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AN EVALUATION OF WATER EXTRACTION AS A SOIL-TESTING PROCEDURE FOR PHOSPHATE

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ABSTRACT

In New Zealand, the fertilizer P requirements of developed pasture, maintained at a steady level of production, are currently calculated using a model which is based on the concept that the size of the P cycling pool remains constant. Consequently, fertilizer P is required only to replace P lost from the cycle through animals and in the soil. A soil test is required to assess whether the amount of available soil P is appropriate for the desired level of production and to monitor the effectiveness of the maintenance fertilizer P programme indicated by the model. A water-extraction procedure offers potential as a soil-testing procedure for this purpose. The water-extraction procedure involves an extraction period of 1 h and a soil: solution ratio of 1:120.

In an initial evaluation in the glasshouse with 20 soils, water-extractable P was highly correlated with plant uptake of P ($r = 0.90^{**}$). Unlike the prediction by the Olsen test, the prediction of plant-available P using water extraction was not improved by inclusion of an estimate of P buffering capacity (P retention value or the slope of the desorption isotherm). Consequently, the water-extraction procedure may have advantages over other soil P tests because the interpretation of the results obtained appears to be independent of buffering capacity and soil type.

The effect of seasonal variations, sampling depth, and fertilizer P additions on water-extractable P values was investigated in field experiments, involving two soils of contrasting P sorption capacity (Ramiha and Tokomaru) under permanent pasture over 12 months. It was found that the levels of water-extractable P in soil were always lower than those of Olsen-extractable P. Over the 12-month period, the average value of water-extractable P in the unfertilized Ramiha soil (0-7.5 cm depth) was 1.8 $\mu g\ g^{-1}$ soil compared to the Olsen-extractable P value of 12.6. The variability

associated with water-extractable P at each sampling time was comparable with that for Olsen-extractable P. However, the relative seasonal variation over 12 months was larger for water-extractable P (coefficient of variation = 23% for the Ramiha soil) than for Olsen-extractable P (coefficient of variation = 16% for the Ramiha soil). Both extractants showed a seasonal fluctuation that was closely related to the pattern of pasture P uptake. Low levels of extractable P were generally associated with autumn and spring flushes of pasture growth, while high values were obtained during periods of slow growth in winter. The levels of water- and Olsen-extractable P were higher in samples taken from the 0-4.0 than the 0-7.5 cm sampling depth. For example, water-extractable P values of the unfertilized Ramiha soil averaged over the 12-month period were 3.7 and 1.8 $\mu g\ g^{-1}$ soil for the 0-4.0 and 0-7.5 cm sampling depths, respectively. The relative variability of P level at each sampling depth varied between soils.

Fertilizer P addition resulted in larger increases in water-extractable P in the 0-4.0 cm sampling depth than those in the 0-7.5 cm depth. Furthermore, the effect of fertilizer P on water-extractable P in the 0-7.5 cm depth became undetectable within a few months of addition, inspite of the continuing response of pasture to fertilizer P. Consequently, water-extractable P in soil sampled from the 0-4.0 cm depth may better reflect the effect of fertilizer P addition than water-extractable P in the 0-7.5 cm depth. The relative increase in water-extractable P as a result of fertilizer P addition was larger than that of Olsen-extractable P. At two weeks after 40 kgP ha^{-1} was added to both the Ramiha and Tokomaru soils, water-extractable P (0-4.0 cm depth) was increased by 150% whereas the increase in Olsen-extractable P was only 100%.

Although seasonal variations were observed in both water-extractable P and soil microbial biomass P in unfertilized and fertilized soils, they were not related. Neither were the seasonal changes in soil microbial biomass P related to P uptake by pasture. It appears that microbial

biomass P may be a less sensitive index of soil P availability than previously thought.

The addition of lime in an incubation and a glasshouse study caused significant decreases in Olsen-extractable P but very little change in water-extractable P in two soils of contrasting P sorption capacities. Decreases in Olsen-extractable P of approximately 20% were obtained for both soils of medium P status as a result of the addition of $Ca(OH)_2$ at rates equivalent to 2,000 and 6,000 kg $CaCO_3$ ha^{-1}, respectively. No such decreases were found in plant data or other soil P tests. Evidence from a laboratory study indicated that the decline was a result of an artifact in the Olsen procedure by which calcium phosphates may be precipitated under the conditions of high calcium concentration and high pH. Results from a field experiment on a Tokomaru soil under permanent pasture over 21 months also confirmed that liming caused a decrease in Olsen-extractable P. In fact, a significant reduction of 30% in the Olsen-extractable P was still obtained at 21 months after the application of 5,000 kg $CaCO_3$ ha^{-1}. Because water-extractable P values are much less influenced by soil pH, water extraction may have an advantage over the Olsen test as a soil-testing procedure for limed soils.

A model of P sorption, based on the Langmuir adsorption equation was used to predict changes in water-extractable P in soils following P addition. The predictive ability of the model was strongly influenced by estimates of sorption energy constants (K) for a high P-sorbing soil. Whereas for a low P-sorbing soil, estimates of sorption maxima (b) were more important. The predictions were satisfactory for a soil with high P sorption capacity but overestimated results were obtained for a low P-sorbing soil. A revised model was developed to use phosphate retention (PR) test data as an estimate of b. When tested on a group of 16 soils with a wide range of P sorption capacities, very good predictions ($r = 0.84^{**}$) of changes in water-extractable P following P addition were obtained. It was found that, in some soils, the amounts of P extracted by

water were still changing rapidly at 1 h but the rate of change became significantly smaller at 24 h. Improved predictions by the model ($r = 0.91^{**}$) were obtained with an extraction period of 24 h compared to the original 1-h period. With such a modelling approach, it may be possible to use the water-extraction procedure to determine whether fertilizer application rates are in excess of the calculated maintenance requirements and also to quantify this estimate.

In a study using a double-labelling technique designed to characterise soil P, the soil was incubated with ^{33}P for a relatively long period of time (51 days) and ^{32}P for a relatively short period of time (5 days). The ^{32}P:^{33}P ratios in the Olsen and water extracts of the high P-sorbing Egmont soil showed a contrasting pattern to that of the low P-sorbing Tokomaru soil. An initial assumption of the technique is that as the exchangeability of soil P decreases, so should the ratio of ^{32}P:^{33}P. The unexpected lower ^{32}P:^{33}P ratios in the water extract as compared to the ratio in the Olsen extract of the Egmont soil appears to be consistent with the larger difference between the amounts of water-extractable P and those of Olsen-extractable P which, in turn, seem to reflect the ratio of loosely-held P to more tightly-held P. A lower ^{32}P:^{33}P ratio in the water extracts can occur when the exchange of ^{32}P between the soil solution and the surface has slowed down and the ^{32}P is redistributed among various surface groups.

The ^{32}P:^{33}P ratios of ryegrass grown on the labelled soils were always lower than the ratios of white clover, indicating that ryegrass can remove P from more tightly-held soil P than can white clover. This may be due to the ability of ryegrass to exploit P from different soil P pools as well as the larger depletion of soil P by ryegrass.

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INTRODUCTION

Most New Zealand soils in their unimproved state are unable to supply sufficient phosphorus (P) for high levels of pasture production. To overcome this problem, fertilizer P, predominantly in the form of superphosphate, is regularly added to most soils. In recent years, the escalating cost of superphosphate, together with increasing transport and spreading costs have drawn attention to ways of improving the efficiency with which phosphate fertilizer is used in New Zealand.

The use of soil testing for making recommendations on the use of superphosphate is well established in New Zealand. Currently, the fertilizer P requirement of a well-developed pasture, maintained at a steady level of production, is calculated using a model which was developed by Cornforth and Sinclair (Cornforth and Sinclair, 1982). The model is based on the concept that, in such a pasture, the size of the cycling pool of P remains constant and therefore fertilizer P is required only to replace P which is lost from the cycle through animals or in the soils. A soil test is required to assess whether the level of available soil P is appropriate for the desired level of production and to monitor the effectiveness of the maintenance fertilizer P programme calculated by the model.

At present, the Olsen P test (Olsen et al., 1954a) is used in New Zealand. Although, over a wide range of soils, the Olsen P test appears to be the most satisfactory of the procedures evaluated so far, its development has been entirely empirical. In other words the relationship between the Olsen test value and probability of obtaining a response has been derived from experimental observations rather than from any theoretical considerations. Thus, although this relationship may be known reasonably accurately, it is

difficult to predict what the soil test value will be at some future date or how it will be affected by addition of fertilizer P or other P inputs. Furthermore, although some data of this type are available on a limited range of soils, it is difficult to extrapolate the information to other soils which may have widely different properties or fertilizer histories.

A soil-testing procedure based on extraction of the soil with water has been developed by Ryden et al. (1976). This procedure was claimed to be specific for a pool of soil P defined by a sorption model based on the Langmuir equation. A potential advantage of this water-extraction procedure over the Olsen method is that origin of the P in a water extract is much better understood than is the case with the more complex Olsen reagent. Thus, it should be easier to develop a model which predicts the behaviour of water-extractable P, as affected by fertilizer P addition. The implication with regard to the maintenance P model is that it may be possible to use the water-extraction procedure to determine not only whether or not fertilizer application rates are in excess of maintenance requirements, but also to quantify the excess or deficit. In addition, because water extraction may be specific for a pool of soil P, it may provide a non-empirical estimate of available soil P which is independent of soil type.

This study is concerned with an evaluation of the potential of water extraction as a soil-testing procedure for P. The influence of P buffering on the prediction of plant-available P in a wide range of soils by the water-extraction procedure is assessed in a glasshouse study. The effects of season, depth of soil sampling, and fertilizer P addition on the amounts of water-extractable P are evaluated at two contrasting sites over one year. Comparisons are made between the effect of soil pH on water- and Olsen-extractable P in glasshouse and field studies. The ability to predict changes in water-extractable P following fertilizer P addition is assessed using a model developed by Rennes (1978). An attempt is also made to use a double-

labelling technique to characterise the short-term plant availability of soil P.

CHAPTER 2

CHAPTER 2

REVIEW OF LITERATURE

The subject of this review is the origin and characterisation of plant-available P in soils. The availability of various forms of P in soils and the influence of different processes affecting their availability are discussed. The characterisation of plant-available P is reviewed with specific reference to laboratory procedures, their objectives, operation, evaluation, and factors which influence the results. Finally, the development and evaluation of a water-extraction procedure is discussed.

2.1 Forms and Availability of Soil P

Soil P can be divided into two broad categories: inorganic and organic P. Numerous approaches have been used to further partition soil inorganic P into various forms. The categorisation of soil P has been discussed in several review articles, such as those of Beckett and White (1964), Larsen (1967), Mattingly (1975), Berkheiser et al. (1980), and Olsen and Khasawneh (1980).

There are two major types of categorisation. The first, based on kinetic considerations, describes soil P in terms of the following relationship (Larsen, 1967):

Soil solution P $\rightleftharpoons$ labile soil P $\rightleftharpoons$ non-labile soil P

where equilibrium is rapidly established between labile and soil solution P, as compared to that between the labile and non-labile pools of soil P. This division of soil P is largely arbitrary, as exact boundaries between pools cannot be delineated precisely (Olsen and Khasawneh, 1980). The second type of categorisation is based on a mechanistic approach which classifies the solid phase of soil P into sorbed P and precipitated P. The first refers to P sorbed on surfaces in the soil and the second to distinct P

compounds either formed as reaction products, or inherently present as a result of the weathering of the parent material. This approach offers a clearer picture of soil P from which further attempts to understand the reactions of P in soils can be made. Hence in this review, soil P is classified into four components: solution P, sorbed P, precipitated P, and organic P (Fig. 2.1). The availability of these forms of soil P and the transformation processes between them are discussed. Particular attention will be given to organic P which increasingly has been the subject of many studies.

2.1.1 Solution P

The immediate source of P for plants growing in a soil is inorganic phosphate ions in the soil solution. Soil solution P in this study refers to the inorganic P present in the soil solution unless stated otherwise. The soil solution phase is the starting and finishing point for a number of P transformation reactions in soils (Fig. 2.1). Therefore, the concentration of P in the soil solution is subject to rapid and continual changes, and varies widely between different soils.

Soil solution concentrations are generally low (approximately 0.1% of total P in soil) due to strong interactions of soluble P species with some soil constituents (Beek and van Riemsdijk, 1979). The concentration of soil solution P can be below 0.0003 $\mu gP\ ml^{-1}$ in some tropical soils and can exceed 3 $\mu gP\ ml^{-1}$ in a well-fertilized soil. Generally, a concentration of 0.3 μg dissolved inorganic P ml^{-1} in the soil solution is considered adequate for plant growth (Mengel and Kirkby, 1982). Although the concentration of soil solution P can be influenced by a number of processes (Fig. 2.1), it is believed that sorption-desorption processes are the most important in controlling reactions in soils which have not recently received phosphate fertilizer (Syers and Iskandar, 1981).

Soil solution P is also referred to as the intensity factor in the concept of nutrient availability (Khasawneh,

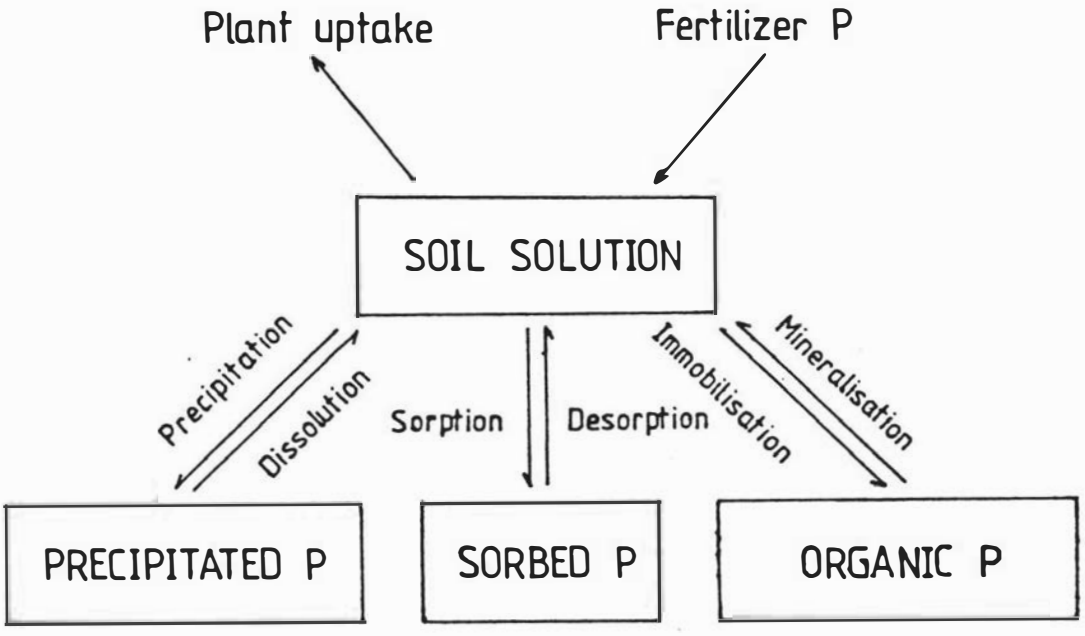

Figure 2.1 Schematic representation of components and reactions of soil P

1971). Some dissolved organic P is also present in the soil solution (Pierre and Parker, 1927; Wild and Oke, 1966). Although organic P in the soil solution can provide P to some plants (Wild and Oke, 1966), it is uncertain whether organic P has to be mineralised to inorganic P before being taken up by plants.

2.1.2 Sorbed P

Sorbed P is defined as phosphate ions which are removed from solution and retained at soil surfaces (Syers and Iskandar, 1981). This process is also referred to as 'adsorption'. When it is followed by a more or less uniform penetration of the adsorbed P into the solid phase, the reaction is called 'absorption'. Because it is difficult to distinguish these two reactions (Glasstone, 1960), the less specific, overall term 'sorption' is often preferred.

The amount of sorbed P in a soil depends on two main factors. Firstly, it is influenced by the ability of a soil to sorb P which, in turn, is governed by the presence of P-sorbing soil components, particularly the short-range order and crystalline hydrous oxides of iron and aluminium, and short-range order aluminosilicates (Williams et al., 1958; Saunders, 1965; Syers et al., 1971). The amounts of these soil components will largely determine the number of sites available for P sorption. There have been numerous studies of the relationships between various soil constituents and P sorption. These have been discussed and reviewed by several workers, including Parfitt (1978), White (1980), and Berkheiser et al. (1980). The second factor influencing the level of sorbed P in a soil is the amount of P that has been added to the soil. In soils with similar P-sorption capacity, the more P is added the greater the amount of sorbed P present.

Sorbed P is released into the soil solution by the process of desorption. There are several factors that influence the rate and extent of desorption of P. They include soil pH; the concentrations and types of cations, and of both inorganic and organic anions present in the soil

solution; the degree of saturation of the sorption complex; and the time allowed for sorption prior to desorption (Barrow, 1974; Syers and Iskandar, 1981). These will be discussed later in the section on sorption-desorption processes (Section 2.2.1).

2.1.3 Precipitated P

Precipitated P is present in soil either as a result of weathering of primary minerals or as reaction products of fertilizer P. In addition certain primary phosphate minerals can be inherited from the parent material. The major sources of primary P in soils are minerals of the apatite group ($Ca_{10}(PO_4)_6Z_2$, where Z = fluoride (F), hydroxyl (OH), chloride (Cl), or 1/2carbonate (CO_3), the most common of these is fluorapatite. Although apatite is initially a major source of P in virgin soils, the rate of weathering is generally too slow to provide adequate P for plant growth (Syers et al., 1967).

A variety of precipitated P compounds have been proposed as fertilizer reaction products in soils. A summary of the types of products is given by Sample et al. (1980). There have been very few studies in which reaction products have successfully been isolated from soil and identified. Most of the compounds identified as probable soil-fertilizer reaction products have been obtained from simulations of the chemical environment near a fertilizer particle. Evidence for the occurrence of precipitated P compounds in soils has also been based on the results of selective fractionation procedures, such as that of Chang and Jackson (1957) and its modifications.

Aluminium, iron, and calcium phosphate compounds are the main types of precipitated P commonly found in soils. As they slowly dissolve in the soil they will become available for plant uptake (Taylor et al., 1963). The rate of dissolution depends largely on their solubilities which are, however, not easy to predict in the complex soil system.

2.1.4 Organic P

The organic P content of soils varies widely, ranging from 4% of total P in some podzolic soils to 90% in alpine soils (Williams and Steinbergs, 1958). However, in most agricultural soils, organic P comprises from 30 to 80% of the total P (McCall et al., 1956). In arable and grassland soils, the application of fertilizer P often results in the buildup of organic P (Jackman, 1955; Walker and Adams, 1958; Rixon, 1966; Cooke and Williams, 1970). Other factors that have been found to influence the content of organic P in soils include rainfall, temperature, P content of the parent material, P sorption capacity of the soil, drainage, soil pH, and cultivation. These are summarised in reviews by Barrow (1961) and Dalal (1977).

The significant contribution of soil organic P to plant-available P in the tropics is well known (Anderson, 1980; Tate, 1984a). This is due to the faster rates of mineralisation at higher temperatures. In contrast, the contribution of soil organic P in temperate regions has generally been assumed to be small (Russell, 1973). However, recent experimental and simulation modelling studies of P cycling in grassland soils have indicated that mineralisation of soil organic P supplies a significant proportion of the total P requirement of plants (Blair et al., 1976; Cole et al., 1977; Blair and Boland, 1978).

The nature, sources, properties, and metabolism of soil organic P have been the subject of many reviews (Anderson, 1967; Cosgrove, 1967; Anderson, 1975; Halstead and McKercher, 1975; Hayman, 1975; Dalal, 1977; Anderson, 1980; Stewart and McKercher, 1982). The diversity and complexity of organic P forms in soil, however, has resulted in the subject remaining only poorly understood, with only 50 to 70% of the organic P in soil having been characterised (Dalal, 1977).

Considerable progress in elucidating the chemical nature and the dynamics of soil organic P has been made in the last 15 years through the application of modern methods

of extraction, concentration, separation, and identification (Cosgrove, 1977; Stewart and McKercher, 1982). Recent studies have suggested that the traditional belief that the organic P in soil is stabilised through incorporation into humic material may not be correct (Dalal, 1977). The fact that organic P is readily dispersed suggests that organic P is not necessarily associated with and stabilised as a constituent of humic materials (Scott and Anderson, 1976). These workers have concluded that the stability of organic P in soil may be due more to the phosphate group than to the carbon moiety. The phosphate group in organic P molecules can be very accessible for sorption by, or reaction with, soil inorganic components. This hypothesis was confirmed by direct evidence of sorption of organic P compounds by soils (Anderson et al., 1974) and observations that organic P content is closely related to the P sorption capacity of soils (Williams, 1959; Jackman, 1964). Furthermore, the observation that the P content of soil organic matter is more variable than that of N and S (Dalal, 1977) suggests that organic P may be stabilised by mechanisms other than those stabilising organic matter in general.

The organic P compounds in soil that have been identified can be grouped into three main categories: inositol P, phospholipids, and nucleic acids. The remaining organic P may be present in small quantities as phosphoproteins and sugar phosphate (e.g., glucose-1-phosphate, Dalal, 1977). Recently, phosphonates (C-P linked compounds) have been detected by nuclear magnetic resonance spectrometry in New Zealand soils (Newman and Tate, 1980). A more detailed discussion on the chemistry of organic P compounds in soil is beyond the scope of this review. The subject is well reviewed by Anderson (1980) and Stewart and McKercher (1982).

The exact origin and transformation of organic P compounds in soils are still uncertain largely because of the lack of methods that can accurately separate and identify these complex forms of organic P in soils. The plant availability of organic P compounds commonly found in

soil has been demonstrated by many workers (e.g., Rogers et al., 1940; Martin, 1973; Tate, 1984a). However, contrasting observations have been made with regard to the mechanisms involved. In the absence of conclusive evidence that plants can absorb P in the organic form, it is assumed that mineralisation by phosphatase enzymes precedes uptake of P (Anderson, 1975). Phosphatase enzymes can be produced by soil microorganisms, mycorrhizae, or plant roots (Speir and Ross, 1978), but the major source has not yet been identified (McGill and Cole, 1981).

It is generally accepted that the transformations between organic and inorganic P in soils are carried out mainly by soil microorganisms. Cosgrove (1967) stated that P-containing organic matter is almost certainly accumulated as a result of microbial activities. The implication is that the organic P in plant and animal remains which are returned to soil is mineralised fairly rapidly and then used for the synthesis of microbial organic P. The study of Martin and Molloy (1971) also indicates that stable organic P in soil originates from microbial synthesis rather than by accumulation of resistant fractions of plant and animal residues.

Approximately 5 to 10% of the organic P in soil is in microbial biomass (Halstead and McKercher, 1975; Jenkinson and Ladd, 1981; Brookes et al., 1982; Hedley and Stewart, 1982). Despite being only a small proportion of total P, soil microbial biomass is a relatively labile constituent of soil organic matter (Cole et al., 1977), and a key site for mineralisation of organic P in soils. The recent development of methods for estimating soil microbial biomass (e.g., Chauhan et al., 1981; Brookes et al., 1982; Hedley and Stewart, 1982) has greatly improved the understanding of the role of microbial P. Results from microbial P studies have suggested that the microbial biomass in some pasture soils could supply significant amounts of available soil P (Halm et al., 1972; Cole et al., 1977; Brookes et al., 1982; Perrott and Sarathchandra, 1982; Tate, 1984a).

2.2 Processes Affecting the Availability of Soil P

Plants growing in a soil absorb inorganic P from the soil solution. The concentrations of P in the soil solution are maintained by replenishment from other forms of soil P, such as sorbed P and organic P (Fig. 2.1). Processes which control the transformations between different forms of soil can be summarised into four groups: (i) sorption-desorption, (ii) precipitation-dissolution, (iii) immobilisation-mineralisation, and (iv) plant uptake. Fertilizer P addition also influences the availability of soil P.

2.2.1 Sorption-desorption

Sorption of P refers to the removal of P from solution and its accumulation at a solid phase, while desorption refers to the release of sorbed P into solution. It is now believed that the balance between sorption and desorption (rather than precipitation-dissolution reactions) largely controls the concentration of P in the soil solution (e.g., Barrow, 1978; Syers and Iskandar, 1981), except in soils which have recently been fertilized. In this section, the influence of various soil properties on sorption-desorption reactions is discussed first. The mechanisms of P sorption are then reviewed and this is followed by a discussion on modelling sorption-desorption reactions.

2.2.1.1 Soil properties

Published work on P sorption indicates that soils can vary appreciably in their ability to sorb P. In a number of studies, attempts have been made to correlate P sorption with soil properties. These have been summarised in review papers by Parfitt (1978), Beek (1979), Berkheiser et al. (1980), White (1980), and Syers and Iskandar (1981). The factors considered to influence P sorption-desorption will be discussed briefly.

(i) Amount and nature of P sorbing components

Sorption of P occurs at exposed hydroxyl groups on the surfaces of soil colloids (Parfitt, 1978; Harrison and Berkhieser, 1982). McLaughlin et al. (1981) have shown that the extent of P sorption by several iron- and

aluminium-containing components are primarily related to the number of functional hydroxyl groups present at the solid-solution interface. Short-range order (amorphous) components generally have abundant exposed hydroxyl groups, so they have a much greater capacity to sorb P than do their crystalline counterparts (Bache, 1963; Ryden, 1975). One short-range component usually found in soils contaminated by volcanic ash is allophane-like (short-range order alumino-silicate) material which is extremely effective in P sorption (Cloos et al., 1968). Crystalline hydrous metal oxides usually sorb more P than layer silicates (Muljadi et al., 1966). In weakly and moderately weathered soils, hydrous ferric oxide gel occurs as coatings on layer silicates (Deshpande et al., 1968; Wada and Harward, 1974), resulting in the sorption of larger amounts of P. Calcium carbonate is reported to have a very limited ability to sorb P (Griffin and Jurinak, 1973), which may be due to hydrous ferric oxide impurities (Holford and Mattingly, 1975).

(ii) Soil pH

Studies on the effect of soil pH on P sorption-desorption reactions have produced contradictory results. It is widely accepted that increasing soil pH by liming generally reduces the sorption of P, but the opposite finding has also been reported in a few studies (Probert, 1980; Sanchez and Uehara, 1980; Haynes, 1982; and Barrow, 1984). The decrease in P sorption following an increase in pH has been attributed to the effect of pH on surface charge, which becomes less positive with increasing pH, and on the species of P present in solution (Hingston et al., 1968, 1972). As soil pH rises, the surface becomes more negative and therefore less attractive to the sorption of phosphate ions. In many soils an increase in soil pH could also lead to an increase in microbial activity and an increased production of organic anions that could reduce P sorption (Earl et al., 1979).

The opposite effect of soil pH on P sorption often occurs in highly-weathered, acid soils (Haynes, 1982). As the pH in these soils increases, P sorption initially

increases and then decreases as the soil pH rises above 6.5 to 7. It is suggested that the high level of exchangeable aluminium (Al^{3+}) present in these soils is an important factor. Haynes (1982) has concluded that an increase in soil pH enhances the hydrolysis and polymerisation of exchangeable Al^{3+} and forms insoluble, polymeric hydroxy-Al cation species which have highly active P-sorbing surfaces (Coleman et al., 1960; Mokwunge, 1975). These hydroxy-Al polymers remove P from the soil solution. As soil pH is raised above six, the previously formed hydroxy-Al sorbing surfaces become more soluble and dissolve, with the release of previously sorbed P. Apparently these hydroxy-Al polymers are not stable and air-drying can reduce their surface activity (probably due to crystallisation) and decrease P sorption capacity (Haynes, 1982). Hence, if a limed soil is air-dried before reaction with P, the sorption of P would be decreased rather than increased.

However, White (1983) has pointed out that there is ample evidence for the stability of hydroxy-Al charged species, so the drying process would have to be extremely severe and prolonged for the activity of the sorbing surfaces to decrease. Furthermore, Hayne's (1982) explanation about the effect of drying on P solubility is inconsistent with the results of Taylor and Gurney (1965), Amarasiri and Olsen (1973), and Friesen et al. (1980), all of whom air-dried and rewetted soils two or more times following the addition of lime. After reviewing data from several studies, White (1983) concluded that the exchangeable Al content of an acid soil is important in determining how P sorption will be affected by pH increase through liming. It is proposed that there is a critical level of exchangeable Al above which soils will show an increase in P sorption when limed (Sumner, 1979; White, 1983).

(iii) The presence of other ions

Various cations and anions can affect the sorption and desorption of P in soils. Several studies have shown that P sorption by soils is influenced by the species

and concentration of cations in the system (Beek and van Riemsdijk, 1979; Syers and Iskandar, 1981; Barrow, 1983c). Generally, high salt concentrations increase P sorption and divalent cations enhance P sorption relative to monovalent cations. The additional effect of divalent cations, such as Ca, on P sorption, as compared with sodium (Na), was attributed to the additional screening of negative charge at the surface provided by the divalent cation, in addition to the effect of specific sorption of calcium on surface charge (Kinniburgh et al., 1975).

Some inorganic and organic anions can compete to a varying extent with P for sorption sites, resulting in a decrease in the sorption of added P or in the desorption of sorbed P. Nitrate and chloride, which are non-specifically sorbed cannot compete with P for sorption sites (Evans and Syers, 1971; Kinjo and Pratt, 1971), although some other inorganic anions have been shown to compete successfully with P. These include arsenate, bicarbonate, fluoride, molybdate, selenite, and hydroxyl. Recently, Ryden et al. (1985) have reported that although P is preferentially sorbed, there is no evidence to suggest that anions, such as arsenate and selenite, are sorbed on different sites from P. They also suggested that the competitive ability of such anions was attributed to the charge relationships of sorption.

Sulphate can desorb little phosphate because of the inability of sulphate to form a stronger bond than phosphate at the surface (Evans and Syers, 1971). It appears that competition between these anions and phosphate for sorption sites in soils involves ligand-exchange reactions (Parfitt, 1978). The competitive ability of the anion is determined by the strength of bonding of the anion with the surface.

Phosphate sorption in soils can also be reduced by the following organic anions: citrate, oxalate, tartrate, and polygalacturonate, and by fulvic and humic acids (Parfitt, 1978; Beek and van Riemsdijk, 1979; Syers and Iskandar, 1981). Studies with organic anions (e.g., Nagarajah et al.,

1968, 1970) have shown that the structure of the anion and the pH of the system are important factors which determine the extent of reduction of P sorption. The effect of these organic anions on P sorption can be attributed to their formation of stable complexes with the Fe and Al of soil components, thus reducing the number of sorption sites (Nagarajah et al., 1970; Earl et al., 1979).

