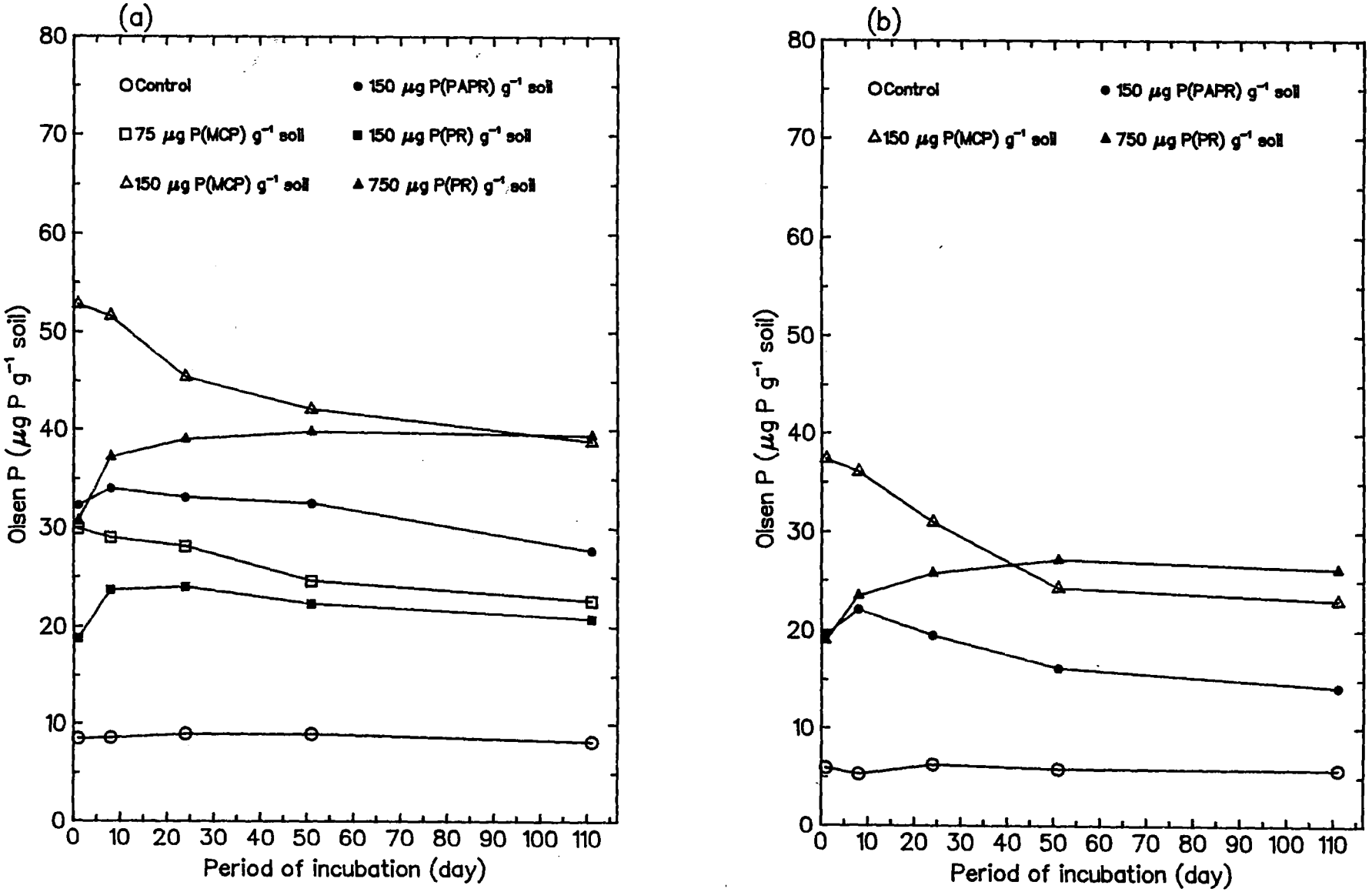


Figure 6.3 Changes of Olsen P with period of incubation: (a) Tekapo soil; (b) Craigieburn soil.

extended periods. In the higher P-retention Craigieburn soil (Figure 6.1 b), the water extractable P in the MCP fertilised samples dropped to a concentration similar to that in the soil which received PAPR at the same rate.

Similar patterns occurred in the Bray I and Olsen P values (Figures 6.2 and 6.3). Whilst the concentrations of Bray I P and Olsen P in the MCP fertilised samples declined with extended periods of incubation, they increased rapidly in the PR fertilised samples before reaching a plateau. The levelling off of the values in the PR-fertilised soils does not necessarily mean the cessation of PR dissolution, rather, it implies that the input of phosphate to these P pools from the PR dissolution was compensated by the output by soil retention. The values of the water, Bray I and Olsen P in the PAPR fertilised soils were intermediate between the MCP and PR treated soils.

The trends in the temporal changes of plant-available P in the soils which received different types of phosphate fertilisers, as measured by the three extraction indices, are in agreement with those predicted by the kinetic parameters derived from the isotopic labelling study (cf. Chapter 5). The temporal variation of water, Bray I and Olsen P pools can be considered in terms of the rates of input to and output from the exchangeable P pools estimated by the isotopic labelling method. Extractable P pools are increased to very high concentrations immediately following the application of MCP (solution) but diminish rapidly because of the high rate of P retention (high F_{out}) by soil components and lack of sustained phosphate input (low F_{in}) from further fertiliser dissolution (cf. Section 5.4.2). Extractable P pools in the soils which received PR and PAPR, in contrast, were not as high as those in the soils which received MCP, but were maintained by the continuous input (comparatively high F_{in}) of P from the dissolution of PR materials for prolonged periods and relatively lower rates of phosphate retention (comparatively low F_{out}).

The relationships between the three chemical indices and the isotopically measured exchangeable P pools are variable (Figures 6.4, 6.5 and 6.6). The symbols in the three figures, P(E), P(W), P(B) and P(O) represent exchangeable P, water

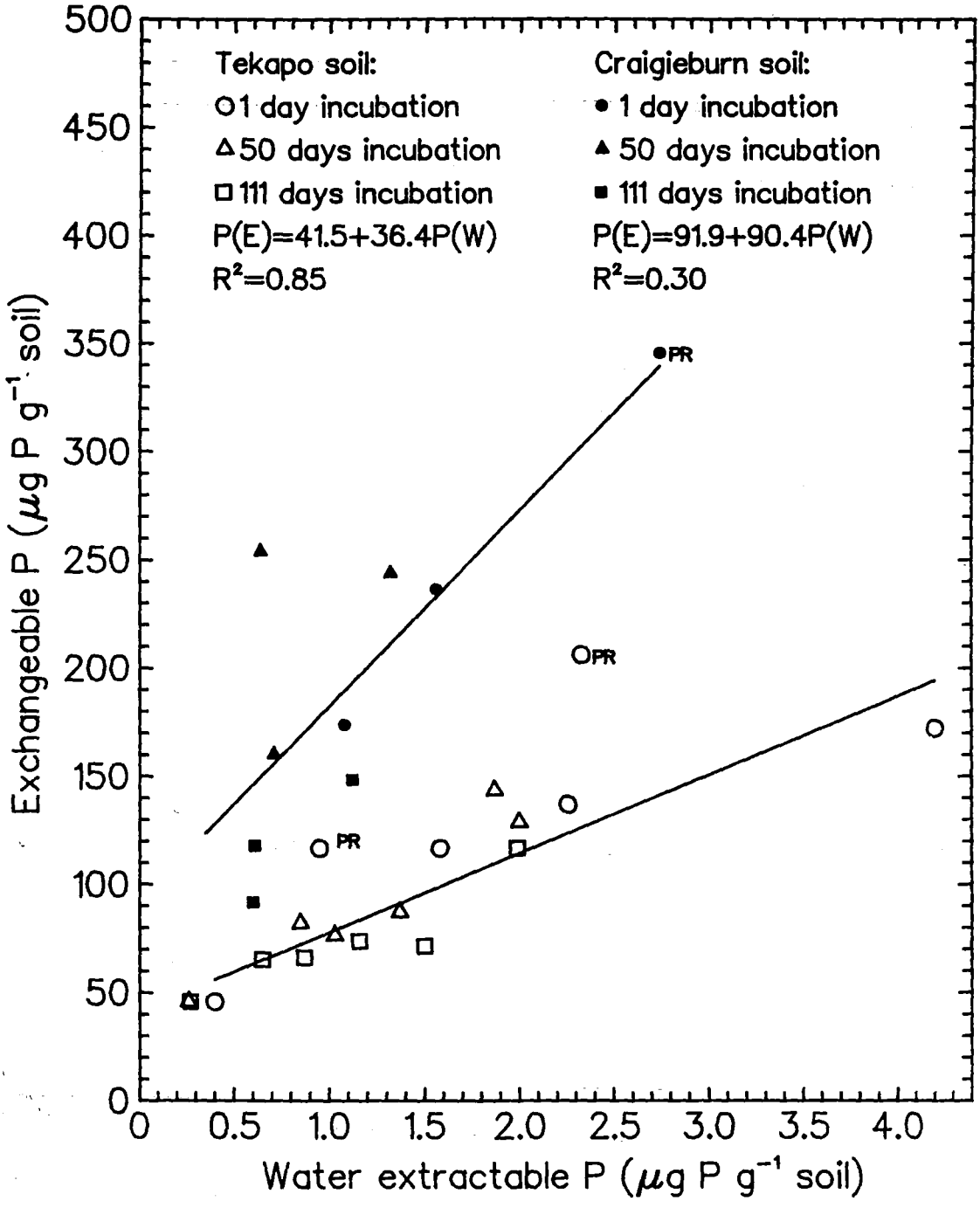


Figure 6.4 Relationships between exchangeable P and water extractable P.

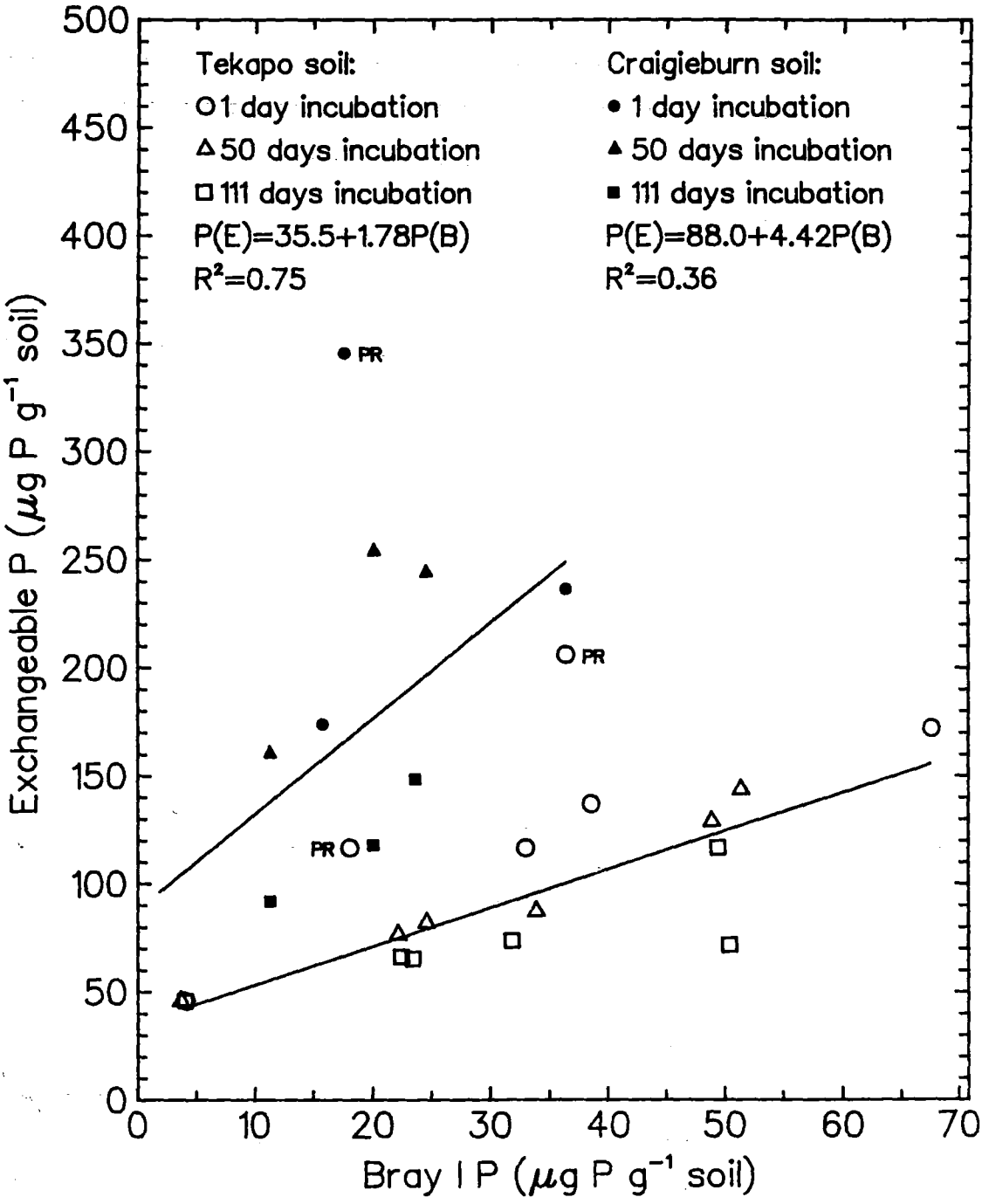


Figure 6.5 Relationships between exchangeable P and Bray I P.

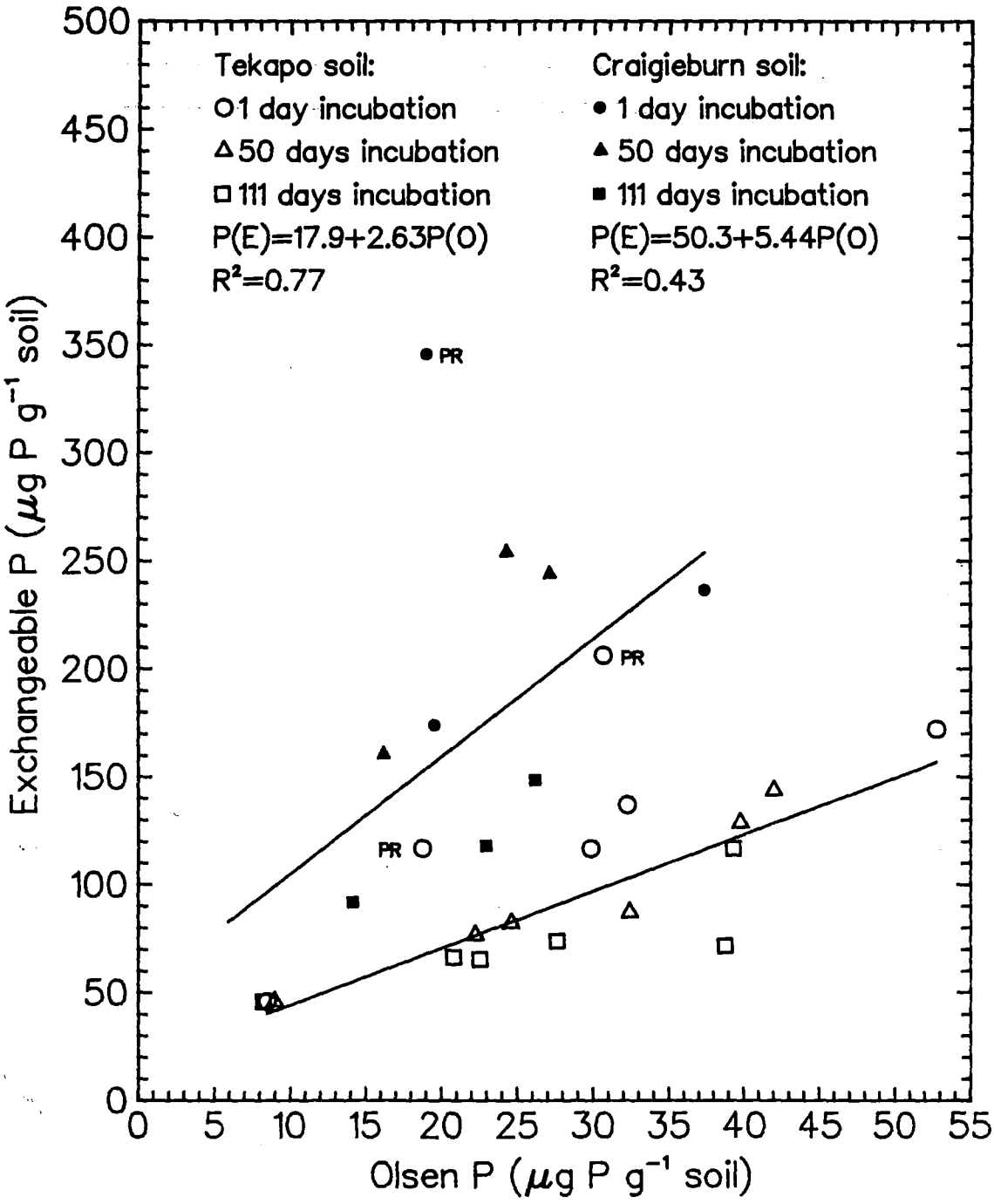


Figure 6.6 Relationships between exchangeable P and Olsen P.

extractable P, Bray I P and Olsen P respectively. It was suggested in Chapter 5 (cf. Section 5.4.2) that the exchangeable P pools of PR-treated soils at the one day incubation ($Q_{t=1}$) were overestimated. This is clearly shown in the figures by the scattered points labelled "PR" located away to the upper-left side of the main frames. These points were excluded from the regression analysis.

Fairly good linear relationships could be established between the three chemical indices and the exchangeable P pool in the Tekapo soil, but not in the Craigieburn soil. The latter may be partly attributable to the limited number of data points available for regression. However, it is obvious that different relationships apply to the two soils (Figures 6.4, 6.5 and 6.6). The values of the water extractable P, Bray I P and Olsen P are higher in the Tekapo soil than in the Craigieburn soil at the same values of exchangeable P pools. This is related to the nature of these P pools. The exchangeable P pool represents a capacity factor (cf. Section 2.4.5) and is relatively large in size. The water, Bray I (0.03 M NH_4F + 0.025 M HCl) and Olsen (0.5 M $NaHCO_3$) reagents are generally weak extractants and only extract the very labile fractions of the exchangeable P pool. The proportion of the exchangeable P pool that may be extracted by these extractants decreases with increasing soil P retention capacities or P buffering capacities (Holford and Mattingly, 1979; Holford, 1980; Holford and Cullis, 1985). The amounts of P extracted by the three extractants therefore were lower in the higher P-retention Craigieburn soil than in the Tekapo soil at the same values of exchangeable P.

The validity of using the Bray I reagent to extract P from soil treated with phosphate rock has been questioned (e.g. Chien, 1978; Cope and Evans, 1985) because the acid contained in the reagent might attack undissolved PR materials remaining in the soil. Figure 6.7 shows that there is a very good relationship between Bray I P and Olsen P in both soils. This suggests that with the high soil:solution ratio (3:20) and the very brief period of extraction (1 minute) the dilute acid might not have attacked the

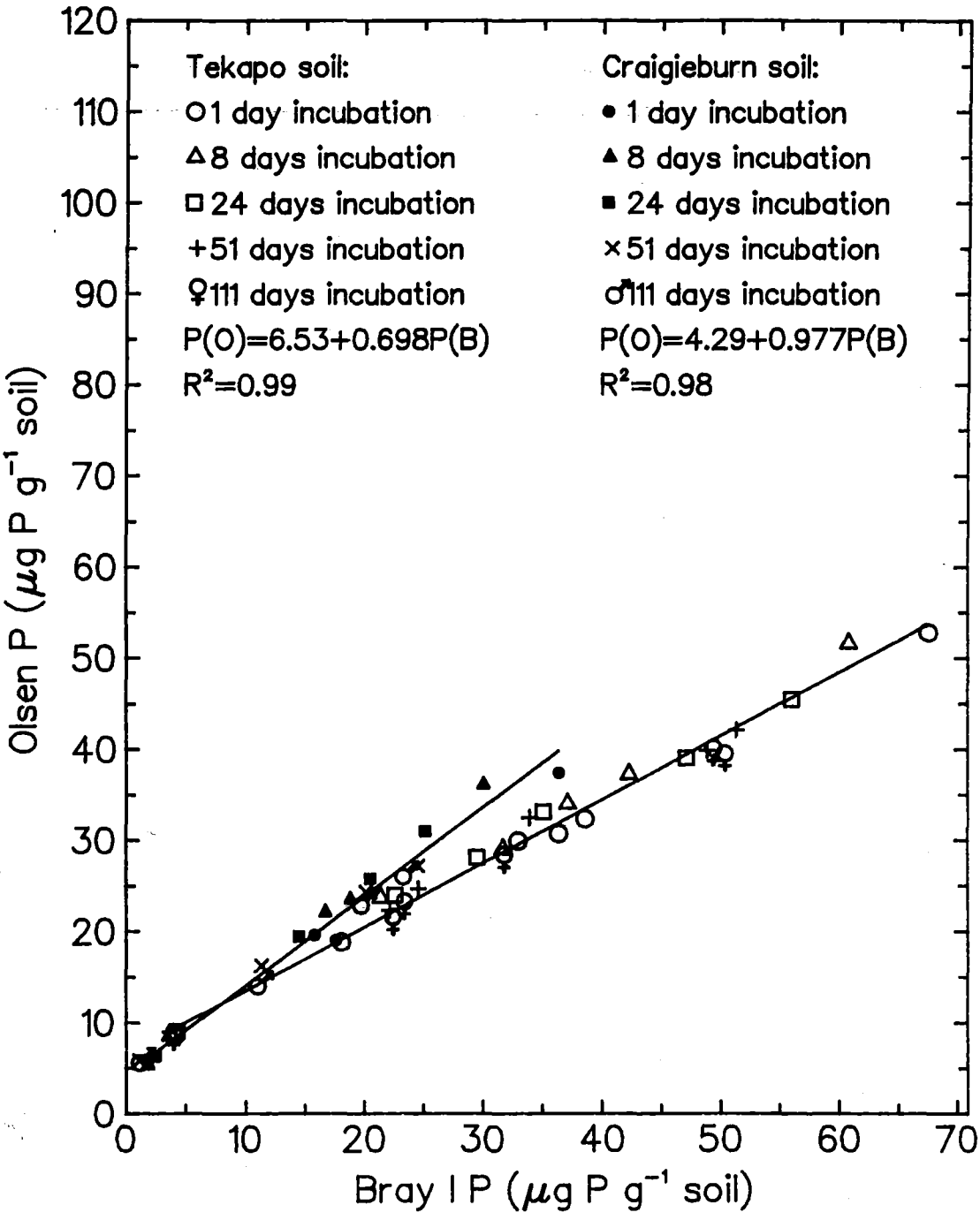


Figure 6.7 Relationships between Olsen P and Bray I P.

undissolved PR residue to any greater extent than did the 0.5 M $NaHCO_3$ solution. If these extraction conditions vary, however, this relationship may no longer hold.

6.3.2 Extractions with 0.5 M NaOH followed by 1 M HCl and with 0.5 M $BaCl_2$/TEA

Figures 6.8 and 6.9 illustrate the total amounts of phosphate extracted by 0.5 M NaOH, and by 1 M HCl following the 0.5 M NaOH extraction respectively. The amounts of phosphate extracted by 0.5 M NaOH and solubilised by 1 M HCl remained steady in the samples treated with MCP solution, as the phosphate added was largely extractable by the 0.5 M NaOH extractant (about 90%). They increased and decreased respectively in the samples treated with PR-containing fertilisers with increasing periods of incubation as more phosphate dissolved from the PR materials. The percentages of the PR-containing fertilisers dissolved and remaining undissolved are presented in Figure 6.10 a and b respectively. These results are calculated on the basis of the increases in the amount of P extracted by the two extractants from the fertilised samples over the controls (ΔP) and the total amounts of P added. Both parameters as a function of incubation period can be described by the Mitscherlich exponential equations 6.1 and 6.2 below fitted by the least squares regression method (Table 6.1):

$$y = a[1 - b \cdot \exp(-ct)] \qquad (6.1)$$

$$y = a[1 + b \cdot \exp(-ct)] \qquad (6.2)$$

where y is the percentage of dissolution in Equation 6.1 and percentage of added P remaining as PR residue in Equation 6.2, a is the asymptote, b and c are coefficients and t is period of incubation (day).

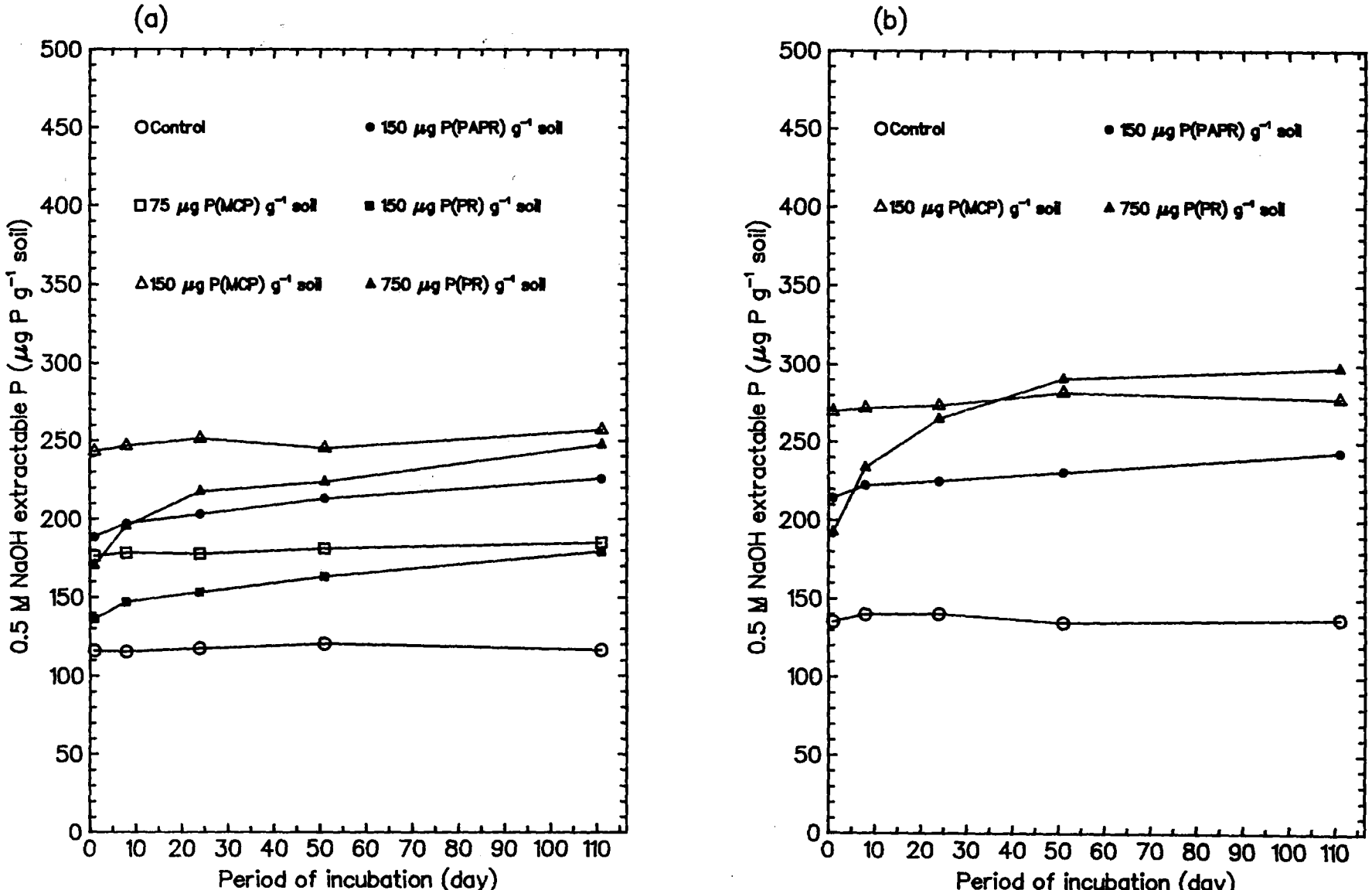


Figure 6.8 Changes of 0.5 M NaOH extractable P with period of incubation: (a) Tekapo soil; (b) Craigieburn soil.

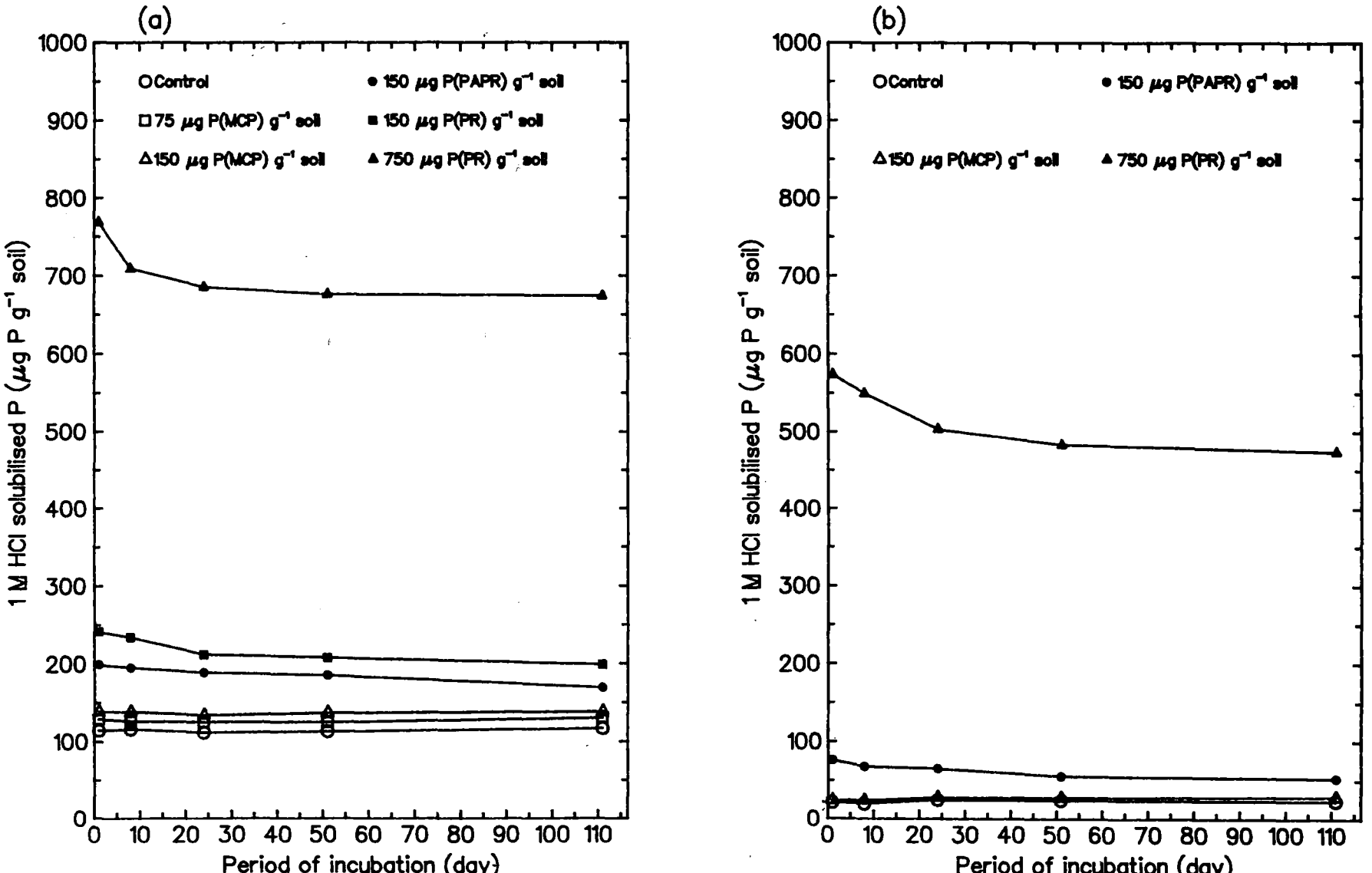


Figure 6.9 Changes of residual P solubilised by 1 M HCl following the extraction with 0.5 M NaOH: (a) Tekapo soil; (b) Craigieburn soil.

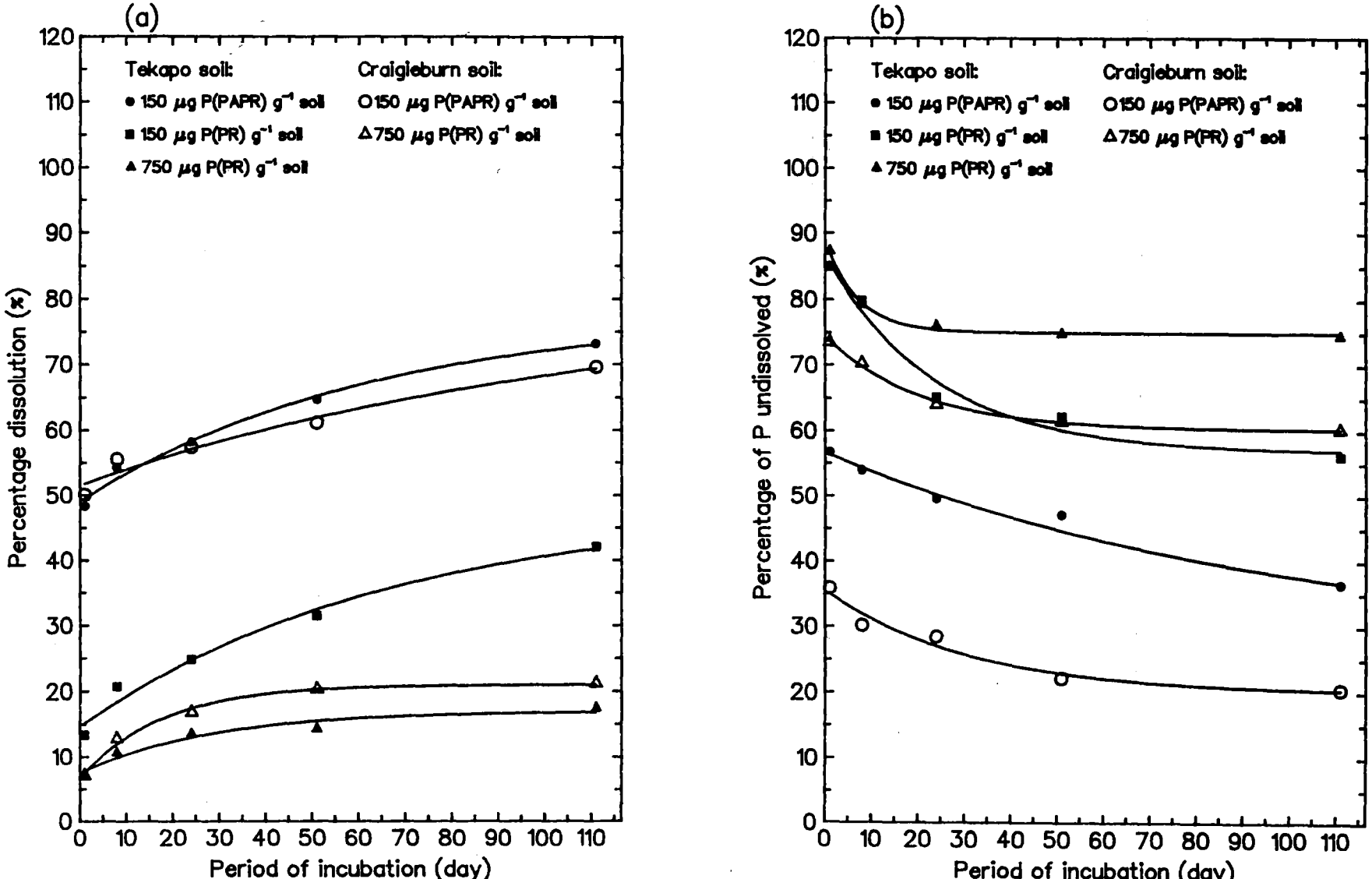


Figure 6.10 Percentage of total fertiliser P dissolved as measured by 0.5 M NaOH extraction (a) and undissolved as measured by 1 M HCl following the extraction with 0.5 M NaOH (b).

Table 6.1 Parameters of the exponential equations, fitted by the least squares regression method, to describe the percentage dissolution of PR-containing fertilisers in the soils as measured by 0.5 M NaOH, and percentage of added P remaining as PR residue measured by 1 M HCl as a function of incubation period.

Treatment	Parameters estimated							
	Percentage dissolution (%)				Percentage undissolved (%)			
	a	b	c	R^2	a	b	c	R^2
Tekapo soil:								
150 μg P(PAPR) g^{-1} soil	77.8	0.370	0.0162	0.99	27.6	1.056	0.0104	0.99
150 μg P(PR) g^{-1} soil	48.4	0.697	0.0147	0.98	56.8	0.531	0.0426	0.98
750 μg P(PR) g^{-1} soil	17.1	0.563	0.0358	0.95	75.0	0.188	0.142	0.99
Craigieburn soil:								
150 μg P(PAPR) g^{-1} soil	79.6	0.353	0.00912	0.96	20.0	0.781	0.0331	0.96
750 μg P(PR) g^{-1} soil	21.0	0.683	0.0577	0.99	60.2	0.236	0.0497	0.99

R^2: A measure of the amount of variation accounted for by the regression.

The a (asymptote) values in Table 6.1 represent the maximum percentage of dissolution or minimum percentage of the added P remaining as PR residue in the soils given a sufficient period of incubation under the same conditions. These values show that the maximum extent of dissolution of the PR-containing fertilisers increases at lower application rate and when applied to soils with higher P-retention capacity. This agrees with the estimates by the rates of dissolution, F_{in}, determined by the isotopic labelling method discussed in Chapter 5 (cf. Section 5.4.2). It also supports findings by other workers (Syers and Mackay, 1986; Hughes and Gilkes, 1986a, b; Kanabo and

Gilkes, 1987b, 1988a). The increased dissolution at the lower application rate is probably due to greater fertiliser-soil contact and lower P and Ca concentrations in the soil solution, whilst that in the higher P-retention soil would be caused by the greater rate of removal of dissolved P by soil retention (cf. Table 5.5).

However, differences in the extent of fertiliser dissolution between the two soils are greater when calculated on the basis of percentage of P remaining as PR residues than when calculated on the basis of percentage PR dissolved (Figure 6.10 and Table 6.1). This is most likely caused by a systematic lower recovery of both dissolved and undissolved P in the higher P-retention Craigieburn soil (Table 6.2), which would moderate the differences between the two soils according to the 0.5 M NaOH extractable P, but exaggerate them in terms of the 1 M HCl solubilised P.

Table 6.2 Percentage of fertiliser P recovered in the extractions with 0.5 M NaOH and 1 M HCl.

Treatment	Percentage recovery (%)[1]				
	Period of incubation (day)				
	1	8	24	51	111
Tekapo soil:					
75 μg P(MCP) g^{-1} soil	100	99	97	101	113
150 μg P(MCP) g^{-1} soil	101	103	103	101	110
150 μg P(PAPR) g^{-1} soil	105	109	108	112	110
150 μg P(PR) g^{-1} soil	98	101	90	94	98
750 μg P(PR) g^{-1} soil	95	90	90	89	92
Craigieburn soil:					
150 μg P(MCP) g^{-1} soil	88	89	93	99	97
150 μg P(PAPR) g^{-1} soil	86	86	86	83	90
750 μg P(PR) g^{-1} soil	81	83	81	82	82

1: Percentage recovery = $\frac{\Delta P(0.5\ M\ NaOH) + \Delta P(1\ M\ HCl)}{\text{total P added}} \times 100$

where ΔP is the difference in the amounts of P extracted between the fertilised treatments and the controls.

The changes in extractable Ca by 0.5 M $BaCl_2$/TEA with pH buffered at 8.1 are shown in Figure 6.11. The amounts of extractable Ca increased with increasing periods of incubation in the soils which received PR, but varied erratically in the soils which received MCP and PAPR fertilisers. The latter observation may be indicative of the incongruent dissolution of the two MCP-containing fertilisers. The method of measuring the changes of extractable Ca by 0.5 M $BaCl_2$/TEA to study fertiliser dissolution in soils may therefore be suitable for PR materials, but inappropriate for PAPR's.

The percentage dissolution calculated, according to the increases of extractable Ca in the PR-fertilised soils over the controls (ΔCa) and the total quantity of Ca applied with the fertilisers, as a function of incubation period, can also be described by the exponential model (Equation 6.1, Figure 6.12 and Table 6.3). The asymptotes (the a values in Table 6.3) show similar trends to those estimated by the 0.5 M NaOH and 1 M HCl extractions, in that more PR would dissolve at a lower rate of application and when applied to higher P-retention soils. However, the specific values obtained from the $BaCl_2$/TEA method differ slightly from those obtained by NaOH and HCl methods.

Table 6.3 Parameters of the exponential equations, fitted by the least squares method, to describe the percentage dissolution of PR materials in the soils, measured by 0.5 M $BaCl_2$/TEA extractions, as a function of incubation period.

Treatment	Parameters estimated			
	a	b	c	R^2
Tekapo soil:				
150 μg P(PR) g^{-1} soil	34.2	0.363	0.167	0.99
750 μg P(PR) g^{-1} soil	21.1	0.541	0.0571	0.97
Craigieburn soil:				
750 μg P(PR) g^{-1} soil	23.5	0.565	0.0263	0.93

R^2: A measure of the amount of variation accounted for by the regression.

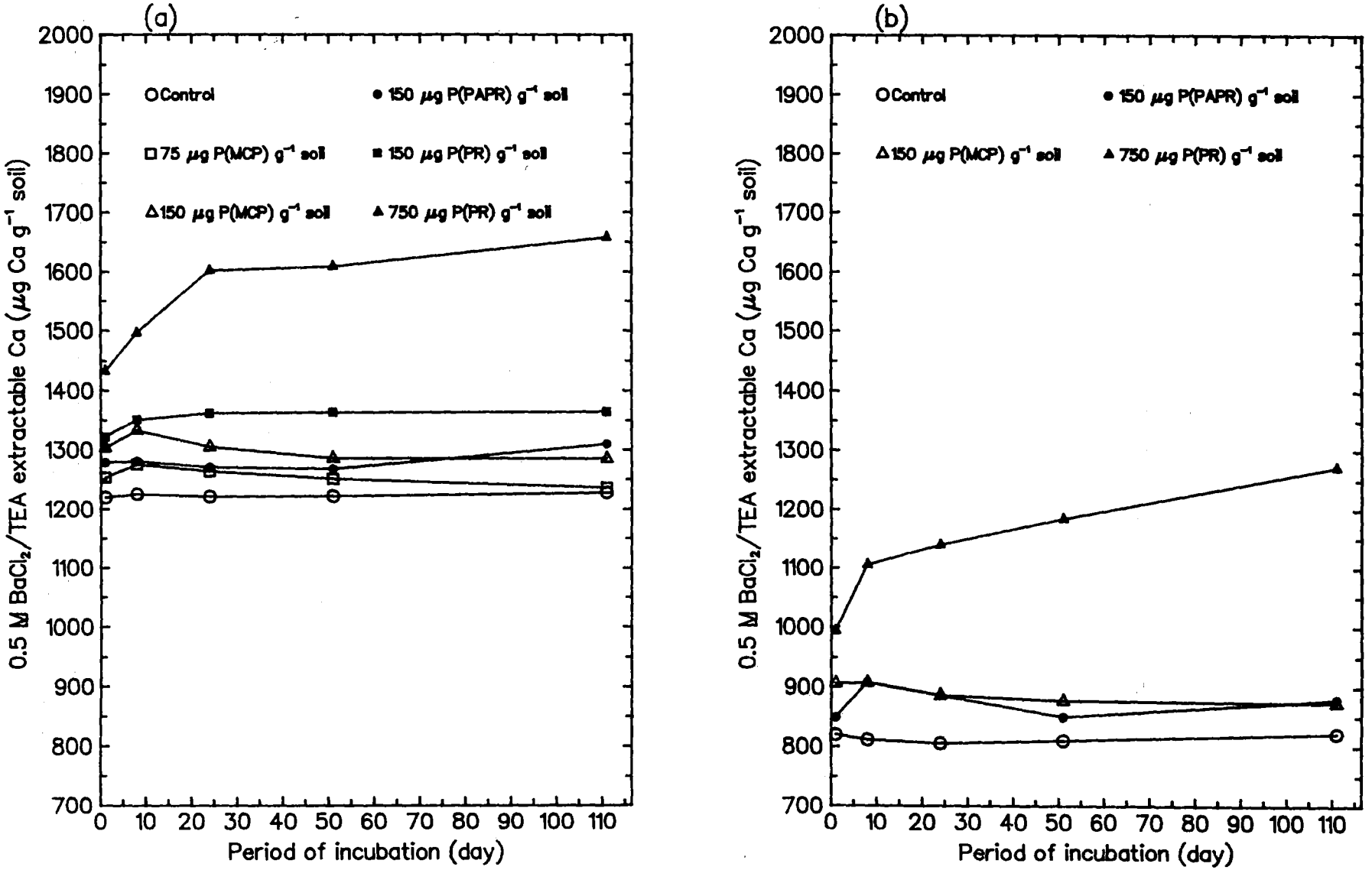


Figure 6.11 Changes of 0.5 M $BaCl_2$/TEA (pH=8.1) extractable Ca with period of incubation: (a) Tekapo soil; (b) Craigieburn soil.

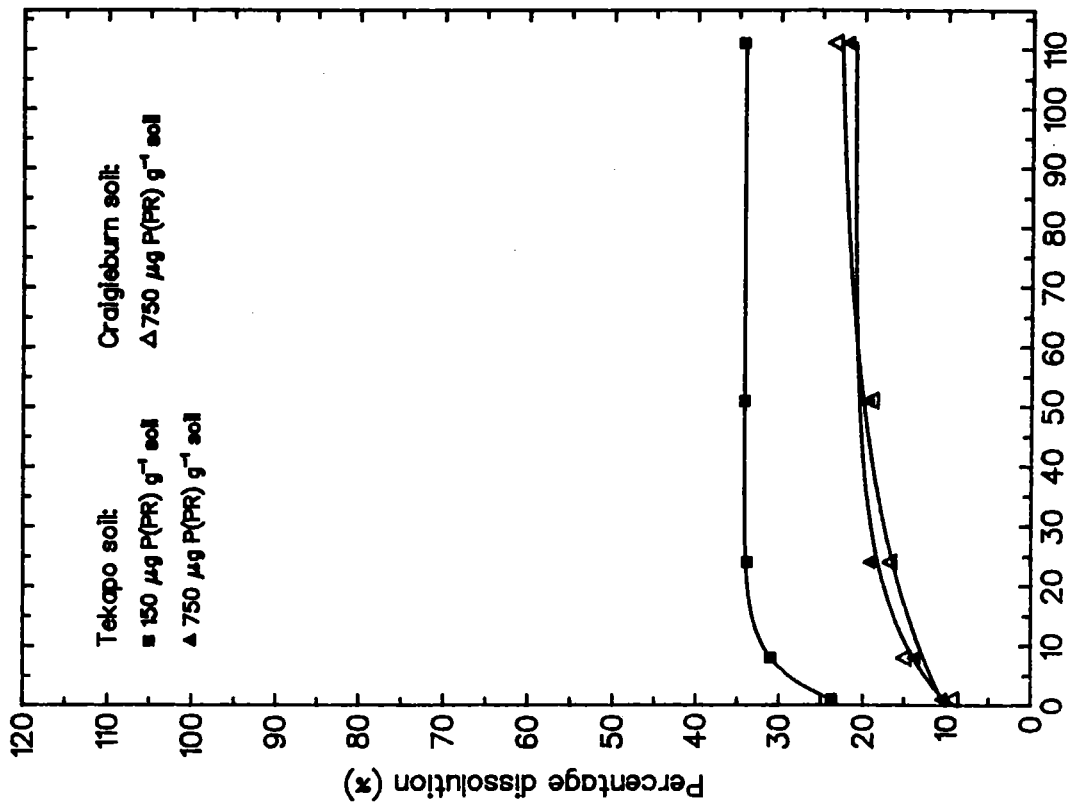


Figure 6.12 Percentage of total fertiliser dissolved as measured by 0.5 M $BaCl_2$/TEA extractable Ca.

Results comparing the percentage dissolution of PR-containing fertilisers, determined by chemical extractions with 0.5 M NaOH, 1 M HCl and 0.5 M $BaCl_2$/TEA are summarised in Table 6.4. For the extractions with 0.5 M NaOH and 0.5 M $BaCl_2$/TEA, the percentage dissolution is calculated on the basis of the increases of P and Ca in the fertilised treatments compared with the controls (ΔP or ΔCa) and the total fertiliser P or Ca added. For the 1 M HCl extraction, it is the difference between 100 percent and the percentage of P remaining as PR residue.

Table 6.4 Percentage dissolution of the PR-containing fertilisers in the soils assessed by chemical extraction methods.

Treatment	Method of estimation	Percentage dissolution (%)				
		Period of incubation (day)				
		1	8	24	51	111
Tekapo soil:						
150 μg P(PAPR) g^{-1} soil	0.5 M NaOH	48.3	54.2	58.1	64.7	73.2
	1 M HCl	43.2	46.0	50.3	52.8	63.4
150 μg P(PR) g^{-1} soil	0.5 M NaOH	13.4	20.7	24.8	31.5	42.1
	1 M HCl	15.0	20.1	34.8	37.7	43.8
	0.5 M $BaCl_2$ /TEA	23.7	31.0	33.8	34.2	34.4
750 μg P(PR) g^{-1} soil	0.5 M NaOH	7.2	10.6	13.5	14.3	17.5
	1 M HCl	12.7	20.7	23.9	25.1	25.4
	0.5 M $BaCl_2$ /TEA	10.4	13.6	19.0	19.3	21.8
Craigieburn soil:						
150 μg P(PAPR) g^{-1} soil	0.5 M NaOH	50.1	55.5	57.3	61.1	69.6
	1 M HCl	64.1	69.8	71.5	77.8	79.5
750 μg P(PR) g^{-1} soil	0.5 M NaOH	7.1	12.8	16.8	20.3	21.2
	1 M HCl	26.5	29.7	35.9	38.5	39.7
	0.5 M $BaCl_2$ /TEA	9.1	14.8	16.5	18.8	23.3

The values of percentage dissolution measured by the three chemical extractions are of the same order. However, values estimated by 1 M HCl extraction are often higher than those determined from 0.5 M NaOH extraction at higher

application rate, particularly in the Craigieburn soil. This is most likely due to the slightly lower recovery rates of phosphate using these two extractants. A lower recovery of dissolved P by NaOH extraction results in a lower percentage of dissolution, whereas that of undissolved P by HCl results in a higher percentage of dissolution estimated. These results and those discussed in preceding paragraphs suggest that, when studying dissolution of phosphate rock in soil by chemical extraction methods, special attention should be paid to the possible variations in the recovery rate, or the extractability of P or Ca which may be influenced by the rate of fertiliser application and/or soil properties. In the PAPR treatment of the Tekapo soil, however, the 1 M HCl estimates are lower than those of the 0.5 M NaOH. Some carry-over of P to the 1 M HCl extractable P may have contributed to this result, as a recovery exceeding 100% was obtained in the treatment (cf. Table 6.2). The estimates by 0.5 M $BaCl_2$/TEA generally lie in between those by 0.5 M NaOH and 1 M HCl.

The extent of NCPR dissolution estimated in this study are lower than those reported by Bolan and Hedley (1989). They estimated, using 0.5 M NaOH and $BaCl_2$/TEA extractions, that about 75-80% of P (NCPR) added to the soil (800 μg P g^{-1}) dissolved after 84 days of incubation. The two studies, however, were carried out under different conditions. Bolan and Hedley (1989) used a higher P-retention soil (89% compared with 30% and 49%), and finer PR particles (125 μm compared with 150 μm) that were incubated under moister conditions (60% compared with 35% moisture content) than in this experiment. The conditions of Bolan and Hedley (1989) favour greater dissolution of PR materials in the soil (cf. Section 2.7).