(iv) Saturation of the sorption complex

The ability of a soil to sorb P is largely related to the saturation of the sorption complex or to the number of sites available for further sorption (Parfitt, 1978; Syers and Iskandar, 1981; White, 1980; Barrow, 1983c). Desorption of P is also strongly influenced by the extent of saturation of the sorption complex (Woodruff and Kamprath, 1965), in addition to the time of contact between added P and the soil (Evans and Syers, 1971; Barrow and Shaw, 1974).

2.2.1.2 Mechanisms of P sorption

A knowledge of mechanisms of P sorption is essential for an understanding of the behaviour of soil and fertilizer P in relation to availability to plants. Research to elucidate the mechanisms of P sorption by soils is hindered by the complex nature of the many different soil components (Berkheiser et al., 1980). Although there is extensive literature on P sorption, there is still some conflict with regard to the mechanisms of P sorption proposed by various workers (Muljadi et al., 1966; Hingston et al., 1972; Rajan, 1975b; Ryden et al., 1977a; Bowden et al., 1980).

Sorption of P by soils and soil components is generally characterised by an initially fast reaction followed by a slow reaction which can continue for some time (Hsu, 1964; Evans and Syers, 1971; Rajan and Fox, 1972; Barrow and Shaw, 1974; Ryden et al., 1977b; Barrow, 1983a). The initial rapid reaction is believed to involve sorption reactions (Munns and Fox, 1976; McLaughlin et al., 1977; Ryden et al., 1977b; Barrow, 1983c), but there are varied opinions on the nature of the slow reaction (e.g., Barrow and Shaw, 1975a; McLaughlin et al., 1977; Barrow, 1983a).

It is generally agreed that P is specifically sorbed by ligand exchange (Hingston et al., 1972; Ryden et al., 1977a); that release of OH^- (and/or H^+) often occurs as a consequence of P sorption (e.g., Breeuwsma and Lyklema, 1973; Rajan, 1975a; Ryden et al., 1977a); and that P sorption is affected by ionic strength (Helyar et al., 1976; Ryden et al., 1977c) and pH (Barrow, 1970; Bowden et al., 1980). Among the several mechanisms proposed by different workers to explain such observations, there are two contrasting approaches to describing P sorption: the Langmuir approach (Ryden et al., 1977a) and the extended double layer model (Bowden et al., 1980; Barrow et al., 1980a,b).

Using a three-surface Langmuir equation to describe P sorption data, Ryden et al. (1977a) proposed that P was sorbed at three energetically different types or regions of sites. They suggested that mechanisms of P sorption at low concentrations involved chemisorption by replacement of $-OH_2^+$ and -OH groups on the surface (regions I and II) by ligand exchange and possible formation of binuclear or bridging complexes (Parfitt, 1977). At high P concentrations, more-physical sorption of P involving a weaker bonding to the surface (region III) was suggested. Rajan and co-workers (Rajan and Fox, 1972; Rajan and Perrot, 1975; Rajan, 1976) have postulated a similar series of ligand exchange mechanisms for P sorption. This group of workers found evidence that surface negative charge did not change in a certain range of sorption and this was explained by the mechanisms proposed (Rajan, 1976; Ryden et al., 1977a).

In contrast, another group of workers has recently suggested that there is no need to postulate more than one type of site on the surface for P sorption and that the changes in P sorption can be explained by a progressive increase in surface negativity as sorption proceeds (Bowden et al., 1977, 1980). These workers used an extended double layer approach to develop a mechanistic model to describe sorption of ions, including P, on an idealised charged

surface (Bowden et al., 1980). It is likely that there will be difficulties in applying the model to soils which is a mixed mineral system. Furthermore, evidence for a consistent increase in surface negative charge on P sorption is by no means conclusive (Marsh, 1983).

A variety of mechanisms has been proposed for the slow reaction of P removal which follows an initial, rapid P sorption reaction. These include the precipitation of discrete P compounds (Larsen and Widdowson, 1971; Chen et al., 1973; Talibudeen, 1974), the shift from monodentate to a bi-dentate form of sorbed P (Kafkafi et al., 1967; Hingston et al., 1974; Barrow and Shaw, 1975b; Munns and Fox, 1976), the penetration (i.e., absorption) of surface-sorbed P into soil components (Holford and Mattingly, 1976), and the shift of P from a loosely-held (i.e., more-physically sorbed) form (Ryden et al., 1977b) to a more strongly-held chemisorbed form, thus regenerating sites for further sorption (McLaughlin et al., 1977). This view is consistent with the three-compartment model (A = solution P, B = weakly-sorbed P, and C = strongly-sorbed P) of Barrow and Shaw (1974), developed from studies of the kinetics of P sorption by soils. According to Barrow and Shaw (1974), the slow reaction involves the shift of sorbed P from compartment B (weakly-sorbed P) to compartment C (strongly-sorbed P), allowing further removal of P from compartment A (solution P).

Recently, Barrow (1983c) postulated a diffusion mechanism for the slow and continuing reaction between P and soil. He proposed that the initial, rapid P sorption reaction induces a diffusion gradient towards the interior of the particle and begins a solid-state diffusion process. Penetration of P into the particle will produce vacancies on the surface for further sorption.

The continuing sorption reaction, involving the shift of a loosely-bound to a more tightly-bound form of sorbed P, is partly responsible for the fact that sorption of P is not completely reversible (Ryden et al., 1977a; Barrow, 1983c).

In contrast to the situation for sorption, the desorption process of P has been studied less frequently. The extent of saturation of the sorption complex has a marked influence on the desorption of P (Ryden et al., 1977a). It is suggested that the greater ease of desorption at higher saturations arises from the decrease in the energy of P sorption with increasing surface coverage. The rate of desorption also decreases as the period of prior reaction increases (Barrow and Shaw, 1975b; Munns and Fox, 1976). The explanation provided by the diffusion mechanism of Barrow (1983c) is that the longer the period before desorption is initiated, the more deeply P will have penetrated, and hence the more slowly it can be desorbed.

2.2.1.3 Modelling P sorption-desorption reactions

Numerous studies have attempted to describe and model sorption-desorption reactions of soil P in an attempt to understand more about the nature and mechanisms of the reactions involved or to characterise the sorption-desorption properties of a soil (Barrow, 1983c). Sorption isotherms have been used to describe the relationship between the amount of P sorbed and that remaining in the soil solution at constant temperature. Several equations have also been used to describe P sorption data and these have been discussed extensively by Barrow (1978). Three commonly used equations are the Freundlich (Russell and Prescott, 1916), the Langmuir (Olsen and Watanabe, 1957), and the Temkin (Bache and Williams, 1971) equations. The most widely used equation is the Langmuir equation.

Applications of the linear form of Langmuir equation to P sorption by soils and soil components over a wide range of solution P concentrations have generally indicated deviations from a single linear relationship (e.g., Olsen and Watanabe, 1957; Shapiro and Fried, 1959). It has been suggested that this deviation arises from more than one mechanism or population of sorption sites (Syers et al., 1973; Rajan et al., 1974). Sorption isotherms for P have often been split into regions, each of which is attributed

to a distinct population of sites and is described by a Langmuir equation. Ryden et al. (1977a) suggested that the sorption data for contrasting soils could be described by three distinct Langmuir equations. Further supporting data relating to the surface charge and pH relationships of sorption, and the effects of pH, other ions, and ionic strength on sorption, allowed them to propose that two chemisorption mechanisms could operate at equilibrium solution P concentrations of approximately 0.2 mg l^{-1} or lower. Above this concentration, a third mechanism, having a substantially lower free energy of sorption, became operative. This was called a more-physical sorption reaction which was reversible upon a reduction in the solution P concentration.

Several criticisms of the use of the Langmuir equation to describe sorption isotherms have recently been made (Bowden et al., 1974, 1977; Harter and Baker, 1977; Veith and Sposito, 1977; Barrow, 1978; Parfitt, 1978). Hope (1978) pointed out that most of the criticisms relate to the failure of the Langmuir equation to consider changes in surface charge during sorption. Rennes (1978) has argued that the consequence of the changes in surface charge may be relatively insignificant. Furthermore, the work of Giles (1970) suggests that the Langmuir equation may be more suitable for describing solute sorption than gas sorption, for which it was developed.

Despite these criticisms, the Langmuir equation has proved useful in developing models to describe several aspects of P sorption by soils, including sorption-desorption relationships (Holford and Mattingly, 1975; Ryden et al., 1977a; Taylor and Ellis, 1978), time-dependent sorption of P (Enfield et al., 1976; Hope and Syers, 1976; Ryden et al., 1977b), and the plant availability of P (Holford and Mattingly, 1976).

Recently, Bowden et al. (1977) has developed a general model for ion sorption on variable charge mineral surfaces. The model, unlike others, accounts for the pH-dependent

charge on the surface and the charge on the sorbing ion. Although the Bowden et al. model has been used successfully to describe P sorption in pure mineral systems, it requires some complicated computations which may limit its use on whole soils.

In most cases, the models for P sorption describe experimental data satisfactorily and often with correlation coefficients of 0.9 or higher (Berkheiser et al., 1980). However, the 'goodness of fit' alone does not constitute proof that sorption mechanisms assumed by the model are in operation exclusively (Veith and Sposito, 1977).

2.2.2 Precipitation-dissolution

Precipitation implies that the solution P concentration is controlled by the solubility product of the least soluble P compounds. From laboratory studies during the 1950's, it was postulated (Cole and Jackson, 1950; Haseman et al., 1950; Kittrick and Jackson, 1955) that the concentration of solution P in neutral and acid soils was controlled by the solubility products of crystalline P compounds. The results of several subsequent studies, however, have indicated that the solubility of such compounds does not satisfactorily explain the concentration of P observed in the soil solution (Wild, 1954; Taylor and Gurney, 1962; Bache, 1963; Murrmann and Peech, 1969b). Precipitation-dissolution reactions appear to be more significant in the vicinity of fertilizer particles than in the bulk soil. The presence of Fe and Al phosphates has been reported as soil-fertilizer reaction products around fertilizer granules (Lindsay and Stephenson, 1959; Huffman, 1969), and it is also well established that dicalcium phosphates can form as reaction products when monocalcium phosphate is added to soils (Lindsay et al., 1959; Moreno et al., 1960). However, these compounds are unlikely to persist in soils for long periods (Huffman and Taylor, 1963; Probert and Larsen, 1970). More detailed discussion of reaction products and their dissolution is given in Section 2.2.5.

2.2.3 Immobilisation-mineralisation

Phosphorus can be removed from the soil solution by microbial transformation (immobilisation) into organic compounds which are unavailable to plants. Some P can also be released from soil organic P into the soil solution after microbial conversion (mineralisation). Both immobilisation and mineralisation processes occur concurrently in soil, and the balance between them will determine the amounts of organic P present in a soil. When soils receive regular applications of fertilizer P they gradually accumulate organic P up to an equilibrium level until the rate of immobilisation balances the rate of decomposition (Jackman, 1955; Walker and Adams, 1958; Rixon, 1966; Quin and Rickard, 1983).

The rates and pathways of P through soil organic matter are poorly understood when compared to physico-chemical processes of soil P, such as sorption-desorption and precipitation-dissolution (Tate, 1984a). The dynamic nature of soil organic P is masked by the fact that only a small portion of the total soil organic P may be biologically active and it is difficult to measure the reactivity of a small portion of labile organic P in the presence of a larger proportion of relatively stable organic P (Stewart and McKercher, 1983).

Soil microorganisms play an important role in the turnover of soil organic P (Dalal, 1977) by being a source and sink of P, as well as the main agents for transformation of soil P. Although the mechanisms of P uptake by microbial population have been examined (Beever and Burns, 1976), the release of P from the microbial cells is less well understood (Stewart and McKercher, 1983). Soil microorganisms can produce a variety of phosphatases (Feder, 1973) capable of releasing inorganic P from organic P compounds. This mechanism is termed 'biological mineralisation' (McGill and Cole, 1981) where a need of soil organisms for energy is the driving force. This is in contrast to 'biochemical mineralisation', which involves the breakdown of organic P by extracellular phosphatases

released from plant roots, plant residues, dead cells of microbial tissues, and soil animals (Skujins, 1967). These concepts can accommodate the well known variability of C:N:S:organic P ratios and the greater variability of organic P in soil organic matter (Tate, 1984a).

Although mineralisation of soil organic P depends primarily on the activity of soil microorganisms, invertebrates, especially earthworms, have an important regulatory function in this process. Surface casting earthworms, for example, can increase the short-term availability of P in plant residues by a factor of two to three through the release of inorganic P in plant material largely by physical decomposition; this is especially important in soils of low P status (Mansell et al., 1981).

The ultimate limit on the availability of organic P to plants and microorganisms is the rate of inorganic P release by mineralisation, rather than the amounts of organic P present (Tate, 1984a). The rate and extent of mineralisation of soil organic P is largely governed by the factors which control the population dynamics and activities of soil microorganisms; the factors include temperature, pH, moisture, aeration, and the presence of plants (for reviews, see Dalal, 1977; Speir and Ross, 1978; Tate, 1984b).

2.2.4 Plant uptake

The transport of phosphate ions towards plant roots involves diffusion, mass flow, and root interception processes (Lewis and Quirk, 1967). The contribution of mass flow, however, is minimal as the concentration of P in the soil solution is normally too low (Bole, 1973). Under most situations, therefore, diffusion of P to the root is the dominant mechanism determining P concentrations at the root surface (Brewster and Tinker, 1972; Bhat and Nye, 1973, 1974; Nye, 1977).

The uptake of P by plants is largely determined by the amount of plant-available P in the soil, the root distribution pattern of the plant, and the environmental

factors influencing plant growth. Factors involved in determining plant uptake of P can be grouped into those related to soil P and to plant attributes. The ability of soil to sorb P influences the concentration of P in the soil solution and the diffusion coefficient, both of which determine P uptake (Lewis and Quirk, 1967; Khasawneh, 1971; Barrow, 1975a; Helyar and Munns, 1975; Nye and Tinker, 1977). Soil texture is another factor affecting diffusion (Olsen and Watanabe, 1963). As the clay content increases, the diffusion coefficients increase due to a decrease in tortuosity. In a model simulating P uptake by corn and soybeans, Silberbush and Barber (1983) concluded that the P concentration in the soil solution affected P uptake more than the diffusion coefficient and sorption capacity of soils. They also found that soil P parameters were more important than root physiological uptake parameters in determining the rate of P uptake. Evidence is accumulating to indicate that internal plant factors may strongly influence P uptake (Loneragan, 1978). It has been suggested that the transport of inorganic P within the plant may also regulate P uptake by roots (White, 1973). The effect of plant growth and the P status of the plant on P uptake, however, is not clearly established (Jungk and Barber, 1975).

The influence of root attributes on uptake of P may involve (i) the ability to absorb P from dilute solution, (ii) the ability to physically explore the soil volume, and (iii) the ability to modify the root environment.

2.2.4.1 Absorption from dilute solution

The minimum concentration of P in soil solution from which P uptake can occur differs between plant species (Barber, 1980). It is known as the threshold concentration of plant uptake. The ability of plant species to absorb P from dilute P solution is particularly important in soils with high P buffering capacity because these soils can rapidly replenish P as it is depleted from the soil solution. Some workers (Mosse et al., 1973; Howeler et al., 1982b) have attributed the increase of P uptake by

mycorrhizal plants to the lower threshold concentration of mycorrhizal roots than of non-mycorrhizal roots. Other workers (Cress et al., 1979; Howeler et al., 1982a) have proposed that the mycorrhizal effect may be due to high affinity of P for absorption sites on the hyphae of the mycorrhiza.

2.2.4.2 Physical exploration of soil volume

Differences in uptake of P among plant species can be attributed to differences in root morphology and density (Nye and Foster, 1958). The superior ability of grasses over clovers to compete for P is due to the better root distribution of grasses including greater root length, higher root density, and more root tips (Mouat and Walker, 1959; Jackman and Mouat, 1972b; Evans, 1977). Consequently, ryegrass can explore a larger soil volume than clover (Evans, 1977; Haynes, 1980). Mouat (1983) has proposed that plants with a low root cation exchange capacity (CEC) would adapt to low P supply by increasing their root growth. Root hairs are known to increase nutrient uptake by increasing root surface area and extending the effective root diameter (Nye, 1966). Improved uptake of P by roots infected with mycorrhizal fungi has been attributed to the large surface area for absorption and the greater volume of soils explored by mycorrhizal hyphae (Sanders and Tinker, 1973). From their P uptake model, Silberbush and Barber (1983) concluded that root growth rate and root radius were the most sensitive root attributes affecting P uptake.

2.2.4.3 Modification of root environment

The metabolic activity of plant roots can modify the root environment (rhizosphere) and thus influences P uptake in several ways (Loneragan, 1978). Excretion from roots (with or without mycorrhiza) of CO_2, organic acids, or stimulants to microbial activity have all been suggested as possible mechanisms. Such organic acids (e.g., citrate) are capable of forming chelates which could compete effectively with P for sorption sites (Nagarajah et al., 1970; Earl et al., 1979; Parfitt, 1979). Organic acids from root exudates can also solubilise some soil P (Stevenson, 1967; Barber,

1968; Kepert et al., 1979). Moghimi et al. (1978) have isolated 2-keto gluconate from the rhizosphere of wheat roots in quantities that could solubilise considerable amounts of P from hydroxyapatite. However, Hedley et al. (1982a) concluded that any release of organic acids by the roots or rhizosphere microorganisms was insufficient to account for the solubilisation of P that occurred during plant growth.

The ability of some plant species and mycorrhizal plants to utilise P from phosphate rocks has been associated with an increase in Ca uptake (Asher and Ozanne, 1961; Ross, 1971; Deist et al., 1971). Robson et al. (1970) have suggested that Ca stimulates P uptake by screening negative charges on the roots, thereby increasing the accessibility of absorption sites to P. Another important influence of roots on P uptake is the effect of pH changes in the rhizosphere. The pH at the root surface is influenced by the balance of cation and anion uptake, which is associated with the release of OH^- and H^+ (Mengel and Kirkby, 1982). When plants take up more cations than anions, H^+ is released into the soil and the rhizosphere pH will decrease. Such changes in acidity could markedly influence P uptake by plants because P solubility in the soil is highly pH dependent. It is commonly observed that when ammonium and urea fertilizers are used as N sources, the rhizosphere pH decreases and uptake of P increases (Blair et al., 1971; Riley and Barber, 1971; McLachlan, 1976; Soon and Miller, 1977). In contrast, no such observation was reported when the N source was nitrate (Hedley et al., 1982a). A number of workers (McLachlan, 1976; Andersen and Thomsen, 1979; Grinsted et al., 1982) have associated an enhanced efficiency of plants to absorb soil and fertilizer P with their ability to reduce the rhizosphere pH. Recently, Hedley et al. (1982c) have demonstrated that the ability of rape plants (Brassica napus) to solubilise the less-soluble fraction of soil P was due to the reduction in rhizosphere pH. The pH reduction was the result of net excretion of H^+ from plant roots caused by an imbalance in cation-anion uptake.

Phosphatase enzymes excreted from, or present on root surfaces, may be important in the uptake of P (Bartlett and Lewis, 1973). Enzyme activity increases when the P concentration in solution is low and is inhibited by high solution P concentration (Speir and Ross, 1978). Therefore the contribution of phosphatases may be important to uptake of P by plants in low P soils (Woolhouse, 1969; Bieleski, 1973).

2.2.5 Fertilizer P addition

Water-soluble P fertilizers are the most common type of fertilizer used to correct P deficiency in soils. Of these, superphosphate is the most extensively used in New Zealand. Other soluble P fertilizers include monoammonium and diammonium phosphates. Recently, there has been increasing interest in the use of reactive phosphate rocks as direct-application P fertilizers for pasture in this country (Gregg et al., 1981).

When particles of a water-soluble P are in contact with moist soil, a complex series of chemical reactions occurs in the fertilizer particles and the surrounding soil. The dissolution of fertilizer P is initiated by soil moisture moving into the particle, thereby forming a saturated or nearly saturated solution in and around the fertilizer particles. The concentrated fertilizer solution then diffuses out from the particles into the soil solution. The pH of the solution diffusing from monocalcium phosphate in superphosphate and ammonium phosphate is about 1.5 (Huffman and Taylor, 1963). During diffusion, the fertilizer solution dissolves Fe, Al, and other cations from the soil and forms complex compounds of phosphate. The types of compounds formed as reaction products depend on the kinds and amounts of cations and anions supplied by both the fertilizer and the soil, the pH, and the soil moisture content (Smith, 1974). A large range of such compounds has been identified (Huffman, 1969) and a summary is given in a review by Sample et al. (1980). These reaction products are not stable and will gradually dissolve to form more stable and less-soluble compounds. Some of the products are

thought to be variscite ($AlPO_4.2H_2O$) and strengite ($FePO_4.2H_2O$) in acid to neutral soils, and hydroxy- and fluorapatites in alkaline and calcareous soils (Sample et al., 1980). As the reaction products dissolve during the alteration process they release P into the soil solution which is then subject to all the processes described earlier. A large proportion of applied fertilizer P is generally sorbed and precipitated by soils, while only a small fraction is taken up by plants (White and Taylor, 1977). Leaching losses of added P are minimal, except in soils with extremely low P-sorbing capacity, such as some sandy or organic soils (Fox and Kamprath, 1971; Humphreys and Pritchett, 1971), or when high rates of fertilizer P are used (Fiskell and Spencer, 1964; Logan and McLean, 1973).

The effectiveness of fertilizer P declines with time as a result of the removal of added P into sorbed or precipitated forms (Ryden et al. (1977b). Barrow (1983c) also suggested that the slow and continuing reaction, or solid-state diffusion, was responsible for the decline in availability of fertilizer P with time. The rate and extent of these slow reactions between soils and added P depend on several factors. Temperature (Barrow, 1974), soil pH (Larsen et al., 1965), and soil texture (Kafkafi et al., 1968) have been found to be important. There have been contradictory reports on the influence of the P sorption capacity (or buffering capacity) on the decline in the availability of fertilizer P. The rate of decline was found to decrease (Barrow, 1973) or increase (Devine et al., 1968; Fitter, 1974; Enwezor, 1977) with increasing ability of the soil to sorb P. Most workers, however, agree that the amounts of P added have no influence on the rate or proportion of P removed by the slow reactions (Barrow, 1973; Barrow and Shaw, 1975b; Rennes, 1978).

2.3 Assessment of the Availability of Soil P using Soil Analysis

The availability of soil P can be assessed by means of soil analysis, plant analysis, and experiments using growing plants (glasshouse and field trials). Of these procedures, soil analysis, usually referred to as soil testing, is the most convenient and the most widely used. Consequently, numerous studies have been carried out to determine the most suitable methods of soil analysis for P. Reviews of this work have been prepared by a number of authors, including Nelson et al. (1953), Bingham (1962), Hesse (1971), Thomas and Peaslee (1973), Kamprath and Watson (1980), Olsen and Khasawneh (1980), and Olsen and Sommers (1982).

In this review it is intended to discuss various aspects of soil testing, including objectives, approaches and techniques, correlation and calibration studies, and factors affecting the interpretation of soil test results. In the section concerning correlation and calibration studies, some glasshouse and field experimental techniques used for evaluation will be discussed briefly.

2.3.1 Objectives

The primary purpose of soil P testing is to determine the available P status of a soil. Such knowledge can then be used in different ways, including (i) grouping of soils into classes for the purpose of making fertilizer P recommendations, (ii) prediction of the probability of obtaining plant responses to an application of fertilizer P, and (iii) providing an index of the amount of P a soil can supply (Kamprath and Watson, 1980). Generally, P responses are obtained on soils with low soil P test values, while soils with high soil P test values are not usually expected to respond to added P. Once it is established that responses to applied P are probable, the next step is to determine the rate of fertilizer P required. Soil test data, in themselves, provide no information about the quantity of fertilizer P required for optimum production. This information must be obtained from response data from

field experiments which are dependent upon several soil, plant, and climatic factors. Methods used to derive fertilizer P recommendations from soil P test values and plant response data have been discussed by Peaslee (1978).

In recent years there has been increasing interest in bringing the available P level in soil to the point where only maintenance rates of fertilizer are required (Kamprath and Watson, 1980). This requires knowledge of the optimum level of available soil P which is needed for a maintenance situation to apply. The role of a soil P test here is to assess whether available soil P is sufficient to maintain a given level of production and to monitor the effectiveness of the fertilizer P programme designed for the maintenance situation (Cornforth and Sinclair, 1982).

Several workers have used soil P analysis as a tool to gain a better understanding of the chemistry of soil P. In such cases interest is focussed on how the available soil P, as indicated by soil P analysis, is influenced by the particular factors being studied. In this instance, soil P analysis has a purely descriptive role as opposed to the predictive role in fertilizer recommendations.

2.3.2 Approaches and techniques

Soil tests for P have usually been designed to extract available forms of soil P. Because soils vary considerably in the forms of P present, a number of methods for soil P analysis have been developed. The mechanisms of P removal by various methods have been discussed by Williams (1962), Thomas and Peaslee (1973), Kamprath and Watson (1980), and Sibbesen (1983). The mechanisms involved can be considered under the following categories:

(i) decreasing the soil:solution ratio, as in the water extraction methods of Bingham (1949), van der Paauw (1971), and Ryden et al. (1976).

(ii) changing pH with dilute acids, pH-buffers, or dilute bases, as in the methods of Dyer (1894) (citric acid), Truog (1930) (sulphuric acid), Morgan (1937)

(acetate-buffer), Bray and Kurtz (1945) (hydrochloric acid), Egner et al. (1960) (lactate-buffer), and Olsen et al. (1954a) (bicarbonate).

(iii) introducing anions that complex and/or precipitate cations (Ca, Fe, Al) in P-containing compounds, as in the methods of Morgan (1937) (acetate), Bray and Kurtz (1945) (fluoride), Egner et al. (1960) (lactate, acetate), and Olsen et al. (1954a) (bicarbonate, hydroxyl).

(iv) introducing anions (as in (iii) above) which promote the desorption of phosphate from surfaces. In the anion-exchange resin method (Amer et al., 1955), phosphate in soil solution is exchanged with chloride (Amer et al., 1955) or bicarbonate (Sibbesen, 1978) on a resin, thereby reducing the P concentrations in the soil solution and promoting continuous desorption of P from the surface.

According to the concept of nutrient availability first proposed by Schofield (1955), the ability of soil to supply P to plants depends on the concentration of P in the soil solution (intensity), the amount of available P (quantity), and the ability of soil to maintain the soil solution P concentration (buffering capacity). Ideally, soil-testing procedures should take into account all three parameters in order to accurately reflect the availability of soil P. However, most soil P analyses characterise only one of these factors. In this review the various methods of soil P analysis will be discussed in relation to the intensity, quantity, or buffering capacity factor. Other approaches, including combinations of measurements that have been used to assess the availability of soil P, are also discussed.

2.3.2.1 Intensity measurements

The intensity factor for soil P is probably most directly and simply reflected in extraction with water or a very dilute acid at a narrow soil:solution ratio (Thomas and Peaslee, 1973). The soil:solution ratios used include 1:1.25 (Olsen and Watanabe, 1970), 1:10 (Olsen and Dean, 1965), 1:40 (Ryden et al., 1976), and 1:60 (van der Paauw,

1971). A 0.01M $CaCl_2$ solution has also been used to extract soil solution P (Aslyng, 1964). The concentration of P in $CaCl_2$ extracts is generally lower than that of water extracts, due to the presence of Ca (Olsen and Watanabe, 1970; Soltanpour et al., 1974).

Schofield (1955) was the first to propose the 'phosphate potential' as an expression for the intensity of soil P. The application of phosphate potential measurements has been discussed in detail by Aslyng (1964) and White and Beckett (1964). Olsen and Khasawneh (1980) concluded that the assumptions required for the application of this phosphate potential are valid only in certain soils and that, because of such a limitation, this procedure offers no advantage over any other measure of P intensity.

Recently, an electro-ultrafiltration (EUF) procedure has been proposed (Nemeth, 1979) to determine the availability of nutrients in soil. The EUF procedure is a combination of electrodialysis and ultrafiltration. It is claimed that EUF-extractable P can be regarded as an index of the intensity of soil P (Nemeth, 1982).

2.3.2.2 Quantity measurements

The amount of solid phase P that acts as a reserve for plant uptake has been referred to as the 'quantity factor' by many authors (Olsen and Khasawneh, 1980). Soil P analyses relating to the quantity factor can be grouped into three categories: chemical extraction, extraction with anion-exchange resins, and isotopic exchange.

(i) Chemical extraction

Methods of soil analysis used for the measurement of the 'quantity factor' of soil P involve stronger extractants than those for intensity measurements. A wide variety of chemical extractants have been used in various countries of the world, and a list of the commonly used reagents and methods is given in Table 2.1. The form of P extracted depends on the mechanism of extraction (see

Table 2.1 Common methods of chemical extraction for assessing available soil P

Name	Extractant	pH	References
Bray 1	0.025M HCl + 0.03 NH_4F	3.5	Bray and Kurtz (1945)
Bray 2	0.1M HCl + 0.03M NH_4F	1.0	Bray and Kurtz (1945)
Egner	0.02M Ca acetate + 0.02M HCl	3.8	Egner et al. (1960)
Morgan	0.054M acetic acid + 0.7M Na acetate	4.8	Morgan (1937)
North Carolina	0.05M HCl + 0.0125M H_2SO_4	1.2	Nelson et al. (1953)
Olsen	0.5M $NaHCO_3$	8.5	Olsen et al. (1954a)
Truog	0.001M H_2SO_4 + $(NH_4)_2SO_4$	3.0	Truog (1930)

Section 2.3.2). A comprehensive review of the relationship between the amounts of P extracted by soil-testing procedures and the various forms of soil P is given by Kamprath and Watson (1980). Generally, it can be concluded that alkaline solutions and NH_4F preferentially extract Al-P and acid solutions preferentially extract Ca-P (Kamprath and Watson, 1980). Consequently, some extractants are better suited to particular soils than others and the choice of an extractant will depend largely on the form of P present in a soil. In New Zealand, the bicarbonate extraction (Olsen et al., 1954a) has been the standard procedure for evaluating the P status of soils since 1976 (During et al., 1981). Prior to 1976, the Truog test was used, but this was found to be unsatisfactory because it extracts mainly Ca-P (Grigg, 1965) which is not readily available to plant.

(ii) Anion-exchange resin procedures

The use of anion-exchange resins to assess the availability of soil P was first suggested by Amer et al. (1955), and later used by several workers (e.g., Cooke and Hislop, 1963; Gunary and Sutton, 1967; Zunino et al., 1972; Dalal and Hallsworth, 1976, and Sibbesen, 1978). The removal of P by resins without chemical alteration or pH changes is believed to closely resemble the process of P withdrawal by plant roots (Amer et al., 1955). Anion-resin extractable P is therefore reported to be a highly successful measure of the 'quantity factor' of soil P (Olsen and Khasawneh, 1980).