The dissolution rates of PR and PAPR in soils, estimated by extractions with 0.5 M NaOH, 1 M HCl and 0.5 M $BaCl_2$/TEA, are compared with those determined by the isotopic labelling method (Chapter 5) in Table 6.5. As the rates of dissolution vary depending on the extraction method used, the range within which the values vary, estimated by the three extraction methods, are provided.

Table 6.5 Dissolution rates of the PR-containing fertilisers in the soils assessed by chemical extraction methods and isotopic labelling method (F_{in}).

Treatment	Method of estimation	Average dissolution rate ($\mu g\ P\ g^{-1}\ soil \cdot day^{-1}$)					
		Period of incubation (day)					
		0-1	1-8	8-24	24-51	1-50	50-111
Tekapo soil:							
150 μg P(PAPR) g^{-1} soil	Extraction[1]	72-85	0.60-1.3	0.37-0.40	0.14-0.37	0.29-0.49	0.21-0.27
	F_{in}[2]	-----	-----	-----	-----	0.80	0.56
150 μg P(PR) g^{-1} soil	Extraction	20-23	1.1-1.6	0.38-1.4	0.16-0.37	0.54-0.68	0.15-0.27
	F_{in}	-----	-----	-----	-----	1.2	0.80
750 μg P(PR) g^{-1} soil	Extraction	54-95	3.6-8.6	1.4-1.5	0.22-0.33	1.1-1.9	0.31-0.40
	F_{in}	-----	-----	-----	-----	3.1	2.7
Craigieburn soil:							
150 μg P(PAPR) g^{-1} soil	Extraction	75-96	1.1-1.2	0.16-0.17	0.21-0.35	0.33-0.41	0.04-0.21
	F_{in}	-----	-----	-----	-----	0.97	1.1
750 μg P(PR) g^{-1} soil	Extraction	53-199	3.4-6.1	1.9-2.9	0.72-0.97	1.8-2.0	0.22-0.56
	F_{in}	-----	-----	-----	-----	4.1	2.9

1: Dissolution rate = $(PD_{t2} - PD_{t1}) \cdot$ application rate/(t2 - t1), where PD_{t1} and PD_{t2} are percentage dissolution at the times t1 and t2 respectively. The two values represent the range of dissolution rates estimated by the three extraction methods.

2: The F_{in} values are as calculated in Chapter 5 (Table 5.5). The values from the control of the Tekapo soil were subtracted from those of the fertilised treatments in this soil.

Both PR and PAPR dissolved very rapidly immediately following addition to soils (0-1 day, Table 6.5), due to low concentrations of P and Ca in soil solution and sufficient soil acidity. The initial surge of PR dissolution might also be partially due to preferential acidulation of the more soluble fractions of PR materials in the soil. As more fertiliser was dissolved, raising the concentrations of P and Ca in soil solution, and consuming soil acidity at the vicinity of PR particles, the rate of dissolution decreased with increasing periods of soil-fertiliser contact. After about 8 days of incubation, the dissolution rates settled to relatively stable values. This verifies the assumption made in Chapter 5 (Section 5.4.2) that the rates of PR dissolution changed rapidly immediately after application to soils, but remained relatively stable after extended periods of incubation.

The average rates of dissolution between 1-50 and 50-111 days estimated by the isotopic method are generally higher than those by extraction. This partially reflects the difference in the conditions under which the measurements were made. F_{in} values were measured under conditions of plant growth. The continued removal of P and Ca from the soil solution, by plant uptake and microbial immobilisation, would create favourable conditions for increased PR dissolution. These conditions contrast with those under which the soil samples used for extractions were incubated. In addition, F_{in} also includes other terms, such as dissolved P sorbed on soil surfaces before labelling entering the exchangeable P pool when the concentration of P in soil solution was lowered by plant uptake.

It seems that both isotopic and extraction methods have advantages and disadvantages. Extraction methods can provide rates of dissolution for a specific period of incubation, but the results may be susceptible to variations, depending on the extractability of P or Ca by the extractants. The extractability may be affected by soil properties and rates of fertiliser applications. The estimates by 0.5 M NaOH and $BaCl_2$/TEA may be invalid if considerable losses of P or Ca occur, as a result of leaching or of plant and microbial uptake. The isotopic labelling method provides an

average rate of dissolution for an extended period. This may be adequate, in practical terms, to assess the amount of P that may be released by PR or PAPR over a period, such as a growing season. The important advantage of this approach is that the estimates of PR dissolution reflect the conditions of growing plants and that it measures both the rates of phosphate retention and dissolution at the same time.

The extent of fertiliser dissolution estimated by the extraction methods may not adequately indicate the amounts of plant available P in the soil. Figure 6.13 shows that the relationships between 0.5 M NaOH extractable P and the water extractable P are very poor. Slightly better correlations are found between 0.5 M NaOH extractable P and the Bray I P (Figure 6.14) and the Olsen P (Figure 6.15). However, separate relationships hold for the two soils. The amounts of available P as indicated by the water extractable P, Bray I P and Olsen P are lower in the higher P-retention Craigieburn soil than in the Tekapo soil, even though the fertilisers dissolved to a greater extent in the former. With increasing periods of incubation, the data points in Figures 6.13, 6.14 and 6.15 tend to move towards the upper-left. This suggests that as increasing amounts of fertiliser dissolved, as measured by the 0.5 M NaOH extraction, the concentrations of available P actually decreased or remained steady with time (cf. Figures 6.1, 6.2 and 6.3). This is because NaOH extracts not only the available fraction of the soil inorganic P but most of the non-apatite inorganic P, including that bound with Al and Fe whose lability is markedly reduced.

Similarly, very poor relationships exist between 0.5 M NaOH extractable P and the exchangeable P pools (Figure 6.16). The three points labelled with PR located in the upper-left side correspond to the exchangeable P pools in the PR-treated soils at the one day incubation ($Q_{t=1}$). This reaffirms the proposition made in Chapter 5 (Section 5.4.2) that the exchangeable P pools at the one day incubation for the PR-treated soils are overestimated.

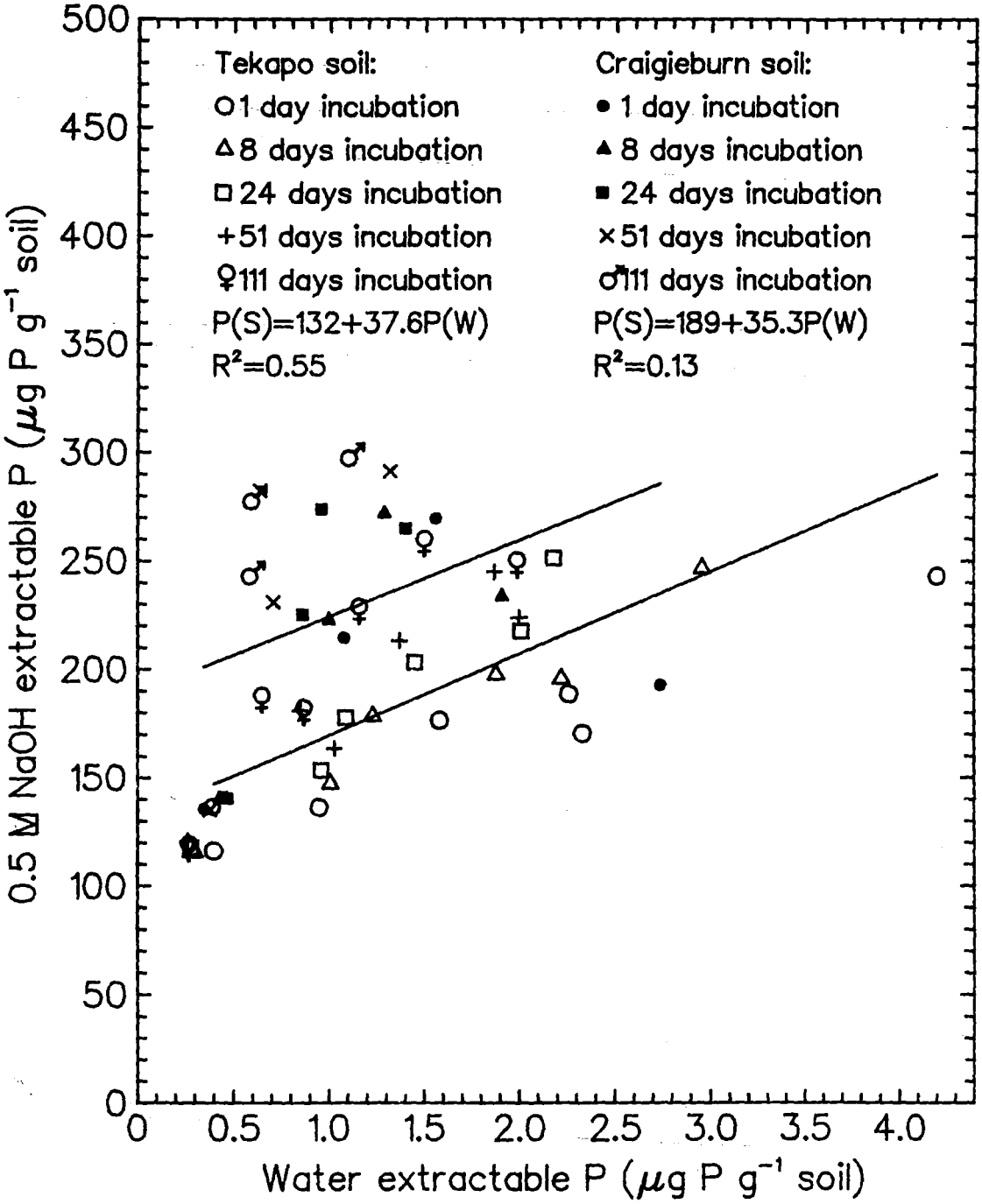


Figure 6.13 Relationships between 0.5 M NaOH extractable P and water extractable P.

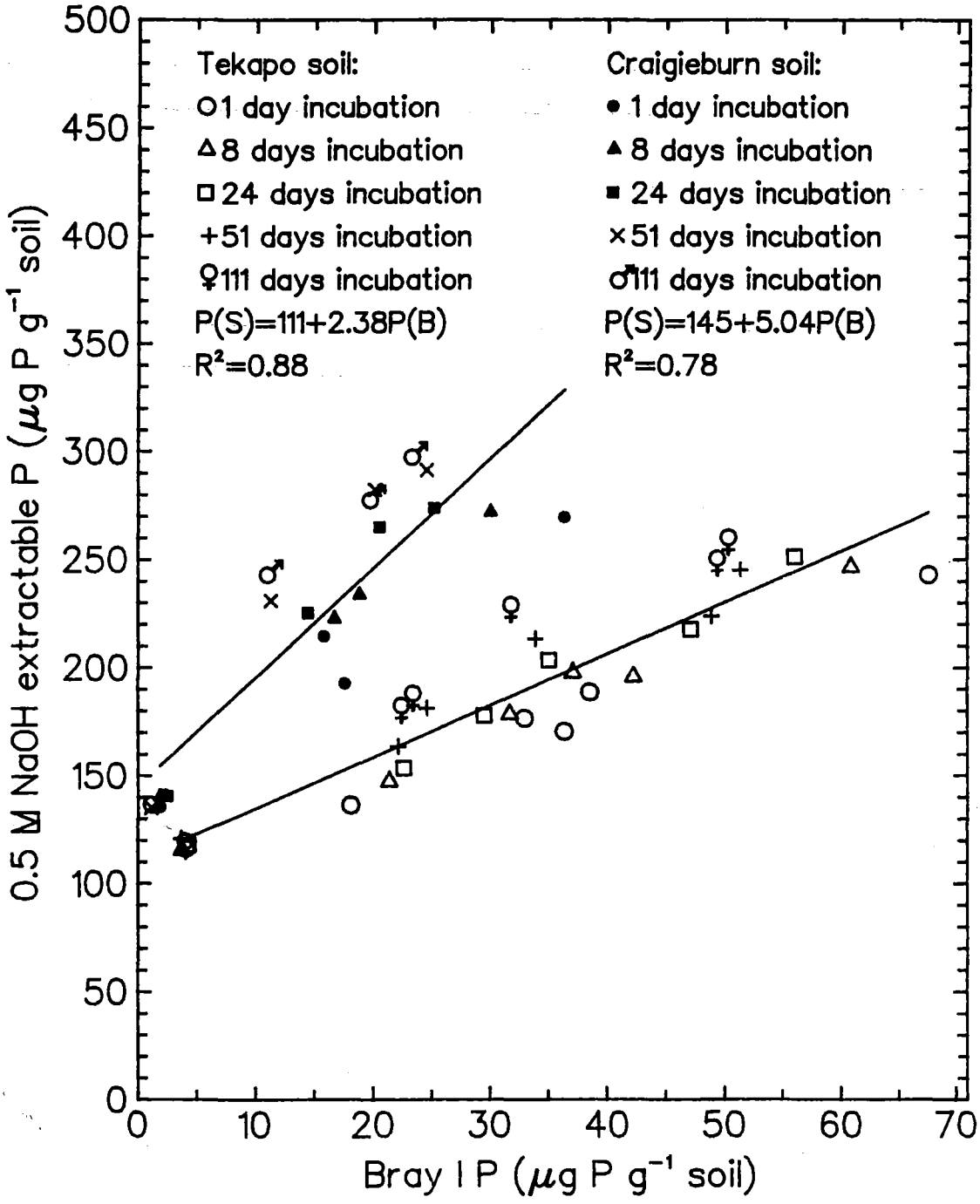


Figure 6.14 Relationships between 0.5 M NaOH extractable P and Bray I P.

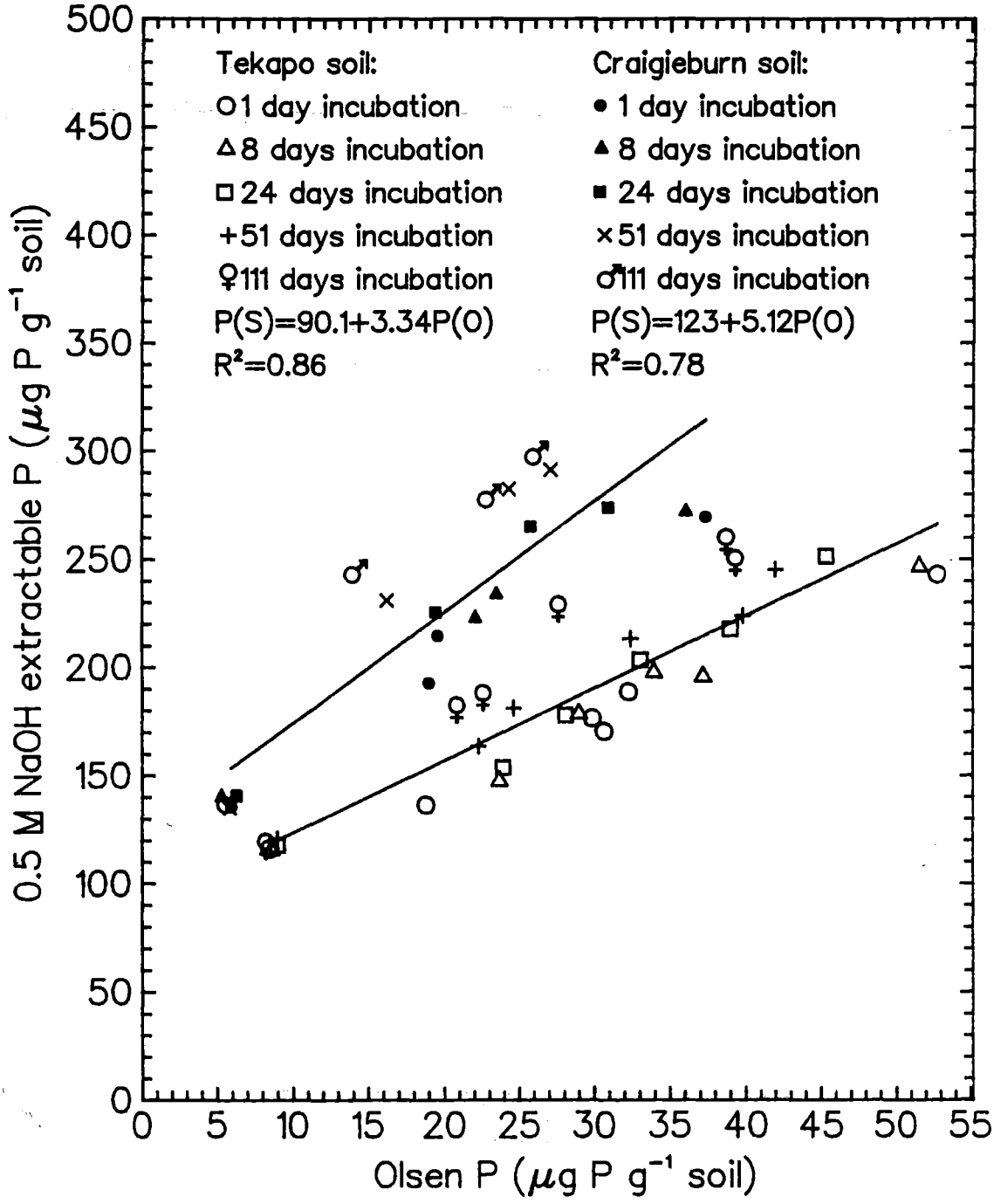


Figure 6.15 Relationships between 0.5 M NaOH extractable P and Olsen P.

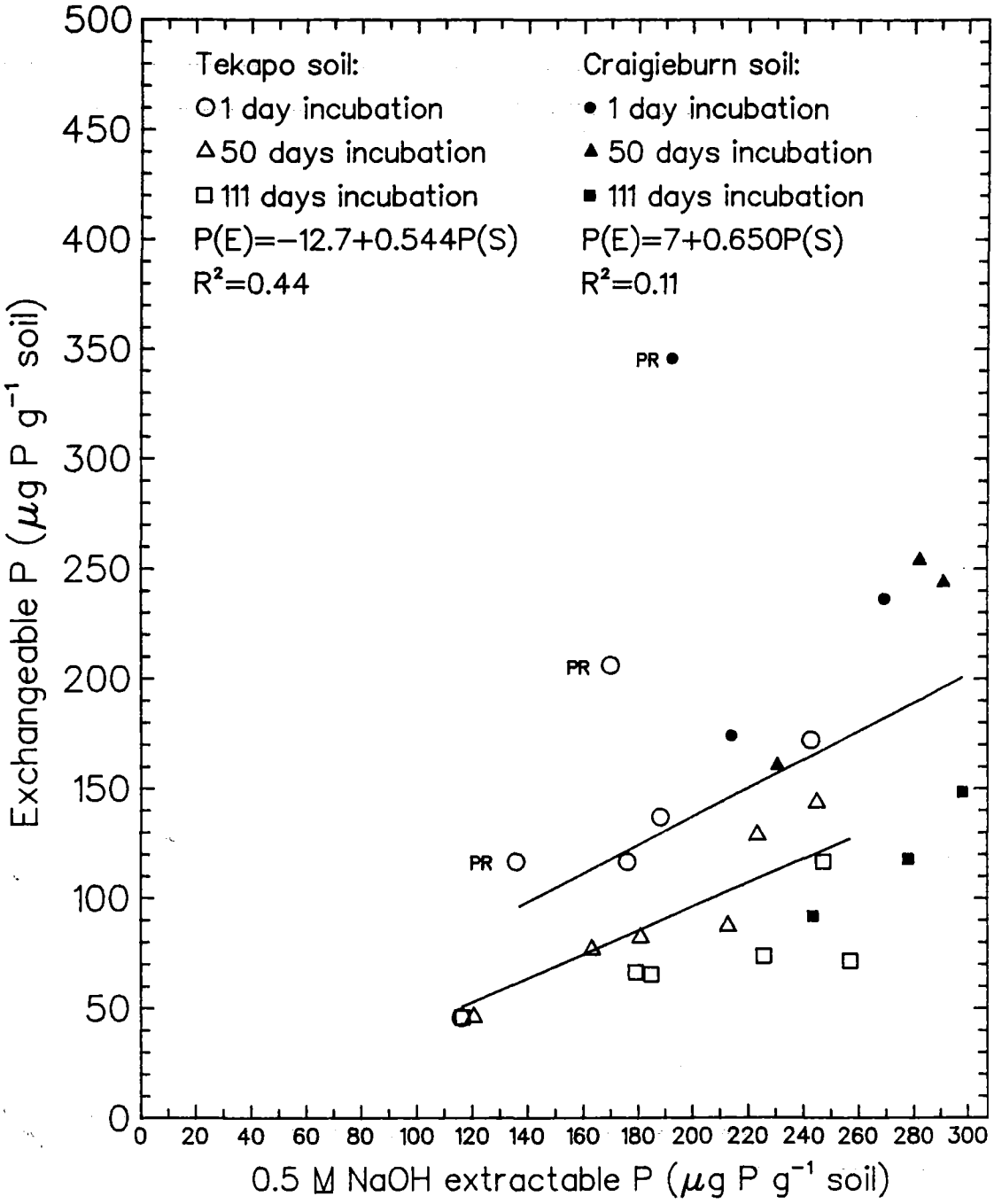


Figure 6.16 Relationships between exchangeable P and 0.5 M NaOH extractable P.

6.4 Summary and conclusions

In the MCP fertilised soils, the water extractable P, Bray I P and Olsen P pools all declined rapidly with increasing periods of incubation. In the PR-treated soils, on the other hand, the three P pools were increased above those of the controls within short periods of incubation and remained relatively stable for extended periods. The soils which received PAPR fertilisers behaved intermediately in the changes of the three P pools between those which received MCP and those which received PR materials. These trends are in accordance with those predicted by the rates of phosphate fertiliser dissolution and retention in the soils, estimated by the isotopic labelling method.

The extent of dissolution of NCPR and NCPAPR in the soils assessed by extractions with 0.5 M NaOH, 1 M HCl and 0.5 M $BaCl_2$/TEA are generally in agreement. The percentage dissolution as a function of time (incubation period) is well described by the Mitscherlich exponential models. These models predict that the PR and PAPR materials would dissolve to greater extents at lower rates of application and when applied to soils with higher P-retention capacity. Increased dissolution in a higher P retention soil, however, may not mean greater amounts of plant available P in the soil, as the concentrations of water extractable P, Bray I P and Olsen P pools contributed by the fertilisers are in fact lower in the higher P retention Craigieburn soil than in the Tekapo soil.

The extraction methods by 0.5 M NaOH, 1 M HCl and 0.5 M $BaCl_2$/TEA may reveal the extent of fertiliser dissolution in the soil for a specific period of incubation, but the values may be subjected to variations due to changes in the rate of recovery or extractability of P or Ca by these extractants, from different soils, and at different application rates. The 0.5 M $BaCl_2$/TEA extraction is not a reliable method for determining the dissolution of PAPR materials. These methods, particularly the 0.5 M NaOH and 0.5 M $BaCl_2$/TEA extractions, may be inappropriate under conditions of plant growth where losses of P and Ca take place by plant uptake, microbial

immobilisation or leaching. In contrast, the measurement of F_{in} values by the isotopic labelling technique is conducted under conditions of plant growth. The plant uptake of phosphate from the soil medium is employed as a sampling mechanism. As the removal of P and Ca from the soil by plant uptake, microbial consumption and leaching accelerates fertiliser dissolution, the rates of dissolution measured by the isotopic labelling method are expected to be higher than those provided by the chemical extractions of samples incubated in the laboratory.

Chapter 7

Plant responses to the application of phosphate fertilisers and relationships with kinetic and chemical parameters of fertiliser dissolution

7.1 Introduction

The prediction of phosphate fertiliser requirements to achieve desired levels of production depends upon knowledge such as the concentration of plant available P in the soil, the rate of dissolution of applied phosphate fertilisers and the relationships between these variables and plant responses. The concentration of plant available P in the soil and the rate of fertiliser dissolution are usually assessed by chemical extraction methods or by isotopic labelling techniques (cf. Sections 2.5 and 2.7.3). The relationships between these assessments and plant responses, however, are complicated by the use of different phosphate fertilisers which vary in solubility. Bolland *et al.* (1988a), for instance, reported that separate calibrations between yield and soil test values were required for different fertilisers and for each combination of fertiliser and plant species. Gregg *et al.* (1987) and Bolan and Hedley (1990) observed poor correlations between the amounts of phosphate rock dissolved and plant P uptake.

This chapter reports the results of plant responses to the application of different types of phosphate fertilisers, obtained from the growth chamber experiments described in Chapter 5. The isotopically and chemically measured parameters regarding the dissolution of the phosphate fertilisers in the soils presented in Chapters 5 and 6 will then be examined in terms of their relationships with plant P uptake. The objective is to assess the ability of these parameters to account for the variations of plant P uptake and explore models representing plant P uptake and soil tests which may be relied upon to predict fertiliser requirements or plant yield.

7.2 Results and discussion

7.2.1 Plant P uptake and dry matter yield

The mean values of plant P uptake and dry matter yield from each treatment are illustrated graphically in Figures 7.1 and 7.2 respectively. The descriptions of the treatments and the conduct of the trials have been detailed in Chapter 5 (cf. Section 5.3). The individual graphs labelled (a), (b) and (c) correspond to the three kinetic experiments (Experiments A, B and C) described in Section 5.3 after the fertilisers were incubated with the soils for 1, 50 and 111 days. The plant P uptake and dry matter yield presented in Figures 7.1 and 7.2 are cumulative values from the individual cuts of each of the three experiments.

Ryegrass, which was used as the test plant, responded very positively to the application of any of the three phosphate fertilisers: MCP; NCPR; and NCPAPR. This reflects the highly deficient P-status of both soils. Immediately following application (1 day incubation), MCP appeared to be superior in supplying P to plants than either NCPR or NCPAPR applied at the same rate (Figure 7.1 a). After 50 and 111 days of incubation, however, the NCPR and NCPAPR were just as effective or more effective in the low P-retention Tekapo soil, in comparison to MCP at the same application rate (Figures 7.1 b and c and 7.2 b and c). In the higher P-retention Craigieburn soil, however, the effectiveness of the NCPAPR did not increase as quickly as that in the Tekapo soil with increasing periods of incubation. These trends are illustrated in Figures 7.3 and 7.4 which show the relative percentage of plant P uptake and dry matter yield respectively from the PR and PAPR treatments compared with 150 μg P(MCP) g^{-1} soil treatment on both soils. The values are calculated using the following equation:

$$RP\% = [(x_f - x_c)/(x_m - x_c)] \cdot 100 \qquad (7.1)$$

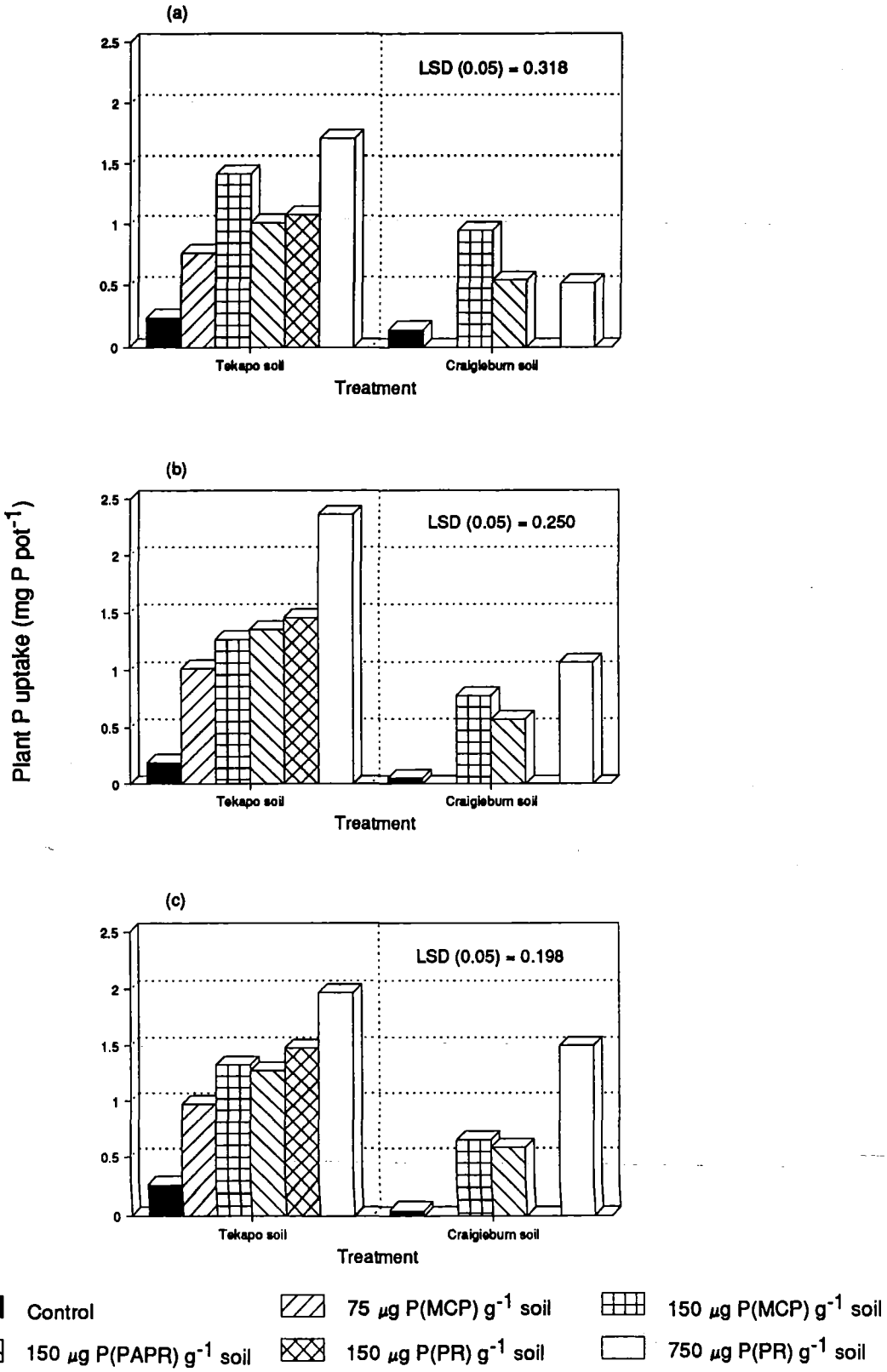


Figure 7.1 Total plant P uptake. (a) Period of incubation = 1 day, period of plant growth = 34 days; (b) period of incubation = 50 days, period of plant growth = 45 days; (c) period of incubation = 111 days, period of plant growth = 43 days.

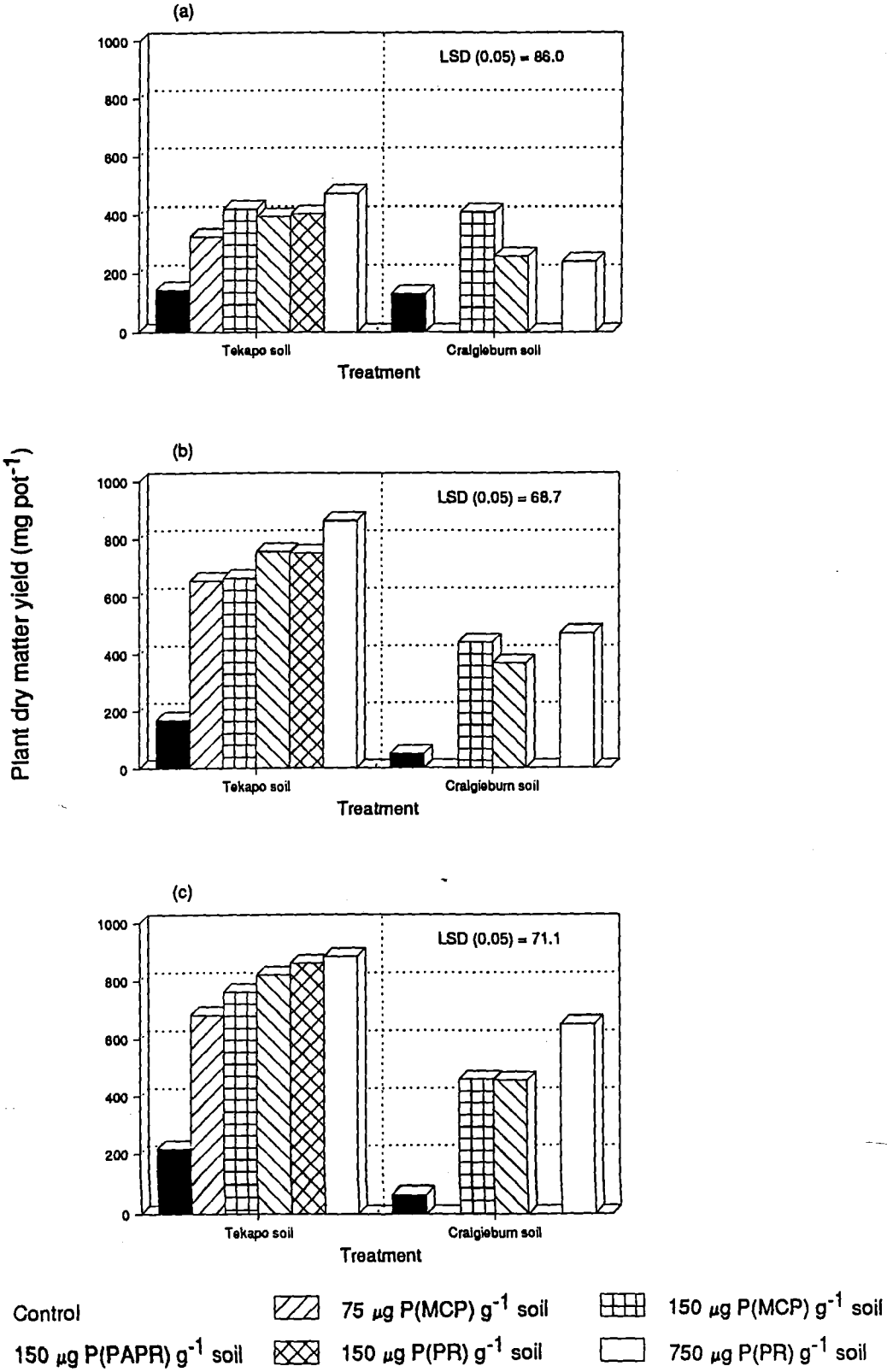


Figure 7.2 Total dry matter yield. (a) Period of incubation = 1 day, period of plant growth = 34 days; (b) period of incubation = 50 days, period of plant growth = 45 days; (c) period of incubation = 111 days, period of plant growth = 43 days.

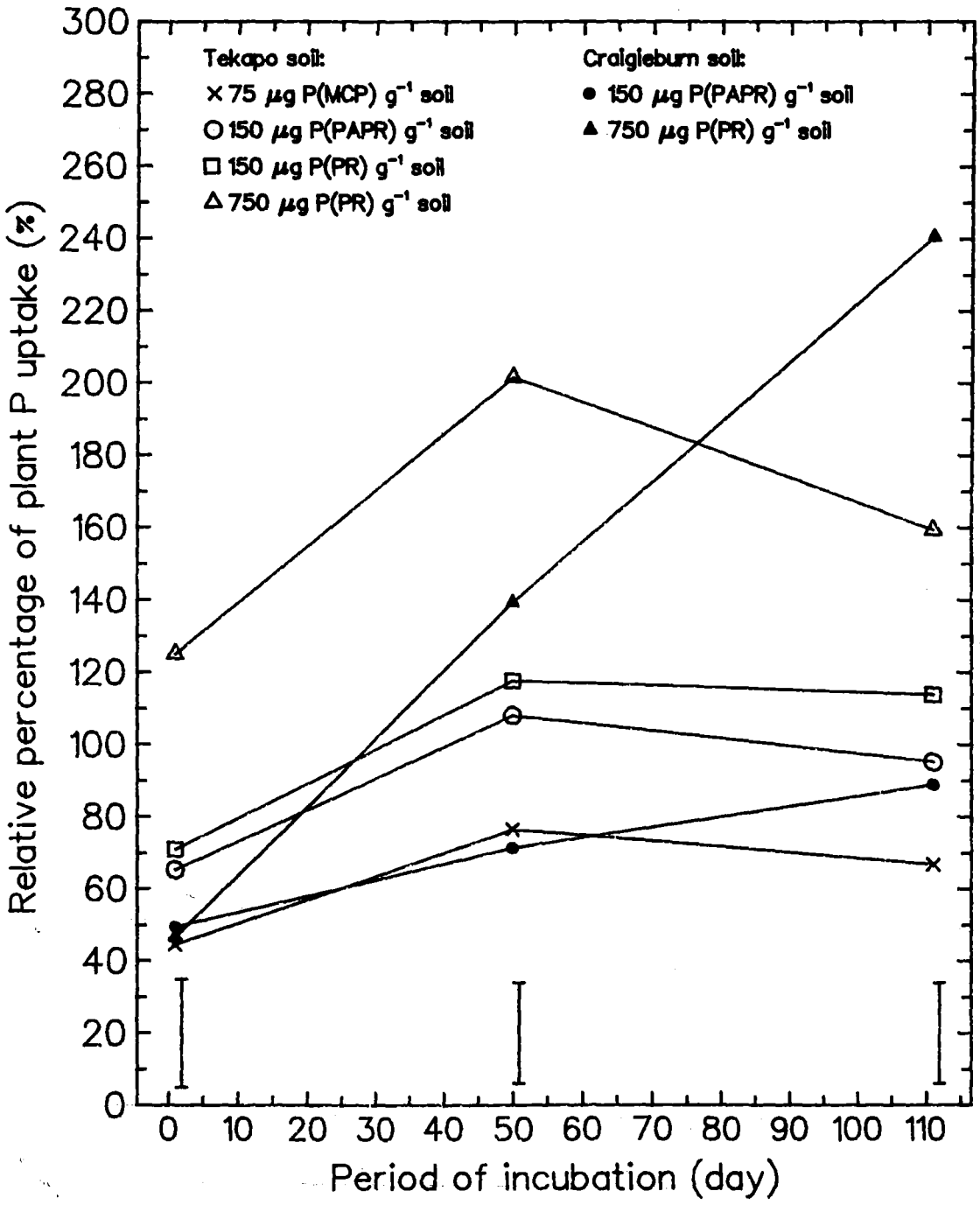


Figure 7.3 Relative percentage of plant P uptake.

The vertical bars represent LSD (0.05).

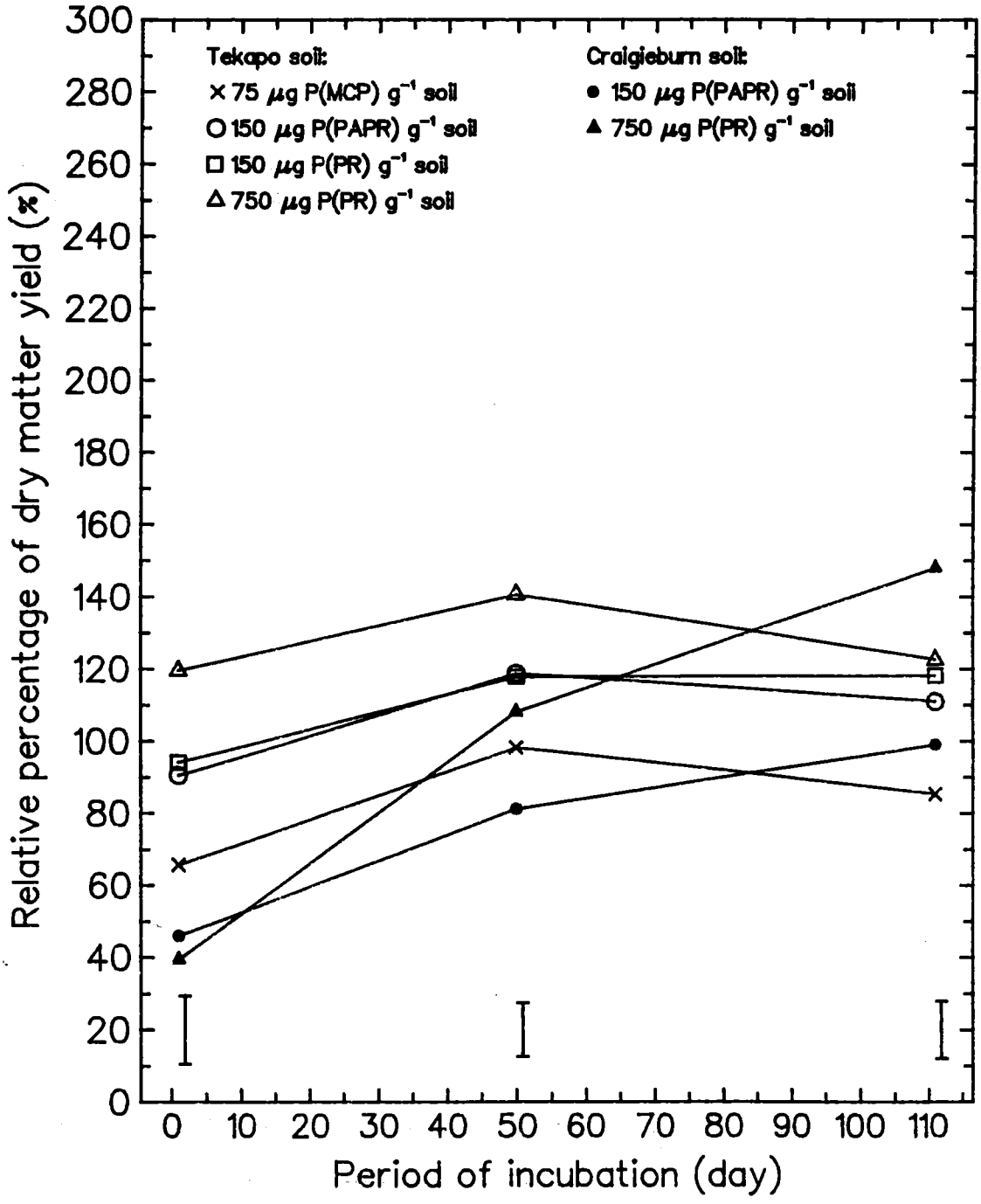


Figure 7.4 Relative percentage of dry matter yield.

The vertical bars represent LSD (0.05).

where RP% is relative percentage of P uptake or dry matter yield, x_f, x_c and x_m are P uptake or dry matter yield in fertilised, controls and in the MCP (150 μg P g^{-1} soil) treatments respectively. The relative percentages in the PR or PAPR treatments at 150 μg P g^{-1} soil exceeded 100% after 50 and 111 days of incubation in the Tekapo soil and drew close to 100% in the Craigieburn soil. This is in line with the findings reported in Chapters 5 and 6. The concentration of plant available P represented by exchangeable P, water extractable P, Bray I P and Olsen P in the MCP-treated soils decreased markedly, with increasing periods of incubation, as a result of P retention by the soils (large F_{out}) and a lack of any sustained phosphate input (small F_{in}) into the available P pool. In the PR and PAPR treated soils, the extractable or exchangeable P pools increased with incubation periods or remained stable due to the substantial input (large F_{in}) of phosphate from the dissolution of PR materials which continued for extended periods after application (cf. Sections 5.4.2 and 6.3.1).

The relative performance of the PR and PAPR compared with MCP is generally poorer in the Craigieburn soil than in the Tekapo soil shortly after application (Figures 7.3 and 7.4). The large amount of free sorption surfaces in the higher P-retention Craigieburn soil means that a considerable proportion of the phosphate initially dissolved from the PR and PAPR materials would be quickly sorbed by soil components rather than taken up by plants. One effect of this might be to limit root development in the early stages of plant growth (Hammond *et al.*, 1986). However, after 111 days of incubation, the relative effectiveness of PAPR is similar between the two soils, but that of PR at the higher application rate is greater in the Craigieburn soil. Therefore, the relative performance of PR and PAPR with respect to water soluble fertilisers in soils which differ in P-retention capacity depends on the period of soil-fertiliser contact and application rate.

It should be noted that the plant response data reported here were collected from pot trials with limited periods of plant growth (34 to 45 days). One of the advantages of pot trials is that as they are carried out under controlled conditions, the

influences of factors other than the ones under investigation are minimised. The results derived should therefore provide a clear indication as to how plants respond to the variations of the factors studied. Moreover, the level of plant production is often controlled by the conditions at the early stages of plant growth, as young plants are more sensitive to changes in growing conditions than plants already established. A short term trial using young plants might detect subtle differences in the ability of different forms of phosphate fertilisers to supply P to the plants. However, the artificially imposed conditions to the plants in the pot trial do not adequately represent those in the field. Relatively long term trials conducted in the field are required to test the findings obtained in pot trials. One of the drawbacks attached to field trials, however, is that plant responses are a function of several uncontrolled conditions which may tend to overshadow the real treatment effect.

7.2.2 Relationships between plant P uptake and kinetic and chemical indices

The relationships between plant P uptake from the kinetic experiments (Experiments A, B and C) and the water extractable P, Bray I P, Olsen P, 0.5 M NaOH extractable P, exchangeable P and the rate of phosphate input to the exchangeable P pool (F_{in}) are illustrated in Figures 7.5 to 7.10 respectively. The values of the extractable P pools are those measured at the beginning of each experiment when the fertilisers and the soils were incubated for 1, 50 and 111 days. The relationships between plant P uptake and exchangeable P pools from Experiment A are not presented as the exchangeable P pools in the PR-treated soils were overestimated (cf. Section 5.4.2). The overestimation of the exchangeable P pools also affects the F_{in} values, but the magnitude of the influence is relatively small. The values of F_{in} in both Experiments A and B are therefore assessed: there were no F_{in} values available in Experiment C. The F_{out} values indicate the rate of phosphate retention by soils which are mainly influenced by the soil P-retention capacity. Since only two soils were used

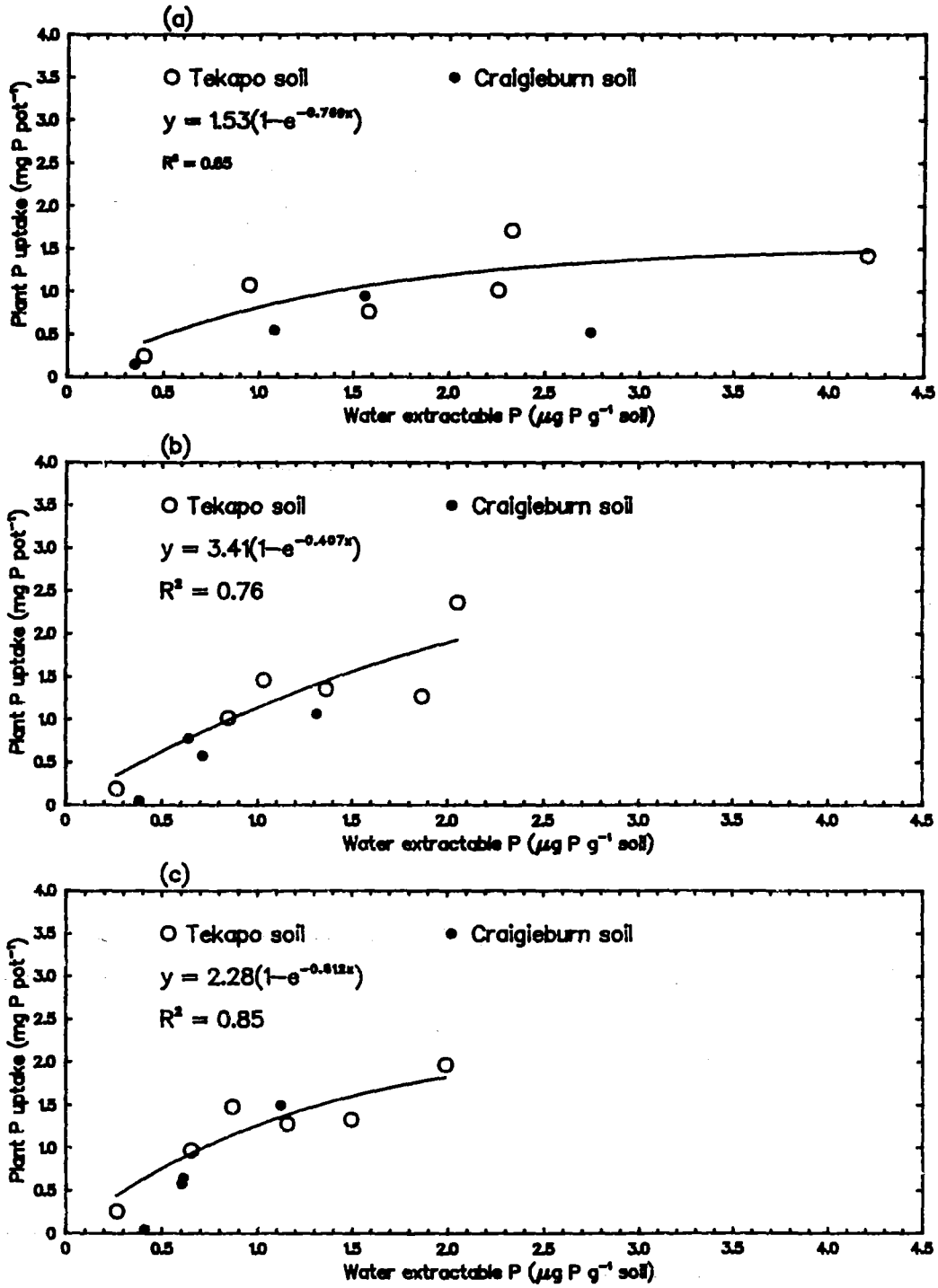


Figure 7.5 Relationships between water extractable P and plant P uptake. (a) period of incubation = 1 day, period of plant growth = 34 days; (b) period of incubation = 50 days, period of plant growth = 45 days; (c) period of incubation = 111 days, period of plant growth = 43 days.

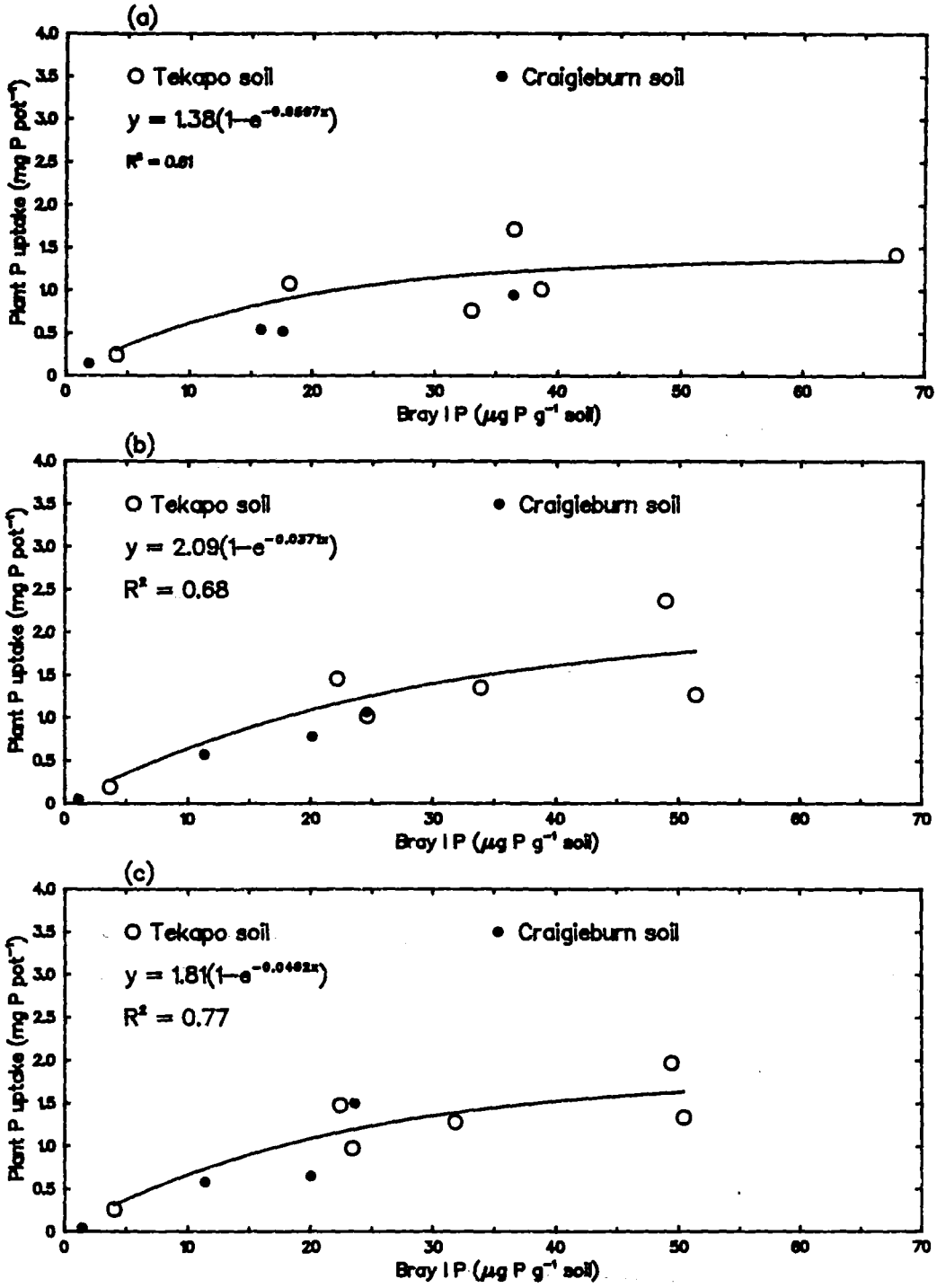


Figure 7.6 Relationships between Bray I P and plant P uptake. (a) period of incubation = 1 day, period of plant growth = 34 days; (b) period of incubation = 50 days, period of plant growth = 45 days; (c) period of incubation = 111 days, period of plant growth = 43 days.