(iii) Isotopic exchange procedures

When a radioactive P is added to the soil, it mixes with soil solution P and exchanges with surface P, which is in equilibrium with P in solution. This process is called isotopic exchange. Isotopic exchange is usually a rapid process in the first 24 hours and decreases to a slow rate of exchange for days thereafter (Jose and Krishnamoorthy, 1972; White, 1976). Any measurements of isotopically-exchangeable P (E-value), therefore, should specify the time period allowed for equilibration. Isotopically-exchangeable P is regarded as a measure of

labile P, because it refers to the form of P which readily exchanges with solution P (Larsen, 1967). Since the introduction of the isotopic exchange principle by McAuliffe et al. (1947), many workers have suggested that the fraction of soil P which is readily accessible to isotopic exchange may represent the P available to the plant.

A similar approach using isotopic exchange to determine available soil P was proposed by Larsen (1952). In this case, isotopically-exchangeable P is assessed by growing plants and this is known as the 'L-value'. The E-value is therefore the laboratory equivalent of the L-value. Although the concept of E and L values is the same in principle, the estimates are not identical since isotopic exchange occurs under different environmental conditions. Comparisons of these two values have been discussed in detail by Fried and Broeshart (1967) and Larsen (1967). The effects of time, addition of carrier P, presence of extracting chemicals, temperature, and time of pre-equilibration on estimates of isotopically-exchangeable P were reviewed by Fried and Broeshart (1967).

2.3.2.3 Buffering capacity

The P sorption capacity of soil influences the concentration of P in the soil solution by buffering it against any changes following the removal of P by plant uptake or the addition of fertilizer P. It is now well recognised that a knowledge of the buffering capacity of soil with respect to P is an essential part of the characterisation of soil P availability (Olsen and Watanabe, 1963; Mattingly, 1965; Barrow, 1967b; Holford and Mattingly, 1976). Buffering capacity is usually measured from the slope of a sorption isotherm or a quantity/intensity (Q/I) curve. Because the slope of an isotherm changes with the solution concentration, various indices have been used to express this parameter, including the slope at a standard equilibrium solution concentration. A detailed discussion of these soil P buffering indices has been given by Holford (1979). In New Zealand, the P sorption capacity of a soil is determined by the P retention test (Saunders, 1965),

which involves measuring the proportion of P sorbed from an added P solution. An index of buffering capacity is used in conjunction with soil P test results to predict P responses. Buffering capacity measures are more commonly used to assist in determining fertilizer P requirements (i.e., amounts) once the need for fertilizer P has been established by conventional soil tests.

2.3.2.4 Other approaches

A number of workers have commented on the inadequacy of using a single parameter (either intensity or quantity) to assess the availability of soil P (Olsen and Khasawneh, 1980). The reason for such observations is that the availability of soil P depends on the interaction of three factors: intensity, quantity, and buffering capacity (see Section 2.3.2). A number of workers have used approaches combining these parameters and, in general, they have been more successful in evaluating the availability of soil P. For example, a study of the rate of P uptake by cotton (Khasawneh and Copeland, 1973) showed that a term combining the factors of intensity, quantity, and buffering capacity was a better measure of soil P status than either quantity or intensity alone. Gunary and Sutton (1967) also reported that P uptake by ryegrass from a range of soils was better correlated when intensity and quantity factors were considered together. Several workers have demonstrated an improvement in estimating fertilizer P requirements or predicting P responses from conventional soil tests when indices of buffering capacity were included (e.g., Ozanne and Shaw, 1968; Peaslee and Fox, 1978; During et al., 1981).

Other soil measurements, such as soil pH, have also been included in calibration equations for soil P tests (Colwell and Esdaile, 1968; Saunders, 1981). The significance of soil pH can be related to its interactions with the reactions of P in soil as well as to its influence on the suitability of soil-testing procedures. The effects of soil pH on processes affecting the availability of soil P have been discussed in Section 2.2. The influence of soil pH on the choice of soil-testing procedures will be considered in Section 2.3.3.3.

In some tropical regions, organic P measurements have been found to be better related to crop response than inorganic P soil tests (Friend and Birch, 1960). In systems where there is a continual input of organic matter (e.g., native grassland, pasture, and forest systems), it is suggested that measurement of plant-available P should ideally include a measure of potentially mineralisable organic P to explain P uptake by plants (Halm et al., 1972; Stewart and McKercher, 1983). Recently, it has been suggested that soil microbial P could be important in supplying significant amounts of available P to plants and that it could be a useful indicator of P availability in a soil (see Section 2.1.4).

2.3.3 Interpretation of soil test results

The practical usefulness of a soil-testing procedure depends on its ability to predict the availability of soil P and fertilizer P requirements. The former aspect can be evaluated by correlation studies with plants while the latter requires field calibration. The interpretation of soil test results is also influenced by a number of factors, such as soil type, fertilizer history, season, and management practices. These aspects will be briefly discussed here.

2.3.3.1 Correlation studies

The suitability of various soil-testing procedures for assessing P availability can be evaluated by correlating the soil test results with plant growth parameters. Plant growth studies are generally carried out in glasshouses or growth chambers where variability in climatic conditions can be eliminated or minimised. In these correlation studies, it is important that the supply of all essential nutrients except P is adequate and that optimum growth conditions are maintained so that the only limiting factor in plant growth is available soil P (Middleton and Toxopeus, 1973). In a conventional glasshouse experiment, plants are generally grown in the soil until the available pool of soil P is exhausted. This may take a long time depending on the types of plants and

soils. Stanford and DeMent ((1957) proposed a short-term technique which involves an initial establishment of plants without added P in sand and, after a reasonable root system has developed, placing intact plants with the exposed root mat in contact with the soil to be tested. When in contact with soil, these P-deficient plants rapidly absorb P from the soil, enabling the measurement of P uptake to be made within a relatively short period. Another short term glasshouse method is the Neubauer technique (Neubauer and Schneider, 1923), which is based on the uptake of nutrients by a large number of (seedling) plants in a small amount of soil. Results from short-term methods usually agree well with those from the conventional glasshouse studies using longer growth periods and larger amounts of soils (Terman et al., 1958; Stanford and Bouldin, 1962).

Plant growth parameters that are commonly used for correlation studies include yield, P concentration, P uptake (Fitts and Nelson, 1956), and L-value (Larsen, 1967). Extraction methods which provide mainly measurements of P quantity tend to correlate better with P uptake than yield, while the reverse is observed with methods which measure P intensity (Williams, 1962; Williams and Knight, 1963). Relative yields are often used to minimise the variability in soil test correlation data caused by differences in other soil properties (Cate and Nelson, 1971). An excellent summary of results from numerous correlation studies with various soil-testing procedures has been given by Kamprath and Watson (1980).

2.3.3.2 Calibration studies

In order to translate soil test values for P into predictions of plant responses and fertilizer P recommendations, it is necessary to determine, from calibration studies, the relationships between soil test values, rates of fertilizer P addition, and plant growth. Field experimentation is the only means by which the integrated effects of all factors influencing the availability of soil P in the field can be reflected in the soil test calibration.

Experimental data obtained from field studies are greatly influenced by environmental conditions so there is likely to be some degree of scatter of points on a calibration curve. To avoid placing too much emphasis on the actual soil test values, a rating system which expresses the status of available soil P as low, medium, and high has been used in many parts of the world (Thomas and Peaslee, 1973). Detailed discussion on calibration studies of soil-testing procedures has been presented by Cope and Rouse (1973) and Hanway (1973).

2.3.3.3 Factors affecting the interpretation of soil test results

An integral part of the interpretation of soil test results is field calibration. In addition, the interpretation of a soil test result to predict fertilizer P requirements in a particular soil-plant-climate system is also influenced by factors relating to soil properties, management practices, seasons, soil sampling and handling.

(i) Soil properties

Certain soil-testing procedures are better suited to some soils than others because different methods remove different forms of soil P. Consequently, the choice of soil-testing procedure depends largely on the forms of P that are present in a particular soil (Kamprath and Watson, 1980). Numerous studies have shown that the interpretation of soil test values can be improved by taking into account the sorption capacity of a soil (Barrow, 1967a; Ozanne and Shaw, 1967; Helyar and Spencer, 1977; Sinclair et al., 1977; Holford and Mattingly, 1979; During et al., 1981). The suitability of various soil-testing procedures is also influenced by soil pH (Kamprath and Watson, 1980). With calcareous soils, the bicarbonate procedure of Olsen et al. (1954a) is particularly suitable while for neutral and acid soils, the acid ammonium fluoride procedure of Bray and Kurtz (1945) gives reliable results (Mengel and Kirkby, 1982). When interpreting soil test results, the density of the soil should also be considered (Mengel and Kirkby, 1982), particularly with organic soils. Because organic

soils generally have a low bulk density, the expression of soil test results on a weight basis can be misleading. Soil texture can also influence the interpretation of soil test results. Novais and Kamprath (1978) have reported that, at the same soil test level, a fine-textured soil has a greater supply of available P than a coarser-textured soil.

(ii) Management practices

Different amounts of fertilizer P are required for different crops. Under grazed pastures, the requirements of fertilizer P input are usually smaller than in the cropping situation because of the influence of the animal in returning P to the soil. Therefore, management practices must be considered when using soil test values to formulate fertilizer P recommendations.

When fertilizer P is added to soils, its effectiveness declines with time due to the conversion of P into less available forms. Consequently, soil test results vary depending on the time when the soil is sampled after fertilizer application.

The ability of soil-testing procedures to estimate the plant availability of P in soils receiving fertilizer P is also influenced by the types of fertilizer P. For example, the bicarbonate procedure of Olsen et al. (1954a), the acid ammonium fluoride procedure of Bray and Kurtz (1945), and the double water-extraction of Ryden and Syers (1977b) appear to be useful indicators of plant-available P in soils to which essentially water-soluble P fertilizers, such as superphosphate, have been added (Williams and Knight, 1963; Blanchar and Caldwell, 1964; Luscombe et al., 1979; Holford, 1980). When phosphate rock is applied, the Bray method appears to give a better prediction of both the initial and residual effectiveness of phosphate rock (Chien, 1978; Quin, 1981; MacKay et al., 1984). Both the Olsen- and water-extraction procedures were found to predict the residual effectiveness of phosphate rock better than the initial effectiveness (Quin, 1981; MacKay et al., 1984).

Soil pH or lime addition has been found to influence the interpretation of soil test results. This is largely related to the influence of soil pH or liming on the availability of soil P, which has been discussed in Section 2.2.1. Among various soil-testing procedures, the Olsen test (Olsen et al., 1954a) has frequently been reported to be affected by soil pH (Colwell and Esdaile, 1968; Allbrook and Stiefel, 1977; Lambert and Grant, 1980; Davis, 1981; Saunders, 1981; Thomson, 1981; Holford, 1983).

(iii) Seasonal variations

It is commonly observed that soil test results change with the time of sampling. Many workers have reported temporal variations of soil test results but did not observe any consistent patterns (Gallagher and Herlihy, 1963; Mountier and During, 1966; Jessop et al., 1977). Other workers, on the other hand, have found some seasonal patterns of variations in soil test results and have concluded that the accuracy of a soil P test result can be influenced by seasonal fluctuations (Yuen and Pollard, 1951; Blakemore, 1966; Grigg, 1966; Childs and Jencks, 1967; Saunders and Metson, 1971). In many of these studies, significant increases in extractable soil P have been observed in summer and autumn. These increases have been attributed to the release of P from the decomposition of organic matter at a time when plant uptake tends to be limited by a soil moisture deficit (Saunders and Metson, 1971). Low levels of extractable soil P have also been reported during winter and sometimes in early spring (Williams and Simpson, 1965; Saunders and Metson, 1971; Sharpley et al., 1977). Van der Paauw (1962) has noted a negative relationship between rainfall and water-extractable P level in soils. He suggested that during periods of high rainfall, soil P was leached out of the soil sampling zone resulting in low measurements of water-extractable P in soils. This would probably only occur in coarse-textured soils having a low P sorption capacity.

(iv) Soil sampling and sample handling

Variability associated with soil sampling and handling of soil samples can significantly affect the reliability of soil testing for fertilizer advisory purposes. Numerous studies have examined various aspects of this problem, including the effect of sampling area size (Hemingway, 1955; Ball and Williams, 1971; Cameron et al., 1971), the effect of various sampling methods (Hammond et al., 1958; McIntyre, 1967), the effect of sampling depth (Halstead et al., 1957; Beckett and Webster, 1971; Sherrell and Saunders, 1974; Friesen and Blair, 1984), and the effect of drying and storage (Barrow and Shaw, 1980; Bartlett and James, 1980; Gillman and Murtha, 1983). Most of these aspects have been discussed in a review by Beckett and Webster (1971). They concluded that most of the soil variability in a uniform field usually expresses itself within a few square metres of a given point and that the variability tends to increase, often slightly, with the size of the area sampled. In reviewing the relative value of various sampling methods, Petersen and Calvin (1965) concluded that systematic sampling was more effective than simple random sampling.

Nutrients accumulate near the soil surface in soils under grazed pastures (Friesen and Blair, 1984). The regular application of fertilizer P to pasture also leads to an accumulation of P in the surface layer of the soil (Sherrell and Saunders, 1974). Plants can absorb different amounts of P from different depths depending upon the pattern of root distribution but it is generally agreed that a high proportion of P is taken up from the top few centimetres of the soil profile (Jackman and Mouat, 1972b; Gillingham et al., 1980; Syers et al., 1984). Friesen and Blair (1984) reported significant decreases in soil test values down the soil profile but found that sampling depth had little effect on the variability of soil test values.

Moist soil samples collected from the field are normally air-dried before analysis. Air-drying can alter the chemical, physical, and microbiological properties of

a soil from its field condition. Many of the changes caused by drying appear to be associated with changes in surface chemical properties and in solubilising organic matter (Bartlett and James, 1980). Air-drying has been reported to both increase (Barrow and Shaw, 1980; Bartlett and James, 1980; Haynes and Swift, 1984) and decrease (Gillman and Murtha, 1983) the P-sorption capacity of soils. Gillman and Murtha (1983) have suggested that the effect of drying on P sorption capacity depends on soil type. Comparing the analysis of field moist and air-dried soil samples, Bartlett and James (1980) found that water-extractable P was considerably higher in air-dried than in moist soils.

2.4 Development of a Water-Extraction Technique as a Soil-Testing Procedure

Water extraction of soil P is one of many empirical soil-testing procedures which have been evaluated by several workers (Bingham, 1949; Martin and Buchanan, 1950; Olsen et al., 1954b; Larsen et al., 1958; Thompson et al., 1960; Hagin et al., 1963; van Diest, 1963; Blanchar and Caldwell, 1964; McLean et al., 1964; Williams, 1967; van der Paauw, 1971; Aura, 1978; Orphanos, 1978; Luscombe et al., 1979). The soil:solution ratio used in these methods has ranged from 1:4 (Bingham, 1949) to 1:400 (Aura, 1978). When a relatively small volume of water is used, the method is believed to reflect the intensity factor of soil P. With a wider soil:solution ratio, both the intensity and capacity of P supply will be reflected (van der Paauw, 1971). The amounts of soil P removed by water extraction are generally small and often present difficulties in the analysis. A common problem encountered in the water-extraction technique is the difficulty in obtaining a clear extract. These analytical problems are probably partly responsible for the variable success in using the water-extraction method as a soil-testing procedure.

In their summary of several water-extraction techniques, Nelson et al. (1953) have concluded that water-extraction techniques are particularly suitable for

prediction of fertilizer P responses in soils with low "ability to fix or release inorganic P" (i.e., low buffering capacity) such as sandy soils. A water-extraction technique developed by van der Paauw (1971) has been used successfully with arable soils in the Netherlands. Although the method was well-correlated with plant responses on a wide range of soils from different countries and was independent of soil type, the correlations were considerably poorer on permanent grassland soils (van der Paauw, 1974). He suggested that differences in uptake characteristics (e.g., uptake zone and root density) between arable crops and pastures may influence the utilisation of soil P, thereby affecting the relationship between soil P and plant growth.

Recently, Ryden et al. (1976) has proposed a non-empirical water-extraction method as a soil-testing procedure for P. The method is based on a sorption model which describes two distinct forms of P, namely chemi-sorbed P, and more-physically sorbed P (see Section 2.2.1.3). The properties of more-physically sorbed P have suggested an identity with the labile pool of P, as defined by other workers. It was found that the more-physically sorbed P was essentially quantitatively removed by water extraction (Ryden et al., 1976; Ryden and Syers, 1977b). Because the water extraction appears to be specific for more-physically sorbed P, it may provide a non-empirical estimate of the amount of readily-available P in a soil which should be independent of soil type. A glasshouse experiment (Luscombe et al., 1979), using perennial ryegrass grown in three contrasting soil types, confirmed that the water-extraction technique is independent of soil type. In contrast, Smith and Gregg (1982) found a marked soil type dependence of the water-extraction method, compared to the relative independence of the Olsen test. In the glasshouse investigation of Smith and Gregg (1982), both intact soil cores and sieved soil samples were collected from a number of sites of varying soil P status, but only two soil types were used. The inconsistency regarding the influence of soil type on water extraction suggests that further

investigations, involving a wider range of soil types are needed.

The original water-extraction method proposed by Ryden et al. (1976) involves two successive 1-hour extractions of 1 g soil with 40 ml of distilled water. It was later modified to a single extraction which would be more suitable as a routine procedure. A single water-extraction technique, which was closely related to the original double water-extraction method, involves a 1-hour extraction of 2 g soil with 240 ml of distilled water (Tillman, pers. comm.). The technique requires high speed centrifugation and filtration using membrane filters (Millipore, <450 nm) to ensure that clear solutions are obtained.

2.5 Summary and Conclusions

This review has focused on the origin and characterisation of plant-available P in soils. There appears to be a general agreement in the literature that sorption-desorption reactions are the most important processes that control the P concentration in the soil solution. Despite the abundant studies of these processes, the mechanisms of sorption-desorption reactions are not fully understood. However, attempts to use various modelling approaches for describing or predicting the behaviour of P in soil have been met with greater success.

A water-extraction technique is a soil-testing procedure which is based on a concept of P sorption (Ryden et al., 1976). Compared to other empirical soil-testing procedures, the water-extraction procedure may therefore be expected to better reflect the availability of soil P. Furthermore, the water-extraction procedure may be of value in modelling the relationships between fertilizer P and soil, and thus the prediction of the availability of fertilizer P. Further investigation into the potential of the water-extraction procedure is needed.

Organic forms of soil P are also an important source of available P for plants following mineralisation. The rates

and pathways of P through soil organic matter are, however, poorly understood when compared to physico-chemical aspects of soil inorganic P. Recent development of methods for measuring microbial P in soil has enabled the contribution of microbial biomass to the availability of soil P to be investigated. Further research into the dynamics of soil organic P and microbial P is required. This will improve our understanding of the P cycle and assist in the assessment of availability of soil P to plants. Ultimately, it should lead to improved fertilizer management practices.

CHAPTER 3

CHAPTER 3

PREDICTION OF PLANT-AVAILABLE P IN SOILS USING A COMBINATION OF WATER-EXTRACTABLE P AND AN ESTIMATE OF P BUFFERING CAPACITY

3.1 Introduction

A number of soil-testing procedures have been used, with varying degrees of success, to determine the P status of soils and to assist in making fertilizer recommendations. Extraction procedures are regarded as being suitable if they successfully predict responses and are sufficiently simple to be used on a routine basis. The origin and amount of soil P extracted by these empirical procedures depend on the chemical nature of the extractant and the extraction conditions used. Some extractants are better suited to certain soil types than others, but all usually require extensive field calibration.

Ideally soil-testing procedures should be based on a sound understanding of nutrient availability. Schofield (1955) proposed that at least three factors interact with each other to determine the relationship between plant uptake of P and soil P status: (i) an intensity factor (I) describes the concentration of P in the soil solution; (ii) a quantity term (Q) is a measure of the amount of P associated with the solid phase; and (iii) a buffering capacity term ($\Delta Q/\Delta I$) measures the ability of a soil to maintain the P concentration of the soil solution against changes caused by plant uptake or fertilizer addition. Most soil-testing procedures characterise either the quantity or the intensity factor, or both (Kamprath and Watson, 1980). Weak extractants, such as water and calcium chloride solutions, are thought to reflect the intensity factor while stronger extractants, such as acids, complexing ions, and alkaline-buffered solutions, measure the quantity factor.

The failure of soil-testing procedures to take into account the interrelationship between all three parameters (Q, I, and buffering capacity) probably explains why a single parameter is inadequate for predicting P availability in a range of soils (Olsen and Khasawneh, 1980).

Because plant roots can only absorb P from the soil solution, the concentration of P in the soil solution must be maintained at a satisfactory level for plant growth. Consequently, P availability depends not only on the concentration of soil solution P at any time, but also on the ability of the soil to maintain that concentration. Several studies of nutrient movement in soils and root uptake (e.g., Barber, 1962; Olsen and Watanabe, 1963; Lewis and Quirk, 1967) have indicated an appreciable depletion of soil P around plant roots and that the soil solution P must be renewed several times each day during the growing season. These workers concluded that the buffering capacity of a soil is potentially a limiting factor for P uptake by plants. More recently there have been several plant uptake studies which have indicated that soil P status can be predicted better when intensity, quantity, and buffering capacity parameters are considered together (e.g., Gunary and Sutton, 1967; Khasawneh and Copeland, 1973; Dalal and Hallsworth, 1976; Holford and Mattingly, 1976).

In New Zealand, there has been a limited number of studies which have examined the use of a combination of intensity or quantity and buffering capacity parameters to describe soil P status. The work of Sinclair et al. (1977) with soils from the Mackenzie Basin, indicated that the sorption properties of the soil strongly modify the availability of both native and applied P to pasture plants. They suggested that bicarbonate P (Olsen et al., 1954a) and buffering capacity measurements should be used together in predicting responses to fertilizer P. During et al. (1981) investigated the effectiveness of the phosphate retention (PR) test (Saunders, 1965), combined with the Olsen or with the Truog soil test, for estimating fertilizer P requirements. It was found that a model in which the PR test was

combined with Olsen P or Truog P values accounted for 56 and 69%, respectively, of the variation in P requirements. Although the inclusion of the PR term improved the accuracy of predicting fertilizer P requirements, the model applied only to a certain soil group with a limited range of sorption capacity values. In another study relating to a programme for the maintenance fertilizer P requirements of a group of Northland soils, Shannon (1981) proposed that the Olsen P test should be used in conjunction with the PR test; however, no results have been made available.

Recently a model for calculating maintenance P requirements of grazed pastures has been proposed by Cornforth and Sinclair (1982). It is based on estimates of P losses with various combinations of stock and land type. Soil P losses due to sorption and immobilisation are among the factors incorporated in the calculation. A soil P test (Olsen) is used in the model to assess whether the level of available soil P is appropriate for a maintenance fertilizer application and to monitor the effectiveness of the maintenance fertilizer P programme calculated by the model.

In the present study, an attempt was made to predict the amount of plant-available P in soils by using a combination of water-extractable P (as an intensity parameter) and an estimate of buffering capacity. Two approaches were used to determine buffering capacity. The first method was the PR test which is designed to measure the proportion of fertilizer P likely to be retained by a soil (Saunders, 1965). The second was based on the desorption characteristics of a soil. It was considered that an estimate of buffering capacity based on desorption, which indicates the ability of the soil to replenish P, might better reflect the real situation than an estimate based on sorption.

3.2 Materials and Methods

3.2.1 Soils

Twenty top soils were chosen to cover a wide range of P sorption capacity, P status, and pH. They were collected from sites under permanent pasture which had received no fertilizer P in the year prior to the sampling. The soils were sampled to a depth of 7.5 cm, air-dried, and sieved (<2 mm).

3.2.2 Soil properties

Soil pH was measured in distilled water at a soil: solution ratio of 1:2.5, after a 24-h equilibration period. Total carbon (C) was determined by the method of Tabatabai and Bremner (1970) using a Leco Gravimetric Carbon Determinator. The soil description and some chemical characteristics of the 20 soils studied are given in Table 3.1.

3.2.3 Glasshouse study

The plant availability of P in the 20 soils was determined in a glasshouse experiment, The technique used was designed to measure the potential amount of plant-available P in the soils. Plant uptake of P is used in this study as a measure of plant-available P in the soil. The air-dried soils (<2 mm) were hand packed into 600-ml pots and filled to a volume of approximately 500 ml. The known weight of each soil per pot varied from 400 to 500 g depending on its bulk density. The soils were then watered to 90% of field capacity. Perennial ryegrass (Lolium perenne L., Grasslands "Nui") was used as the test plant and approximately 30 seeds were sown and later thinned to 20 plants per pot. A minus-P nutrient solution (Middleton and Toxopeus, 1973) was applied regularly and moisture was maintained at 90% of field capacity by daily watering. Four harvests were taken at 7, 12, 16, and 21 weeks after sowing. Plants were cut to a level of 1 cm above the soil surface. At each harvest, two pots of each soil were removed from the trial and the roots separated from the soil by washing with water. The soils were air-dried, sieved (<2 mm), and

Table 3.1 Description and some chemical characteristics of the 20 soils used in this study

Soil type	New Zealand Soil Group	Total carbon (%)	pH water
1. Carnarvon black sandy loam	yellow-brown sand	8.1	5.74
2. Dannevirke silt loam	yellow-brown earth/ yellow-brown loam intergrade	8.7	5.80
3. Egmont brown loam (low P)	yellow-brown loam	7.5	5.69
4. Egmont black loam (high P)	yellow-brown loam	8.2	5.80
5. Hamilton clay loam	brown granular loam	6.0	5.07
6. Kiwitea silt loam	yellow-brown earth/ yellow-brown loam intergrade	3.5	5.64
7. Konini silt loam	yellow-brown earth/ yellow-brown loam intergrade	4.0	5.55
8. Kumeroa silt loam (low P)	yellow-grey earth/ yellow-brown earth intergrade	5.8	5.83
9. Kumeroa silt loam (high P)	yellow-grey earth/ yellow-brown earth intergrade	4.6	5.27
10. Manawatu fine silt loam	recent soil	2.1	5.12
11. Okaihau gravelly clay	brown granular loam	7.0	5.46
12. Patua loam	yellow-brown loam	11.3	5.51
13. Ramiha silt loam (low P)	yellow-brown earth/ yellow-brown loam intergrade	6.7	5.16
14. Ramiha silt loam (high P)	yellow-brown earth/ yellow-brown loam intergrade	6.6	5.42
15. Taupo sandy silt (low P)	yellow-brown pumice soil	6.7	5.41
16. Taupo sandy loam (high P)	yellow-brown pumice soil	9.6	5.42
17. Tokomaru silt loam (low P)	yellow-grey earth	3.0	5.36
18. Tokomaru silt loam (medium P)	yellow-grey earth	3.3	5.24
19. Tokomaru silt loam (high P)	yellow-grey earth	4.5	6.37
20. Wainui silt loam	yellow-grey earth/ yellow-brown earth intergrade	4.5	5.25

analysed for pH (Section 3.2.2), water-extractable P (Section 3.2.4.1), and Olsen-extractable P_i (Section 3.2.4.2). The above-soil herbage and the root material were dried at 60°C, weighed, and analysed for P by the method of Twine and Williams (1971).

Four pots of each soil received a complete nutrient solution. Ryegrass from these pots was harvested at the same time as that from pots receiving minus-P nutrient solution. The above-soil herbage was analysed for P at all four harvests but the root material was not collected and analysed for P until the final harvest. The relative P uptake was calculated from P uptake on a soil receiving a minus-P nutrient solution, expressed as a percentage of P uptake by plants growing in pots receiving a complete nutrient solution. Relative yield was also calculated in the same way. As a control, two more pots of each soil were not sown with ryegrass but received an identical treatment to the ones with plants. At each harvest, two cores (2-cm diameter) of soil were taken from each plant-free pot, combined, air-dried, sieved (<2 mm), and analysed for water-extractable P (Section 3.2.4.1), Olsen-extractable P_i (Section 3.2.4.2), and pH (Section 3.2.2). The pots were completely randomised and re-positioned every week to minimize any effects of uneven environmental factors, such as light and temperature. After the second harvest, all pots were leached with 2,000 ml of distilled water to remove any excess nutrients which had accumulated. A total of 14 pots was used for each soil.

3.2.4 Soil P analysis

3.2.4.1 Water-extractable P (Single-water extraction)

The procedure involves shaking 2 g of air-dried soil (<2 mm) with 240 ml of distilled water at 20°C for 1 h. The samples were shaken in 250-ml polyethylene bottles on an end-over-end shaker at 28 r.p.m. On the completion of shaking, the suspension was filtered through a membrane filter (Millipore, <450 nm).

3.2.4.2 Olsen-extractable P_i (Olsen et al., 1954a)

One g of air-dried soil (<2 mm) was shaken with 20 ml of 0.5M $NaHCO_3$ (pH 8.5) at 20°C for 30 min. The suspension was then centrifuged at 10,000 r.p.m. for 2 min and filtered through a Whatman No. 5 filter paper. A 4-ml aliquot of the extract was then taken for analysis of inorganic P. Total P in the extract was also determined after the conversion of organic P to inorganic P by acid persulphate digestion (Environmental Protection Agency, 1971). Organic P in the Olsen extract was calculated from the difference between inorganic P in the extract before and after acid digestion.

3.2.4.3 Bray$_1$-extractable P (Bray and Kurtz, 1945)

Three g of air-dried soil (<2 mm) was shaken with 21 ml of 0.03M NH_4F and 0.025M HCl solution for 5 min. The suspension was centrifuged and filtered as above.

3.2.4.4 Truog-extractable P (Truog, 1930)

One g of air-dried soil (<2 mm) was shaken with 200 ml of 0.001M H_2SO_4 (pH 3.0) for 30 min and then centrifuged and filtered as above.

3.2.4.5 Isotopically-exchangeable P

1.5g of air-dried soil (<2 mm) was shaken with 30 ml of distilled water containing approximately 2 μCi ^{32}P (as carrier-free $H_3{}^{32}PO_4$) at 20°C for 24 h. After centrifugation at 10,000 r.p.m. for 5 min, the soil suspension was filtered through a membrane filter (Millipore, < 450 nm), and the extract analysed for ^{31}P and ^{32}P. The activity of ^{32}P was determined by liquid scintillation counting using a Triton-toluene scintillation cocktail (Patterson and Greene, 1965).

3.2.4.6 Total organic P (Walker and Adams, 1958)

Samples of 0.8 g of air-dried soil (<2 mm) were ashed at 550°C for 1 h, then shaken with 40 ml of 0.5M H_2SO_4

for 16 h, and centrifuged at 10,000 r.p.m. for 10 min. Samples were also extracted without prior ashing. Total organic P was calculated as the difference between the amounts of P in the extracts from samples with and without an ashing pretreatment.