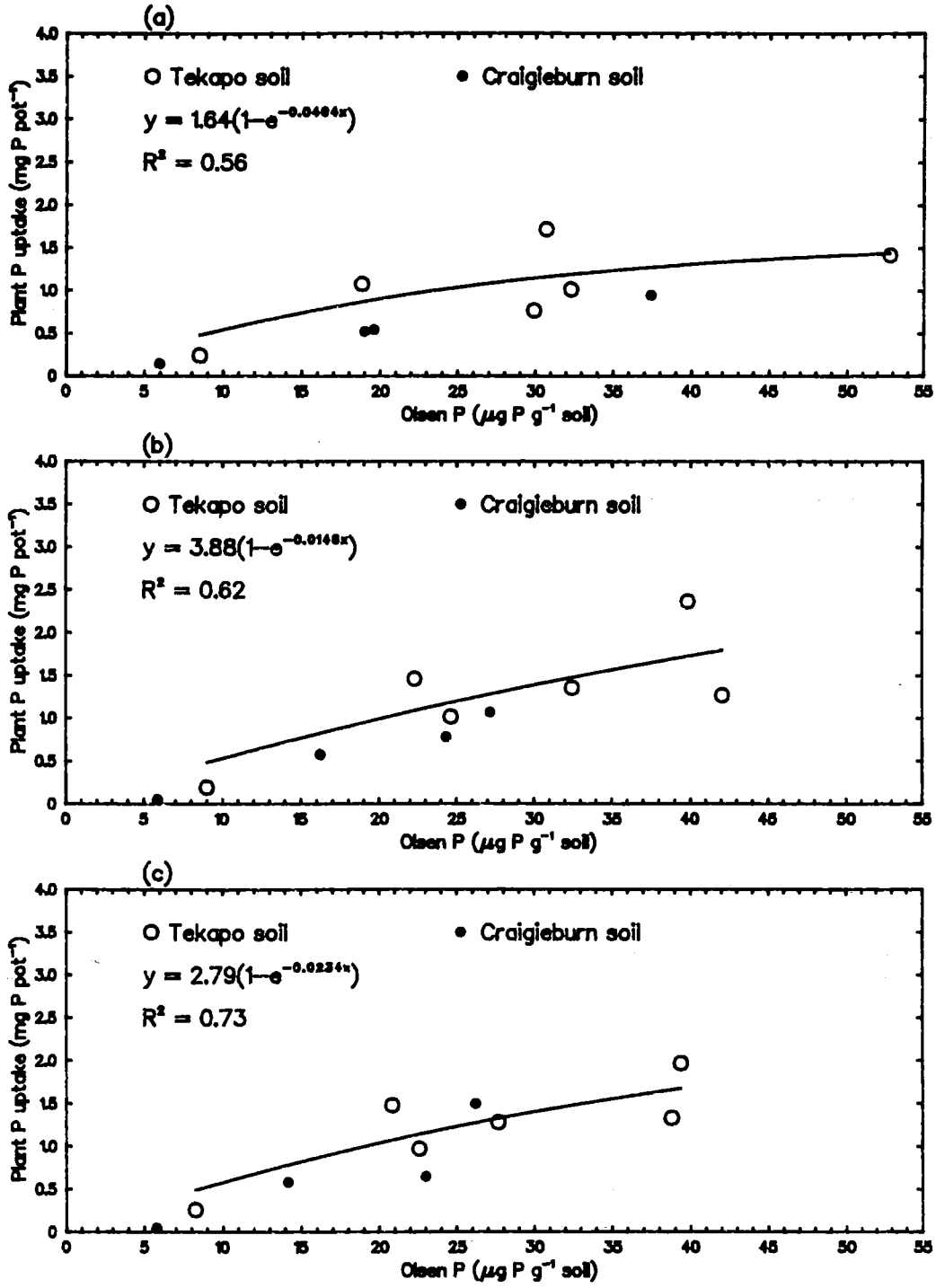


Figure 7.7 Relationships between Olsen P and plant P uptake. (a) period of incubation = 1 day, period of plant growth = 34 days; (b) period of incubation = 50 days, period of plant growth = 45 days; (c) period of incubation = 111 days, period of plant growth = 43 days.

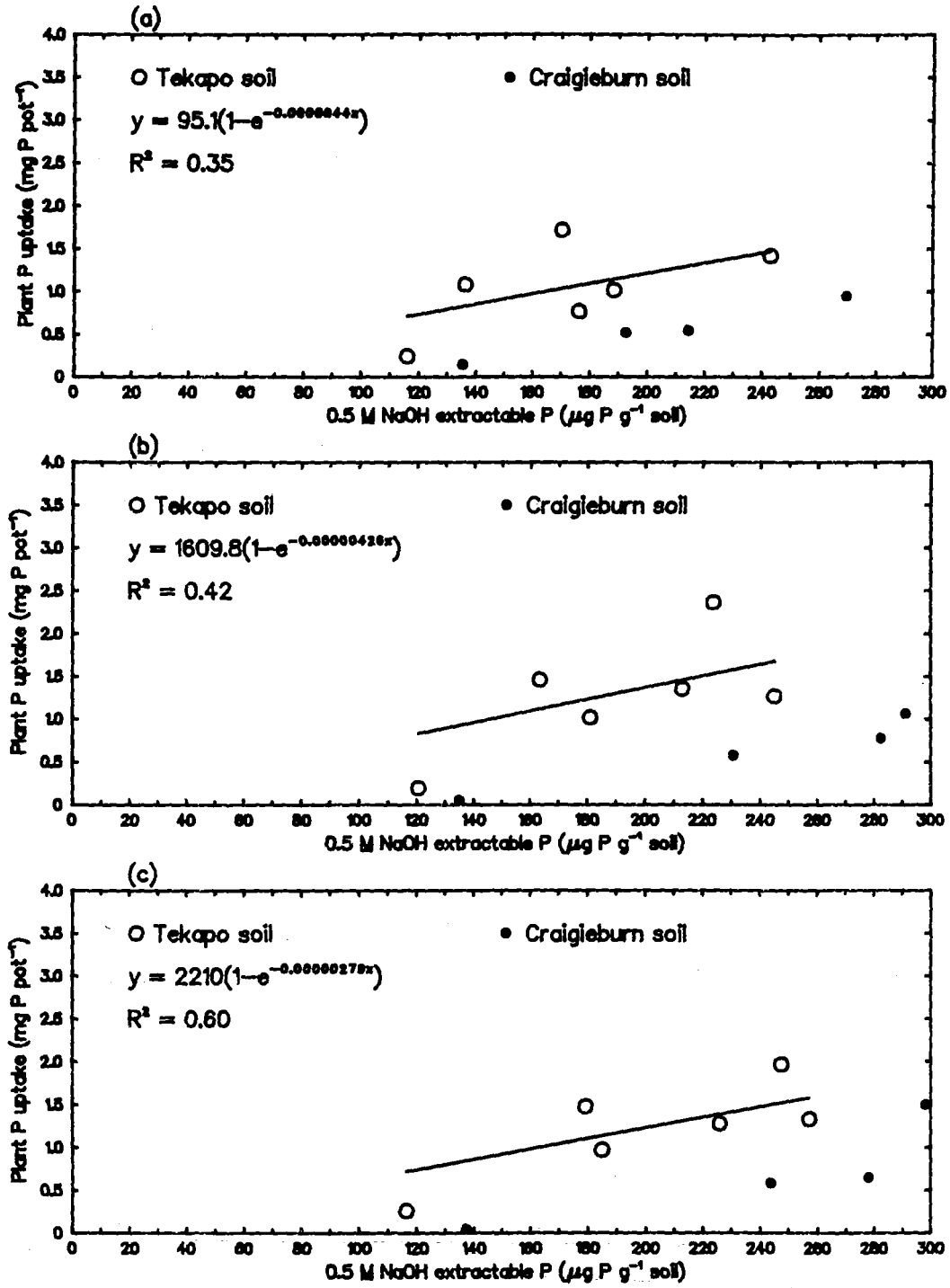


Figure 7.8 Relationships between 0.5 M NaOH extractable P and plant P uptake. (a) period of incubation = 1 day, period of plant growth = 34 days; (b) period of incubation = 50 days, period of plant growth = 45 days; (c) period of incubation = 111 days, period of plant growth = 43 days.

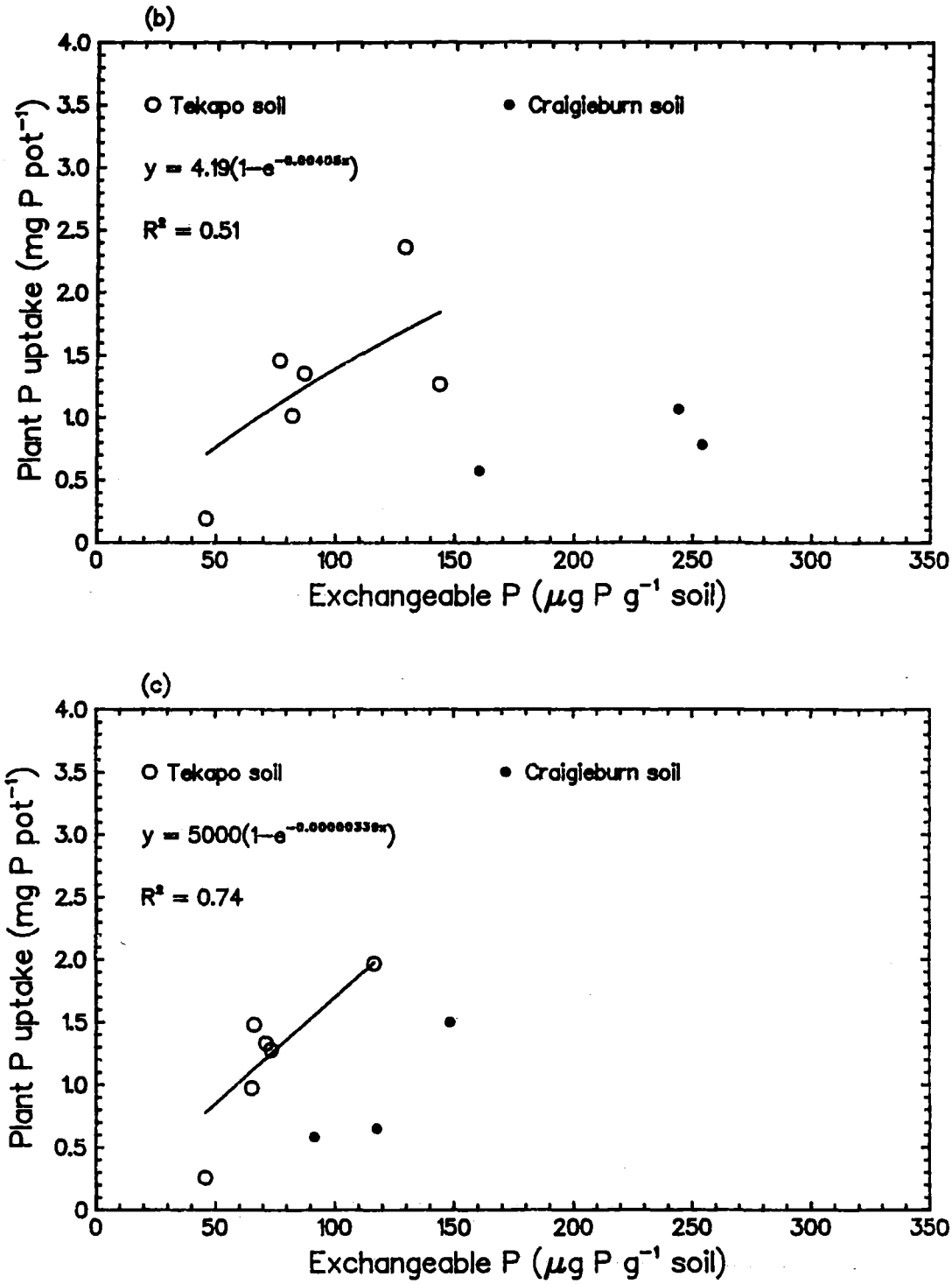


Figure 7.9 Relationships between exchangeable P and plant P uptake. (b) period of incubation = 50 days, period of plant growth = 45 days; (c) period of incubation = 111 days, period of plant growth = 43 days.

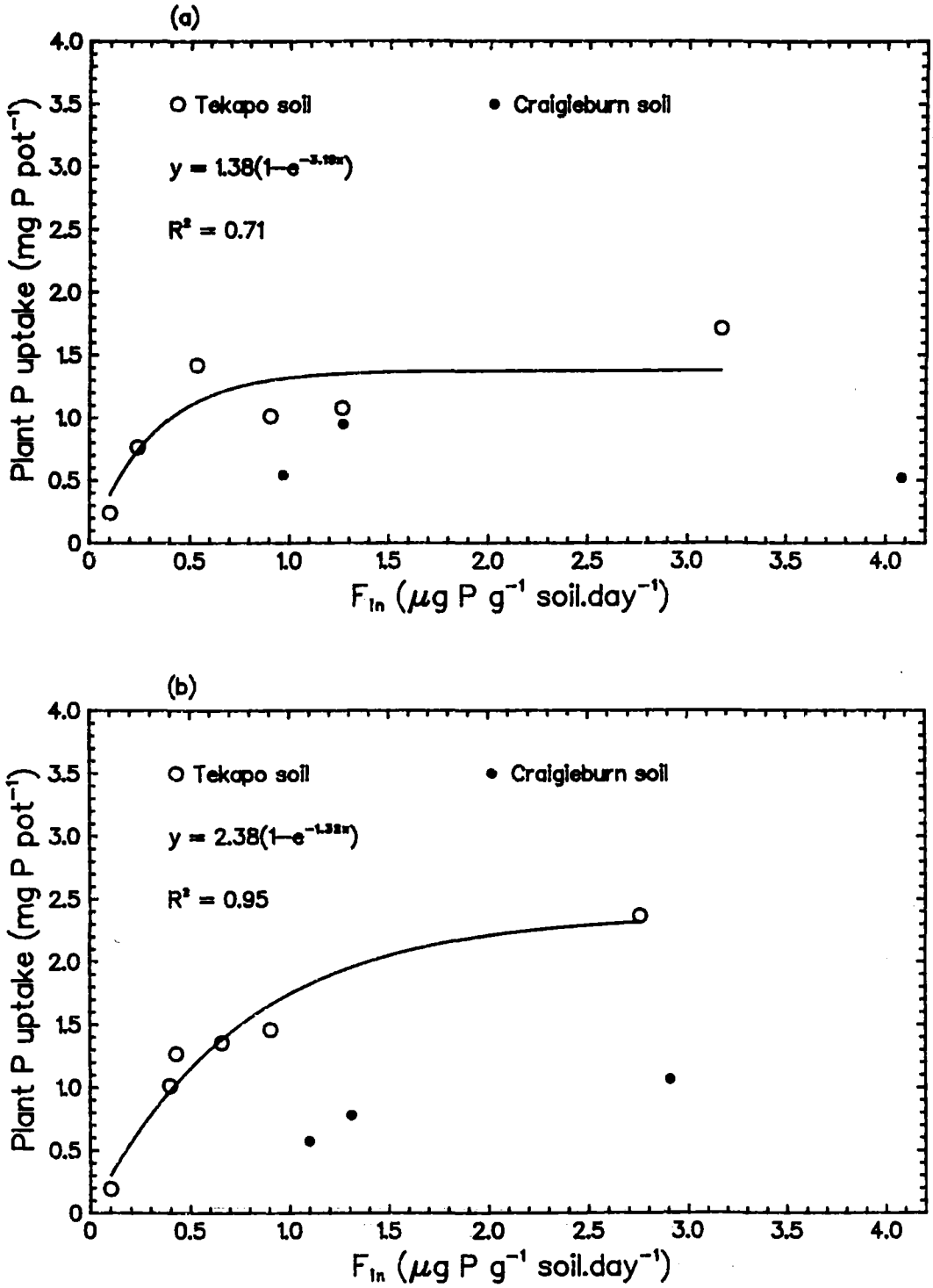


Figure 7.10 Relationships between F_{In} and plant P uptake. (a) period of incubation = 1 day, period of plant growth = 34 days; (b) period of incubation = 50 days, period of plant growth = 45 days.

in this study, the relationships between plant P uptake and F_{out} values are not examined.

Three mathematical models which are commonly used to describe plant responses to fertiliser applications were fitted to the relationships of plant P uptake and the kinetic and chemical parameters by the least squares methods:

(i) the Mitscherlich negative exponential model:

$$y = a(1 - e^{-bx}) \qquad (7.2)$$

(ii) the polynomial quadratic model:

$$y = a + bx + cx^2 \qquad (7.3)$$

and, (iii) the power function model:

$$y = ax^b \qquad (7.4)$$

where y in these models is plant P uptake, x is the values of the kinetic or chemical indices, and a, b and c are coefficients.

The Mitscherlich model is conceived by some workers as reflecting the biological mechanism of plant responses to fertilisers (Nelson *et al.*, 1985). The model defines an asymptotic maximum yield, the a value. The polynomial and the power function models are usually regarded as empirical.

The regressions are only performed using observations from the Tekapo soil as there are insufficient numbers of data points to obtain meaningful regressions in the Craigieburn soil. The relationships between plant P uptake and the indices in the latter soil are only examined in a descriptive manner.

The model parameters along with the values of R^2 which provide a measure of the fit of the models are summarised in Table 7.1. The variables, P(W), P(B), P(O), P(S), P(E) and F_{in} in the table represent water extractable P, Bray I P, Olsen P, 0.5 M NaOH extractable P, exchangeable P, and the rate of phosphate input to the exchangeable P pool. The regression lines fitted by the Mitscherlich model are shown in Figures 7.5 to 7.10.

The values of R^2 in Table 7.1 suggests that no one single soil test parameter is better than the others in accounting for the variations of plant P uptake. The amount of variation explained by these indices is mostly less than 80% no matter which of the three models are fitted. Amongst the noticeable exceptions is the particularly good correlation between the F_{in} values and the plant P uptake fitted by the Mitscherlich and quadratic models in Experiment B. Also noticeable is the poor relationship between the 0.5 M NaOH extractable P (P(S)) and plant P uptake when the fertilisers were incubated for short periods.

The relationships between the kinetic or chemical indices and plant P uptake improved with increasing periods of incubation. The poor relationship shortly after the application of the phosphate fertilisers reflect the diverse forms or phases of phosphate occurring in the soil medium and the inability of any one single measurement to take this into account. As the period of soil - fertiliser contact increases, the forms and phases in which phosphate occurs become more similar between soils treated with different forms of fertilisers. The ability of the kinetic and chemical indices to predict plant responses improves accordingly. This clearly demonstrates the difficulty of choosing a single soil test parameter to estimate plant production when various forms of phosphate fertilisers are applied to the soils.

Table 7.1 Parameters of the models fitted by the least squares methods to describe the relationships between plant P uptake and kinetic and chemical indices.

x variable	Model type	Experiment					
		A		B		C	
		Parameters	R^2	Parameters	R^2	Parameters	R^2
P(W)	I	a 1.53	0.65	3.41	0.76	2.28	0.85
		b 0.769		0.407		0.812	
	II	a 0.0554	0.65	-0.0895	0.75	-0.0121	0.84
		b 0.823		1.46		1.63	
		c -0.118		-0.232		-0.352	
	III	a 0.647	0.73	0.989	0.89	1.15	0.87
		b 0.730		1.09		0.944	
P(B)	I	a 1.38	0.61	2.09	0.68	1.81	0.77
		b 0.0597		0.0371		0.0462	
	II	a 0.172	0.59	-0.0409	0.68	0.0308	0.77
		b 0.042		0.069		0.0644	
		c -3.53×10^{-4}		-6.64×10^{-4}		-6.52×10^{-4}	
	III	a 0.114	0.79	0.0714	0.89	0.101	0.90
		b 0.637		0.842		0.735	
P(O)	I	a 1.64	0.56	3.88	0.62	2.79	0.73
		b 0.0404		0.0148		0.0234	
	II	a -0.184	0.57	-0.705	0.66	-0.418	0.75
		b 0.0676		0.113		0.097	
		c -7.18×10^{-4}		-1.32×10^{-3}		-1.14×10^{-3}	
	III	a 0.041	0.72	0.0112	0.83	0.0271	0.85
		b 0.953		1.40		1.16	
P(S)	I	a 95.1	0.35	1609.8	0.42	2210	0.60
		b 6.44×10^{-5}		4.26×10^{-6}		2.79×10^{-6}	
	II	a -2.62	0.45	-5.68	0.62	-2.79	0.74
		b 0.036		0.0673		0.034	
		c -8.09×10^{-5}		-1.55×10^{-4}		6.67×10^{-5}	
	III	a 5.12×10^{-5}	0.49	4.56×10^{-7}	0.69	9.17×10^{-6}	0.80
		b 1.91		2.80		2.20	
P(E)	I	a ------	---	4.19	0.51	5000	0.74
		b ------		4.05×10^{-3}		3.39×10^{-6}	
	II	a ------	---	-2.695	0.73	-2.866	0.91
		b ------		0.0759		0.0864	
		c ------		-3.19×10^{-4}		-3.86×10^{-4}	
	III	a ------	---	3.89×10^{-4}	0.68	1.73×10^{-4}	0.72
		b ------		1.76		2.04	
F_{in}	I	a 1.38	0.71	2.38	0.95	------	---
		b 3.19		1.32		------	
	II	a 0.497	0.65	0.191	0.93	------	---
		b 0.792		2.036		------	
		c -0.131		-0.454		------	
	III	a 1.14	0.75	1.59	0.86	------	---
		b 0.494		0.74		------	

A: Period of incubation = 1 day; period of plant growth = 34 days.
B: Period of incubation = 50 days; period of plant growth = 45 days.
C: Period of incubation = 111 days; period of plant growth = 43 days.
R^2: A measure of the amount of variation explained by the regression.
I: $y = a(1 - e^{-bx})$; II: $y = a + bx + cx^2$; III: $y = ax^b$

The power function model seems to fit the data slightly better than the other two models judged by the majority of the R^2 values. The fit of a particular model, however, is likely to be influenced by the range of fertiliser application rates. If the rates of the fertilisers applied cover a wide range sufficient to produce a complete plant response curve rather than fragments of it, the other two models might be more appropriate.

Figures 7.5, 7.6 and 7.7 suggest that similar lines might be fitted for the Craigieburn soil as those in the Tekapo soil between plant P uptake and water extractable P, Bray I P and Olsen P. This is not so in the cases of 0.5 M NaOH extractable P, exchangeable P and F_{in} (Figures 7.8, 7.9 and 7.10). This suggests that the very labile fractions of the soil phosphate extracted by water, Bray I and Olsen reagents are similar in plant availability between the two soils. The 0.5 M NaOH extractable P and exchangeable P, however, are comparatively larger P pools and represent the soil P reserves or the capacity factor. The proportion of these P reserves that may be taken up by plants per unit time decreases with increasing soil P-retention or soil P buffering capacity (Holford and Mattingly, 1979; Holford, 1980; Holford and Cullis, 1985). The quantity of phosphate that plants can absorb from the higher P-retention Craigieburn soil is therefore lower than that in the Tekapo soil within the periods of plant growth in the experiment at the same quantities of 0.5 M NaOH extractable P or exchangeable P.

As no one single variable could adequately account for the variation of plant P uptake, an attempt was made to construct models involving more than one variables by the stepwise regression method (Draper and Smith, 1981). Traditionally, it is believed that the intensity factor (the concentration of P in soil solution) and the capacity factor (the amount of P in soil solid phase that may be readily released to replenish the soil solution P) are required to adequately describe the soil phosphorus supply to plants when a range of soils which differ in P-retention capacity are dealt with (Russell *et al.*, 1957; Gunary and Sutton, 1967; Larsen, 1967). If soils are similar

in their P-retention capacity, then only one of the two factors may be related to plant P uptake. However, if slowly-soluble phosphate fertilisers such as PR or PAPR are applied to soils, the phosphate supply to plants by the soil would not only depend on the intensity and the capacity factors, but also the rates of fertiliser dissolution. This last term may be regarded as a kinetic factor. It is therefore assumed that plant P uptake may be a function of three factors: the intensity factor (phosphate concentration in soil solution), the capacity factor (the reserves for solution P) and the kinetic factor (rate of phosphate input from other P pools, mainly from fertiliser dissolution, to plant available P pool).

The isotopically and chemically derived parameters are separated into three categories: water extractable P as an intensity factor; Bray I P, Olsen P, 0.5 M NaOH extractable P and exchangeable P as capacity factors; and the F_{in} values as a kinetic factor. Three variable groups are then formed by matching each of the capacity factors with the water extractable P and F_{in} values. These grouped variables are stepwise regressed with the plant P uptakes.

The model fitted is based on the power function model (Equation 7.4). The adoption of this equation is not only because of its better fit to the data compared to the other two equations but also because it can be easily transformed into a multiple regression model:

$$y = ax_1^b \cdot x_2^c \cdot x_3^d \qquad (7.5)$$

where y is the dependent variable, plant P uptake, x_1, x_2, and x_3 are three independent variables representing the intensity, the capacity and the kinetic factors, a, b, c and d are coefficients. This equation can be easily converted to a linear form by a logarithmic transformation:

$$\ln y = \ln a + b\ln x_1 + c\ln x_2 + d\ln x_3 \qquad (7.6)$$

The data are therefore natural-log transformed before regression.

In the stepwise procedure, the independent variables (the intensity, capacity and kinetic factors) in each group are added one by one to the model and the F statistic for a variable to be added must be significant at a specified level (entry level). The order of entry is determined by using the partial correlation coefficient as a measure of the importance of the variables not yet in the equation. The independent variable best correlated with the dependent variable is entered in the equation first and tested for F statistic significance. The second most correlated variable is then entered to produce a new regression equation. The overall regression is checked for significance and the improvement in the R^2 value is noted. After a variable is added, however, the stepwise procedure examines all the variables already in the model and deletes any variable that does not produce the F statistic significant at a specified level (stay level). The regression process finishes when none of the variables outside the model has an F statistic significant at the entry level, and every variable in the model is significant at the stay level. Since the purpose is to choose a model that provides the best prediction using the data available, a moderate entry and stay level is desirable.

Since the F_{in} values are only available in Experiments A and B, the regression is only performed with data from these two experiments, and the results are summarised in Table 7.2.

In most cases, the plant P uptake can be adequately predicted by a model involving two variables (Table 7.2). The amount of variation in plant P uptake explained by the two term models is significantly higher than that accounted for by the single variable models: more than 96% of the variation can be explained by the regression of any of the two variable models.

Table 7.2 Summary of results from the stepwise regression.

(a) Period of incubation = 1 day; period of plant growth = 34 days.

Variables regressed	Step	Variable entered	Model fitted	Partial R^2	Model R^2
P(W), P(B)	1	P(B)	$y=0.114P(B)^{0.637}$	0.79	0.79
and F_{in}	2	F_{in}	$y=0.267P(B)^{0.421} \cdot F_{in}^{0.303}$	0.19	0.98
P(W), P(O)	1	F_{in}	$y=1.14F_{in}^{0.494}$	0.75	0.75
and F_{in}	2	P(O)	$y=0.14P(O)^{0.626} \cdot F_{in}^{0.336}$	0.23	0.98
P(W), P(S)	1	F_{in}	$y=1.14F_{in}^{0.494}$	0.75	0.75
and F_{in}	2	P(W)	$y=0.853P(W)^{0.468} \cdot F_{in}^{0.323}$	0.21	0.96

(b) Period of incubation = 50 days; period of plant growth = 45 days.

Variables regressed	Step	Variable entered	Model fitted	Partial R^2	Model R^2
P(W), P(B)	1	P(W)	$y=0.989P(W)^{1.09}$	0.89	0.89
and F_{in}	2	F_{in}	$y=1.24P(W)^{0.664} \cdot F_{in}^{0.359}$	0.06	0.96
P(W), P(O)	1	P(W)	$y=0.989P(W)^{1.09}$	0.89	0.89
and F_{in}	2	F_{in}	$y=1.24P(W)^{0.664} \cdot F_{in}^{0.359}$	0.06	0.96
P(W), P(S)	1	P(W)	$y=0.989P(W)^{1.09}$	0.89	0.89
and F_{in}	2	F_{in}	$y=1.24P(W)^{0.664} \cdot F_{in}^{0.359}$	0.06	0.96
P(W), P(E)	1	P(W)	$y=0.989P(W)^{1.09}$	0.89	0.89
and F_{in}	2	F_{in}	$y=1.24P(W)^{0.664} \cdot F_{in}^{0.359}$	0.06	0.96

Partial R^2: Square of the partial correlation coefficient associated with the variable entered at the step.
Model R^2: Square of the multiple correlation coefficients.
The significance probability of the overall F values for every model regressed is <0.05.

In Experiment A which was conducted after the fertilisers were incubated with the soils for 1 day, the plant P uptake is best predicted from a function containing a capacity factor (the Bray I P, and Olsen P) and the kinetic factor (F_{in}). The intensity factor(water extractable P) was only included in the model in one case replacing the 0.5 M NaOH extractable P as a variable because of the latter variable's very poor relationship with plant P uptake. This shows that the concentration of phosphate in soil solution immediately following the application of fertilisers is not a reliable indicator of the amount of plant available P in the soil. This is because the concentration of soil solution P is very unstable shortly after the application of phosphate fertilisers, particularly water soluble ones as it declines rapidly with increasing periods of fertiliser - soil contact (cf. Section 6.3.1).

However, with increasing periods of incubation, the concentration of soil solution P becomes relatively stable. As plant takes up P directly from the soil solution in the immediate vicinity of plant roots, the concentration of P in the soil solution becomes an important indicator of soil phosphate supply. Table 7.2 b shows that after 50 days of incubation, water-soluble P followed by F_{in} are most closely related to plant P uptake. All the capacity factors are left out of the equation. The exclusion of the capacity factors from the models reflect the fact that the data regressed were from experiments conducted using the same soil. The capacity factor is therefore similar in the various treatments. Holford (1991) has also suggested that where the P concentration in the soil solution is controlled more by the dissolution of phosphate minerals than by the desorption of soil P, which is very likely in the case of PR or PAPR treated soils, the intensity factor is a better index of available P than the capacity factor.

It should be noted that the F_{in} variable is included in all the models regardless of the period of incubation. Plant P uptake is not just controlled by the concentration of P in the soil solution and its immediate reserves, but also by the rate of phosphate entering the exchangeable P pool from other sources. The F_{in} values mainly reflect

fertiliser dissolution in the soil; thus, a prediction model which incorporates the kinetic factor as well as the intensity or capacity factors would reflect the nature of the fertilisers applied in addition to the soil P status. This is particularly important when dealing with situations where different forms of phosphate fertilisers which differ in solubility are involved. The amount of plant available P in a soil which received PR fertilisers is not only determined by the soil P status, but also by the rate of PR dissolution. The inclusion of F_{in} in all the models may also reflect the fact that F_{in} was determined under plant growing conditions.

It is clear that plant P uptake is not a function of one single variable. A reliable prediction model should incorporate at least two variables amongst the intensity, capacity and kinetic factors. Although the results reported here are from relatively short-term experiments, they clearly suggest the necessity of including the kinetic factor in the multi-variable models depicting the relationships between plant production and soil test indices when different types of phosphate fertilisers are applied to soils.

7.3 Summary and conclusions

When applied at the same rate, MCP is superior to NCPR and NCPAPR in supplying P to plants after being incubated for 1 day in both the Tekapo and the Craigieburn soils. The NCPR and NCPAPR, however, are just as effective as, or more effective than MCP after 50 days of incubation in the Tekapo soil. The relative effectiveness of the PR and PAPR in comparison to MCP in the high P-retention Craigieburn soil is slightly lower than that in the low P-retention Tekapo soil immediately following the application, but improved markedly with increasing periods of incubation. This is particularly true for the PR applied at the higher rate. The improvement of the PR-containing fertilisers compared with MCP is due to the steady input of phosphate into the plant available P pool from the dissolution of PR materials and the rapid decline of available P in the MCP-treated soils.

No one single kinetic or chemical parameter is clearly better in predicting plant P uptake. The amount of variation in plant P uptake accounted for by the single variable models, however, improved with increasing periods of incubation. This is due to the development of more homogeneous and stable systems in terms of the forms and phases of P in the soil medium following the application of different forms of phosphate fertilisers. Of the three equations regressed, the power function model seems to fit the data slightly better than the Mitscherlich and the quadratic models.

The amount of variation accounted for by regression is greatly improved by including more than one variable in the model. More than 96% of the variation in plant P uptake can be explained by models incorporating two variables amongst the intensity, capacity and kinetic factors. The concentration of P in soil solution is an more important indicator after extended periods of fertiliser - soil contact than immediately after fertilisation. The F_{in} values which indicate the rate of fertiliser dissolution in the soil is included in all the models. This indicates the importance of fertiliser dissolution rate in affecting phosphate supply to plants, particularly when PR-containing fertilisers are applied. This also suggests that the isotopic dilution technique developed in Chapter 5 from which the F_{in} values were derived is a credible methodology.

Part four

General conclusions

Chapter 8

Summary and general conclusions

An injection technique, by which undisturbed soil cores are isotopically labelled with ^{32}P to study dissolution of phosphate fertilisers in soil, was investigated in both field and greenhouse trials. The specific activity, as sampled by plants, was influenced by the P content in the original plant material before labelling and the spatial distribution of ^{32}P and ^{31}P in the soil, as well as by the specific activity in the exchangeable P pool. The original P content effect may be eliminated by encouraging rapid plant growth with frequent harvests. When ^{32}P was injected between 0-150 mm in natural soil columns and phosphate fertilisers were applied at the surface, the amounts of plant available P dissolved from the fertilisers were overestimated. This overestimation was due to at least three mechanisms which reduce the specific activity in the plant material: (i) the interaction between surface-applied fertiliser, ^{32}P injected through the whole soil column, and the vertical decline in root density, (ii) the decline of specific activity in the exchangeable P pool associated with losses of ^{32}P to non-exchangeable P pools, and (iii) non-uniform distribution of ^{32}P vis-a-vis ^{31}P. The first and third mechanisms do not occur if the fertilisers and the tracer are completely mixed with the soil. The second effect may be reduced by obtaining a plant specific activity free from the effect of the original plant P content as early as practically possible, and using this to calculate the exchangeable P pool.

The injection technique can be adopted to assess the effectiveness of phosphate fertilisers by introducing a concept known as the fertilising equivalent (FE). The FE value is not a measure of the absolute amounts of P dissolved from the fertilisers, rather, it is a measure of the amounts of soil exchangeable P that the fertilisers are equivalent to in supplying P to plants, when applied at the specific location. The FE values may be larger, equal to, or smaller than the fertiliser

application rate, depending on the location of the fertiliser applied and thus its availability to plants. The FE values obtained indicated that when applied at the surface of an established grassland soil, the water-soluble fertiliser, single superphosphate (SSP), was much more effective than the surface-applied unground North Carolina phosphate rock (NCPR) and 30% acidulated NCPR with phosphoric acid (NCPAPR) within the period of experimentation. The limited effectiveness of NCPR and NCPAPR was probably due to inadequate contact between the PR and soil materials, which is prerequisite for the dissolution of PR materials.

The association of the FE value concept with the injection technique provides a convenient tool for assessing the effectiveness of phosphate fertilisers on intact established soil-plant systems. The technique may be employed to evaluate the effectiveness or availability of phosphate fertilisers as influenced by fertiliser types, soil types, plant species or environmental factors.

A technique based on isotopic dilution and kinetic principles was developed to study the rates of phosphate fertiliser dissolution (F_{in}) and retention (F_{out}) by soils. The calculation of F_{in} and F_{out} required determining the corresponding values of the specific activities of the exchangeable P pools, SA_1 and SA_2, at times t_1 and t_2 for a given labelling operation, and the respective sizes of the exchangeable P pools at the two times, Q_1 and Q_2. The SA_1 and SA_2 values were determined by sampling the exchangeable P pool with plants over a period of time after labelling. The Q values were calculated using the instantaneous specific activity values immediately after labelling, extrapolated from the specific activity-time (SA-t) curves. The SA-t curves were generated from individual labelling experiments, conducted after the fertilisers were incubated with the soils for 1, 50 and 111 days. The extrapolation was carried out on a semi-log linear basis.

The technique was applied to study the rates of dissolution and retention of ground North Carolina phosphate rock (<150 μm, NCPR) and 30% partially acidulated North Carolina phosphate rock with phosphoric acid (NCPAPR) in comparison with

MCP (solution). The soils used for the study were a Tekapo sandy loam with a low P retention and a Craigieburn silt loam with a higher P retention capacity.

The sizes of the exchangeable P pools measured at 1, 50 and 111 days of incubation, and the average values of F_{in} and F_{out} between 1-50 and 50-111 days of incubation, showed that most of the phosphate from the MCP solution entered the exchangeable P pool immediately after being added to the soil. Further supply of phosphate to the exchangeable P pool was small. With increasing periods of incubation, phosphate was quickly transformed to less rapidly exchangeable forms. The result of the imbalanced inflow and outflow was the rapid decline of the exchangeable P pool. The use of water soluble fertiliser therefore causes a sharp rise in the soil exchangeable P pool immediately after addition of the fertiliser and a subsequent sharp fall. In contrast, the exchangeable P pools in the soils treated with NCPR and NCPAPR were initially not as large as those in the soils treated with MCP. The P pools, however, were maintained at relatively stable levels for extended periods. This was due to the continuous dissolution of PR materials at considerable rates and relatively smaller rates of P-retention by the soils.

The rate of fertiliser dissolution and subsequent retention is influenced by soil P retention capacity and fertiliser application rate. An increase in soil P retention capacity caused a slight rise in the rate of fertiliser dissolution, but also a rise in the rate of P retention by the soil. The PR dissolved more rapidly at a lower application rate, in relative terms, but more slowly in absolute terms.

The trend in temporal changes of plant-available P in the soils receiving different types of phosphate fertilisers were measured by the water, Bray I and Olsen P extractions. These trends were in agreement with those predicted by the F_{in} and F_{out} values. Changes in extractable P pools can be interpreted in terms of rates of input and output to and from the plant available P pool. Extractable P pools were increased to very high concentrations immediately following the application of MCP solution, but diminished rapidly because of the high rate of P retention (high F_{out}) by the soil, and

insufficient sustained phosphate input (small F_{in}) from further fertiliser dissolution. The extractable P pools in the soils which received the NCPR and the NCPAPR were not as high as those in the soils which received MCP, but were maintained by the continuous input (comparatively high F_{in}) of P from the dissolution of PR materials for prolonged periods, and relatively lower rates of P retention (comparatively low F_{out}).

Percentage dissolution of PR-containing fertilisers as measured by 0.5 M NaOH, 1 M HCl and 0.5 M $BaCl_2$/TEA extractions generally corresponded to the trends predicted from the F_{in} values. Percentage dissolution, as a function of period of incubation, is well described by the Mitscherlich exponential model. This model predicts that PR and PAPR fertilisers dissolve to a greater extent at a lower application rate and when applied to a soil with a higher P-retention capacity. This agreed with the estimates based on F_{in} values. However, the average rates of dissolution between 1-50 and 50-111 days of incubation, estimated by the F_{in} values, were systematically higher than those estimated by the chemical extraction methods. It is suggested that this may be because F_{in} values were measured under growing plants. The continuous removal of phosphate and calcium from the soil solution by plant uptake and microbial immobilisation favours PR dissolution. This contrasts with the conditions under which the soil samples used for the chemical extractions were incubated. In addition, F_{in} includes other terms, such as desorption.

Extraction methods may provide estimates of the extent of fertiliser dissolution in the soil for a specific period of incubation, but the values are subjected to variations which depend on the extractability of P or Ca by the extractants. In addition, results may be influenced by soil properties and the rates of fertiliser application, and estimates by 0.5 M NaOH and 0.5 M $BaCl_2$/TEA may be invalid if considerable losses of P or Ca occur as a result of plant uptake or leaching.

In comparison, the isotopic labelling method provides an average rate of dissolution. This may be adequate in practical terms to assess the amount of P that may be released by a PR or PAPR through a period, such as a growing season. The

important attribute of the technique is that it measures the rates of phosphate retention as well as dissolution under growing plants using comparatively large volumes of soil. The uptake of phosphate from the soil by plants was used as a sampling mechanism. It provides quantitative information for the understanding of the dynamics of different types of phosphate fertilisers applied to soils.

Plant responses to the application of the different types of phosphate fertilisers also corresponded to the trend predicted by the F_{in} and F_{out} values. Immediately following the application (1 day incubation), the MCP (solution) appeared to be superior in supplying P to plants compared to either the NCPR or the NCPAPR applied at the same rate. After 50 and 111 days of incubation, however, the NCPR and NCPAPR were just as effective or more effective than MCP at the same application rate in the lower P-retention Tekapo soil. This is in line with the findings that the concentration of plant available P in the MCP-treated soils decreased markedly with increasing periods of incubation, as a result of P fixation by the soils (large F_{out}), and a lack of sustained input (small F_{in}) into the available P pool. The concentration of plant available P in the NCPR and NCPAPR-treated soils increased with incubation period or remained stable, due to substantial input (large F_{in}) of phosphate from the dissolution of PR materials, which continued for extended periods after application. The relative performance of the PR-containing fertilisers, compared with that of MCP, was generally poorer in the Craigieburn soil than in the Tekapo soil shortly after application, but improved with time of incubation.

Relationships between the isotopically and chemically measured parameters, and plant P uptake are complicated by the application of different types of phosphate fertilisers. The amounts of variation explained by individual kinetic or chemical indices are mostly less than 80%, no matter which of the three single variable models, the Mitscherlich, the quadratic or the power function was fitted. The relationships, however, improved with increasing periods of incubation. This is probably due to the

development of more homogeneous and stable systems, in terms of the forms and phases of P, in the soil medium with increasing periods of soil-fertiliser contact.

The amount of variation, accounted for by the regression, may be greatly improved by including more than one variable in the model. More than 96% of the variation in plant P uptake could be explained by the models involving two variables amongst the intensity, capacity and kinetic factors. The concentration of P in soil solution is a more important indicator after sufficient soil fertiliser contact than immediately after the addition of the fertilisers. After 50 days of incubation, this intensity factor together with the kinetic factor is adequate to account for most of the variations in plant P uptake. The F_{in} values were included in all the two variable models irrespective of the period of incubation. This indicated the importance of fertiliser dissolution rate in affecting the phosphate supply to plants when PR-containing fertilisers are applied to the soil. Assessment of soil P supply to plants therefore needs to consider the kinetic factor (fertiliser dissolution rate) in addition to the intensity and capacity factors.

The isotopic dilution technique developed in this study (Chapter 5) was only tested on two soils using a limited number of fertilisers, due to time constraint. The experiments involving sampling of specific activity in the exchangeable P pool by plants were conducted in a growth chamber. The ultimate aim is to develop this technique into a method that is applicable to field studies. Because of the many variables associated with field trials, direct application of the technique to field situations requires further investigations in future studies. However, the growth chamber technique can be adopted to study dissolution and retention of phosphate fertilisers applied to field soils. This involves collecting soil samples from field plots which have received phosphate fertilisers of differing solubility, and conducting the labelling experiments in the growth chamber. As the interest with PR-containing fertilisers lies in their long term effectiveness, the combined field-growth chamber trials may continue as long as necessary, e.g. for a number of years after fertiliser

application. The relationships between determined dissolution and retention parameters and plant responses may be established by correlating kinetic parameters with plant yield data from harvested field plots.

In the kinetic study described in the thesis, both SA_2 and SA_1 were extrapolated to calculate F_{in} and F_{out}. The forward extrapolation to the beginning of the next succeeding labelling experiment to derive SA_2 is not necessary, if the successive labelling experiments are arranged to overlap in time.

Both soils used in the kinetic study were P-deficient. However, the isotopic dilution technique may also be applied to high P-status soils. As the isotopic dilution technique operates on the basis of the ratio of the two isotopes, ^{32}P and ^{31}P, in the soil exchangeable P pool as sampled by plants, a clear plant response to fertiliser addition in dry matter production is not required. In fact, the technique is particularly suitable for soils with conditions favourable for rapid plant growth, where the changes of specific activity in the exchangeable P pool can be revealed in a short time by plant sampling. The technique may therefore be applicable to soil-plant systems operating at maintenance production levels.

References

Amer, F., Bouldin, D.R., Black, C.A. and Duke, F.R. 1955. Characterization of soil phosphorus by anion exchange resin adsorption and P^{32} equilibration. Plant and Soil 6: 391-408.

Anderson, G. 1960. Factors affecting the estimation of phosphate esters in soil. Journal of Science of Food and Agriculture 11: 497-503.

Anderson, G. 1967. Nucleic acids, derivatives and organic phosphates. In: Soil Biochemistry. A.D. McLaren and G.H. Peterson, Editors. Marcel Dekker, New York. 67-90.

Anderson, G. 1980. Assessing organic phosphorus in soils. In: The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath, Editors. ASA-CSSA-SSSA, Madison, Wisconsin, USA. 411-431.

Anderson, G., Williams, E.G. and Moir, J.O. 1974. A comparison of the sorption of inorganic orthophosphate and inositol hexaphosphate by six acid soils. Journal of Soil Science 25: 51-62.

Andrew, C.S. and Robins, M.F. 1969. The effect of P on the growth and chemical composition of some tropical legumes. II. N, Ca, Mg, K and Na contents. Australian Journal of Agricultural Research 20: 675-685.

Appelt, H., Coleman, N.T. and Pratt, P.F. 1975. Interactions between organic compounds, minerals and ions in volcanic-ash-derived soils: II. Effects of organic compounds on the adsorption of phosphate. Soil Science Society of America Proceedings 39: 628-630.

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.

Asea, P.E.A., Kucey, R.M.N. and Stewart, J.W.B. 1988. Inorganic phosphate solubilization by two *Penicillium* species in solution culture and soil. Soil Biology and Biochemistry 20: 459-464.

Avdeeva, T.A. and Andreeva, T.F. 1974. Effect of conditions of phosphorus nutrition on photosynthesis and activity of carboxylating enzymes in bean and corn plants. Soviet Plant Physiology 21: 753-757.

Bache, B.W. 1963. Aluminium and iron phosphate studies relating to soils. I. Solution and hydrolysis of variscite and strengite. Journal of Soil Science 14: 113-123.

Baligar, C.V. and Barber, S.A. 1979. Genotipic differences of corn for ion uptake. Agronomy Journal 71: 870-883.

Barber, S.A. 1958. Relation of fertilizer placement to nutrient uptake and crop yield. I. Interaction of row phosphorus and the soil level of phosphorus. Agronomy Journal 50: 535-539.

Barber, S.A. 1962. A diffusion and mass-flow concept of soil nutrient availability. Soil Science 93: 39-49.

Barber, S.A. 1980. Soil-plant interactions in the phosphorus nutrition of plants. In: The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath, Editors. ASA-CSSA-SSSA, Madison, Wisconsin, USA. 591-615.

Barber, S.A., Walker, J.M. and Vasey, E.H. 1963. Mechanisms for the movement of plant nutrients from the soil and fertilizer to the plant root. Journal of Agricultural and Food Chemistry 11: 204-207.

Barea, J.M. 1991. Vesicular-arbuscular mycorrhizae as modifiers of soil fertility. Advances in Soil Science 15: 1-40.

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

Barrow, N.J. 1979. Three effects of temperature on the reactions between inorganic phosphate and soil. Journal of Soil Science 30: 271-279.

Barrow, N.J. 1980. Evaluation and utilization of residual phosphorus in soils. In: The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath, Editors. ASA-CSSA-SSSA, Madison, Wisconsin, USA. 333-359.

Barrow, N.J. 1985. Reactions of anions and cations with variable-charge soils. Advances in Agronomy 38:183-230.

Barrow, N.J. and Shaw, T.C. 1975a. The slow reactions between soil and anions. 3. The effects of time and temperature on the decrease in isotopically exchangeable phosphate. Soil Science 119: 190-197.

Barrow, N.J. and Shaw, T.C. 1975b. The slow reactions between soil and anions. 5. Effects of period of prior contact on the desorption of phosphate from soils. Soil Science 119: 311-320.

Barrow, N.J. and Shaw, T.C. 1979. Effects of ionic strength and nature of the cation on desorption of phosphate from soil. Journal of Soil Science 30: 53-65.

Barrow, N.J., Bowden, J.W., Posner, A.M. and Quirk, J.P. 1980. Describing the effects of electrolyte on adsorption of phosphate by a variable charge surface. Australian Journal of Soil Research 18: 395-404.

Bekele, T., Cino, B.J., Ehlert, P.A.I., 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.

Berkheiser, V.E., Street, J.J., Rao, P.S.C. and Yuan, T.L. 1980. Partitioning of inorganic orthophosphate in soil-water systems. CRC Critical Reviews in Environmental Control 10: 179-224.

Bieleski, R.L. 1973. Phosphate pools, phosphate transport and phosphate availability. Annual Review of Plant Physiology 24: 225-252.

Bieleski, R.L. and Ferguson, I.B. 1983. Physiology and metabolism of phosphate and its compounds. In: Inorganic Plant Nutrition. A. Lauchli and R.L. Bieleski, Editors. Springer-Verlag, Berlin. 422-449.

Blair, G.J., Till, A.R. and Smith, R.C.G. 1976. The phosphorus cycle - what are the sensitive areas?. In: Prospects for Improving Efficiency of Phosphorus Utilization, Proceedings of a Symposium Held at the University of New England, Armidale, Australia. G.J. Blair, Editor. Reviews in Rural Science III: 9-19.

Blakemore, L.C., Searle, P.L. and Daly, B.K. 1987. Methods for Chemical Analysis of Soils. New Zealand Soil Bureau Scientific Report 80: 31-45.

Blal, B., Morel, C., Gianinazzi-Pearson, V., Fardeau, J.C. and Gianinazzi, S. 1990. Influence of vesicular-arbuscular mycorrhizae on phosphate fertilizer efficiency in two tropical acid soils planted with micropropagated oil palm (*Elaeis guineensis* jacq.). Biology and Fertility of Soils 9: 43-48.

Bloom, P.R. 1981. Phosphorus adsorption by an aluminium-peat complex. Soil Science Society of America Journal 45: 267-272.

Bolan, N.S. and Hedley, M.J. 1989. Dissolution of phosphate rocks in soils. 1. Evaluation of extraction methods for the measurement of phosphate rock dissolution. Fertilizer Research 19: 65-75.

Bolan, N.S. and Hedley, M.J. 1990. Dissolution of phosphate rocks 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., Hedley, M.J., Harrison, R. and Braithwaite, A.C. 1990b. Influence of manufacturing variables on characteristics and the agronomic value of partially acidulated phosphate fertilizers. Fertilizer Research 26:119-138.

Bolan, N.S., Hedley, M.J., Syers, J.K. and Tillman, R.W. 1987. Single superphosphate-reactive phosphate rock mixtures. 1. Factors affecting the chemical composition. Fertilizer Research 13: 223-239.