3.2.4.7 Phosphate retention (PR) (Saunders, 1965)

Five g of air-dried soil (<2 mm) was shaken for 24 h with 25 ml of 0.2M sodium acetate solution containing 1,000 μgP ml^{-1} (as KH_2PO_4) and adjusted to pH 4.65 with glacial acetic acid. After centrifugation and filtration, the extracts were analysed for P. Phosphate retention was calculated from the amount of P removed from solution by the soil, expressed as a percentage of the amount originally added.

3.2.4.8 An estimate of buffering capacity based on desorption

When the concentration of P in the soil solution is decreased, more P will invariably be desorbed from the soil and released into the soil solution. In this study, the soil solution P concentration was decreased by increasing the soil:solution ratio. Soils were shaken with distilled water containing 40 μg $HgCl_2$ ml^{-1} to suppress microbial activity. The soil:solution ratios were 1:5, 1:20, 1:40, 1:80, and 1:120. A preliminary experiment was carried out on four soils (Dannevirke, Kumeroa-low P, Kumeroa-high P, and Ramiha-low P) to determine the period of time required for shaking. It was found that, initially, desorption of P occurred rapidly but after 24 h the change became significantly slower, except at the soil:solution ratio of 1:5 (Fig. 3.1). The rapid rate of P desorption at this soil:solution ratio continued after 24 h in three soils. Consequently, a shaking period of 24 h was adopted for this desorption study. Samples were shaken on an end-over-end shaker at 20°C. After 24 h they were centrifuged at 10,000 r.p.m. for 10 min, and filtered

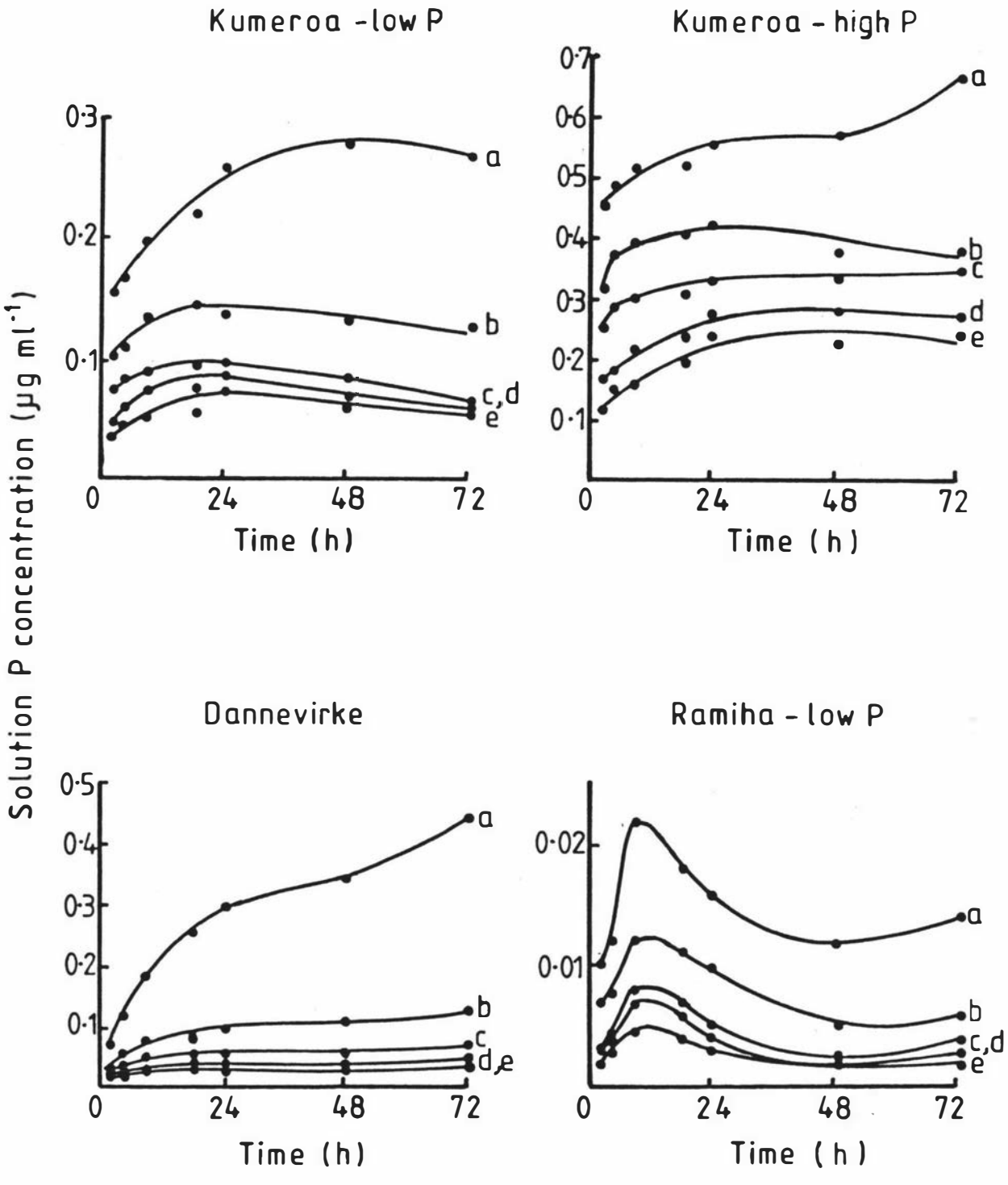

Figure 3.1 Relationship between solution P concentration and time of desorption at a soil:solution ratio of 1:5 (a), 1:20 (b), 1:40 (c), 1:80 (d), and 1:120 (e) for four soils

through membrane filters (Millipore, <450 nm). To prevent any interference from mercury (Hg), 1 ml of NaCl solution containing 5,000 μgCl was added to the aliquot of extract before the analysis of P (Tillman and Syers, 1975). The amounts of P desorbed were calculated and plotted against the concentrations of P in solution, giving a desorption isotherm for each soil.

If required, suspensions were centrifuged in a Sorvall RC2-B refrigerated centrifuge (at 10°C). The method of Murphy and Riley (1962) was used for the analysis of inorganic P (^{31}P) in all soil extracts. Absorbance was measured at 712 nm using either a Pye Unicam 1800B or SP8-300 spectrophotometer.

3.3 Results and Discussion

3.3.1 Plant-available P

Total P uptake by ryegrass from the 20 soils after a growth period of 21 weeks in the glasshouse experiment ranged from 7.5 μg g^{-1} soil with Ramiha-low P soil to 150 μg g^{-1} soil with Egmont-high P soil (Table 3.2). The ryegrass plants became very P deficient as the trial progressed. At the end of 21 weeks the rate of P uptake was only a small fraction of the rate maintained by plants growing in pots receiving a complete nutrient solution, including P (Table 3.3). Consequently, it is suggested that the pool of plant-available P in most of the soils was virtually at or near exhaustion after 21 weeks. However, in soils of high P status, this pool may not be exhausted completely. For example, similarly large amounts of P were taken up from Egmont-high P soil in the final harvest (harvest 4) in comparison with earlier harvests (Table 3.4). It is possible that in such high P soils plant uptake data may underestimate the pool of plant-available P. The implication of this possibility will be discussed later.

3.3.2 Water-extractable P

The amount of water-extractable P in the 20 soils before cropping ranged from 1.2 μg g^{-1} soil in the

Table 3.2 Plant-available P and various measurements of soil P for the 20 soils used in the study (All units are $\mu g\ g^{-1}$ except where indicated)

Soil	Plant available P*	Water-extractable P	Olsen-extractable** P_i	Olsen-extractable** P_o	Isotopically-exchangeable P	Bray P	Truog P	PR# (%)	$Slope_{DI}$## ($ml\ g^{-1}$)	Organic P
1. Carnarvon	15.8	3.8	8.9	17.3	26.7	10.7	25.6	45	15.5	560
2. Dannevirke	20.6	4.6	22.7	19.2	121.4	18.8	48.7	91	2.1	1235
3. Egmont-low P	8.1	1.8	12.0	12.3	119.9	16.1	28.3	82	0.8	1300
4. Egmont-high P	150.2	18.4	58.6	66.2	182.4	79.5	82.5	75	4.8	1531
5. Hamilton	11.6	3.2	13.6	19.7	44.7	14.1	21.0	66	8.5	371
6. Kiwitea	27.3	3.7	10.7	15.0	43.1	13.9	27.8	40	2.8	649
7. Konini	30.3	4.4	12.3	13.9	42.7	10.6	17.0	43	25.0	396
8. Kumeroa-low P	18.0	5.7	9.0	13.4	31.4	10.6	15.6	30	24.5	589
9. Kumeroa-high P	68.4	13.0	32.6	19.3	67.0	44.1	38.6	30	27.2	568
10. Manawatu	67.9	5.1	25.4	6.0	74.7	46.4	87.6	19	-	309
11. Okaihau	43.5	5.6	20.6	9.4	107.1	30.1	64.1	45	5.4	223
12. Patua	8.6	2.2	11.8	12.5	66.0	4.7	12.1	98	0.1	1229
13. Ramiha-low P	7.5	1.2	6.2	15.7	20.9	2.4	5.7	88	14.9	585
14. Ramiha-high P	78.5	6.7	25.7	10.0	71.6	43.6	43.2	55	9.4	653
15. Taupo-low P	18.0	3.0	18.0	16.8	45.7	25.3	37.0	53	21.0	596
16. Taupo-high P	90.9	7.8	40.0	18.6	91.5	37.4	94.0	67	25.0	853
17. Tokomaru-low P	34.8	6.7	16.3	17.0	32.0	21.0	19.4	19	43.7	417
18. Tokomaru-medium P	70.5	9.9	21.1	14.6	42.3	30.7	34.0	14	28.0	437
19. Tokomaru-high P	136.8	23.6	35.2	16.2	102.2	44.9	74.3	21	54.2	499
20. Wainui	41.7	4.9	12.7	22.1	57.2	7.0	12.4	36	34.2	482

* Determined by uptake of P by ryegrass in 21 weeks in the glasshouse.

** Inorganic and organic fractions in Olsen extracts (Olsen et al., 1954).

Phosphate retention test (Saunders, 1965).

An estimate of buffering capacity derived from slope of desorption isotherm (Section 3.2.3 (vii)).

Table 3.3 Relative P uptake by ryegrass from the 20 soils studied in the glasshouse experiment at harvest 4 (21 weeks)

Soil	Relative P uptake (%)
1. Carnarvon	9
2. Dannevirke	12
3. Egmont-low P	5
4. Egmont-high P	59
5. Hamilton	7
6. Kiwitea	14
7. Konini	13
8. Kumeroa-low P	7
9. Kumeroa-high P	23
10. Manawatu	25
11. Okaihau	19
12. Patua	6
13. Ramiha-low P	6
14. Ramiha-high P	31
15. Taupo-low P	9
16. Taupo-high P	33
17. Tokomaru-low P	15
18. Tokomaru-medium P	24
19. Tokomaru-high P	40
20. Wainui	21

Table 3.4 Uptake of P by ryegrass from the 20 soils used in the glasshouse experiment at each harvest

	Soil	Plant P uptake ($\mu g\ g^{-1}$)			
		Harvest 1	Harvest 2	Harvest 3	Harvest 4
1.	Carnarvon	4.7	3.9	4.9	2.3
2.	Dannevirke	4.7	8.1	7.5	0.3
3.	Egmont-low P	3.3	1.1	4.3	-0.6*
4.	Egmont-high P	34.6	39.0	37.0	39.6
5.	Hamilton	6.3	0.5	6.8	-2.0
6.	Kiwitea	14.5	4.9	6.8	1.1
7.	Konini	12.6	10.3	2.0	5.4
8.	Kumeroa-low P	7.4	5.4	-0.4	5.6
9.	Kumeroa-high P	15.5	15.6	15.0	22.3
10.	Manawatu	17.7	16.4	12.9	20.9
11.	Okaihau	12.9	8.4	12.9	9.3
12.	Patua	5.8	1.8	1.1	-0.1
13.	Ramiha-low P	4.5	0.6	0.8	1.6
14.	Ramiha-high P	19.9	26.1	18.5	14.0
15.	Taupo-low P	9.5	1.6	7.9	-1.0
16.	Taupo-high P	22.7	24.0	18.7	25.5
17.	Tokomaru-low P	14.9	8.8	3.8	7.3
18.	Tokomaru-medium P	27.9	15.9	10.7	16.0
19.	Tokomaru-high P	41.8	40.7	30.8	23.5
20.	Wainui	19.5	8.7	6.8	6.7

* Negative uptake was due to death of existing roots exceeding new growth.

Ramiha-low P soil to 23.6 μg g^{-1} soil in the Tokomaru-high P soil (Table 3.2). Water-extractable P values were considerably smaller than estimates of plant-available P indicated by total P uptake by ryegrass over 21 weeks. The relatively low values were expected because water or other weak extractants are considered to reflect the intensity parameter (i.e., soil solution P) which is normally small (Williams and Knight, 1963). Nevertheless, water-extractable P in the 20 soils was closely related to plant-available P ($r = 0.90^{**}$)(Fig. 3.2a). This high correlation supports the findings of a number of workers who have also reported that the water-extraction method provides a good indication of P availability in a wide range of soils (e.g., Bingham, 1949; Thompson et al., 1960; van der Paauw, 1971; Luscombe et al., 1979). In these studies, the amount of soil P extracted by water was found to correlate well with relative yield, yield responses to applied P, or with prediction of fertilizer P requirements. In the present study, significant correlations were also found between water-extractable P and a number of other plant growth parameters, including total dry matter yield, relative dry matter yield, relative P uptake, and herbage P content (Table 3.5). The 20 soils used in this study covered a wide range of soil types and textures (Table 3.1), and varied considerably in their P status and buffering capacity (Table 3.2). The results are consistent with the findings of Ryden et al. (1976) and Luscombe et al. (1979) who confirmed the suggestion of van der Paauw (1971) that the water-extraction method is not greatly affected by soil type. In contrast, Smith and Gregg (1982) reported that water-extractable P was dependent on soil type. They examined, in a glasshouse experiment, the relationship between water-extractable P and relative yield of pasture on two soil types which had different buffering capacities and were collected from sites of varying P status. It was found that closer relationships were obtained among samples of the same soil type than when the two soil types were considered together. Although there was a large number of samples of different P status for each soil type, only two soil types were used. In the present

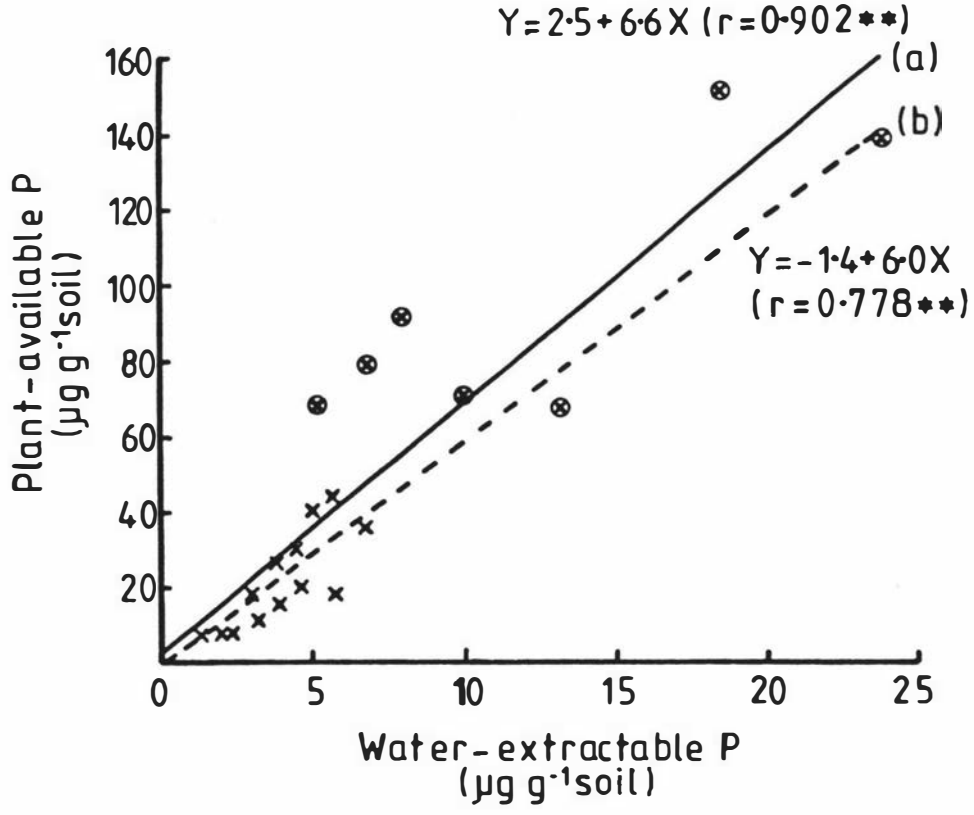

Figure 3.2 Relationship between plant-available P and water-extractable P for the 20 soils (a) and for the 13 selected soils (b), excluding seven soils of high P status (⊕ = excluded soils)

Table 3.5 Correlation coefficients between water-extractable P and various parameters relating to ryegrass growth on the 20 soils studied

Parameter	r
Total P uptake	0.90**
Relative P uptake	0.83**
Total dry matter yield	0.85**
Relative dry matter yield	0.81**
% herbage P	0.90**

* Significant at 5% level

** Significant at 1% level

study, 14 different soil types were used, including soils of different P status for some soil types. When a comparison was made between relative yield and water-extractable P, some differences were obtained between soil types (Fig. 3.3a). However, the differences were within the error limit of the overall relationship (Fig. 3.3b), which was found to be highly significant ($r = 0.87^{**}$). It appears that the limited number of soil types used in the study of Smith and Gregg (1982) explains their finding of the dependence of the water-extraction procedure on soil type.

Evidence from the glasshouse experiment suggests that some high P status soils may not have been exhausted completely after ryegrass was grown for 21 weeks (Section 3.3.1). Water-extractable P values in the 20 soils after 21 weeks (Table 3.6) suggested that 13 soils were at or near exhaustion while the other seven still had water-extractable P values of more than 2 $\mu g\ g^{-1}$ soil. The effect of incomplete exhaustion would be to underestimate plant-available P in soils with high initial water-extractable P values. A regression line between plant-available P and water-extractable P would then have a lower slope than normal. However, in this study there was very little difference in the slopes of the regression lines whether the seven high P soils were included or not (Fig. 3.2). Furthermore, the exclusion of these seven soils did not improve the correlation coefficient for the relationship between plant-available P and water-extractable P ($r = 0.90^{**}$ for all 20 soils, $r = 0.78^{**}$ for 13 soils only). Therefore, herbage data for all 20 soils will be considered in this study.

3.3.3 Olsen-extractable P

The amount of Olsen-extractable P_i in the 20 soils studied varied between 6.2 $\mu g\ g^{-1}$ soil in the Ramiha-low P soil and 58.6 $\mu g\ g^{-1}$ soil in the Egmont-high P soil (Table 3.2). The quantity of Olsen-extractable P_i was less than the amount of plant-available P in most, but not all soils. Exceptions include the Dannevirke, Egmont-low P, Hamilton, Patua, and Taupo-low P soils. In these soils, values of

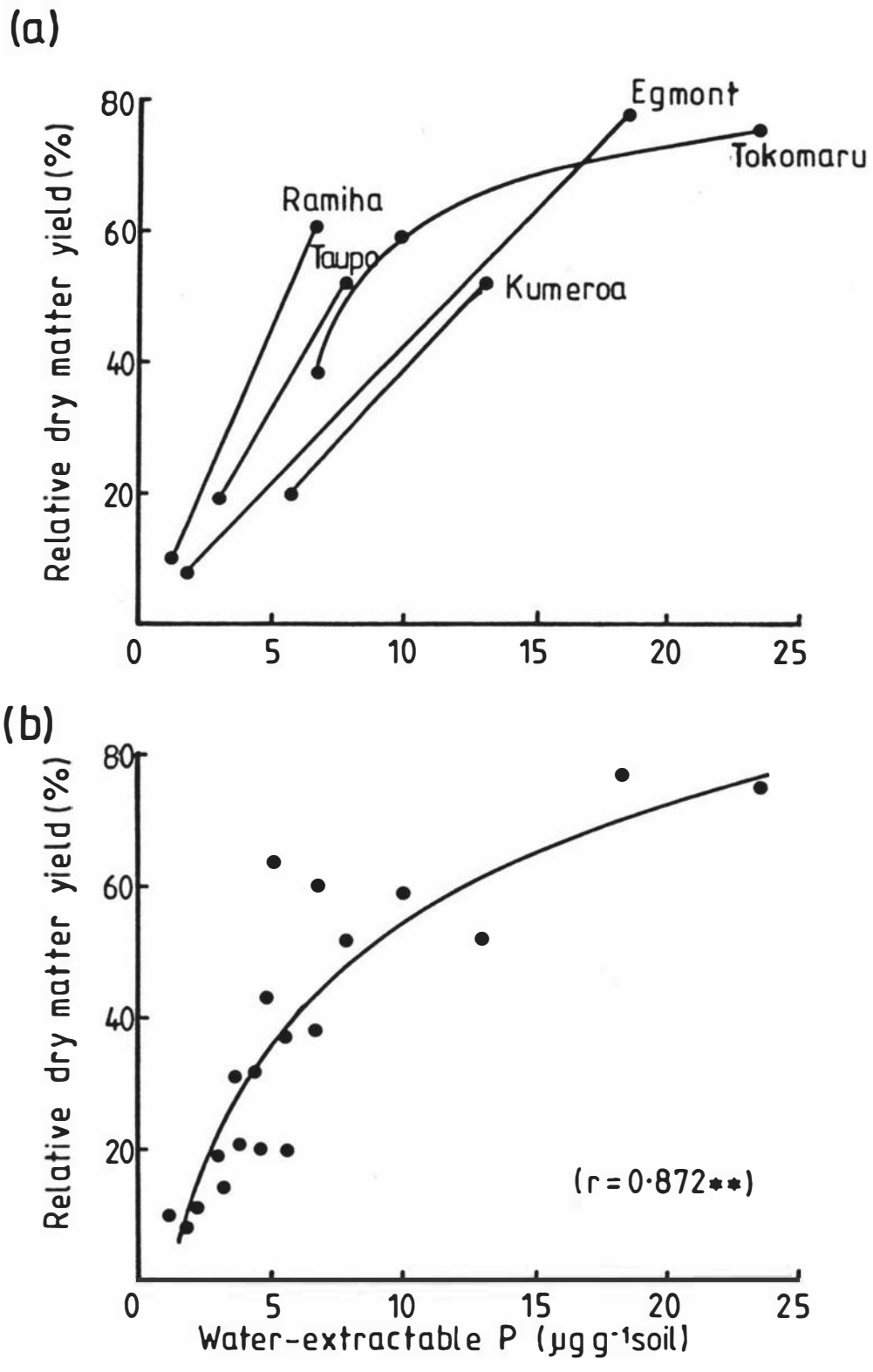

Figure 3.3 Relationship between relative dry matter yield of ryegrass and water-extractable P for individual soil types (a) and for the 20 soils studied (b)

Table 3.6 Water-extractable P in the 20 soils studied before and after growing ryegrass for 21 weeks in the glasshouse

Soil	Water-extractable P ($\mu g\ g^{-1}$)	
	Initial	After 21 weeks
1. Carnarvon	3.8	1.3
2. Dannevirke	4.6	0.7
3. Egmont-low P	1.8	0.5
4. Egmont-high P	18.4	7.6
5. Hamilton	3.2	0.9
6. Kiwitea	3.7	1.3
7. Konini	4.4	1.2
8. Kumeroa-low P	5.7	1.3
9. Kumeroa-high P	13.0	6.4
10. Manawatu	5.1	5.1
11. Okaihau	5.6	1.8
12. Patua	2.2	0.4
13. Ramiha-low P	1.2	0.4
14. Ramiha-high P	6.7	2.4
15. Taupo-low P	3.0	1.0
16. Taupo-high P	7.8	2.2
17. Tokomaru-low P	6.7	1.7
18. Tokomaru-medium P	9.9	3.3
19. Tokomaru-high P	23.6	7.6
20. Wainui	4.9	1.3

Olsen-extractable P_i were slightly higher than, or similar to those for plant-available P. There was no apparent reason for these exceptions apart from the fact that they are all low P status soils and have medium to high PR (Table 3.2).

Plant-available P in the 20 soils studied was highly correlated with Olsen-extractable P_i ($r = 0.90^{**}$, Table 3.7). This is consistent with the results of a number of studies which indicate that the Olsen procedure is a reliable index of plant-available P in soils (Olsen et al., 1954a; Blanchar and Caldwell, 1964; Kamprath and Watson, 1980). The correlation coefficient for the relationship between plant-available P and Olsen-extractable P_i was found to be as high as that for the water-extractable P (Table 3.7).

3.3.4 Estimate of buffering capacity

The buffering capacity of the 20 soils, as measured by the PR method, varied from 14% in the Tokomaru-medium P soil to 98% in the Patua soil (Table 3.2). For soils with the same amount of water-extractable P, plant P uptake was found to increase with increasing PR. This is illustrated by the first two examples in Table 3.8, where comparisons were made between the Tokomaru-low P and the Ramiha-high P soils, and between the Kumeroa-low P and the Okaihau soils. This finding supports the concepts proposed by Khasawneh (1971) that, in soils of equal P intensity, P uptake should be proportional to buffering capacity. This is the case because the higher the buffering capacity the more P is desorbed as the intensity is decreased by root uptake. However, the opposite effect was observed in the third example (Table 3.8), where there was only a small difference between the PR values of the two soils. In this case differences in other factors, such as organic P levels, pH, and texture, may have a more significant influence on plant growth than the small difference in P buffering capacity. It appears that PR values help to explain the differences in P uptake from soils having similar water-extractable P value only when their PR values differ widely. In other words, such relationship between water-extractable P, PR, and plant uptake of P is not universal to all soils.

Table 3.7 Correlation coefficients for the relationships between various measurements of available soil P and plant-available P for the 20 soils studied

Available soil P	r
Water-extractable P	0.90**
Olsen-extractable P_i	0.90**
Bray P	0.89**
Truog P	0.76**
Isotopically-exchangeable P	0.59**

Table 3.8 Comparison of plant uptake of P from soils with equal amounts of water-extractable P and contrasting P retention (PR) values

Example	Soil	Water-extractable P ($\mu g\ g^{-1}$)	PR (%)	Uptake P ($\mu g\ g^{-1}$)
1	Tokomaru-low P	6.7	19	34.8
	Ramiha-high P	6.7	55	78.5
2	Kumeroa-low P	5.7	30	18.0
	Okaihau	5.6	45	43.5
3	Kiwitea	3.7	40	27.3
	Carnarvon	3.8	45	15.8

The PR test was developed to measure P sorption capacity and to give a measure of the ability of a soil to retain P from added fertilizer (Saunders, 1965). However, uptake of P by plants is governed by the ability of a soil to supply P to plant roots or by the desorption capacity of a soil. Many workers have shown that desorption does not follow the same pathway as sorption (e.g., Kafkafi et al., 1967; Syers et al., 1970; Hingston et al., 1974; Munns and Fox, 1976; Barrow, 1983b). Consequently, it was considered in this study that an estimate of buffering capacity based on the desorption process should reflect the P-supplying power of soils more closely than an estimate derived from the sorption process.

In the desorption study, final P concentrations in the extracting solution were plotted against the amounts of P desorbed from soil after 24 h at various soil:solution ratios to give a desorption isotherm. Examples of some desorption isotherms of the soils studied are shown in Fig. 3.4. Generally, the shape of the desorption isotherms are curvilinear, being relatively flat at high P concentrations and steeper at lower P concentrations. The desorption isotherm of the Manawatu soil (data not presented here) is exceptional because it is essentially vertical, indicating constant concentrations of solution P regardless of the amounts of P being desorbed. This behaviour is consistent with the results from the glasshouse experiment where water-extractable P in the Manawatu soil remained constant throughout the period of ryegrass growth despite the removal of 67.9 $\mu g\ g^{-1}$ soil by plants (Tables 3.2 and 3.6). It appears that the release of P from the Manawatu soil is controlled either by desorption from essentially saturated, sorbing surfaces or by dissolution of some P-containing solid phase. The Manawatu soil is a recent soil and has a low P sorption capacity. It seems likely that the dissolution of a calcium phosphate, possibly resulting from fertilizer P addition, is a more likely explanation. The exceptional P-release pattern of the Manawatu soil meant that it was not possible to derive the slope of the

desorption isotherm which was required to indicate the buffering capacity of the soil.

The slope of the desorption isotherm at the highest solution P concentration was used to indicate the buffering capacity of the soil, because at that concentration the soil: solution ratio (i.e., 1:5) was narrowest and closest to the real soil solution condition. The slope, which is the amount of P desorbed per unit decrease in solution P concentration, should therefore closely represent the ability of the soil to replenish P in the soil solution when the level is reduced by plant uptake.

It was found that the slopes of the desorption isotherms ($slope_{DI}$) varied from 0.1 ml g^{-1} for the Patua soil to 54.2 ml g^{-1} for the Tokomaru-high P soil (Table 3.2). There was a negative relationship between $slope_{DI}$ and PR values ($r = -0.73^{**}$). For each soil in this study, the $slope_{DI}$ changed with the concentration of P in the soil solution (Fig. 3.4). It was then considered that the $slope_{DI}$ might reflect not only the buffering capacity of a soil, but also the level of P already present in the soil solution (i.e., intensity). However, it was found that the inclusion of a measure of intensity, such as the amount of P extracted at a soil:solution ratio of 1:5, did not improve the variance accounted for.

When either the PR value or the $slope_{DI}$ was included in the regression of plant uptake of P on water-extractable P, there were no significant increases in the variance accounted for (Table 3.9). It appears that the success of the PR test in explaining differences in P uptake from soils with similar water-extractable P values was limited to a few soils, as shown previously (Table 3.8) and does not apply to the overall range of soils used in this study. The failure of both estimates of buffering capacity to significantly improve the variation of plant P uptake accounted for by water-extractable P, which is already substantial, may also suggest that the availability of soil P in these soils is controlled mainly by the intensity factor. This situation

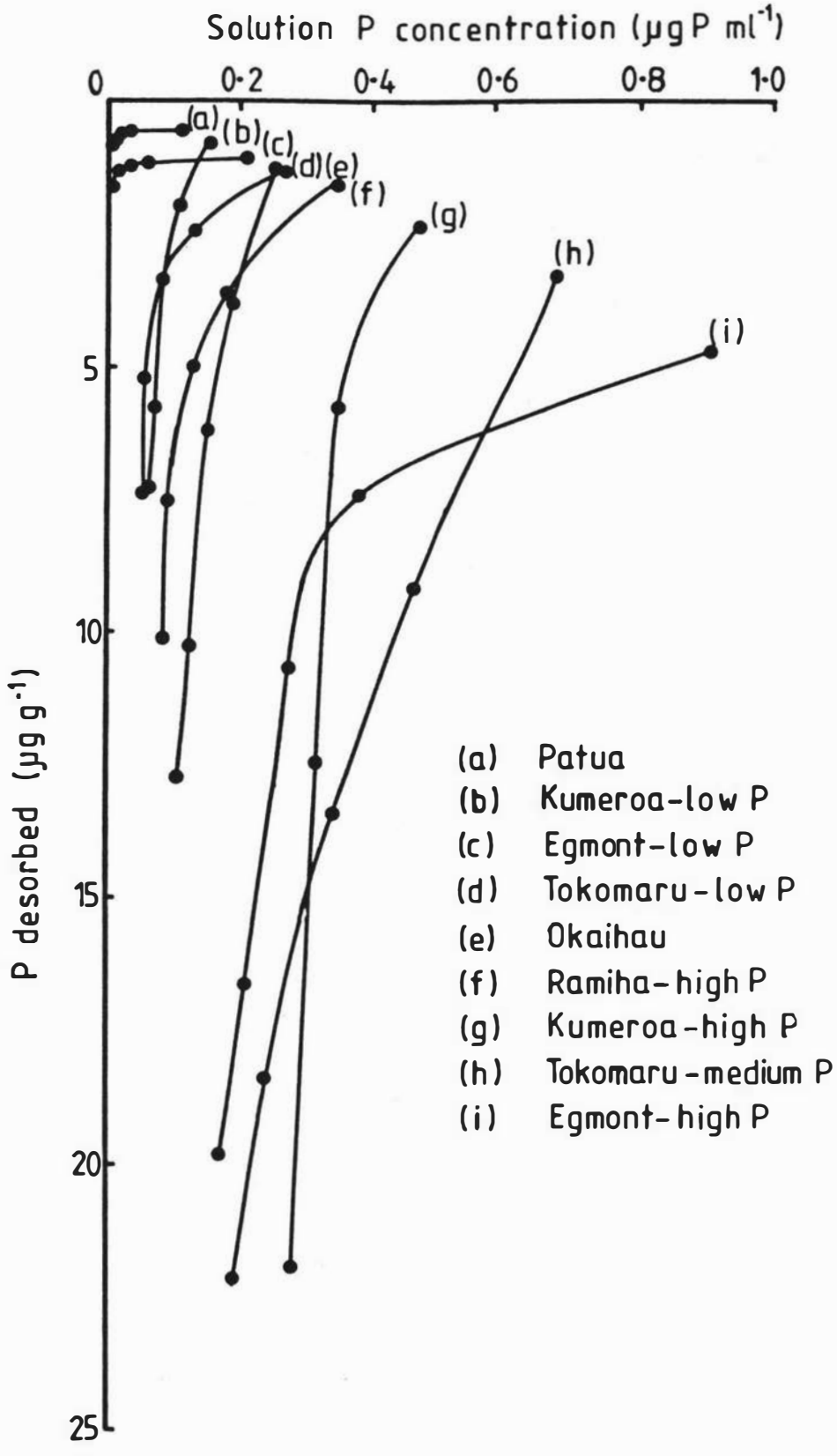

Figure 3.4 Desorption isotherms (24 h) for nine soils selected from the 20 soils studied

Table 3.9 Percentage variance in plant uptake of P accounted for by water-extractable P with and without the inclusion of P retention (PR) or slope of the desorption isotherms ($slope_{DI}$) for the 20 soils studied

Parameters	% variance accounted for
Water-extractable P	81
Water-extractable P + $slope_{DI}$	86
Water-extractable P + PR	81

is commonly found in P-enriched soils (Mengel and Kirkby, 1982) but in the present study the 20 soils used varied widely in P status from extremely low to very high (Table 3.2).

Another possible explanation is that the water-extraction procedure may represent not just the intensity factor, but also gives a measure of buffering capacity. Thomas and Peaslee (1973) stated that the intensity factor for soil P is generally reflected in extraction with water or a very dilute acid at a narrow soil:solution ratio. The water-extraction procedure used in the present study employs a wide soil:solution ratio (i.e., 1:120). The suggestion that the water extraction may reflect part of the capacity factor as well as the intensity factor is supported by the finding that the correlation between the amounts of P extracted at a soil:solution ratio of 1:5 and at 1:120 was increased significantly from 0.86 to 0.90 by including PR values in the regression equation. Therefore, the close correlation between plant-available P and water-extractable P can probably be attributed to the fact that water-extractable P reflects both the intensity and capacity factors to some degree.

This finding is in accord with the study of Rennes (1978), who developed a kinetic model for P sorption to describe the decline in water-extractable P in soil following P addition. The model was based on the concept of P sorption proposed by Ryden et al. (1977a), who suggested that the amount of P removed by water extraction includes P in the soil solution, more-physically sorbed P, and some chemisorbed P. The amount of more-physically sorbed P is influenced by the degree of saturation of the chemisorption sites. According to this P sorption model, the overall buffering capacity of a soil is related to the number of sites available for chemisorption which, in turn, determine the amount of more-physically sorbed P. Significantly, water extraction has been shown to essentially quantitatively remove the more-physically sorbed P. This concept strongly supports the suggestion that water-

extractable P reflects both the intensity and capacity factors of soil P.

The influence of buffering capacity on P availability in the 20 soils studied is more clearly demonstrated by the results for Olsen-extractable P_i than by those for water-extractable P. For soils with similar Olsen-extractable P_i, plant P uptake was inversely proportional to PR values (Table 3.10 and Plate 3.1). This finding again confirms the suggestion of Khasawneh (1971) who stated that for soils of equal quantities (as opposed to intensity) of soil P, plant uptake will be inversely proportional to buffering capacity because the higher the capacity the lower will be the P concentration in solution. Furthermore, when PR values were included in the regression of plant-available P on Olsen-extractable P_i, the variance accounted for was significantly improved from 82 to 89%. Similarly, the inclusion of $slope_{DI}$ values in such regression also improved the variance accounted for from 82 to 88%. The marked influence of buffering capacity on the value of Olsen-extractable P_i as an estimate of plant-available P is consistent with a number of studies in New Zealand (Sinclair et al., 1977; During et al., 1981), as well as from overseas (Barrow, 1967a; Helyar and Spencer, 1977; Holford and Mattingly, 1979).

3.3.5 Other soil P measurements

During the first seven weeks of ryegrass growth, there were significant increases in Olsen-extractable P_i in a number of the soils (Table 3.11). These increases were more marked in the absence of plants. The increases suggest that some P was released from less-available forms of soil P, probably as a result of mineralisation of soil organic P and/or desorption of sorbed P. In the glasshouse, the soils experienced relatively high temperatures (average minimum and maximum air temperatures were 18 and 25°C, respectively), and several drying and wetting cycles. These conditions are known to enhance the mineralisation of soil organic matter (Dalal, 1977). It is possible that soil organic P may make a significant contribution to the supply

Table 3.10 Comparison of plant uptake of P from soils with similar amounts of Olsen-extractable P_i and contrasting P retention (PR) values

Example	Soil	Olsen-extractable P_i ($\mu g\ g^{-1}$)	PR (%)	Plant uptake ($\mu gP\ g^{-1}$)
1	Egmont-low P	12.0	82	8.1
	Hamilton	13.6	66	11.6
	Wainui	12.7	36	41.7
2	Dannevirke	22.7	91	20.6
	Okaihau	20.6	45	43.5
	Manawatu	25.4	19	67.9

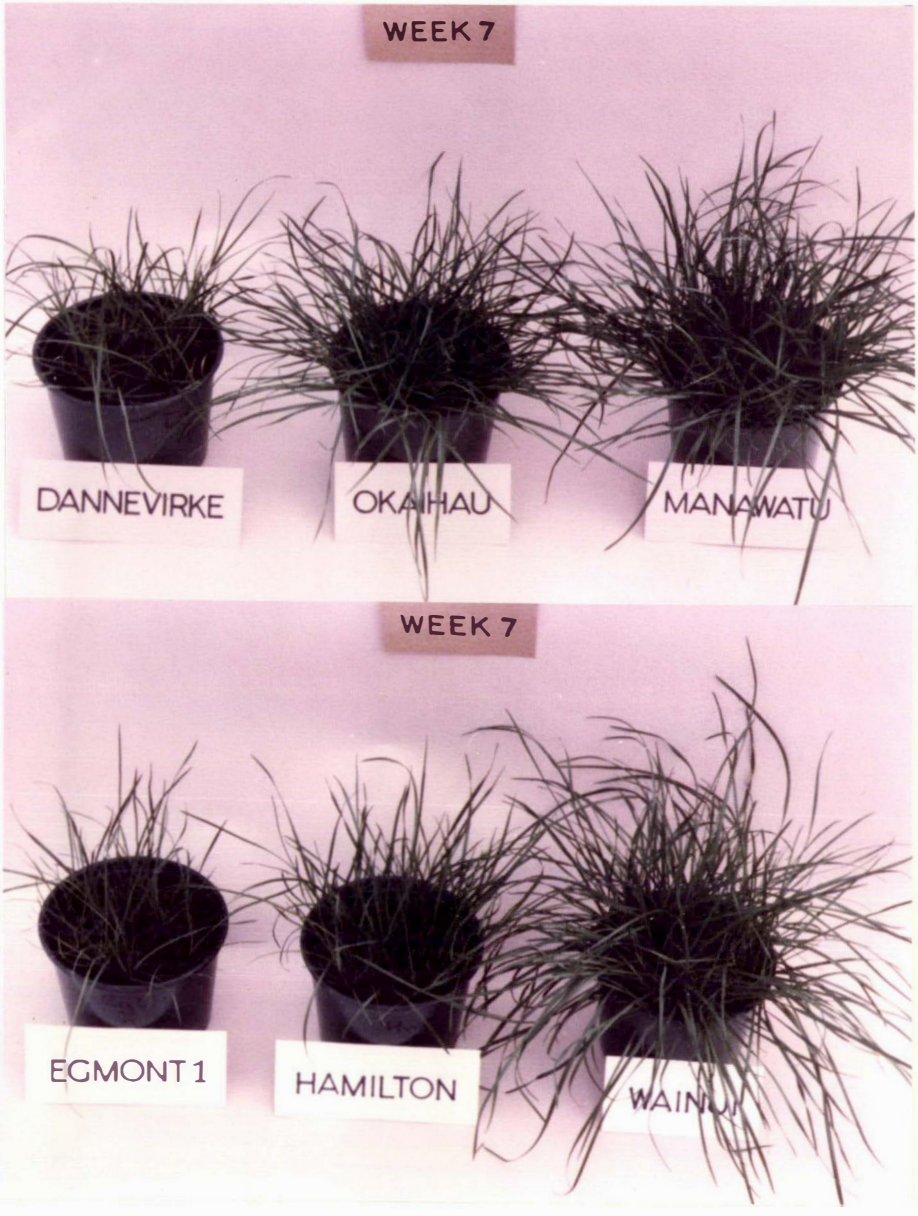

Plate 3.1 Comparison of ryegrass growth at week seven on soils with similar amounts of Olsen-extractable P_i and contrasting phosphate retention (PR) values

Table 3.11 Comparison of the amounts of Olsen-extractable P_i present initially and after seven weeks (harvest 1) in the presence and absence of plants for the 20 soils studied

Soil	Olsen-extractable P_i ($\mu g\ g^{-1}$)		
		After 7 weeks (harvest 1)	
	Initial	With plant	Without plant
1. Carnarvon	8.9	11.5	13.2
2. Dannevirke	22.7	24.0	27.8
3. Egmont-low P	12.0	13.7	16.7
4. Egmont-high P	58.6	63.6	78.1
5. Hamilton	13.6	13.2	14.4
6. Kiwitea	10.7	8.2	14.3
7. Konini	12.3	10.0	13.9
8. Kumeroa-low P	9.0	10.8	14.5
9. Kumeroa-high P	32.6	36.5	46.5
10. Manawatu	25.4	29.0	38.1
11. Okaihau	20.6	21.1	26.9
12. Patua	11.8	11.3	13.1
13. Ramiha-low P	6.2	6.3	7.5
14. Ramiha-high P	25.7	28.3	37.5
15. Taupo-low P	18.0	18.4	22.3
16. Taupo-high P	40.0	36.1	47.8
17. Tokomaru-low P	16.3	10.9	16.4
18. Tokomaru-medium P	21.1	26.3	37.7
19. Tokomaru-high P	35.2	36.4	48.5
20. Wainui	12.7	13.8	19.5

of available P in soil because the decreases in Olsen-extractable P_i in most soils during the whole growth period could only account for a small fraction of total plant P uptake. Because the Olsen extraction removes mostly inorganic sources of available P, it is suggested that the supply of available P from soil P reserves, such as soil organic P and sorbed P, probably accounted for a large proportion of plant P uptake. The amount of P uptake that was not accounted for by the decreases in Olsen-extractable P_i during the growth period is referred to as 'mobilised P'. A highly significant correlation was found between 'mobilised P' and Olsen-extractable P_i (Table 3.12), indicating that the inorganic pool of soil P may be an important source of the 'mobilised P'.

It is probable that soil organic P also contributed to the 'mobilised P'. To examine whether the amount of 'mobilised P' is related to any soil organic P parameters, correlations between a number of these parameters and 'mobilised P' were determined (Table 3.12). The two significant soil organic P parameters were the organic fraction of the Olsen-extractable P (Olsen-extractable P_o) and the % organic P (i.e., organic P expressed as a percentage of total P), which showed significant positive and negative correlations with 'mobilised P', respectively (Table 3.12). However, Olsen-extractable total P ($P_i + P_o$) was better correlated with 'mobilised P' than was any of the organic P parameters alone. These results suggest that the input into the pool of the plant-available P came from the inorganic P reserve (sorbed P), with some contribution also from soil organic P.

When % organic P was included in the regression of plant-available P on water-extractable P, the variance accounted for was significantly improved from 81 to 85%. Similarly, the improvement in variance resulting from the inclusion of the absolute amount of soil organic P in the regression of plant-available P on the Olsen-extractable P_i was from 82 to 86%. These findings suggest that organic P in the 20 soils studied also makes a contribution to the supply of available soil P to plants.

Table 3.12 Correlation coefficients for the relationships between various parameters of soil organic P and 'mobilised P'[#] for the 20 soils studied

Soil organic P parameter	r
Olsen-extractable P_i	0.91**
Olsen-extractable P_o	0.54*
Olsen-extractable $P_i + P_o$	0.80**
Total soil organic P	0.13
% soil organic P[##]	-0.45*
C:P	-0.44
C:organic P	-0.16

Calculated from total P uptake - changes in Olsen-extractable P_i before and after plant growth.

Soil organic P expressed as a percentage of total soil P.

The results of a multiple regression analysis show that soil pH is another factor which, in conjunction with Olsen-extractable P_i and PR, can significantly increase the variance in plant-available P accounted for. The inclusion of soil pH in the regression on Olsen-extractable P_i and PR significantly ($P<0.05$) improved the variance accounted for from 89 to 92%. The regression equation was:

$$\text{Plant-available P} = -91.4 + 2.74\ \text{Olsen-extractable } P_i - 0.44\ \text{PR} + 19.1\ \text{pH}$$

This equation implies that for soils with the same amount of Olsen-extractable P_i and the same PR values but with different pH values, the soil with a higher pH will have a greater amount of plant-available P. A similar trend was also observed with the regression on water-extractable P and PR, although the improvement was not statistically significant. It appears from these results that soil pH, together with either water-extractable P or Olsen-extractable P_i, can account for most of the variation of plant-available P in the 20 soils studied.

Among the other measurements of available soil P considered, $Bray_1$-extractable P was the most strongly correlated with plant-available P, followed by Truog-extractable P and isotopically-exchangeable P (Table 3.7). The correlation coefficient for the relationship between plant-available P and $Bray_1$-extractable P was only slightly lower than those for water-extractable P or Olsen-extractable P_i. There was a significant influence of buffering capacity on the regression of plant-available P on $Bray_1$-extractable P. Inclusion of the $slope_{DI}$ increased the variance accounted for from 79 to 88%. However, there was no significant improvement from the inclusion of PR, indicating that, when used in conjunction with the $Bray_1$ test, the $slope_{DI}$ reflects the replenishment capacity of soil P better than PR.

A similar result was also found with the Truog test. The variance accounted for was improved from 57 to 71% when the $slope_{DI}$ was included in the regression of plant-

available P on Truog-extractable P. There was no improvement from the inclusion of PR. The correlation of Truog-extractable P with plant-available P was relatively weak, partly because the Truog reagent extracts unavailable calcium-bound P (such as apatite) which is commonly found in recent soils, certain yellow-grey earth soils, and some brown-grey earth soils (Grigg, 1965, 1972; Syers, 1974). This was clearly demonstrated in the present study by the exceptionally high value for Truog-extractable P in the Manawatu soil, which is a recent soil (Table 3.2). The finding that the Truog test is less satisfactory than other soil-testing procedures is in accordance with the results of a number of glasshouse, (Grigg, 1968; Sherrell, 1970) and field studies (During, 1969; Grigg, 1972; Grigg and Stephen, 1974).

The correlation between plant-available P and isotopically-exchangeable P (24 h) was the weakest among the estimates of available soil P considered (Table 3.7). Exchangeable P overestimated the amount of plant P uptake in a number of soils, particularly in soils with a high P sorption capacity (Table 3.2). A few other workers have also obtained excessive estimates of isotopically-exchangeable P for soils with high P-fixing capacity (Amer et al., 1969; McConaghy et al., 1966; Dalal and Hallsworth, 1977). In the present study, this was clearly evident for the Dannevirke, Egmont-low P, Patua, and Ramiha-low P soils which have very high P sorption capacities, and in the Okaihau soil which is rich in free iron oxides (Table 3.2). When these soils were omitted, the relationship between exchangeable P and plant-available P approached a ratio of 1:1 (Fig. 3.5) and the correlation coefficient was significantly improved from 0.59 to 0.89. Although there may be appreciable amounts of P on the sorbing surfaces of these high P-sorbing soils, the amounts would be small compared to the number of vacant sites remaining on the surfaces. Consequently, the P concentration in the soil solution would be maintained at a level that is too low for optimum plant growth.

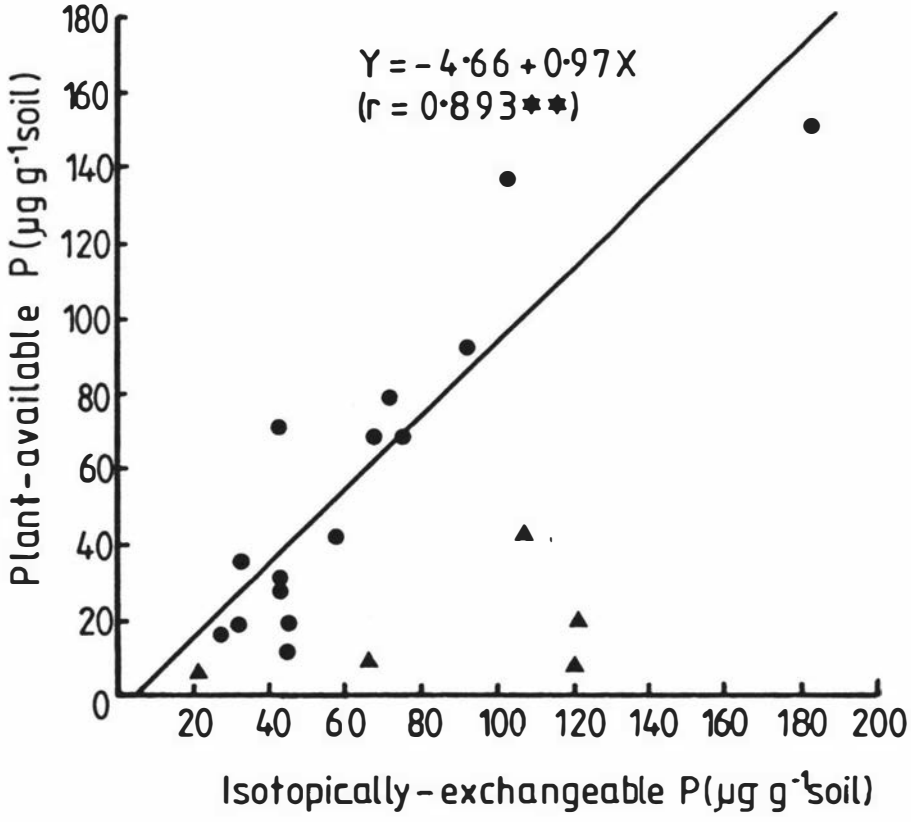

Figure 3.5 Relationship between plant-available P and isotopically-exchangeable P for the 20 soils studied, excluding four soils with very high P-sorption capacity (Dannevirke, Egmont-low P, Patua, and Ramiha-low P) and a soil with high free iron oxide content (Okaihau) (▲ = excluded soils)

For the 20 soils studied, the influence of buffering capacity on the relationship between plant-available P and exchangeable P is similar to that for the other available soil P parameters studied. The inclusion of $slope_{DI}$ values in the regression of plant-available P on exchangeable P significantly improved the variance accounted for from 35 to 66%. Similarly, the variance accounted for was improved from 35 to 62% by including PR values in the regression.

3.4 Conclusions

The plant availability of P in a group of 20 soils, varying widely in their P sorption capacity and P status, was evaluated in a glasshouse experiment, using an exhaustive cropping technique involving four harvests. Among the soil P measurements examined, water-extractable P and Olsen-extractable P_i were the most highly correlated with plant-available P, followed by the $Bray_1$ test, the Truog test, and isotopically-exchangeable P. It was initially thought that the water-extraction procedure would reflect the intensity factor of soil P and that, when combined with an estimate of buffering capacity, it could be used to predict the amount of plant-available P in soils. However, it was found that the inclusion of either PR or $slope_{DI}$ did not improve the ability of water-extractable P to predict plant-available P. It appears that when a wide soil:solution ratio is used in the water-extraction procedure, not only is the intensity factor measured but also a part of the buffering capacity of soil P. This suggestion was supported by the finding that the correlation between the amounts of P extracted at a soil:solution ratio of 1:5 and that at 1:120 was significantly improved by including an estimate of buffering capacity (PR). It has been shown (Ryden and Syers, 1977b) that water extraction essentially removes the more-physically sorbed P, the level of which is determined by the number of vacant sites available for chemisorption. This could explain how water-extractable P may reflect both the intensity and buffering capacity factors. The significant relationship

between plant-available P and water-extractable P was also not influenced by soil type.

Buffering capacity had some influence on the ability of all other soil P measurements (Olsen-extractable P_i, $Bray_1$ test, Truog test, and isotopically-exchangeable P) to predict plant-available P in the 20 soils studied. The inclusion of $slope_{DI}$ improved the correlation between all of these soil P measurements and plant-available P, while the inclusion of PR improved the prediction given by Olsen-extractable P_i and isotopically-exchangeable P only.

The decreases in most soil P measurements after growing ryegrass accounted for only a small fraction of plant P uptake, suggesting that some P was supplied by other sources, such as soil organic P and more tightly-held inorganic P.

Water extraction appears to have a useful role as a soil-testing procedure for the prediction of plant-available P. It may have advantages over other soil P tests because it appears to be independent of soil type and is not greatly influenced by the buffering capacity of soils.

CHAPTER 4

CHAPTER 4

EFFECTS OF SEASON, DEPTH OF SAMPLING, AND FERTILIZER P ADDITION ON THE AMOUNTS OF WATER-EXTRACTABLE P IN SOILS

4.1 Introduction

One of the major sources of variation in soil testing is seasonal or temporal variation. Most workers have reported significant effects of season and concluded that the accuracy of a soil P test result can be influenced by seasonal fluctuations (see Section 2.3.3.3 (iii)). However, in New Zealand, Mountier and During (1966) found that seasonal variations in Truog soil P test (Truog, 1930) results were generally lower than variations associated with laboratory analysis. Saunders and Metson (1971) postulated that soil P tests might be higher in spring than in autumn and winter but failed to obtain any supporting evidence.

The availability of P in most soils varies with depth, especially in soils under grazed pasture in which nutrients accumulate near the soil surface (Friesen and Blair, 1984). The accumulation of soil organic matter in the topsoil also means that there is the potential for larger amounts of soil P to be made available from the organic pool through the mineralisation process near the soil surface.

The importance of mineralisation of soil organic P in providing plant-available P has been well established (Dormaar, 1972; Dalal, 1977). Soil microbial biomass is a relatively labile fraction of soil organic matter (Cole et al., 1977) and results from recent studies have indicated that significant amounts of available soil P could be supplied from this source in pasture soils (Halm et al., 1972; Cole et al., 1977; Brookes et al., 1982; Perrott and Sarathchandra, 1982). Consequently, it is possible that changes in available soil P are related to soil microbial biomass P.

Most agricultural soils cannot provide adequate amounts of available P for plant growth, and require regular applications of fertilizer P. The availability of fertilizer P depends on a number of factors, including the types and forms of fertilizer, methods of application, and soil properties. Furthermore, the effectiveness of fertilizer P declines with time following application (Barrow, 1980). It is therefore important to understand how available soil P changes after fertilizer application.

In the past in New Zealand, the role of soil testing has been to predict responses to fertilizer P during pasture development and in maintenance situations. This has changed since the recent introduction of the new fertilizer recommendation scheme based on a model proposed by Cornforth and Sinclair (Syers, 1982). In this model, soil P tests are used to assess whether the level of soil P is appropriate for the level of production required, as well as to monitor the effectiveness of the maintenance fertilizer P programme (Sinclair and Cornforth, 1982).

A good soil test should be sufficiently sensitive to indicate whether the rate of fertilizer application is appropriate. At the same time, it should be precise and independent of variables such as season.

The objective of this study was to evaluate the variation in the amounts of water-extractable P in soils. Field trials were established on two contrasting soils and were used to investigate the variations in water-extractable P values in relation to season and depth of sampling. The effect of fertilizer P addition on the amounts of water-extractable P in soil was also determined. Comparisons were made with the currently used Olsen P test. Measurements of pasture uptake of P and soil microbial biomass P were made in an attempt to explain changes in the soil test values with time.

4.2 Materials and Methods

4.2.1 Trial site description

Field trials were located on two contrasting soils: a high P-sorbing Ramiha soil and a low P-sorbing Tokomaru soil. Both trial sites were on flat areas under established pastures which had regularly been grazed by sheep. The pasture composition on the Tokomaru site was predominantly a mixture of perennial ryegrass (Lolium perenne) and white clover (Trifolium repens). On the Ramiha site there was a significant amount of browntop (Agrostis tenuis), together with ryegrass and white clover. The soils at both sites had previously received small amounts of fertilizer P (as superphosphate), and therefore had a moderately low P status. The locations and soil descriptions of the two field trial sites are given in Table 4.1.

4.2.2 Trial design and fertilizer treatments

Three rates of superphosphate were surface applied to each site in January, 1983. The rates of superphosphate addition are given in Table 4.2. The treatments were replicated four times on plots of 6 m x 6 m. Preliminary soil sampling was carried out on each plot so that the plots could be grouped into four blocks of similar initial soil P test values. Treatments were then assigned to the plots using a randomised block design.

A combination of sheep grazing and mowing was used on the trials. Grazing allows for the return of nutrients and so the effects of recycled nutrients on changes in the soil test can be studied. It has also been shown that grazing causes less changes in pasture composition than continuous mowing (Sears, 1953; Harris, 1978). Occasional mowing was carried out to provide some indications of plant uptake and yield in relation to changes in the soil test parameters. At the Ramiha site, however, difficulties were experienced in the control of sheep grazing, and the trial was accidentally grazed during the initial period of the experiment. It was then decided to continue the trial at the Ramiha site as a mowing trial only.

Table 4.1 Locations and soil descriptions[a] of the Ramiha and Tokomaru trial sites

	Ramiha trial	Tokomaru trial
Location	10 km east of Palmerston North (Tararua range)	5 km south of Palmerston North (High river terrace)
Soil type	Ramiha silt loam	Tokomaru silt loam
New Zealand Soil Group	Yellow-brown earth/ yellow-brown loam intergrade	Yellow-grey earth
Bulk density (0-5 cm) (kg m^{-3})	963	1305
Soil pH[c] (water)	5.51 ± 0.04[b]	5.69 ± 0.04
Total carbon[c] (%)	7.6	4.5
Organic P[c] (µg g^{-1})	585	420
P retention[c] (%)	88	20
Extractable P in soil[c] (µg g^{-1})		
Water	1.9 ± 0.3	6.0 ±0.3
Olsen	10.4 ± 0.5	8.6 ± 0.3

a - For methods of soil analysis see Chapter 3.

b - Standard error.

c - 0-7.5 cm sampling depth.

Table 4.2 Rates of superphosphate[a] addition (kgP ha^{-1}) for the Ramiha and Tokomaru trials

Trial site	Treatment		
	P0	P1	P2
Ramiha	0	40	80
Tokomaru	0	20	40

a - Superphosphate contains 9.2% total P.

4.2.3 Sampling technique

4.2.3.1 Soil sampling

To monitor the changes in soil parameters, soil sampling was carried out initially at two-week intervals during the first three months after the application of P and then at monthly intervals for a further nine months. The effect of depth of soil sampling on the soil test parameters was examined by sampling the soils to two depths: 0-4.0 and 0-7.5 cm. Twelve soil cores (2.5 cm diameter) were taken randomly from each plot to a depth of 4.0 cm and 10 cores to a depth of 7.5 cm. Soil cores from the same plot were bulked for each depth. A subsample was taken from the bulked 0-7.5 cm depth sample and passed through a 2-mm sieve, while field moist, for the determination of soil microbial biomass P (Section 4.2.4) and soil moisture content. The remaining soil samples were air-dried, sieved (<2 mm), and analysed for water-extractable P (Section 3.2.4.1), Olsen-extractable P (Section 3.2.4.2), and soil pH (Section 3.2.2). A standard soil sample was also included in the analysis of soil samples taken at each sampling in order to assess variability in the laboratory.