Bolan, N.S., White, R.E. and Hedley, M.J. 1990a. A review of the use of phosphate rocks as fertilizers for direct application in Australia and New Zealand. Australian Journal of Experimental Agriculture 30: 297-313.

Bolland, M.D.A. and Barrow, N.J. 1988. Effect of level of application on the relative effectiveness of rock phosphate. Fertilizer Research 15: 181-192.

Bolland, M.D.A. and Gilkes, R.J. 1990. Rock phosphates are not effective fertilizers in Western Australian soils: a review of one hundred years of research. Fertilizer Research 22: 79-95.

Bolland, M.D.A., Gilkes, R.J. and Allen, D.G. 1988a. The residual value of superphosphate and rock phosphates for lateritic soils and its evaluation using three soil phosphate tests. Fertilizer Research 15: 253-280.

Bolland, M.D.A., Gilkes, R.J. and D'Antuono, M.F. 1988b. The effectiveness of rock phosphate fertilizers in Australian agriculture: a review. Australian Journal of Experimental Agriculture 28: 655-668.

Bolland, M.D.A., Weatherley, A.J. and Gilkes, R.J. 1989. The long-term residual value of rock phosphate and superphosphate fertilizers for various plant species under field conditions. Fertilizer Research 20: 89-100.

Bowden, J.W., Posner, A.M. and Quirk, J.P. 1974. A model for ion adsorption on variable charge surfaces. In: 10th International Congress of Soil Science Transitions. 2: 29-36.

Bowden, J.W., Posner, A.M. and Quirk, J.P. 1977. Ionic adsorption on variable charge mineral surfaces. Theoretical charge development and titration curves. Australian Journal of Soil Research 15: 121-136.

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 estimators of available phosphorus in fertilizer products. Fertilizer Research 19: 175-181.

Bray, R.H. and Kurtz, L.T. 1945. Determination of total, organic and available forms of phosphorus in soils. Soil Science 59: 39-45.

Brown, W.E. and Lehr, J.R. 1959. Application of phase rule to the chemical behaviour of monocalcium phosphate monohydrate in soils. Soil Science Society of America Proceedings 23: 7-12.

Burns, R.G. 1978. Soil Enzymes. Academic Press, London.

Caradus, J.R. 1983. Genetic differences in phosphorus absorption among white clover populations. Plant and Soil 72: 379-383.

Caro, J.H. and Hill, W.L. 1956. Characteristics and fertilizer value of phosphate rock from different fields. Journal of Agricultural and Food Chemistry 4: 684-687.

Chang, S.C. and Jackson, M.L. 1957. Fractionation of soil phosphorus. Soil Science 84: 133-144.

Charleston, H.G., Condron, L.M. and Brown, I.W.M. 1989. The nature of the residual apatites remaining after partial acidulation of phosphate rocks with phosphoric and sulphuric acids. Fertilizer Research 18: 257-273.

Chen, R.Y.S., Butler, J.N. and Stumm, W. 1973. Kinetic study of phosphate reaction with aluminium oxide and kaolinite. Environmental Science and Technology 7: 327-332.

Chien, S.H. 1978. Interpretation of Bray I-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. and Hammond, L.L. 1988. Agronomic Evaluation of Partially Acidulated Phosphate Rocks in the Tropics, IFDC's Experience. International Fertilizer Development Center, Muscle Shoals, Alabama. Paper series, IFDC-P-7. 10 p.

Chien, S.H. and Hammond, L.L. 1989. Agronomic effectiveness of partially acidulated phosphate rock as influenced by soil phosphorus-fixing capacity. Plant and Soil 120: 159-164.

Chien, S.H., Adams, F., Khasawneh, F.E. and Henao, J. 1987. Effects of combinations of triple superphosphate and a reactive phosphate rock on yield and phosphorus uptake by corn. Soil Science Society of America Journal 51: 1656-1658.

Chien, S.H., Leon, L.A. and Tejeda, H.R. 1980. Dissolution of North Carolina phosphate rock in acid Colombian soils as related to soil properties. Soil Science Society of America Journal 44: 1267-1271.

Chu, C.R., Moschler, W.W. and Thomas, G.W. 1962. Rock phosphate transformations in acid soils. Soil Science Society of America Proceedings 26: 476-478.

Clark, C.J. and McBride, M.B. 1984. Cation and anion retention by natural and synthetic allophane and imogolite. Clays and Clay Minerals 32: 291-299.

Cole, C.V. and Jackson, M.L. 1950. Solubility equilibrium constant of dihydroxy aluminium dihydrogen phosphate relating to a mechanism of phosphate fixation in soil. Soil Science Society of America Proceedings 15: 84-89.

Cole, C.V., Olsen, S.R. and Scott, C.O. 1953. The nature of phosphate sorption by calcium carbonate. Soil Science Society of America Proceedings 17: 352-356.

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.

Condron, L.M. and Goh, K.M. 1989. Effects of long-term phosphatic fertilizer applications on amounts and forms of phosphorus in soils under irrigated pasture in New Zealand. Journal of Soil Science 40: 383-395.

Cooke, I.J. and Hislop, J. 1963. Use of anion-exchange resin for the assessment of available soil phosphate. Soil Science 96: 308-312.

Cope, J.T. and Evans, C.E. 1985. Soil testing. Advances in Soil Science I: 201-228.

Cosgrove, D.J. 1967. Metabolism of organic phosphates in soil. In: Soil Biochemistry. A.D. McLaren and G.H. Peterson, Editors. Marcel Dekker, New York. 216-228.

Cosgrove, D.J. 1970. Inositol phosphate phosphatases of microbiological origin. Inositol phosphate intermediates in the dephosphorylation of the hexaphosphates of myo-inositol, scyllo-inositol and D-chiro-inositol by a bacterial (*Pseudomonas* sp.) phytase. Australian Journal of Biological Sciences 23: 1207-1220.

Cosgrove, D.J. 1977. Microbial transformations in the phosphorus cycle. Advances in Microbial Ecology 1: 95-134.

Cox, J.E. 1978. Soils and Agriculture of Part Paparua County, Canterbury, New Zealand. Soil Bureau Bulletin 34: 128p.

Dalal, R.C. 1977. Soil organic phosphorus. Advances in Agronomy 29: 85-117.

Dalal, R.C. and Hallsworth, E.G. 1976. Evaluation of the parameters of soil phosphorus availability factors in predicting yield response and phosphorus uptake. Soil Science Society of America Journal 40: 541-546.

Dalal, R.C. and Hallsworth, E.G. 1977. Measurement of isotopic exchangeable soil phosphorus and interrelationship among parameters of quantity, intensity and capacity factors. Soil Science Society of America Journal 41: 81-86.

Davies, G.R. 1984. Comparison of water-insoluble phosphate fertilizers with superphosphate - a review. Journal of Science of Food and Agriculture 35: 265-271.

Di, H.J. and Kemp, R.A. 1989. Variation in soil physical properties between and within morphologically defined series taxonomic units. Australian Journal of Soil Research 27: 259-273.

Draper, N.R. and Smith, H. 1981. Applied Regression Analysis. Second Edition. John Wiley and Sons Inc., New York. 709 p.

Earl, K.D., Syers, J.K. and McLaughlin, J.R. 1979. Origin of the effects of citrate, tartrate, and acetate on phosphate sorption by soils and synthetic gels. Soil Science Society of America Journal 43: 674-678.

Eghball, B. and Sander, D.H. 1989. Distance and distribution effects of phosphorus fertilizer on corn. Soil Science Society of America Journal 53: 282-287.

Engelstad, O.P. and Terman, G.L. 1980. Agronomy effectiveness of phosphate fertilizers. In: The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath, Editors. ASA-CSSA-SSSA, Madison, Wisconsin, USA. 311-332.

Evans, T.D. and Syers, J.K. 1971. Application of autoradiography to study the fate of ^{33}P-labeled orthophosphate added to soil crumbs. Soil Science Society of America Proceedings 35: 906-909.

Fageria, N.K., Morais, O.P., Baligar, V.C. and Wright, R.J. 1988. Response of rice cultivars to phosphorus supply on an oxisol. Fertilizer Research 16: 195-206.

Fitter, A.H. and Sutton, C.D. 1975. The use of the Freundlich isotherm for soil phosphate sorption data. Journal of Soil Science 26: 241-246.

Fox, R.L. and Kamprath, E.J. 1970. Phosphate sorption isotherms for evaluating the phosphate requirements of soils. Soil Science Society of America Proceedings 34: 902-907.

Fox, R.L., Nishimoto, R.K., Thompson, J.R. and de la Pena, R.S. 1974. Comparative external phosphorus requirements of plants growing in tropical soils. In: 10th International Congress of Soil Science Transitions. IV: 232-239.

Fried, M. 1953. The feeding power of plants for phosphates. Soil Science Society of America Proceedings 17: 357-359.

Fried, M. 1954. Quantitative evaluation of processed and natural phosphates. Journal of Agricultural and Food Chemistry 2: 241-244.

Fried, M. 1964. 'E', 'L' and 'A' values. In: 8th International Congress of Soil Science Transitions. IV: 29-39.

Fried, M. and Dean, L.A. 1952. A concept concerning the measurement of available soil nutrients. Soil Science 73: 263-271.

Fried, M. and Shapiro, R.E. 1961. Soil plant relationships in ion uptake. Annual Review of Plant Physiology 12: 91-112.

Friesen, D.K. and Blair, G.J. 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.

Friesen, D.K., Sale, P.W.G. and Blair, G.J. 1987. Long-term greenhouse evaluation of partially acidulated phosphate rock fertilizers. I. Effect of acidulant and degree of acidulation on availability of P from two phosphate rocks. Fertilizer Research 13: 31-44.

Frossard, E., Stewart, J.W.B. and St. Arnaud, R.J. 1989. Distribution and mobility of phosphorus in grassland and forest soils of Saskatchewan. Canadian Journal of Soil Science 69: 401-416.

Fuller, W.H. and McGeorge, W.T. 1951. Phosphates in calcareous Arizona soils: II. Organic phosphorus content. Soil Science 71: 45-49.

Garbouchev, I.P. 1981. The manufacture and agronomic efficiency of a partially acidulated phosphate rock fertilizer. Soil Science Society of America Journal 45: 970-974.

Gillingham, A.G., Syers, J.K. and Gregg, P.E.H. 1980. Phosphorus uptake and return in grazed, steep hill pastures. II. Above-ground components of the phosphorus cycle. New Zealand Journal of Agricultural Research 23: 323-330.

Godwin, D.C. and Wilson, E.J. 1976. Prospects for selecting plants with increased P efficiency. In: Prospects for Improving Efficiency of Phosphorus Utilization, Proceedings of a Symposium Held at the University of New England, Armidale, Australia. G.J. Blair, Editor. Reviews in Rural Science III: 131-139.

Goh, K.M. and Williams, M.R. 1982. Distribution of carbon, nitrogen, phosphorus, sulphur, and acidity in two molecular weight fractions of organic matter in soil chronosequences. Journal of Soil Science 33: 73-87.

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: 219-234.

Gregg, P.E.H., Mackay, A.D., Tillman, R.W. and Currie, L.D. 1987. A summary of reactive phosphate rock research at Massey University. In: The Use of Reactive Phosphate Rocks and Their Derivatives as Fertilizers. Proceedings of the Workshop Organized by FLRC in co-operation with MAF. Massey University, Palmerston North. R.E. White and L.D. Currie, Editors. Occasional Report No. 1: 115-124.

Griffin, R.A. and Jurinak, J.J. 1967. The interaction of phosphate with calcite. Soil Science Society of America Proceedings 37: 847-850.

Griffin, R.A. and Jurinak, J.J. 1974. Kinetics of the phosphate interaction with calcite. Soil Science Society of America Proceedings 38: 75-79.

Grinsted, M.J., Hedley, M.J., White, R.E. and Nye, P.H. 1982. Plant-induced changes in the rhizosphere of rape (*Brassica napus* var. Emerald) seedlings. I. pH change and the increase in P concentration in the soil solution. New Phytologist 91: 19-29.

Gunary, D. and Sutton, C.D. 1967. Soil factors affecting plant uptake of phosphate. Journal of Soil Science 18: 167-173.

Hagin, J. 1985. Partially Acidulated Phosphate Rock, A Review. Israel Institute of Technology, Haifa, Israel. 64 p.

Hagin, J. and Katz, S. 1985. Effectiveness of partially acidulated phosphate rock as a source to plants in calcareous soils. Fertilizer Research 8: 117-127.

Halstead, R.L. and McKercher, R.B. 1975. Biochemistry and cycling of phosphorus. In: Soil Biochemistry, Volume 4. E.A. Paul and A.D. McLaren, Editors. Marcel Dekker, Inc., New York. 31-63.

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.

Hammond, L.L., Chien, S.H. and Polo, J.R. 1980. Phosphorus availability from partial acidulation of phosphate rocks. Fertilizer Research 1: 37-49.

Hammond, L.L., Chien, S.H., Roy, A.H. and Mokwunye, A.U. 1989. Solubility and agronomic effectiveness of partially acidulated phosphate rocks as influenced by their iron and aluminium oxide content. Fertilizer Research 19: 93-98.

Harrison, R. and Hedley, M.J. 1987. Phosphate rock dissolution during the manufacture and hydrolysis of partially acidulated phosphate rocks. In: The Use of Reactive Phosphate Rocks and Their Derivatives as Fertilizers. Proceedings of the Workshop Organised by FLRC in co-operation with MAF, Massey University, Palmerston North. R.E. White and L.D. Currie, Editors. 3-17.

Harrison, R. and Swift, R.S. 1985. The Properties and Fertility of High Country Yellow-Brown Earths Found Under Natural Vegetation. A Report to the Miss E.L. Hellaby Indigenous Grasslands Research Trust. Department of Soil Science, Lincoln College, Canterbury, New Zealand. 189 p.

Harter, R.D. and Baker, D.E. 1977. Application and misapplication of the Langmuir equation to soil adsorption phenomena. Soil Science Society of America Journal 41: 1077-1080.

Hayman, D.S. and Mosse, B. 1972. Plant growth responses to vesicular-arbuscular mycorrhiza. III. Increased uptake of labile P from soil. New Phytologist 71: 41-47.

Haynes, R.J. 1982. Effects of liming on phosphate availability in acid soils. A critical review. Plant and Soil 68: 289-308.

Haynes, R.J. 1984. Lime and phosphate in the soil-plant system. Advances in Agronomy 37: 249-315.

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

Haynes, R.J. and Swift, R.S. 1988. Effects of lime and phosphate additions on changes in enzyme activities, microbial biomass and levels of extractable nitrogen, sulphur and phosphorus in an acid soil. Biology and Fertility of Soils 6: 153-158.

Hedley, M.J. 1988. Personal communication.

Hedley, M.J., Bolan, N.S. and Braithwaite, A.C. 1988. Single superphosphate-reactive phosphate rock mixtures. 2. The effect of phosphate rock type and denning time on the amounts of acidulated and extractable phosphate. Fertilizer Research 16: 179-194.

Hedley, M.J., Nye, P.H. and White, R.E. 1982a. Plant-induced changes in the rhizosphere of rape (*Brassica napus* var. Emerald) seedlings. II. Origin of the pH change. New Phytologist 91: 31-44.

Hedley, M.J., Stewart, J.W.B. and Chauhan, B.S. 1982c. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and laboratory incubations. Soil Science Society of America Journal 46: 970-976.

Hedley, M.J., White, R.E. and Nye, P.H. 1982b. Plant-induced changes in the rhizosphere of rape (*Brassica napus* var. Emerald) seedlings. III. Changes in L value, soil phosphate fractions and phosphatase activity. New Phytologist 91: 45-56.

Hingston, F.J, Atkinson, R.J., Posner, A.M. and Quirk, J.P. 1967. Specific adsorption of anions. Nature 215: 1459-1461.

Hingston, F.J., Atkinson, R.J., Posner, A.M. and Quirk, J.P. 1968. Specific adsorption of anions on goethite. In: 9th International Congress of Soil Science Transitions. 1: 669-678.

Hingston, F.J., Posner, A.M. and Quirk, J.P. 1972. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. Journal of Soil Science 23: 177-192.

Hingston, F.J., Posner, A.M. and Quirk, J.P. 1974. Anion adsorption by goethite and gibbsite. II. Desorption of anions from hydrous oxide surfaces. Journal of Soil Science 25: 16-26.

Holford, I.C.R. 1980. Effects of phosphate buffer capacity on critical levels and relations between soil tests and labile phosphate in wheat-growing soils. Australian Journal of Soil Research 18: 405-414.

Holford, I.C.R. 1991. Comments on intensity-quantity aspects of soil phosphorus. Australian Journal of Soil Research 29: 11-14.

Holford, I.C.R. and Crocker, G.J 1988. Efficacy of various soil phosphate tests for predicting phosphate responsiveness and requirements of clover pastures on acidic tableland soils. Soil Fertility and Plant Nutrition 26: 479-488.

Holford, I.C.R. and Cullis, B.R. 1985. Effects of phosphate buffer capacity on yield response curvature and fertilizer requirements of wheat in relation to soil phosphate tests. Australian Journal of Soil Research 23: 417-427.

Holford, I.C.R. and Mattingly, G.E.G. 1975a. The high- and low- energy phosphate absorbing surfaces in calcareous soils. Journal of Soil Science 26: 407-417.

Holford, I.C.R. and Mattingly, G.E.G. 1975b. Phosphate sorption by Jurassic oolitic limestones. Geoderma 13: 257-264.

Holford, I.C.R. and Mattingly, G.E.G. 1976a. A model for the behaviour of labile phosphate in soil. Plant and Soil 44: 219-229.

Holford, I.C.R. and Mattingly, G.E.G. 1976b. Phosphate adsorption and plant availability of phosphate. Plant and Soil 44: 377-389.

Holford, I.C.R. and Mattingly, G.E.G. 1979. Effects of phosphate buffering on the extraction of labile phosphate by plants and by soil tests. Australian Journal of Soil Research 17: 511-514.

Holford, I.C.R., Morgan, J.M., Bradley, J. and Cullis, B.R. 1985. Yield responsiveness and response curvature as essential criteria for the evaluation and calibration of soil phosphate tests for wheat. Australian Journal of Soil Research 23: 167-180.

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

Huffman, E.O. 1962. Reactions of phosphate in soils: Recent research by TVA. Proceedings of the Fertilizer Society 71: 5-35.

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 fertilizer dissolution in soils. 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 the dissolution of Sechura rock phosphate in some soils from Brazil, Colombia, Australia and Nigeria. Australian Journal of Soil Research 24: 219-227.

Jackman, R.H. 1955. Organic phosphorus in New Zealand soils under pasture. I. Conversion of applied phosphorus to organic forms. Soil Science 79: 207-213.

Johnston, W.B. and Olsen, R.A. 1972. Dissolution of fluorapatite by plant roots. Soil Science 114: 29-36.

Jose, A.I. and Krishnamoorthy, K.K. 1972. Isotopic exchange of phosphates in soil: 'E' value. Soil and Fertilizers 35: 620-627.

Junge, A. and Werner, W. 1989. Investigation on interactions of phosphorus compounds in partially acidulated phosphate rock and fertilizer effectiveness. Fertilizer Research 20: 129-134.

Kafkafi, U., Posner, A.M. and Quirk, J.P. 1967. Desorption of phosphate from kaolinite. Soil Science Society of America Proceedings 31: 348-353.

Kamprath, E.J. and Watson, M.E. 1980. Conventional soil and tissue tests for assessing the phosphorus status of soils. In: The Role of Phosphorus in

Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath, Editors. ASA-CSSA-SSSA, Madison, Wisconsin, USA. 433-469.

Kanabo, I.A.K. and Gilkes, R.J. 1987a. The role of soil pH in the dissolution of phosphate rock fertilizers. Fertilizer Research 12: 165-173.

Kanabo, I.A.K. and Gilkes, R.J. 1987b. A comparison between plant response and chemical measurements of the dissolution of reactive phosphate rock in soils of different pH and phosphorus retention. Australian Journal of Soil Research 25: 451-460.

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-soluble phosphorus. Fertilizer Research 15: 137-145.

Kanabo, I.A.K. and Gilkes, R.J. 1988b. The effect of soil texture on the dissolution of North Carolina phosphate rock. Journal of Soil Science 39: 191-198.

Kanabo, I.A.K. and Gilkes, R.J. 1988c. The effects of moisture regime and incubation period on the dissolution of North Carolina phosphate rock in soil. Australian Journal of Soil Research 26: 153-163.

Katznelson, H. and Bose, B. 1959. Metabolic activity and phosphate-dissolving capability of bacterial isolates from wheat roots, rhizosphere, and non-rhizosphere soil. Canadian Journal of Microbiology 5: 79-85.

Khasawneh, F.E. and Doll, E.C. 1978. The use of phosphate rock for direct application to soils. Advances in Agronomy 30: 159-206.

Kinjo, T. and Pratt, P.F. 1971. Nitrate adsorption: II. In competition with chloride, sulphate and phosphate. Soil Science Society of America Proceedings 35: 725-728.

Kirk, G.J.D. and Nye, P.H. 1986. The dissolution and dispersion of dicalcium phosphate dihydrate in soils. IV. Experimental evaluation of the model for particles. Journal of Soil Science 37: 525-528.

Kittrick, J.A. and Jackson, M.L. 1955. The common ion effect on phosphate solubility. Soil Science 79: 415-421.

Kucey, R.M.N. 1988. Effect of *Penicillium bilaji* on the solubility and uptake of P and micronutrients from soil by wheat. Canadian Journal of Soil Science 68: 261-270.

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 value and total P uptake methods. Soil Science 138: 180-188.

Kucey, R.M.N. and Leggett, M.E. 1989. Increased yields and phosphorus uptake by Westar Canola (*Brassica napus* L.) inoculated with a phosphate-solubilizing isolate of *Penicillium bilaji*. Canadian Journal of Soil Science 69: 425-432.

Kucey, R.M.N., Janzen, H.H. and Leggett, M.E. 1989. Microbially mediated increases in plant-available phosphorus. Advances in Agronomy 42: 199-228.

Kuo, S. and Lotse, E.G. 1972. Kinetics of phosphate adsorption by calcium carbonate and Ca-kaolinite. Soil Science Society of America Proceedings 36: 725-729.

Kuo, S. and Lotse, E.G. 1974. Kinetics of phosphate adsorption and desorption by hematite and gibbsite. Soil Science 116: 400-406.

Kurtz, T., de Turk, E.E. and Bray, R.H. 1946. Phosphate adsorption by Illinois soils. Soil Science 61: 111-124.

Kyle, J.H., Posner, A.M. and Quirk, J.P. 1975. Kinetics of isotope exchange of phosphate adsorbed on gibbsite. Journal of Soil Science 26: 32-43.

L'Annunziata, M.F. 1984. The detection and measurement of radionuclides. In: Isotopes and Radiation in Agricultural Sciences, Volume 1: Soil - Plant - Water Relations. M.F. L'Annunziata and J.O. Legg, Editors. Academic Press, London. 141-231.

Larsen, S. 1952. The use of P^{32} in studies on the uptake of phosphorus by plants. Plant and Soil 4: 1-10.

Larsen, S. 1967. Soil phosphorus. Advances in Agronomy 19: 151-210.

Legg, J.O. and Black, C.A. 1955. Determination of organic phosphorus in soils: II. Soil Science Society of America Proceedings 19: 139-143.

Lehr, J.R. and Brown, W.E. 1958. Calcium phosphate fertilizers. II. A petrographic study of their alteration in soils. Soil Science Society of America Proceedings 22: 29-32.

Lehr, J.R. and McClellan, G.H. 1972. A Revised Laboratory Reactivity Scale for Evaluating Phosphate Rocks for Direct Application. Tennessee Valley Authority, Muscle Shoals, Alabama, USA. Bulletin Y-43. 36 p.

Lehr, J.R., Brown, W.E. and Brown, E.H. 1959. Chemical behaviour of monocalcium phosphate monohydrate in soils. Soil Science Society of America Proceedings 23: 3-7.

Lindsay, W.L. and Taylor, A.W. 1960. Phosphate reaction products in soil and their availability to plants. In: 7th International Congress of Soil Science Transitions. III: 580-589.

Lindsay, W.L., Frazier, A.W. and Stephenson, H.F. 1962. Identification of reaction products from phosphate fertilizers in soils. Soil Science Society of America Proceedings 26: 446-452.

Logan, T.J. and McLean, E.O. 1977. Diffusion of ^{32}P from partially acidulated rock phosphate. Soil Science 123: 203-206.

Loneragan, J.F. and Asher, C.J. 1967. Response of plants to phosphate concentration in solution culture: II. Rate of phosphate absorption and its relation to growth. Soil Science 103: 311-318.

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. 1984. Ability of chemical extraction procedures to predict the agronomic effectiveness of phosphate rock materials. New Zealand Journal of Agricultural Research 27: 219-230.

Mackay, A.D., Syers, J.K. and Gregg, P.E.H. 1987. Potential losses of fertilizer phosphorus by animal transfer. Fertilizer Research 14: 125-134.

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.

Martin, J.K. 1973. The influence of rhizosphere microflora on the availability of ^{32}P myo-inositol hexaphosphate phosphorus to wheat. Soil Biology and Biochemistry 5: 473-483.

Martin, J.K. and Cartwright, B. 1971. The comparative plant availability of ^{32}P myo-inositol hexaphosphate and $KH_2{}^{32}PO_4$ added to soils. Communications in Soil Science and Plant Analysis 2: 375-381.

Mattingly, G.E.G. 1975. Labile phosphate in soils. Soil Science 119: 369-375.

McAuliffe, C.D., Hall, N.S., Dean. L.A. and Hendricks, S.B. 1948. Exchange reactions between phosphates and soil: Hydroxylic surfaces of soil minerals. Soil Science Society of America Proceedings 12: 119-123.

McClellan, G.H. and Gremillion, L.R. 1980. Evaluation of phosphatic raw materials. In: The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath, Editors. ASA-CSSA-SSSA, Madison, Wisconsin, USA. 43-80.

McGill, W.B., and Cole, C.V. 1981. Comparative aspects of cycling of organic C, N, S and P through soil organic matter. Geoderma 26: 267-286.