4.2.3.2 Assessment of plant uptake and pasture production

The uptake of P by plants was determined by means of herbage cuts which were carried out at the times of soil sampling whenever there was sufficient pasture growth. At the Tokomaru site, pasture was hand-cut to a level of 1 cm above ground using a quadrat (50 cm x 20 cm). Three quadrats were taken from each plot and the fresh weights were recorded. The herbage samples from the three quadrats were combined, thoroughly mixed, and two subsamples (approximately 100 g) were taken for the assessment of dry matter, P content, and botanical composition. The first subsample was weighed, oven-dried at 60°C for 24 h, and reweighed. Dry matter percentages were calculated and then converted to total pasture production expressed in terms of kg of dry matter per ha. After the reweighing, the dry herbage sample was then ground and analysed for P (Section 3.2.3). The

second subsample was dissected into clover (mainly white clover), and grasses. After drying separately at 60°C for 24 h, the grass and clover samples were weighed, and clover content was calculated as a percentage of total dry weight of grass and clover combined. After each herbage cut, sheep were allowed to quickly graze the plots, leaving approximately 1 cm of pasture behind. The amount of pasture removed by sheep was assumed to be the same as the amount measured at the time of sampling.

In the Ramiha trial, pasture production was assessed using a rotary mower. A hand-cut herbage sample was also taken from each plot for assessments of moisture content, P content, and botanical composition, as described previously.

4.2.4 Measurement of microbial biomass P in soil

The method used for measuring microbial biomass P in this study was developed by modifying the procedures used by Hedley and Stewart (1982) and Brookes et al. (1982). The amount of P in soil microbial biomass was estimated by adding chloroform ($CHCl_3$) to soil to lyse microbial cells and measuring the amount of microbial P released to 0.5M $NaHCO_3$ (pH 8.5) extracts. Calculations of total microbial P were based on the difference between P removed by $NaHCO_3$ extraction of $CHCl_3$-treated and untreated samples. The fumigation and extraction procedures were basically as described by Hedley and Stewart (1982) except for the omission of the pre-incubation step. It was considered that the pre-incubation would invalidate any possible effects of season which was one of the main objectives of this study. It has been suggested that some $CHCl_3$-released P is sorbed by soil during fumigation and extraction (Hedley and Stewart, 1982; Hedley et al., 1982b; Brookes et al., 1982). A technique proposed by Brookes et al. (1982) was adopted in this study to overcome this problem. The procedure involved adding a known amount of inorganic P during extraction and correcting for recovery.

The modified method used to measure microbial biomass P in this study is as follows. A set of eight samples (3 g)

of sieved, field-moist soil was placed in 250-ml polyethylene bottles. One ml of $CHCl_3$ was added to three samples and the bottle caps were replaced for 1 h during which the bottles were hand-shaken every 15 min. This was to ensure optimum contact between soil and $CHCl_3$. After 1 h, the caps were removed and the $CHCl_3$ was allowed to evaporate overnight in a fume hood at room temperature (20±5°C). The remaining five untreated samples were also placed in the fume hood overnight. Samples in all eight bottles were then shaken with 120 ml of 0.5M $NaHCO_3$ (pH 8.5) for 16 h at 20°C on an end-over-end shaker. Before shaking, 1 ml of KH_2PO_4 solution containing 150 g P ml^{-1} was added with the 0.5M $NaHCO_3$ to three of the untreated samples (no chlorform added). After centrifugation at 10,000 r.p.m. for 2 min (10°C), the extract was filtered through a Whatman No.5 filter paper. Inorganic P (P_i) in the extract was analysed by the method of Murphy and Riley (1962). The extract was also analysed for total P following a persulphate digestion (Environmental Protection Agency, 1971). An aliquot (4 ml) of the extract was placed in a 50-ml Erlenmyer flask containing 30 ml of distilled water. After the addition of 0.4 g ammonium persulphate and 1 ml of 5.5M H_2SO_4, the flask was brought to the boil gently for 30 min. The digest was then neutralised with 5M NaOH using p-nitrophenol as an indicator before being analysed for P_i by the method of Murphy and Riley (1962).

Microbial biomass P in soil was calculated as follows:

$$\text{microbial biomass } P^{*} = (a - b) \times C.F. \times 10 \times (1 - \omega)/Kp$$

(* - expressed as µg P g^{-1} oven-dried soil)

where
- a = µg P_i in 4 ml of $CHCl_3$-treated sample
- b = µg P_i in 4 ml of untreated sample
- C.F. = correction factor for P sorption
  - = P_i added ml^{-1} extract/P_i recovered ml^{-1} extract
- K_p = recovery factor = 0.4 (Brookes et al., 1982)
- D.F. = dilution factor
  - = 120 ml extract/(3 g soil x 4 ml aliquot) = 10
- ω = gravimetric water content of soil.

It has been suggested that 0.5M $NaHCO_3$ extracts some relatively labile organic P as well as inorganic P (Halm et al., 1972; Perrott and Sarathchandra, 1982). Halm et al. (1972) showed that $NaHCO_3$-extractable organic P was positively correlated with soil phosphatase activity and microbial biomass during the growing season. Bowman and Cole (1978) evaluated the $NaHCO_3$ extraction method and found that labile organic compounds, such as RNA, nucleotides, and glycerophosphates, were recoverable from the extract. Perrott and Sarathchandra (1982) reported a highly significant correlation of microbial biomass P and total P (organic + inorganic) in the $NaHCO_3$ extract. These workers therefore proposed that total P in $NaHCO_3$ extracts could be a better measure of P availability in a soil than the presently determined inorganic P in the $NaHCO_3$ extract (i.e., Olsen-extractable P). Their suggestions, however, were not based on any plant studies.

In this study the procedures for measuring soil microbial biomass P involved the use of 0.5M $NaHCO_3$ (pH 8.5) as an extracting solution and the analysis of both inorganic and organic P in the extract (Section 4.2.4). This extracting solution is identical to that used in the Olsen method (Section 3.2.4.2). The amounts of inorganic and organic P in extracts of the untreated sample (no chloroform or P added) from the microbial biomass study were examined. These are referred to as $NaHCO_3$-extractable inorganic P and $NaHCO_3$-extractable organic P, and the combined total as $NaHCO_3$-extractable total P.

4.2.5 Statistical analysis

All results from field trials in this study were checked for homogeneity using Bartlett's Test (Little and Hills, 1972), and when necessary, a logarithmic transformation was applied before analysis of variance was carried out.

4.3 Results and Discussion

4.3.1 Seasonal variations

Water-extractable P showed significant ($P<0.01$) seasonal variations in both the 0-4.0 and 0-7.5 cm depths of the unfertilized Ramiha and Tokomaru soils (Fig. 4.1). For the Tokomaru soil, the coefficients of variation of water-extractable P over the 12-month period were similar to those of the Olsen-extractable P but in the Ramiha soil the former were considerably greater (Table 4.3). A similar finding was also obtained for the variability between plots at each sampling (Table 4.4). It is possible that the relatively low values of water-extractable P in the Ramiha soil are partly responsible for the high coefficients of variation. This is supported by the evidence that the variability of the absolute values was higher for the Olsen-extractable P than for water-extractable P. For example, during the 12-month period, water-extractable P in the 0-4.0 cm depth of the Ramiha soil varied from 1.3 to 7.9 $\mu g\ g^{-1}$ soil whereas Olsen-extractable P ranged from 9.6 to 21.8 $\mu g\ g^{-1}$ soil.

Variability during the 12 months in water- and Olsen-extractable P was greater in the 0-4.0 cm than in the 0-7.5 cm depth of the Ramiha soil, but was similar in both depth intervals of the Tokomaru soil (Table 4.3). Within the 0-4.0 cm zone, nutrient uptake by roots (Jackman and Mouat, 1972a) and microbial activity (Anderson, 1975) are the most active. As these activities are strongly affected by environmental factors, such as moisture and temperatures, availability of nutrients in this zone is therefore expected to be sensitive to changes in environmental conditions occurring between seasons. The Ramiha soil contained high amounts of roots and organic matter, particularly in the top 4-5 cm. This could explain the higher seasonal variability in extractable soil P in the 0-4.0 cm than in the 0-7.5 cm depth. In contrast, there were no significant effects of sampling depth on the variability of water- and Olsen-extractable P in the Ramiha soil within each sampling (Table 4.4).

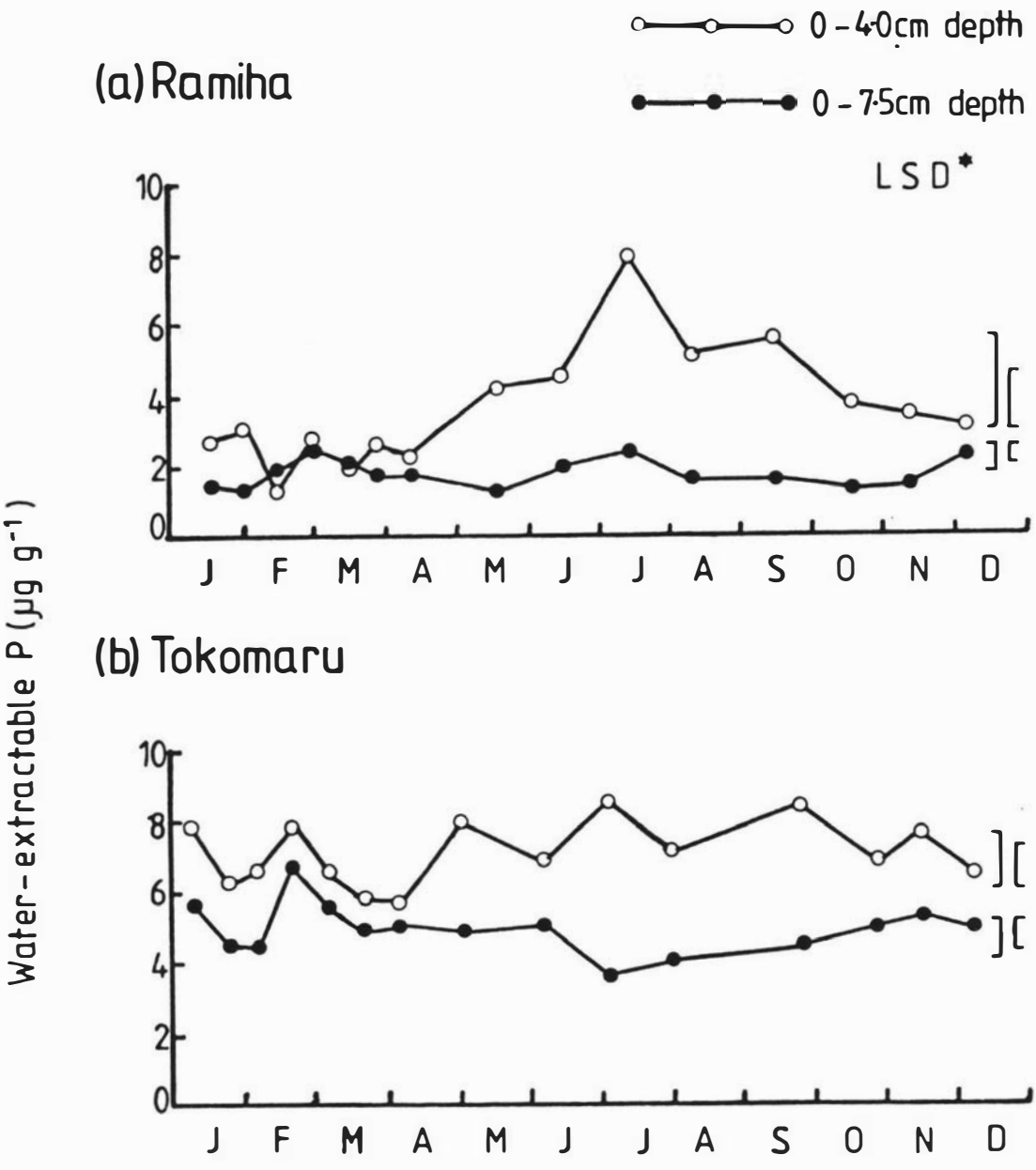

Figure 4.1 Changes in water-extractable P over the 12-month period in unfertilized Ramiha (a) and Tokomaru (b) soils at the 0-4.0 and 0-7.5 cm sampling depths

* Least significant difference at 1 and 5% levels

Table 4.3 Coefficients of variation (%) of the means of water- and Olsen-extractable P during the 12-month period in the Ramiha and Tokomaru soils at the 0-4.0 and 0-7.5 cm sampling depths

	Depth (cm)	Ramiha	Tokomaru
Water-extractable P	0-4.0	45.4	12.5
	0-7.5	22.9	14.8
Olsen-extractable P	0-4.0	21.6	9.0
	0-7.5	16.4	12.4

Table 4.4 Average values for coefficients of variation (%) of water- and Olsen-extractable P within each sampling in the unfertilized Ramiha and Tokomaru soils at the 0-4.0 and 0-7.5 cm sampling depths

Parameter	Depth (cm)	Ramiha	Tokomaru
Water-extractable P	0-4.0	21.3	10.1
	0-7.5	19.2	10.8
Olsen-extractable P	0-4.0	13.2	11.5
	0-7.5	10.0	13.0

Sampling depth also had a significant effect on the amounts of water- and Olsen-extractable P in both soils. Values for both extractable soil P parameters were always higher in the 0-4.0 cm than in the 0-7.5 cm depth (Fig. 4.1 and 4.2). This finding is consistent with the general observation that a grazed permanent pasture system encourages the accumulation of nutrients near the soil surface. When comparisons were made between the average values of the two sampling depths over the 12-month period, water-extractable P was 45-106% higher in the 0-4.0 cm than in the 0-7.5 cm depth while in the case of Olsen-extractable P, the differences were only 18-29% (Table 4.5). This implies that most of the soil P in the 0-7.5 cm depth which was removed by water extraction was present in the 0-4.0 cm depth.

4.3.2 Effect of fertilizer P addition

For both the Ramiha and Tokomaru soils, the addition of fertilizer P significantly increased ($P<0.01$) water- and Olsen-extractable P at both the 0-4.0 cm and 0-7.5 cm sampling depths. Generally the increases were largest immediately following the addition of fertilizer P and then gradually became smaller with time (Fig. 4.3, 4.4, 4.5, and 4.6). The initial increases in water- and Olsen-extractable P in the 0-4.0 cm of both soils (Table 4.6) were found to be proportional to the rate of fertilizer P addition. The increases were approximately doubled when the rates of P addition were increased twofold. This is consistent with the study of Rennes (1978) who reported proportional increases in water-extractable P with increasing rates of P addition. This relationship, however, was not found for the 0-7.5 cm depth of either soil. These different increases could partly be attributed to the fact that the soils were sampled only two weeks after the application of fertilizer. During this short period, it is unlikely that fertilizer P would have penetrated to and reacted with soil material in the lower depth, thus resulting in the inconsistent pattern of increases in extractable soil P at the 0-7.5 cm depth. Furthermore, if the added P had not penetrated to the lower

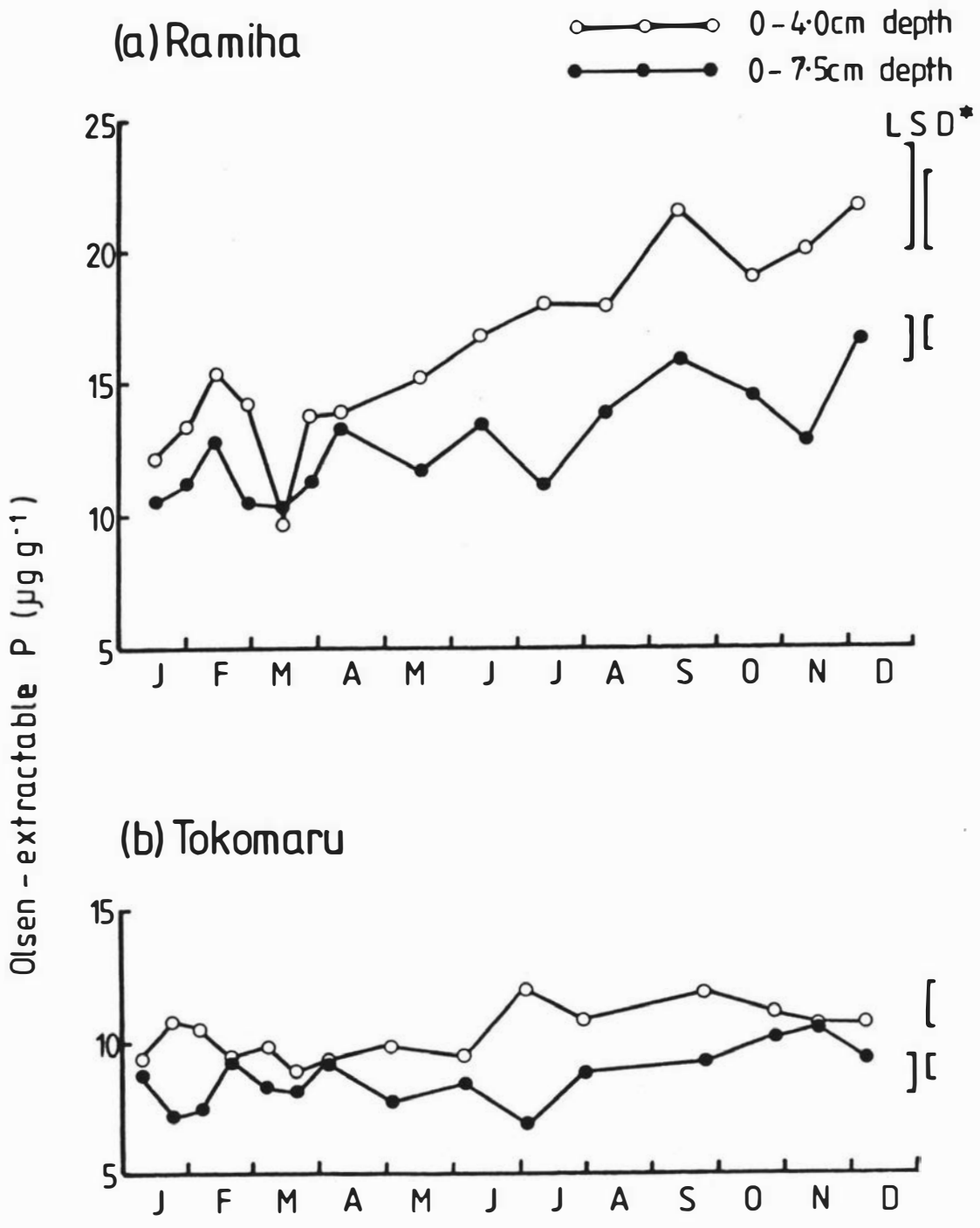

Figure 4.2 Changes in Olsen-extractable P over the 12-month period in unfertilized Ramiha (a) and Tokomaru (b) soils at the 0-4.0 and 0-7.5 cm sampling depths

* Least significant difference at 1 and 5% levels

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Table 4.5 Average values of water- and Olsen-extractable P over the 12-month period in the Ramiha and Tokomaru soils at the 0-4.0 and 0-7.5 cm sampling depths

Soil	Depth (cm)	Water-extractable P ($\mu g\ g^{-1}$)	Olsen-extractable P ($\mu g\ g^{-1}$)
Ramiha	0-4.0	3.7	16.2
	0-7.5	1.8	12.6
	(% difference relative to value at 0-7.5 cm)	(+106)	(+29)
Tokomaru	0-4.0	7.1	10.3
	0-7.5	4.9	8.7
	(% difference relative to value at 0-7.5 cm)	(+45)	(+18)

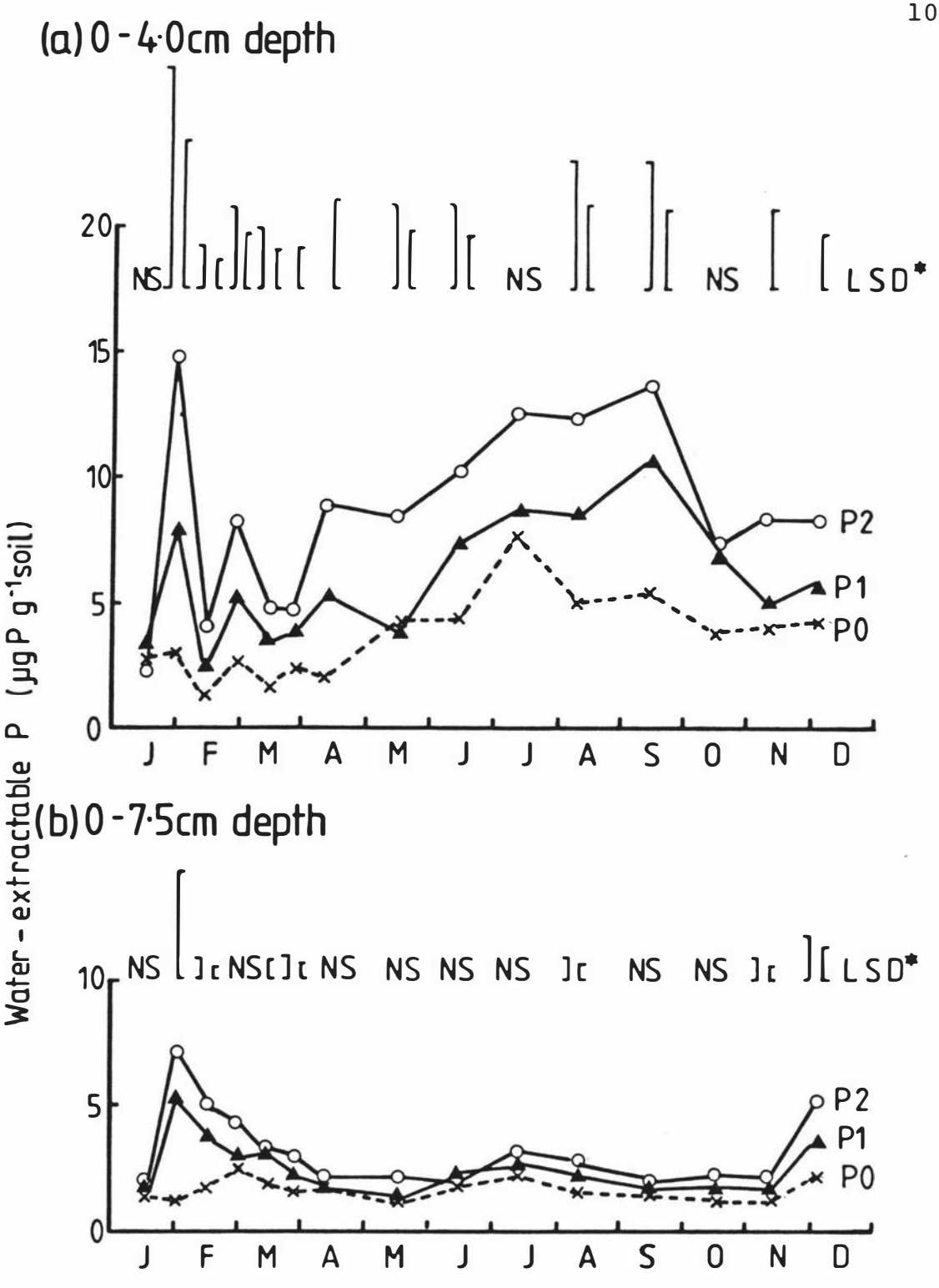

Figure 4.3 Changes in water-extractable P over the 12-month period in the Ramiha soil at the 0-4.0 (a) and 0-7.5 (b) cm sampling depths following the additions of 0 (P0), 40 (P1), and 80 (P2) kgP ha^{-1} of superphosphate

* Least significant difference at 1 and 5% levels

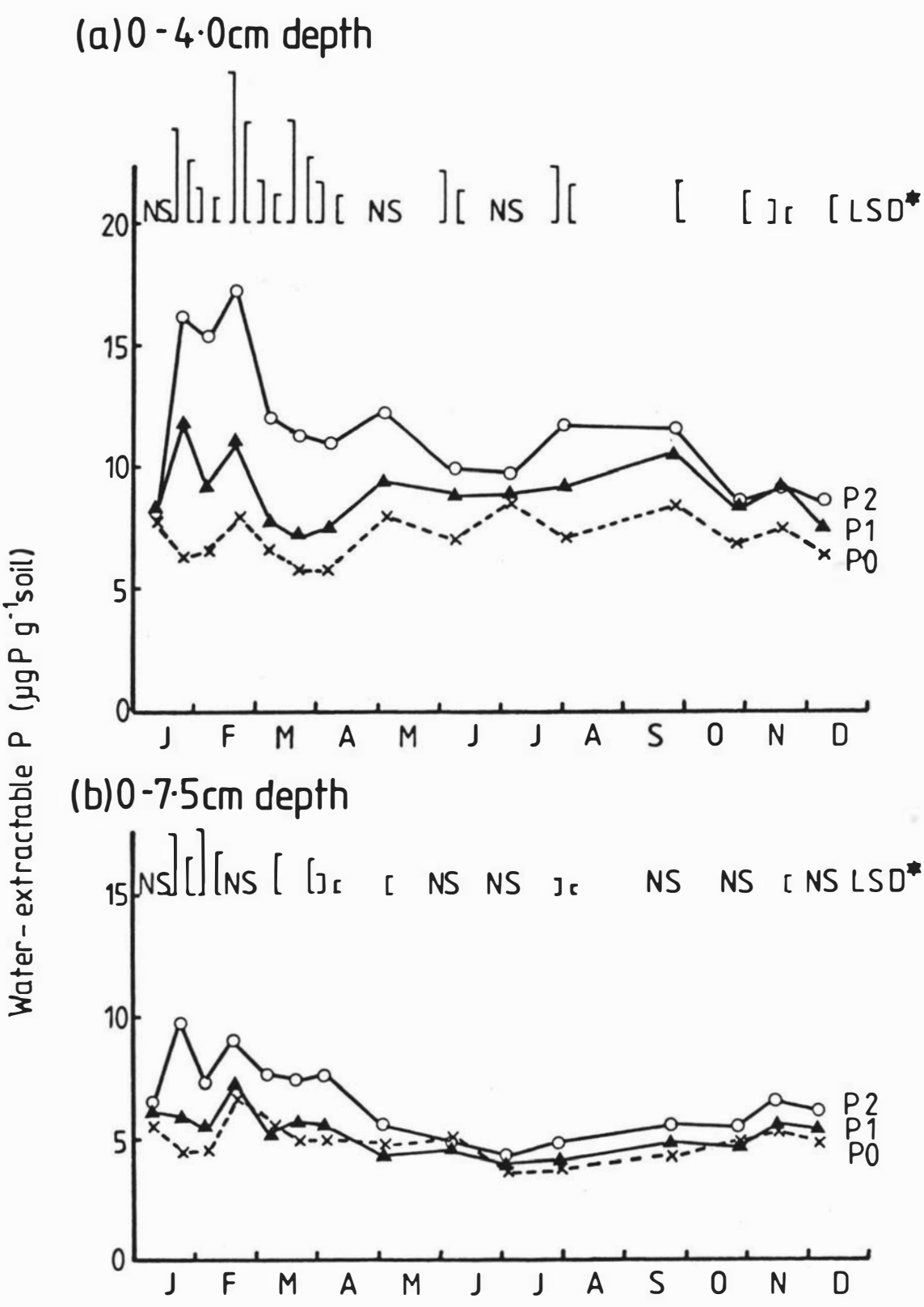

Figure 4.4 Changes in water-extractable P over the 12-month period in the Tokomaru soil at the 0-4.0 (a) and 0-7.5 (b) cm sampling depths following the additions of 0 (P0), 20 (P1), and 40 (P2) kgP ha^{-1} of superphosphate

* Least significant difference at 1 and 5% levels

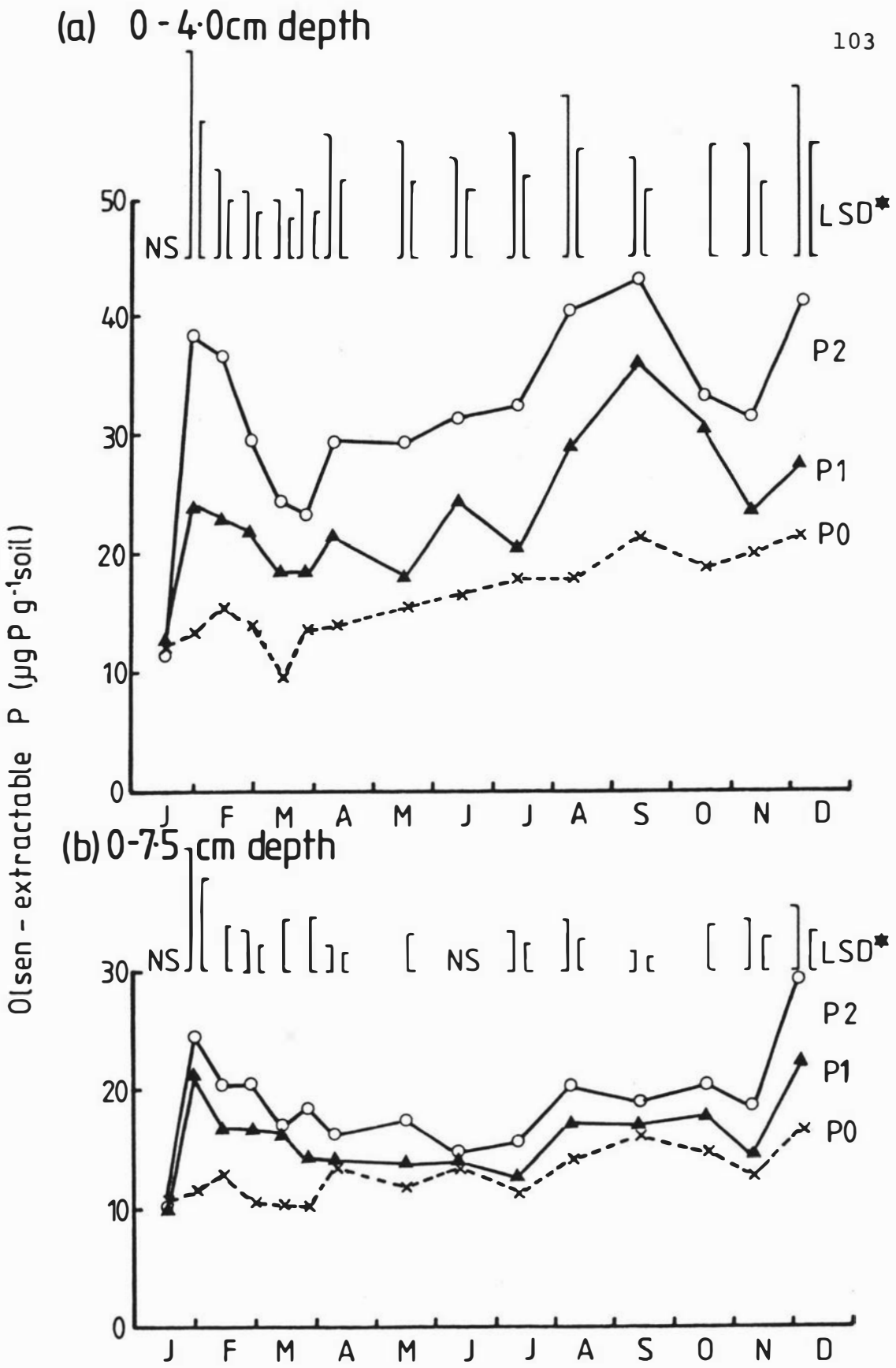

Figure 4.5 Changes in Olsen-extractable P over the 12-month period in the Ramiha soil at the 0-4.0 (a) and 0-7.5 (b) cm sampling depths following the additions of 0 (P0), 40 (P1), and 80 (P2) kgP ha^{-1} of superphosphate