McKercher, R.B. 1968. Studies on soil organic phosphorus. In: 9th International Congress of Soil Science Transitions. III: 547-553.

McLaughlin, J.R., Ryden, J.C. and Syers, J.K. 1977. Development and evaluation of a kinetic model to describe phosphate sorption by hydrous ferric oxide gel. Geoderma 18: 195-207.

McLaughlin, M.J., Alston, A.M. and Martin, J.K. 1988. Phosphorus cycling in wheat-pasture rotations. III. Organic phosphorus turnover and phosphorus cycling. Australian Journal of Soil Research 26: 343-353.

McLean, E.O. and Balam, B.S. 1967. Partially acidulated rock phosphate as a source of phosphorus to plants. III. Uptake by corn from soils of different calcium status. Soil Science Society of America Proceedings 31: 811-814.

McLean, E.O. and Logan, T.J. 1970. Sources of phosphorus for plants grown in soils of differing phosphorus fixation tendencies. Soil Science Society of America Proceedings 34: 907-911.

McLean, E.O. and Wheeler, R.W. 1964. Partially acidulated rock phosphate as a source of phosphorus to plants: I. Growth chamber studies. Soil Science Society of America Proceedings 28: 545-550.

McLean, E.O., Wheeler, R.W. and Watson, J.D. 1965. Partially acidulated rock phosphate as a source of phosphorus to plants. II. Growth chamber and field corn studies. Soil Science Society of America Proceedings 29: 625-628.

McSweeney, G. and Charleston, A.G. 1985. Partially acidulated phosphate rocks - reactions with water. Fertilizer Research 8: 75-83.

Mehta, N.C., Legg, J.O., Goring, C.A.I. and Black, C.A. 1954. Determination of organic phosphorus in soils: I. Extraction method. Soil Science Society of America Proceedings 18: 443-449.

Mengel, K. 1985. Dynamics and availability of major nutrients in soils. Advances in Soil Science 2: 65-131.

Menon, R.G., Chien, S.H. and Hammond, L.L. 1989. Comparison of Bray I and P_i tests for evaluating plant-available phosphorus from soils treated with different partially acidulated phosphate rocks. Plant and Soil 114: 211-216.

Menzel, R.G. and Smith, S.J. 1984. Soil fertility and plant nutrition. In: Isotopes and Radiation in Agricultural Sciences, Volume 1. Soil-Plant-Water relationships. M.F. L'Annunziata and J.O. Legg, Editors. Academic Press, London. 1-34.

Middleton, K.R. and Toxopeus, M.R.J. 1973. Diagnosis and measurement of multiple soil deficiencies by a subtractive technique. Plant and Soil 38: 219-226.

Mokwunye, A.U. and Chien, S.H. 1980. Reaction of partially acidulated phosphate rock with soils from the tropics. Soil Science Society of America Journal 44: 477-482.

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

Muljadi, D., Posner, A.M. and Quirk, J.P. 1966b. The mechanism of phosphate adsorption by kaolinite, gibbsite, and pseudoboehmite. Part II. The location of the adsorption sites. Journal of Soil Science 17: 230-237.

Muljadi, D., Posner, A.M. and Quirk, J.P. 1966c. The mechanism of phosphate adsorption by kaolinite, gibbsite, and pseudoboehmite. Part III. The effect of temperature on the adsorption. Journal of Soil Science 17: 238-247.

Munns, D.N. and Fox, R.L. 1976. The slow reaction which continues after phosphate adsorption: kinetics and equilibrium in some tropical soils. Soil Science Society of America Journal 40: 46-51.

Murphy, J. and Riley, J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta 27: 31-36.

Murrmann, R.P. and Peech, M. 1969. Relative significance of labile and crystalline phosphates in soil. Soil Science 107: 249-255.

Nagarajah, S., Posner, A.M. and Quirk, J.P. 1970. Competitive adsorption of phosphate with polygalacturonate and other organic anions on kaolinite and oxide surfaces. Nature 228: 83-84.

Nelson, L.A., Voss, R.D. and Pesek, J. 1985. Agrononic and statistical evaluation of fertilizer response. In: Fertilizer Technology and Use. Third Edition. D.P. Engelstad, Editor. Soil Science Society of America Inc., Madison, Wisconsin, U.S.A. 53-90.

Nielson, N.E. and Barber, S.A. 1978. Differences among genotypes of corn in the kinetics of P uptake. Agronomy Journal 70: 695-698.

NZ Soil Bureau, 1968. Soils of New Zealand, Part 2. NZ Soil Bureau Bulletin 26 (2).

Olsen, S.R. and Sommers, L.E. 1982. Phosphorus. In: Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. Second Edition. A.L. Page, Editor. ASA-SSSA, Madison, Wisconsin, USA. 403-430.

Olsen, S.R. and Watanabe, F.S. 1957. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir equation. Soil Science Society of America Proceedings 21: 144-149.

Olsen, S.R., Cole, C.V., Watanabe, F.S. and Dean, L. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circular 939.

Ozanne, P.G. 1980. Phosphate nutrition of plants - a general treatise. In: The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath, Editors. ASA-CSSA-SSSA, Madison, Wisconsin, USA. 559-589.

Parfitt, R.L. 1978. Anion adsorption by soils and soil materials. Advances in Agronomy 30: 1-50.

Parfitt, R.L. 1989. Phosphate reactions with natural allophane, ferrihydrite and goethite. Journal of Soil Science 40: 359-369.

Parfitt, R.L. 1990. Allophane in New Zealand - a review. Australian Journal of Soil Research 28: 343-360.

Parfitt, R.L. and Hemni, T. 1980. Structure of some allophanes from New Zealand. Clays and Clay Minerals 28: 285-294.

Pathiratna, L.S.S., De, U.P., Waidyanatha, S. and Peries, O.S. 1989. The effect of apatite and elemental sulphur mixtures on growth and P content of *Centrocema pubescens*. Fertilizer Research 21: 37-43.

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: 566-570.

Pierre, W.H. and Parker, F.W. 1927. Soil phosphorus studies. 2. The concentration of organic and inorganic phosphorus in the soil solution and soil extracts and the availability of the organic phosphorus to plants. Soil Science 24: 119-128.

Rajan, S.S.S. 1975. Adsorption of divalent phosphate on hydrous aluminium oxide. Nature 253: 434-436.

Rajan, S.S.S. 1976. Phosphate reactions with soil constituents and prospects for manipulation. In: Prospects for Improving Efficiency of Phosphorus Utilization, Proceedings of a Symposium Held at the University of New England, Armidale, Australia. G.J. Blair, Editor. Reviews in Rural Science III: 35-39.

Rajan, S.S.S. 1982. Availability to plants of phosphate from "biosupers" 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. 1985. Partial acidulation of an 'unground' phosphate rock: I. Preparation and characteristics. Fertilizer Research 8: 147-155.

Rajan, S.S.S. 1986. Partial acidulation of an 'unground' phosphate rock: II. Plant availability of phosphate. Fertilizer Research 8: 219-229.

Rajan, S.S.S. 1987. Partially acidulated phosphate rock as fertilizer and dissolution in soil of the residual rock phosphate. New Zealand Journal of Experimental Agriculture 15: 177-184.

Rajan, S.S.S. and Edge, E.A. 1980. Dissolution of granulated low grade phosphate rock, phosphate rock/sulphur (Biosuper), and superphosphate in soil. New Zealand Journal of Agricultural Research 23: 451-456.

Rajan, S.S.S. and Quin, B.F.C. 1985. Partially phosphoric-acidulated phosphate rocks as fertilizers for pastures. In: Proceedings of the Twentieth Technical Conference, Volume 2. New Zealand Fertilizer Manufacturers' Research Association. 411-424.

Rajan, S.S.S., Gillingham, A.G., O'Connor, M.B., Percival, N.A. and Gray, M.G. 1987. Ground phosphate rock as fertilizers for pastures. In: The Use of Reactive Phosphate Rocks and Their Derivatives as Fertilizers. Proceedings of the Workshop Organised by FLRC in co-operation with MAF, Massey University, Palmerston North, New Zealand. R.E. White and L.D. Currie, Editors. Occasional Report No. 1. 78-83.

Rajan, S.S.S., Perrott, K.W. and Saunders, W.M.H. 1974. Identification of phosphate-reactive sites of hydrous alumina from proton consumption during phosphate adsorption at constant pH values. Journal of Soil Science 25: 438-447.

Raju, A.S. 1988. Influence of some factors on measurement of "A" value for available soil phosphorus. Journal of Nuclear Agriculture and Biology 17: 195-201.

Resseler, H. and Werner, W. 1989. Properties of unreacted rock residues in partially acidulated phosphate rocks affecting their reactivity. Fertilizer Research 20: 135-142.

Riley, D. and Barber, S.A. 1969. Bicarbonate accumulation and pH changes at the soybean [*Glycine max* (L.) Merr.] root-soil interface. Soil Science Society of America Proceedings 33: 905-908.

Riley, D. and Barber, S.A. 1971. Effect of ammonium and nitrate fertilization on phosphorus uptake as related to root-induced pH changes at the root-soil interface. Soil Science Society of America Proceedings 35: 301-306.

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.

Rogers, H.T., Pearson, R.W. and Pierre, W.H. 1940. Absorption of organic phosphorus by corn and tomato plants and the mineralizing action of exo-enzyme systems of growing roots. Soil Science Society of America Proceedings 5: 285-291.

Rowarth, J.S., Gillingham, A.G., Tillman, R.W. and Syers, J.K. 1985. Release of phosphorus from sheep faeces on grazed, hill country pastures. New Zealand Journal of Agricultural Research 28: 497-504.

Russell, E.W. 1973. Soil Conditions and Plant Growth. 10th Edition. Longmans, Green, New York. 263 p.

Russell, R.S., Rickson, J.B. and Adams, S.N. 1954. Isotope equalibria between phosphates in soil and their significance in the assessment of fertility by tracer methods. Journal of Soil Science 5: 85-105.

Russell, S.S., Russell, E.W. and Marais, P.G. 1957. Factors affecting the ability of plants to absorb phosphate from soils. I. The relationship between labile phosphate and absorption. Journal of Soil Science 8: 248-267.

Ryan, A.P. 1987. The climate and weather of Canterbury. New Zealand Meteorological Service 115(17).

Ryden, J.C. and Pratt, P.F. 1980. Phosphate removal from waste water applied to land. Hilgardia 48: 1-36.

Ryden, J.C. and Syers, J.K. 1975. Rationalization of ionic strength and cation effects on phosphate sorption by soils. Journal of Soil Science 26: 395-406.

Ryden, J.C. and Syers, J.K. 1977. Desorption and isotope exchange relationships of phosphate sorbed by soils and hydrous oxide gel. Journal of Soil Science 28: 596-609.

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

Ryden, J.C., McLaughlin, J.R. and Syers, J.K. 1977c. Time-dependent sorption of phosphate by soils and hydrous ferric oxides. Journal of Soil Science 28: 585-595.

Ryden, J.C., Syers, J.K. and Harris, R.F. 1973. Phosphorus in runoff and streams. Advances in Agronomy 25: 1-45.

Ryden, J.C., Syers, J.K. and McLaughlin, J.R. 1977a. Effects of ionic strength on chemisorption and potential-determining sorption of phosphate by soils. Journal of Soil Science 28: 62-71.

Sadler, J.M. and Stewart, J.W.B. 1975. Changes with time in form and availability of residual fertilizer phosphorus in a catenary sequence of Chernozemic soils. Canadian Journal of Soil Science 55: 149-159.

Saggar, S., Hedley, M.J. and White, R.E. 1990. A simplified resin membrane technique for extracting phosphorus from soils. Fertilizer Research 24: 173-180.

Salih, H.M., Yahya, A.I., Abdul-Rahem, H.M. and Munam, B.H. 1989. Availability of phosphorus in a calcareous soil treated with rock phosphate or superphosphate as affected by phosphate-dissolving fungi. Plant and Soil 120: 181-185.

Sample, E.C., Soper, R.J. and Racz, G.J. 1980. Reactions of phosphate fertilisers in soils. In: The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath, Editors. ASA-CSSA-SSSA, Madison, Wisconsin, USA. 263-310.

Sanchez, P.A. and Uehara, G. 1980. Management considerations for acid soils with high phosphorus fixation capacity. In: The Role of Phosphorus in Agriculture. F.E.Khasawneh, E.C. Sample and E.J. Kamprath, Editors. ASA-CSSA-SSSA, Madison, Wisconsin, USA. 471-514.

Sanders, F.E. and Tinker, P.B. 1971. Mechanism of absorption of phosphate from soil by *Endogone* mycorrhizas. Nature 233: 278-279.

Saunders, W.M. and Williams, E.G. 1955. Observations on determination of total organic phosphorus in soils. Journal of Soil Science 6: 254-267.

Shipley, R.A. and Clark, R.E. 1972. Tracer Methods for *in vivo* Kinetics, Theory and Applications. Academic Press, New York. 239 p.

Sibbesen, E. 1977. A simple ion exchange resin procedure for extracting plant available elements from soil. Plant and Soil 46: 665-669.

Sibbesen, E. 1983. Phosphate soil tests and their suitability to assess the phosphate status of soil. Journal of Science of Food and Agriculture 34: 1368-1374.

Sleight, D.M., Sander, D.H. and Peterson, G.A. 1984. Effect of fertilizer placement on the availability of phosphorus. Soil Science Society of America Journal 48: 336-340.

Smeck, N.E. 1985. Phosphorus dynamics in soils and landscapes. Geoderma 36: 185-199.

Smyth, T.J. and Sanchez, P.A. 1982. Phosphate rock dissolution and availability 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 Cornforth, 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 Research 15: 225-236.

Sperber, J.I. 1958. The incidence of apatite-solubilizing organisms in the rhizosphere and soil. Australian Journal of Agricultural Research 9: 778-781.

Stanford, G. and Dement, J.D. 1957. A method for measuring short-term nutrient absorption by plants: I. Phosphorus. Soil Science Society of America Proceedings 21: 612-617.

Stephen, R.C. 1985. The agronomic value of products resulting from the partial acidulation of North Carolina phosphate rock with phosphoric acid. Fertilizer Research 8: 67-73.

Stephen, R.C. and Condron, L.M. 1986. An assessment of the agronomic efficiency of partially acidulated phosphate rock fertilizers. Fertilizer Research 10: 269-282.

Stevenson, F.J. 1986. Cycles of Soil: Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients. John Wiley and Sons, New York. 231-284.

Stewart, J.W.B., Hedley, M.J. and Chauhan, B.S. 1980. The immobilization, mineralization and redistribution of phosphorus in soils. In: Proceedings of the Western Canada Phosphate Symposium. J.T. Harapiak, Editor. Alberta Soil Science Society, Edmonton, Alberta. 276-306.

Swaby, R.J. 1975. Biosuper - biological superphosphate. In: Sulphur in Australian Agriculture. K.D. McLachland, Editor. Sydney University Press, Sydney. 213-220.

Swift, R.S. and Posner, A.M. 1972. Nitrogen, phosphorus and sulphur contents of humic acids fractionated with respect to molecular weight. Journal of Soil Science 23: 50-57.

Syers, J.K. and Gregg, P.E.H. 1981. Proceedings of the Technical Workshop on Potential of Phosphate Rock as a Direct Application Fertilizer in New Zealand. Massey University, Palmerston North. Occasional Report No. 3. 168 p.

Syers, J.K. and Iskandar, I.K. 1981. Soil-phosphorus chemistry. In: Modeling Wastewater Renovation. I.K. Iskandar, Editor. John Wiley and Sons, New York. 571-599.

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. and Walker, T.W. 1969. Phosphorus transformations in a chronosequence of soils developed on wind-blown sand in New Zealand. II. Inorganic phosphorus. Journal of Soil Science 20: 318-324.

Syers, J.K., Browman, M.G., Smillie, G.W. and Corey, R.B. 1973. Phosphate sorption by soils evaluated by the Langmuir adsorption equation. Soil Science Society of America Proceedings 37: 358-363.

Syers, J.K., Murdoch, J.T. and Williams, J.D.H. 1970. Adsorption and desorption of phosphate by soils. Communications in Soil Science and Plant Analysis 1: 57-62.

Syers, J.K., Smillie, 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.

Szember, A. 1960. Influence on plant growth of the breakdown of organic phosphorus compounds by micro-organisms. Plant and Soil 13: 147-158.

Taylor, R.W. and Ellis, B.G. 1978. A mechanism of phosphate adsorption on soil and anion exchange resin surfaces. Soil Science Society of America Journal 42: 432-436.

Terman, G.L. and Allen, S.E. 1967. Response of corn to phosphorus in underacidulated phosphate rock and rock-superphosphate fertilizers. Journal of Agricultural and Food Chemistry 15: 354-358.

Terman, G.L., Moreno, E.C. and Osborn, G. 1964. Acidulation of phosphate rock in soil. Soil Science Society of America Proceedings 28: 104-107.

Thomas, G.W. and Peaslee, D.E. 1973. Testing soils for phosphorus. In: Soil Testing and Plant Analysis. Revised Edition. L.M. Walsh and J.D. Beaton, Editors. SSSA, Madison, Wisconsin, USA. 115-132.

Tinker, P.B. 1980. Role of rhzosphere microorganisms in phosphorus uptake by plants. In: The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C.

Sample and E.J. Kamprath, Editors. ASA-CSSA-SSSA, Madison, Wisconsin, USA. 617-654.

Tisdale, S.L., Nelson, W.L. and Beaton, J.D. 1985. Soil Fertility and Fertilizers. Fourth Edition. Macmillan Publishing Company, New York. 754 p.

Tonkin, P.J. 1990. Personal communication.

Truog, E. 1930. Determination of the readily available phosphorus of soils. Journal of the American Society of Agronomy 22: 874-882.

Van Der Paauw, F. 1971. An effective water extraction method for the determination of plant-available soil phosphorus. Plant and Soil 34: 467-481.

Van Diest, A. 1968. Biological immobilization of fertilizer phosphorus. II. Evaluation of factors involved in phosphorus transformation. Plant and Soil 29: 248-256.

Van Ray, B. and Van Diest, A. 1979. Utilization of phosphate from different sources by six plant species. Plant and Soil 51: 577-589.

Van Riemsdijk, W.H., Westrate, F.A. and Beek, K.J. 1977. Phosphates in soils treated with sewage water: III. Kinetic studies on the reaction of phosphate with aluminium compounds. Journal of Environmental Quality 6: 26-29.

Van Riemsdijk, W.H., Westrate, F.A. and Bolt, G.H. 1975. Evidence for a new aluminium phosphate phase from reaction rate of phosphate with aluminium hydroxide. Nature 257: 473-474.

Veith, J.A. and Sposito, G. 1977. On the use of the Langmuir equation in the interpretation of adsorption phenomena. Soil Science Society of America Journal 41: 697-702.

Vose, P.B. 1980. Introduction to Nuclear Techniques in Agronomy and Plant Biology. Pergamon Press, Oxford. 391 p.

Walker, T.W. 1965. The significance of phosphorus in pedogenesis. In: Experimental Pedology. S.G. Hallsworth and D.V. Crawford, Editors. Butterworths, London. 295-315.

Walker, T.W. and Adams, A.F.R. 1958. Studies on soil organic matter. 1. Influence of phosphorus content of parent materials on accumulation of carbon, nitrogen, sulfur and organic phosphorus in grassland soils. Soil Science 85: 307-318.

Walker, T.W. and Adams, A.F.R. 1959. Studies on soil organic matter. 2. Influence of increased leaching at various stages of weathering on levels of carbon, nitrogen, sulfur and organic and total phosphorus. Soil Science 87: 1-10.

Walker, T.W. and Syers, J.K. 1976. The fate of phosphorus during pedogenesis. Geoderma 15: 1-19.

Walker, T.W., Thapa, B.K. and Adams, A.F.R. 1959. Studies on soil organic matter. 3. Accumulation of carbon, nitrogen, sulfur, organic and total P in improved grassland soils. Soil Science 87: 135-140.

White, R.E. 1980. Retention and release of phosphate by soil and soil constituents. In: Soils and Agriculture. P.B. Tinker, Editor. Blackwell Scientific Publications, London. 71-114.

White, R.E. and Taylor, A.W. 1977. Reactions of soluble phosphate with acid soils: the interpretation of adsorption-desorption isotherms. Journal of Soil Science 28: 314-328.

White, R.E. and Thomas, G.W. 1981. Hydrolysis of aluminium on weakly acidic organic exchangers: implications for phosphate adsorption. Fertilizer Research 2: 159-167.

Wiklander, L. 1950. Kinetics of phosphate exchange in soils. Annals of the Royal Agricultural College of Sweden 17: 407-424.

Wild, A. 1950. The retention of phosphate by soil. A review. Journal of Soil Science 1: 221-238.

Wild, A. 1954. The concentration of phosphate in the soil solution. In: 5th International Congress of Soil Science Transitions. 2: 500-504.

Wild, A. and Oke, O.L. 1966. Organic phosphate compounds in calcium chloride extracts of soils: Identification and availability to plants. Journal of Soil Science 17: 356-371.

Williams, C.H. and Steinbergs, A. 1958. Sulphur and phosphorus in some eastern Australian soils. Australian Journal of Agricultural Research 9: 483-491.

Williams, J.D.H. and Walker, T.W. 1969. Fraction of phosphate in a maturity sequence of New Zealand basaltic soil profiles: 2. Soil Science 107: 213-219.

Williams, J.D.H., Syers, J.K. and Walker, T.W. 1967. Fraction of soil inorganic phosphate by a modification of Chang and Jackson's procedure. Soil Science Society of America Proceedings 31: 736-739.

Appendix

Semilog linear functions of specific activity against time fitted to estimate the readily exchangeable P pools for the calculation of F_{in} and F_{out} in Chapter 5.

Treatment	Experiment	Semilog linear functions	R^2
Tekapo soil:			
75 μg P(MCP) g^{-1}1 soil	A	lnSA = 1.67 - 0.00243t	0.90
	B	lnSA = 2.75 - 0.00544t	1.00
	C	lnSA = 3.20 - 0.01010t	0.99
150 μg P(MCP) g^{-1} soil	A	lnSA = 1.28 - 0.00340t	0.91
	B	lnSA = 2.19 - 0.00414t	0.81
	C	lnSA = 3.26 - 0.0244t	0.95
150 μg P(PAPR) g^{-1} soil	A	lnSA = 1.51 - 0.00823t	0.98
	B	lnSA = 2.67 - 0.00715t	0.95
	C	lnSA = 3.08 - 0.0123t	0.99
150 μg P(PR) g^{-1} soil	A	lnSA = 1.67 - 0.0133t	0.99
	B	lnSA = 2.82 - 0.0126t	0.95
	C	lnSA = 3.35 - 0.0189t	0.98
750 μg P(PR) g^{-1} soil	A	lnSA = 1.10 - 0.0193t	0.99
	B	lnSA = 2.29 - 0.0222t	0.92
	C	lnSA = 2.62 - 0.0221t	0.99
Craigieburn soil:			
150 μg P(MCP) g^{-1} soil	A	lnSA = 0.963 - 0.00518t	0.98
	B	lnSA = 1.62 - 0.00737t	0.93
	C	lnSA = 2.61 - 0.0164t	0.98
150 μg P(PAPR) g^{-1} soil	A	lnSA = 1.27 - 0.00581t	0.96
	B	lnSA = 2.08 - 0.00895t	0.64
	C	lnSA = 2.86 - 0.0160t	0.98
750 μg P(PR) g^{-1} soil	A	lnSA = 0.583 - 0.0140t	0.97
	B	lnSA = 1.66 - 0.0151t	0.93
	C	lnSA = 2.38 - 0.0207t	0.97

Total dry matter yield and plant uptake of ^{32}P and P obtained from the field trial as described in Chapter 3.

Treatment No.	Dry matter yield (g pot^{-1})	^{32}P uptake (kBq pot^{-1})	P uptake (mg P pot^{-1})
1	6.05	248.6	24.2
	5.12	159.2	21.4
	6.02	---	--
	5.59	155.1	24.5
2	5.90	176.1	25.0
	7.97	180.3	27.1
	6.34	167.4	28.6
	5.97	134.5	24.7
3	--	---	--
	5.10	89.9	25.6
	5.26	75.0	13.5
	9.49	205.7	40.9
4	7.67	121.1	31.2
	6.86	126.4	32.4
	6.02	143.2	35.7
	7.52	117.6	29.1
5	9.27	181.4	48.0
	3.76	---	--
	5.39	70.2	16.6
	4.79	104.9	24.5
6	8.66	189.0	40.2
	5.06	122.9	25.1
	6.90	162.4	26.9
	10.16	234.8	40.2
7	7.38	187.9	34.5
	6.95	223.7	33.6
	5.95	123.4	23.5
	5.37	96.2	27.6
8	10.02	179.9	44.6
	5.09	86.5	24.5
	5.36	135.9	32.4
	6.57	103.4	30.2

Total dry matter yield and plant uptake of ^{32}P and P obtained from the pot trial as described in Chapter 4.

Treatment No.	Dry matter yield (g pot^{-1})	^{32}P uptake (kBq pot^{-1})	P uptake (mg P pot^{-1})
1	0.627	58.4	0.96
	0.421	25.6	1.21
	0.203	11.1	0.57
	0.443	26.5	1.08
2	1.158	83.5	5.66
	0.685	38.7	3.39
	0.969	49.8	4.62
	0.680	45.1	3.04
3	0.537	25.5	5.64
	0.986	58.3	6.07
	0.964	39.1	5.36
	0.861	38.3	5.49
4	1.216	59.6	7.02
	1.084	91.4	6.29
	0.683	61.8	2.41
	1.112	--	6.45
5	0.281	26.8	1.55
	0.911	83.6	4.43
	0.452	36.7	2.28
	0.516	42.3	2.56
6	0.418	27.7	1.42
	0.364	25.6	1.24
	0.231	10.9	1.66
	0.828	45.7	2.31
7	0.738	31.5	5.35
	--	--	--
	0.404	18.3	2.55
	0.652	26.5	4.63
8	0.455	24.9	1.49
	0.461	20.4	1.41
	0.444	24.2	1.43
	0.397	18.1	1.25
9	0.485	26.6	1.89
	0.484	17.2	1.81
	0.358	15.8	1.20
	0.257	9.1	0.70