* Least significant difference at 1 and 5% levels

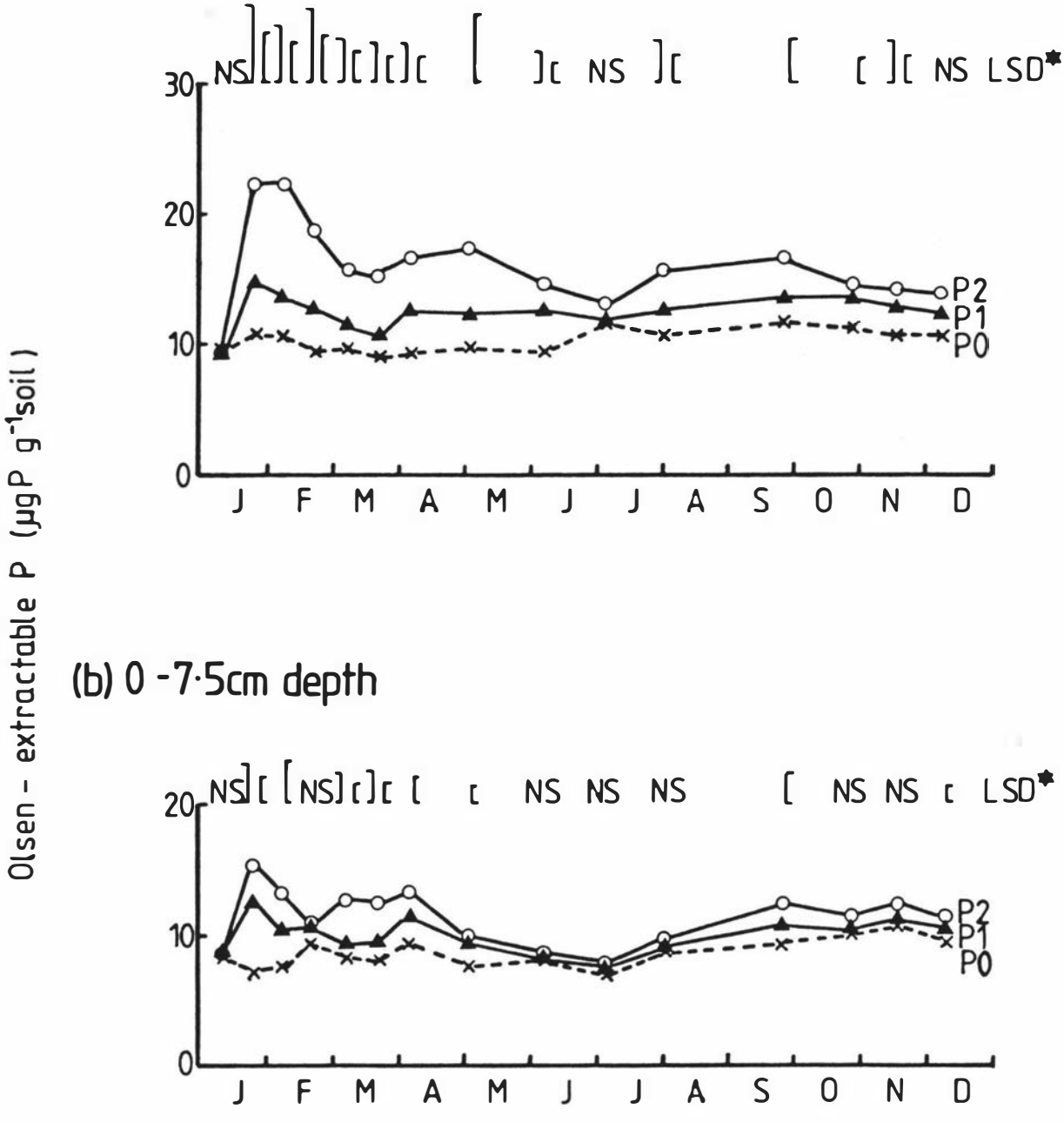

Figure 4.6 Changes in Olsen-extractable P over the 12-month period in the Tokomaru soil at the 0-4.0 (a) and 0-7.5 (b) cm sampling depths following the additions of 0 (P0), 20 (P1), and 40 (P2) kgP ha^{-1} of superphosphate

* Least significant difference at 1 and 5% levels

Table 4.6 Amounts of water- and Olsen-extractable P in the Ramiha and Tokomaru soils at the 0-4.0 and 0-7.5 cm sampling depths two weeks after the addition of fertilizer P

Soil	P addition kg ha^{-1}	Water-extractable P µg g^{-1}				Olsen-extractable P µg g^{-1}			
		0-4.0 cm depth		0-7.5 cm depth		0-4.0 cm depth		0-7.5 cm depth	
Ramiha	0	3.1		1.4		13.4		11.3	
	40	8.1	(5.0)[a]	5.5	(4.1)	24.0	(10.6)	21.3	(10.0)
	80	14.9	(11.8)	7.2	(5.8)	38.5	(25.1)	24.5	(13.2)
Tokomaru	0	6.3		4.5		10.8		7.1	
	20	11.8	(5.5)	6.0	(1.5)	15.0	(4.2)	12.5	(5.4)
	40	16.2	(9.9)	9.8	(5.3)	22.1	(11.3)	15.1	(8.0)

a - Number in brackets is the increase from control treatment.

depth, it is likely that some resorption of P could occur during the extraction of the soil sample taken from the 0-7.5 cm depth. The initial effect of fertilizer P addition on extractable soil P was therefore less variable in the 0-4.0 cm than in the 0-7.5 cm sample.

The effect of fertilizer P addition on water-extractable P in the 0-4.0 cm depth of both soils persisted throughout the 12-month period, while in the 0-7.5 cm depth the differences became insignificantly small during the winter-spring period (Fig. 4.3 and 4.4). The effect of added P on Olsen-extractable P was also more pronounced and more consistent in the 0-4.0 cm than in the 0-7.5 cm depth (Fig. 4.5 and 4.6). There were also highly significant interactions ($P<0.01$) between the effect of fertilizer P addition and the effect of sampling time in both soils at both sampling depths. These strong interactions imply that the effect of added P on extractable P values would vary depending on the time when the soil is sampled in relation to season as well as the time after fertilizer application.

4.3.3 Relationship between extractable soil P and P uptake by pasture

Two important features were observed in the seasonal pattern of water-extractable P in the soils studied (Fig. 4.3 and 4.4). Firstly, low levels of water-extractable P were obtained in the autumn (March), and secondly, a build-up occurred during the winter months. This pattern was not found in the analysis of the standard soil sample, so the effect was not a result of variability in the laboratory. These features in the seasonal pattern of water-extractable P were more pronounced in the fertilized than in the unfertilized soils.

It is suggested that the low level of water-extractable P in autumn was associated with the autumn flush of pasture growth, which resulted from increases in rainfall and available soil moisture after a relatively dry summer period. The rainfall data and soil moisture contents shown in Fig. 4.7 and 4.8 indicated that heavy rains in March

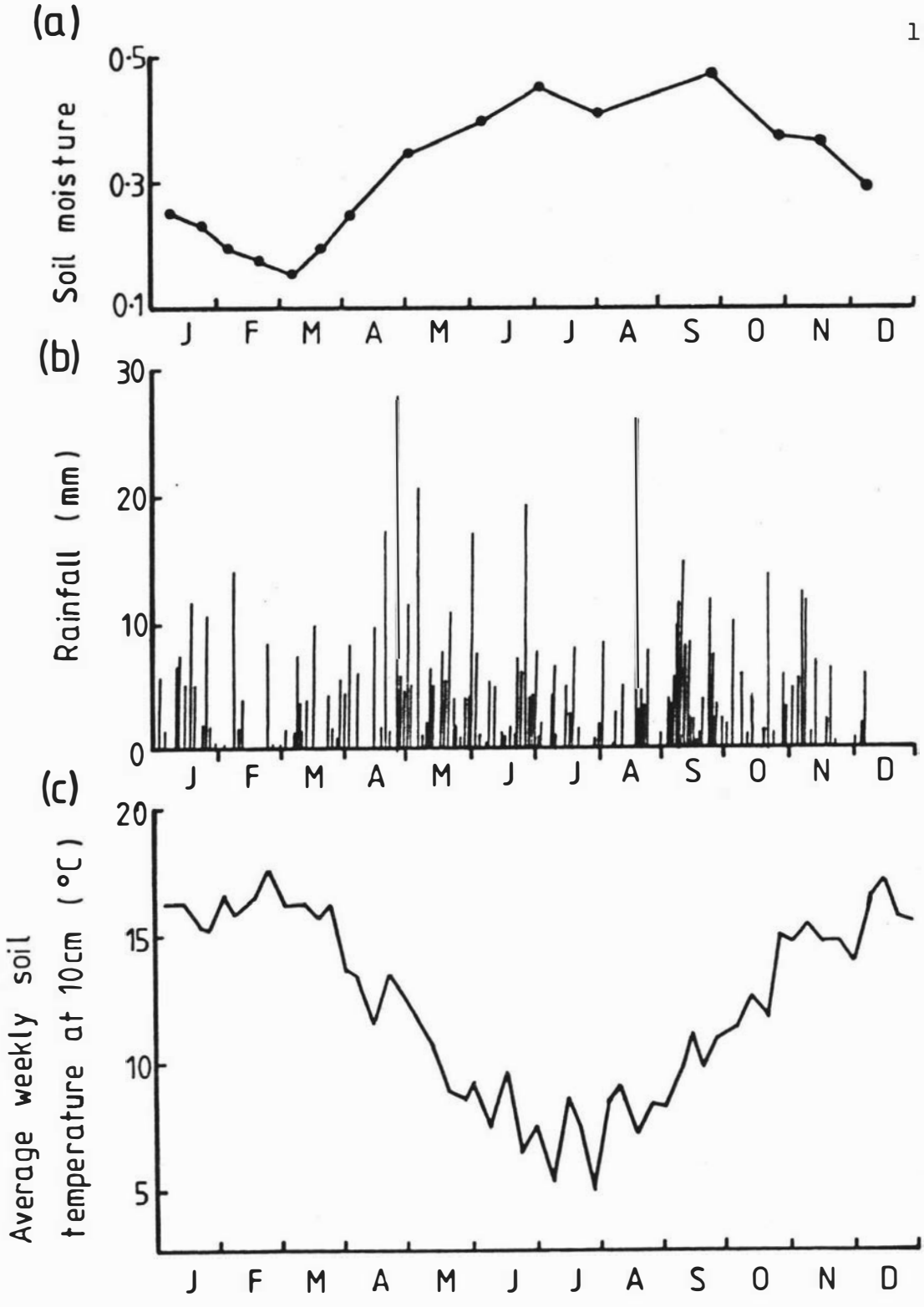

Figure 4.7 Gravimetric soil moisture content at 0-7.5 cm depth (a), rainfall (b), and average weekly soil temperature at 10 cm (c) at the Tokomaru site during the 12-month period

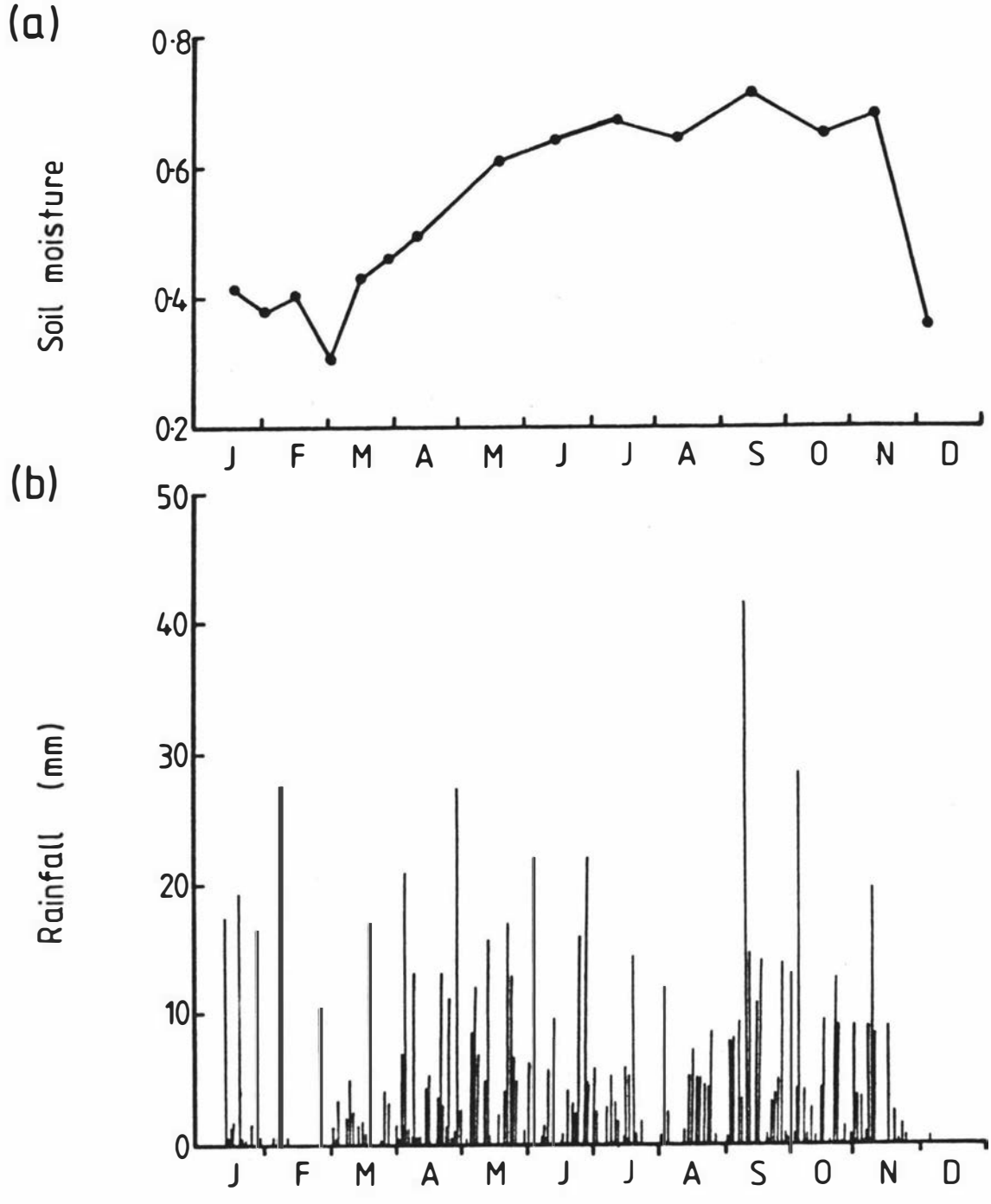

Figure 4.8 Gravimetric soil moisture content at 0-7.5 cm depth (a) and rainfall (b) at the Ramiha site during the 12-month period

resulted in significant increases in soil moisture content which were associated with low water-extractable P (Fig. 4.1). Visual assessment of pasture indicated rapid pasture growth during March.

A similar seasonal pattern for extractable soil P was obtained by Saunders and Metson (1971) who reported that, after heavy rains in March, there was a marked autumn flush of growth. During the autumn flush the increased P concentration in the pasture was accompanied by a fall in extractable soil P values. This concept has previously been suggested by Larsen (1967) and Wilson (1968) who considered that the readily-available sources of P were depleted during periods of rapid growth and then restored from more slowly available sources during subsequent periods of slow growth.

The build-up of water-extractable P during winter was evident in the 0-4.0 cm depth, particularly in the Ramiha soil (Fig. 4.3). During winter months, pasture growth was very slow (Fig. 4.9), and hence the utilisation of soil P would be relatively low. During this period of low soil temperatures (Fig. 4.7(c)) and high soil moisture content (Fig. 4.7(a) and 4.8(a)), conversion of various forms of soil phosphate into a plant-available form would still proceed, even though at a sub-optimum rate. Consequently, readily-available soil P would accumulate over the winter period resulting in high plant availability of soil P in spring. This was also indicated by high P concentration in pasture over the winter period (Fig. 4.10). A similar suggestion made by Scott and Cullen (1965) is that available P accumulates in the soil during the winter period of slow growth and is then able to support the rapid increase in spring growth. An attempt by Saunders and Metson (1971) to examine this hypothesis has failed to show any significant variations in soil P measured over the winter-spring period that could indicate a build-up of available P_i in the late winter and early spring. They suggested that the rapid release of P from organic residues and soil organic matter in the spring could provide sufficient available phosphate to maintain a high rate of pasture growth without any

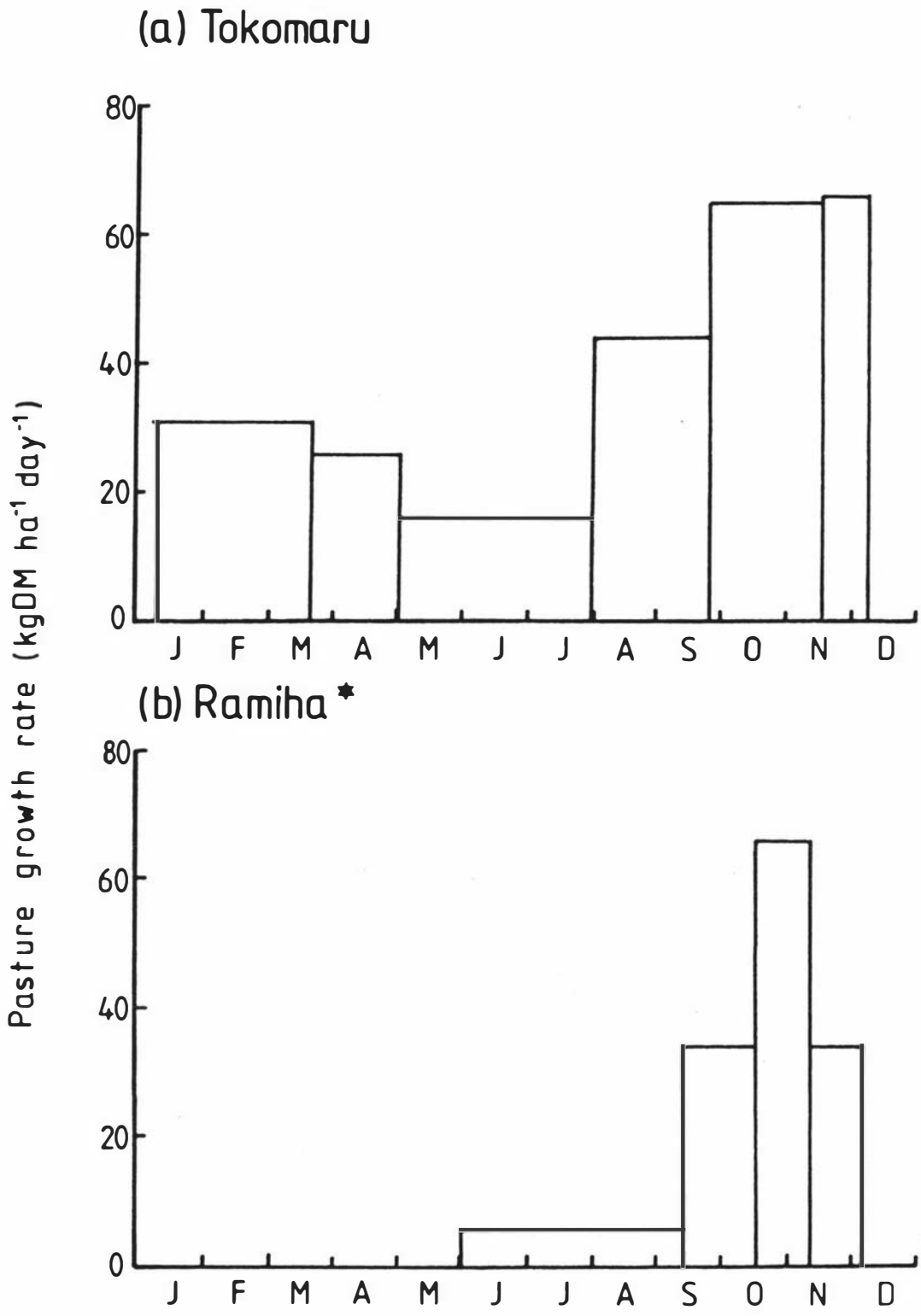

Figure 4.9 Changes in average pasture growth rate on the unfertilized Tokomaru (a) and Ramiha (b) soils

* Data available from June

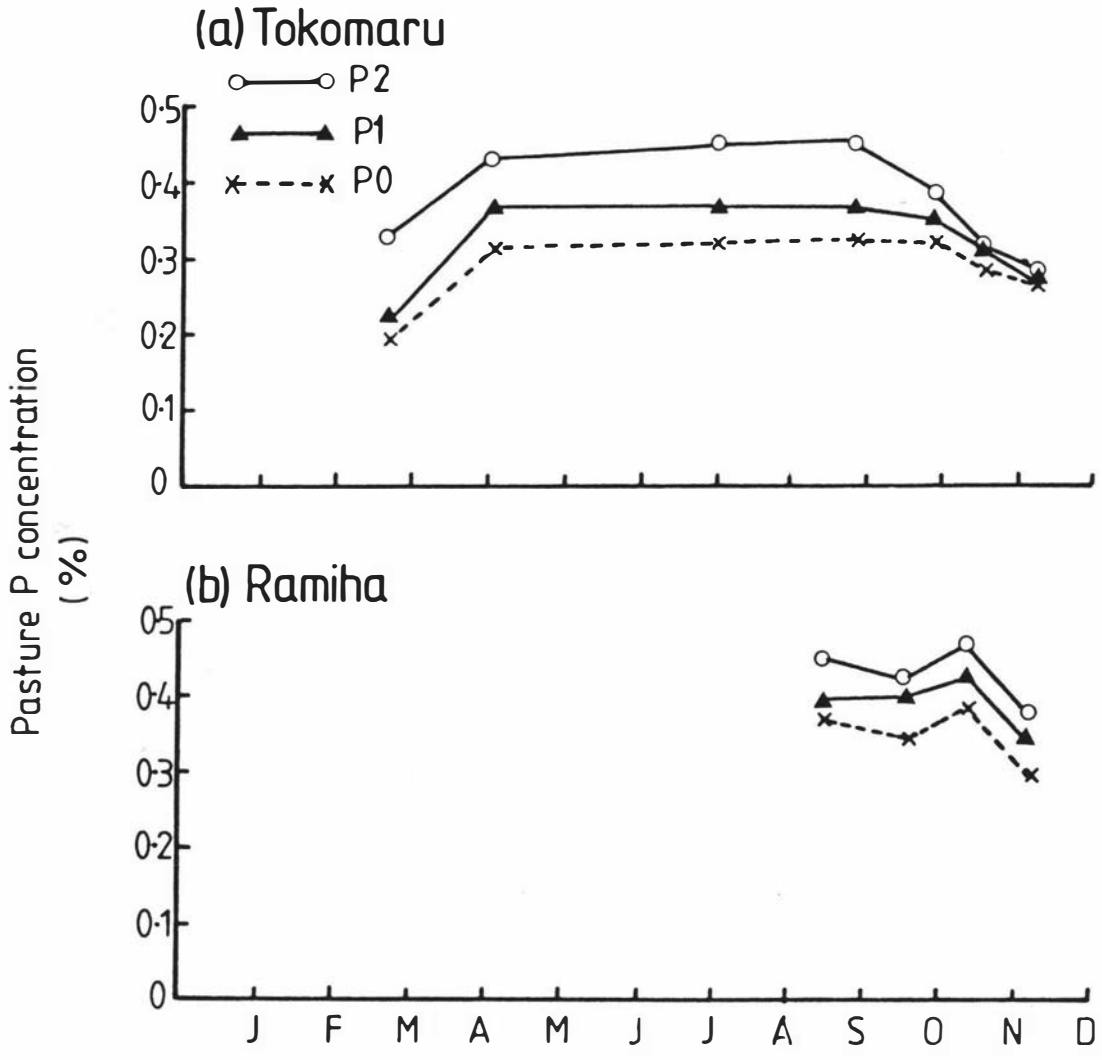

Figure 4.10 Changes in pasture P concentration on the Tokomaru soil (a) following the additions of 0 (P0), 20 (P1), and 40 (P2) kgP ha^{-1} of superphosphate; and Ramiha soil (b) following the additions of 0 (P0), 40 (P1), and 80 (P2) kgP ha^{-1} of superphosphate

appreciable change occurring in the level of soil P measured. These features were also observed in the seasonal pattern of the Olsen-extractable P in both soils (Fig. 4.5 and 4.6).

The decline in water-extractable P in spring was probably a result of spring flush growth. On both soils, the rates of pasture growth (Fig. 4.9) and P uptake (Fig. 4.11) increased considerably over the spring period. If it is assumed that most of the plant P is taken up from the 0-4.0 cm depth (Gillingham et al., 1980; Syers et al., 1984), then the total uptake of P during spring could not be accounted for by decreases in water-extractable P in this zone alone. For example, during September-November a decrease in water-extractable P of 0.9 $\mu g\ g^{-1}$ in the Tokomaru soil from the 0-4.0 cm depth (Fig. 4.1) would be equivalent to 0.5 kgP ha^{-1} (based on a bulk density of 1,305 kg m^{-3}, Table 4.1). However, pasture P uptake during this period was 9.8 kg ha^{-1} (Fig. 4.11(a)). Therefore more than 9 kgP ha^{-1} must have been made available to the plants from less readily-available sources of soil P, such as adsorbed P and soil organic P. There is considerable evidence that soil conditions in spring are most suitable for a high level of biological activity which enhances mineralisation of soil organic matter (e.g., Halm et al., 1972).

In the Ramiha soil the temporary depletion of extractable soil P in spring was followed by sudden increases in early summer (Fig. 4.3 and 4.5). It was found that after the spring period of rapid growth, the rate of pasture growth, P concentration, and P uptake on the Ramiha soil decreased markedly (Fig. 4.9(b), 4.10(b), and 4.12(b)) probably due to water stress caused by lack of rainfall (Fig. 4.8(b)) and increasing temperatures (Fig. 4.7(c)) during November-December. The resultant decreased P uptake apparently led to significant increases in extractable P in the Ramiha soil at the beginning of December (Fig. 4.3(b) and 4.5), with the exception of the water-extractable P in the 0-4.0 cm depth (Fig. 4.3(a)). It is possible that the small amounts of rain during November-December may have been

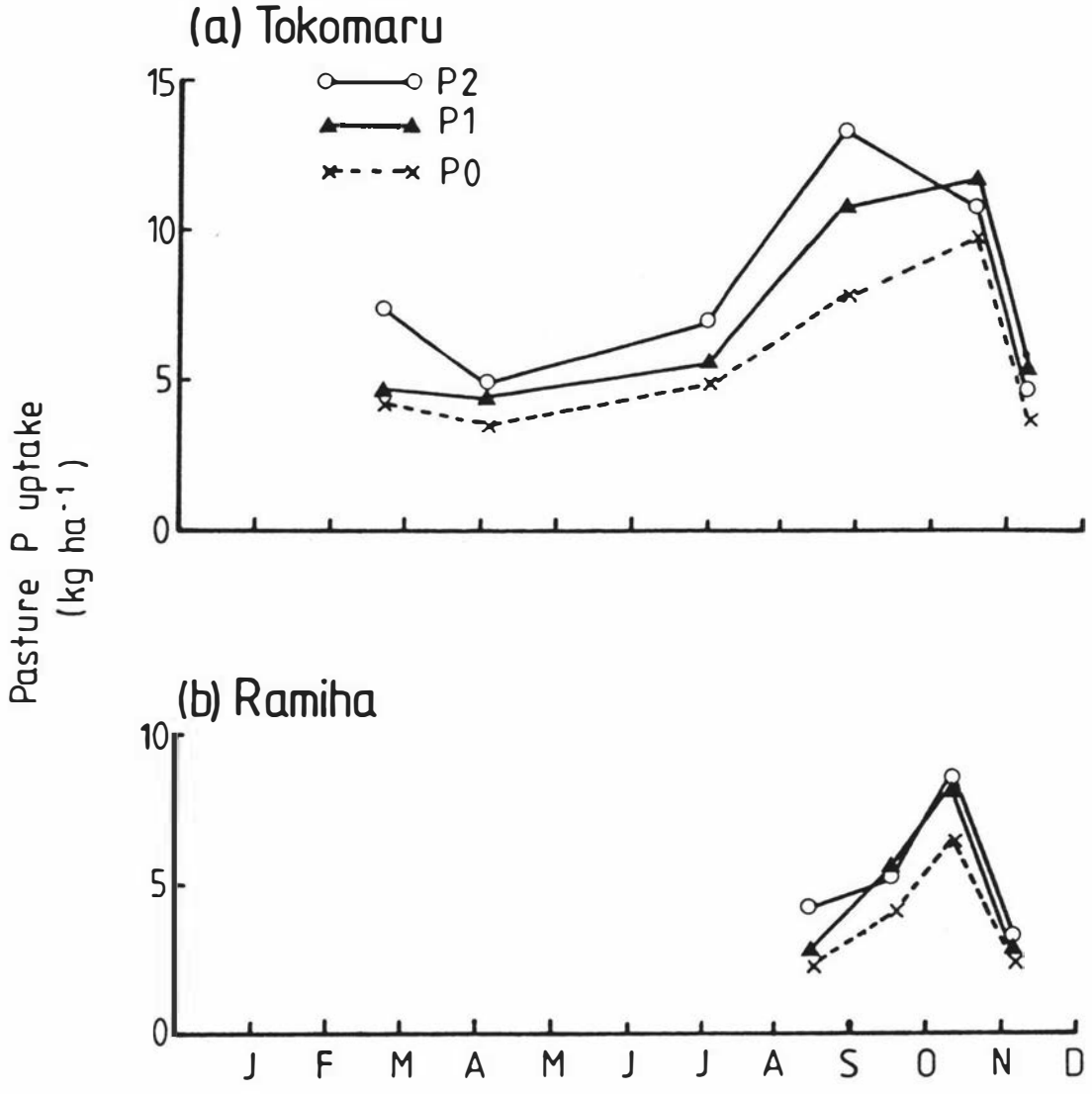

Figure 4.11 Changes in pasture P uptake on the Tokomaru soil (a) following the additions of 0 (P0), 20 (P1), and 40 (P2) kgP ha^{-1} of superphosphate; and Ramiha soil (b) following the additions of 0 (P0), 40 (P1), and 80 (P2) kgP ha^{-1} of superphosphate

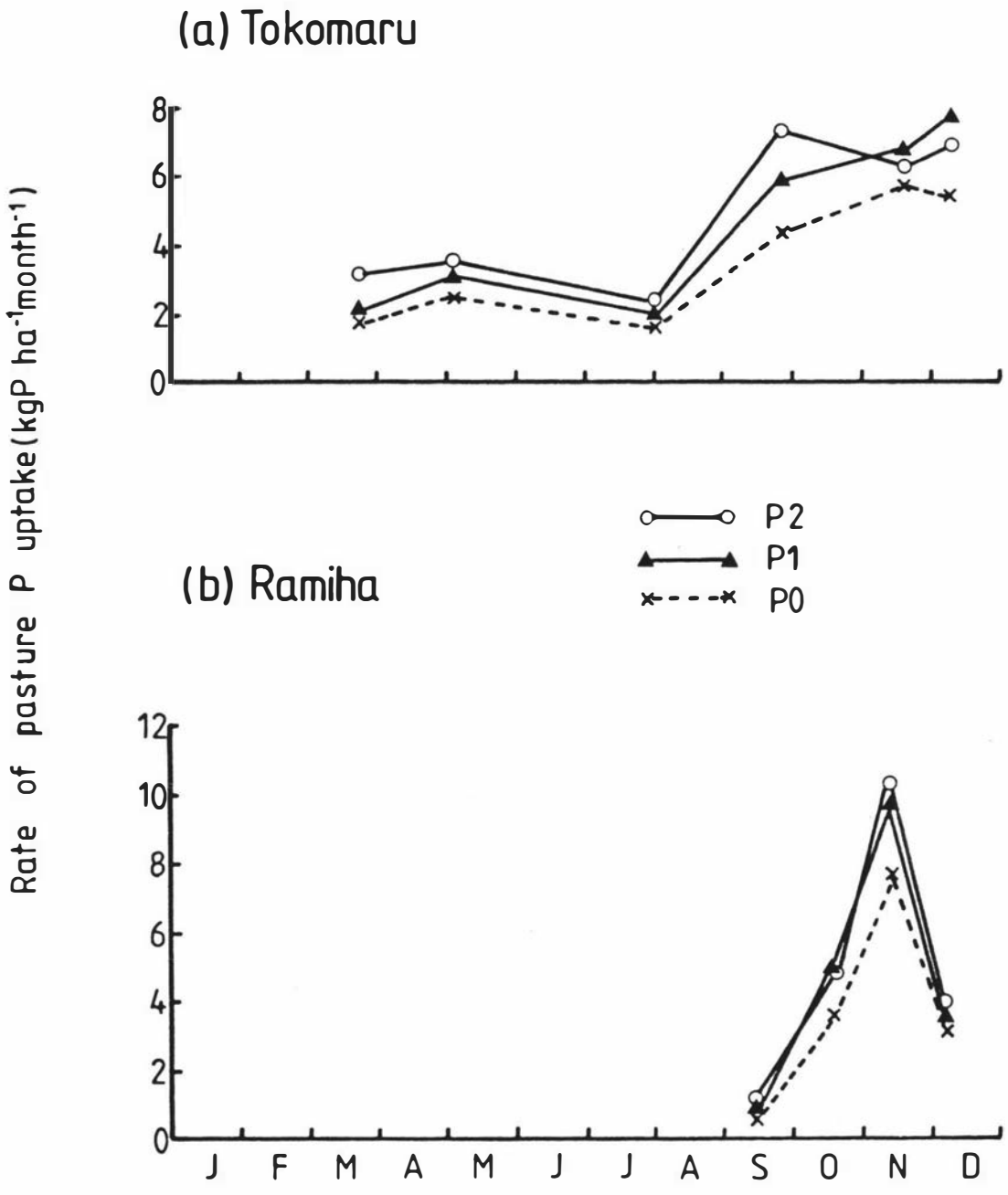

Figure 4.12 Changes in rate of pasture P uptake on the Tokomaru soil (a) following the additions of 0 (P0), 20 (P1), and 40 (P2) kgP ha^{-1} of superphosphate; and Ramiha soil (b) following the additions of 0 (P0), 40 (P1), and 80 (P2) kgP ha^{-1} of superphosphate

sufficient to wet the top 1-2 cm of the soil only. As a result, plant uptake of P would continue from within this top layer of soil, thus allowing no accumulation of water-extractable P in the top 4 cm layer. In contrast, such increases in extractable P in early summer were not observed in the Tokomaru soil (Fig. 4.4 and 4.6). This can be explained by the continually high pasture growth rate (Fig. 4.9(a)) and high P uptake (Fig. 4.11(a)) after spring. In the Tokomaru soil, the soil moisture content (Fig. 4.7(a)) was not so markedly reduced as to adversely affect pasture growth.

The effect of fertilizer P addition on plant availability of P is evident in the increases of total pasture uptake of P which resulted mainly from an increase in P concentration in the plants rather than from an increase in pasture dry matter. Following the addition of fertilizer P, significant increases ($P<0.01$) were found in the P concentration (%P) of pasture. However, there were no significant differences in the pasture dry matter production (Appendices I and II). This could be due to limitations of other nutrients.

4.3.4 Relationship between soil microbial biomass P and water-extractable P

Microbial biomass P in both Ramiha and Tokomaru soils fluctuated considerably throughout the growing season (Fig. 4.13 and 4.14). It ranged from 87 to 154 $\mu g\ g^{-1}$ soil (oven-dried basis) for the Ramiha soil and from 87 to 135 $\mu g\ g^{-1}$ soil for the Tokomaru soil. Of particular interest is the fact that the addition of fertilizer P had no influence on the amounts of microbial biomass P in either soil. The highest rate of fertilizer P added was 80 kgP ha^{-1} to the Ramiha soil, which was equivalent to 111 $\mu gP\ g^{-1}$. Therefore it is surprising that the addition of fertilizer P did not have any measurable effect on the pool of microbial biomass P which averaged approximately 118 $\mu g\ g^{-1}$. Although water-extractable P showed significant seasonal fluctuations, no direct relationship was obtained between changes in water-extractable P and those of microbial biomass P. ($r=0.29$ and 0.26 for the Ramiha and Tokomaru soils at 0-7.5 cm sampling depth, respectively). In

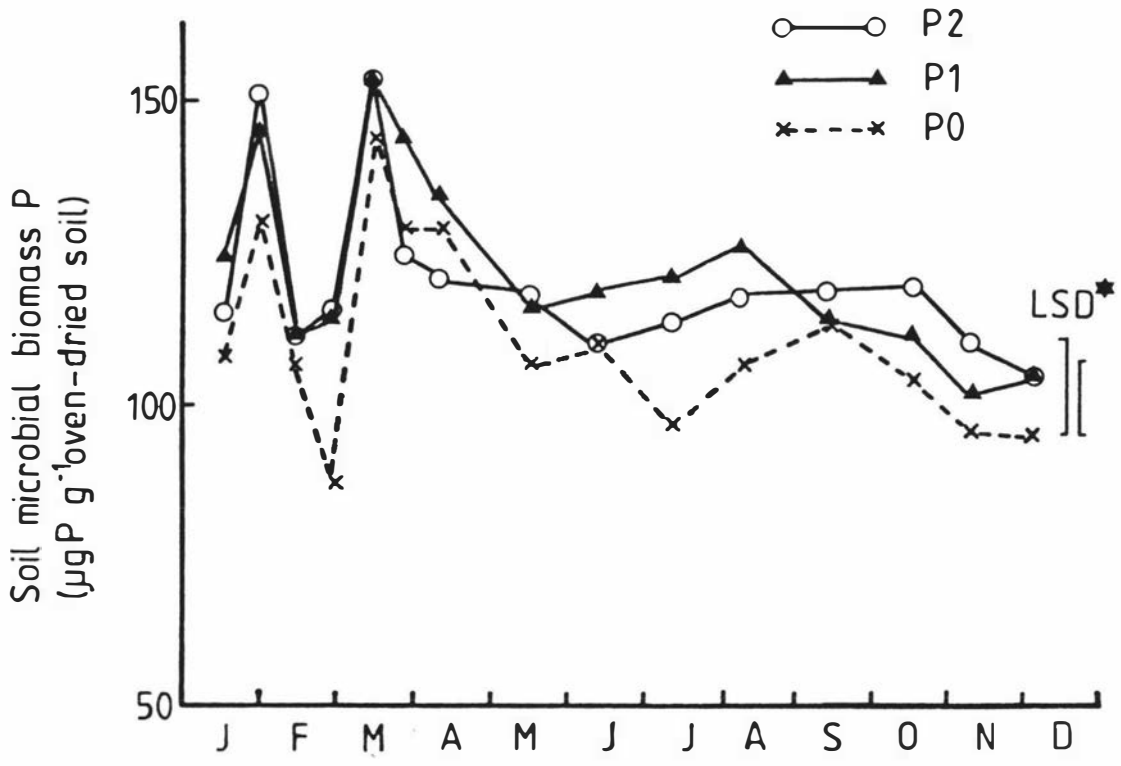

Figure 4.13 Changes in soil microbial biomass P in the Ramiha soil following the additions of 0 (P0), 40 (P1), and 80 (P2) kgP ha^{-1} of superphosphate

* Least significant difference at 1 and 5% levels

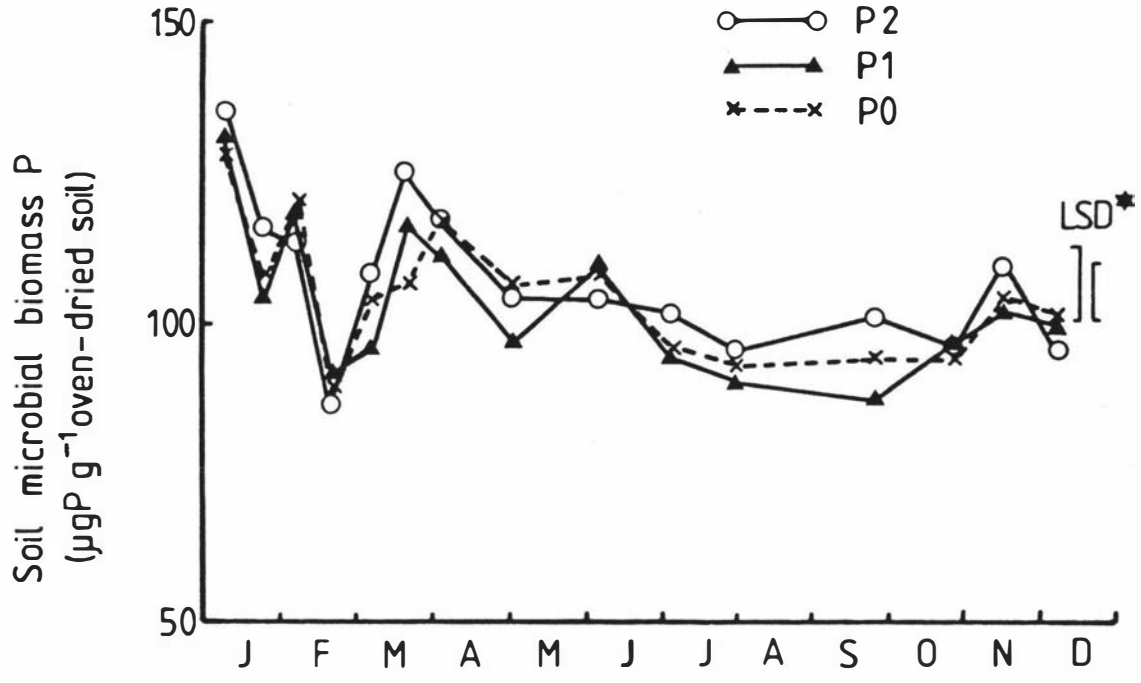

Figure 4.14 Changes in soil microbial biomass P in the Tokomaru soil following the additions of 0 (P0), 20 (P1), and 40 (P2) kgP ha^{-1} of superphosphate

* Least significant difference at 1 and 5% levels

other words, variations in water-extractable P could not be explained by changes in microbial biomass P in these soils. This may be due to the fact that the changes in water-extractable P was too small to be explained by a much larger pool of soil microbial biomass P. For example, during the 12 months the standard error of water-extractable P in the unfertilized Ramiha soil in the 0-7.5 cm depth was 0.4 $\mu g\ g^{-1}$ as compared to the standard error of soil microbial biomass within each sampling of 6.2 $\mu g\ g^{-1}$.

Although soil microbial biomass was determined in the soil samples taken from the 0-7.5 cm depth, which is the standard sampling depth, it is considered with hindsight that the determination of soil microbial biomass P in soil samples from the 0-4.0 cm depth may be more useful in attempts to explain variations in water-extractable P. This is because the amounts of water-extractable P in the 0-4.0 cm depth appeared to be more sensitive to fertilizer P addition and seasons than those in the 0-7.5 cm depth. The absence of significant relationship between water-extractable P and microbial biomass P seems to conflict with the suggestion that soil microbial biomass P, being a measure of labile organic P, should be a useful indicator of P availability in a soil (Halm et al., 1972; Brookes et al., 1982; Hedley and Stewart, 1982; Perrott and Sarathchandra, 1982). These workers obtained good correlations between soil microbial biomass P and available soil P, when comparing across a range of different soils. Although only two soil types were used in this study, they represent soils of contrasting properties, including P sorption capacity (Table 4.1).

It is likely that microbial biomass is strongly influenced by environmental factors, such as moisture and temperature, hence its value will vary considerably with changes in those factors. In this study, greatest fluctuations in microbial biomass P occurred between January and May (Fig. 4.13 and 4.14) when there were also significant variations in soil moisture contents (Fig. 4.7(a) and 4.8(a)). Sharp increases in microbial biomass P in March

appear to be associated with the drying and wetting of soils. It is known that one of the most important factors influencing microbial activity under field conditions is fluctuations in soil moisture (Lund and Goksoyr, 1980), and that the most significant consequence of the drying/wetting effect is the accelerated release of plant nutrients (Marumoto et al., 1982). Dalal (1977) suggested that part of the organic matter which decomposes during the drying period later disperses into the soil solution upon wetting and also that drying and wetting breaks up water-stable soil aggregates such that the humic matter that has been inaccessible to the soil microorganisms becomes exposed for decomposition.

During the winter period the variations in microbial biomass P became relatively small, possibly due to low microbial activity caused by a combination of cold temperature (Fig. 4.7(c)) and excessively high soil moisture (Fig. 4.7(a) and 4.8(a)). Microbial activity can be inhibited not only by unfavourably low temperatures but also by excessive soil moisture which restricts aeration (Russell, 1973).

Results for microbial biomass P in both the Ramiha and Tokomaru soils seem to be high compared with published data from New Zealand and overseas studies (Anderson and Domsch, 1980; Brookes et al., 1982; Hedley and Stewart, 1982; Perrott and Sarathchandra, 1982). Brookes et al. (1982) recorded soil biomass P values of 5.3 to 72.3 $\mu g\ g^{-1}$ from the top 0-10 cm of seven English soils, whereas Perrott and Sarathchandra (1982) obtained a range of 20 to 88 $\mu g\ g^{-1}$ (mean = 51) for a group of 20 New Zealand soils under well-established pasture. In Canada, Hedley and Stewart (1982) reported a value of 18.2 $\mu g\ g^{-1}$ of microbial P. Using C:P ratios ranging from 7:1 to 17:1, Anderson and Domsch (1980) estimated that the average quantity of microbial P in the top 12.5 cm of forest soils is 70 kg ha^{-1} which is equivalent to 56 $\mu g\ g^{-1}$ soil assuming a bulk density of 1,000 kg m^{-3}. Similarly, Chauhan et al. (1981) calculated that microbial P values in soil could range from 1.5 to 50 $\mu g\ g^{-1}$ soil.

It is inevitable that variations in the procedures used by different workers to measure microbial biomass P in soils would contribute to differences in the estimates. It is likely that soils sampled from a lower depth would give lower estimates of microbial biomass P. The method used by Brookes et al. (1982) and Perrott and Sarathchandra (1982) employed a soil:solution ratio of the extracting solution of 1:20 and an extraction time of 30 min. The method chosen for the present study used a soil:solution of 1:40 and an extraction time of 16 h. The wider ratio was adopted following the recommendation by Hedley and Stewart (1982) that the ratio should be between 1:30 and 1:60. They also reported that an extraction time of 16 h gave higher results for microbial P than did the 30 min period. It was decided that the larger amount of P extracted during a longer extraction time would help to improve the accuracy when calculating the amount of microbial biomass P from the difference of two measurements. The modification of the procedure probably contributed to the comparatively high values of microbial biomass P measured in this study.

Another possible source of variation is the manner in which results are expressed. Estimates of various forms of soil P are usually expressed in units of P per unit weight of soil on an air-dried basis, as soils are normally air-dried before the analysis. The measurement of soil microbial biomass P, however, involves the use of field-moist samples so the results must be corrected for variations in soil moisture contents. While some workers (Brookes et al., 1982) have corrected for this and expressed their results as per unit weight of soil on an oven-dried basis, others have given no indication whether or not the correction has been made or whether the results are expressed on an air-dried or oven-dried basis (Anderson and Domsch, 1980; Hedley and Stewart, 1982; Perrott and Sarathchandra, 1982). Both the modification of the procedures and the fact that results are expressed on an oven-dried basis possibly account for the higher values of microbial biomass P obtained in this study compared with the published data.

4.3.5 Relationship between changes in $NaHCO_3$-soluble organic P and water-extractable P

It was found that $NaHCO_3$-extractable organic P was not affected by the addition of fertilizer P in both the Ramiha and Tokomaru soils, but varied significantly with sampling time ($P<0.01$) (Fig. 4.15(a) and 4.16(a)). In the Ramiha soil, $NaHCO_3$-extractable organic P tended to decrease from high values in late summer to relatively low values during autumn and winter, and then increased again towards summer (Fig. 4.15(a)). The relatively low values during the winter period may be the result of a low level of microbial activity. In contrast to the Ramiha soil, variations in $NaHCO_3$-extractable organic P in the Tokomaru soil did not show any definite seasonal patterns (Fig. 4.16(a)).

Also there was no relationship between microbial biomass P (Fig. 4.13 and 4.14) and $NaHCO_3$-extractable organic (Fig. 4.15(a) and 4.16(a)) or total P (Fig. 4.15(b) and 4.16(b)). This finding is inconsistent with those of Halm et al. (1972) and Perrott and Sarathchandra (1982) who obtained significant correlations between these parameters. Furthermore, changes in $NaHCO_3$-extractable total P (Fig. 4.15(b) and 4.16(b)) bear no relation to changes in water- or Olsen-extractable P (Fig. 4.3, 4.4, 4.5, and 4.6). It appears that, in these soils, estimates of $NaHCO_3$-extractable organic or total P did not relate either to the availability of soil P as indicated by water- or Olsen-extractable P or to microbial biomass P.

4.3.6 Relationship between changes in soil pH and water-extractable P

Soil pH at both the 0-4.0 and 0-7.5 cm depths showed significant variations ($P<0.01$) with sampling times for both soils (Appendices III and IV). Variations in soil pH, however, did not help explain the seasonal fluctuations of water-extractable P (Fig. 4.3 and 4.4). The addition of superphosphate appeared to lower the pH of both soils at both depths. However, only in the 0-7.5 cm depth of the Ramiha soil were the decreases sufficiently consistent to be statistically significant ($P<0.05$).

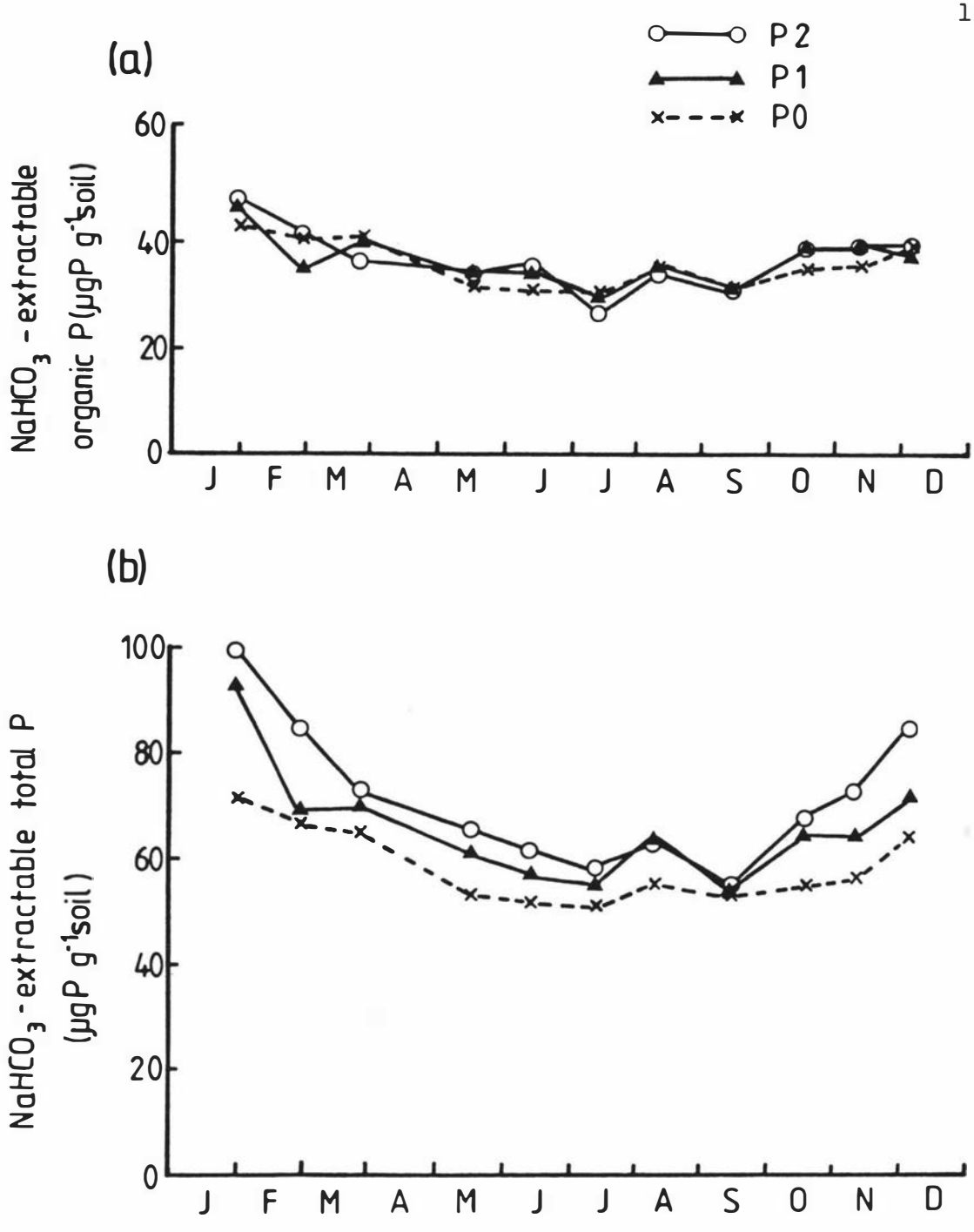

Figure 4.15 Changes in $NaHCO_3$-extractable organic (a) and total (b) P in the Ramiha soil following the additions of 0 (P0), 40 (P1) and 80 (P2) kgP ha^{-1} of superphosphate

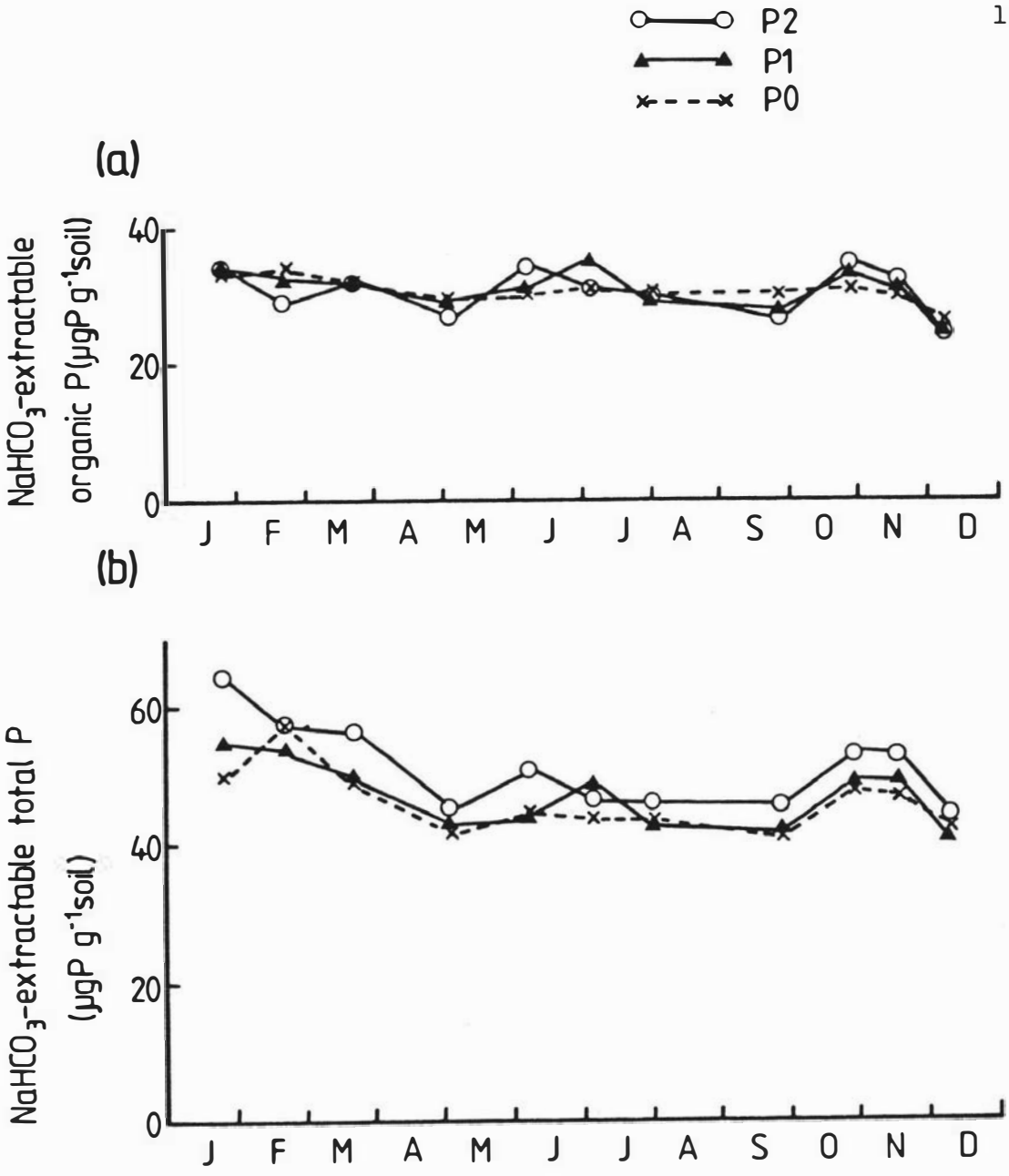

Figure 4.16 Changes in $NaHCO_3$-extractable organic (a) and total (b) P in the Tokomaru soil following the additions of 0 (P0), 20 (P1), and 40 (P2) kgP ha^{-1} of superphosphate

4.4 Conclusions

The Ramiha and Tokomaru soils showed significant seasonal variations in water- and Olsen-extractable P. The variations during the 12-month period of study were larger for water-extractable P than for Olsen-extractable P. For example, the coefficient of variation of water-extractable P during the 12-month period in the Ramiha soil (0-4.0 cm depth) was 45.4% compared with 21.6% for Olsen-extractable P. Seasonal fluctuations were closely related to the pattern of pasture P uptake which, in turn, was influenced by seasonal factors such as rainfall and temperature. Low values of extractable P were associated with autumn and spring flushes of pasture growth, while high values were obtained during periods of slow growth in winter and in one case in summer also.

In contrast to the seasonal variations, the variability of water-extractable P within each sampling was similar to that of Olsen-extractable P. The implication of this finding is that, although levels of water-extractable P in soil are generally smaller than those of Olsen-extractable P, the variability associated with water-extractable P within each sampling is comparable with that of Olsen-extractable P.

Sampling depth affected the levels of water- and Olsen-extractable P in both soils. The values in the 0-4.0 cm depth were higher than those in the 0-7.5 cm depth. The seasonal variability of water-extractable P in the 0-4.0 cm depth was lower in the Tokomaru soil and higher in the Ramiha soil than in the 0-7.5 cm depth. The effect of sampling depth on the variability of water-extractable P, therefore, varied with soil. Further studies on a wider range of soils may provide a more conclusive result. It appears that the effect of sampling depth in this study was mainly on the absolute levels of extractable soil P. There was no significant influence of sampling depth on the variability within sampling of extractable soil P in both soils.

The addition of fertilizer P to the Ramiha and Tokomaru soils caused significant increases in water- and Olsen-extractable P. The effect of added P, however, varied considerably with sampling time during the growing season. Initially there were marked fluctuations in the months immediately following the addition of fertilizer P. These variations became smaller with time. These results support the general recommendation that soil sampling should not be carried out within the first few months after fertilizer application. The seasonal pattern in fertilized soils was essentially the same as in the unfertilized soils. With the addition of fertilizer P, the depletion in the autumn and the winter build-up of extractable P were more pronounced. The relatively high values of water-extractable P in late winter also accentuated the effect of fertilizer P addition. Therefore values of water-extractable P in soil samples collected in late winter or early spring (i.e., before spring flush) should best reflect the potential availability of soil P as affected by P addition.

It was found that increases in water-extractable P in the 0-7.5 cm depth due to added P were not as marked as in the 0-4.0 cm depth. The effect of fertilizer P addition became insignificant in the 0-7.5 cm depth within a few months of addition. This was despite the continuing responses to added P as indicated by higher P concentration of pasture in the fertilized than in the control treatment. It appears that water-extractable P in the 0-7.5 cm depth was not a sufficiently sensitive indicator which could accurately or fully reflect the effect of fertilizer P addition on these two soils. Hence it is proposed that, to monitor the effect of fertilizer P addition, water-extractable P should be determined from the 0-4.0 rather than the 0-7.5 cm depth.

Seasonal fluctuations in water-extractable P were not related to changes in soil microbial biomass P which averaged 118 and 105 $\mu g\ g^{-1}$ soil (oven-dried basis) for the Ramiha and Tokomaru soils, respectively. It is unlikely that variations in water-extractable P could be explained by

changes in a much larger pool of microbial biomass P. The addition of fertilizer P had no effect on soil microbial biomass P in either soil. The results obtained suggest that microbial biomass P may be a less sensitive index of soil P availability than previously thought.

CHAPTER 5

CHAPTER 5

EFFECT OF SOIL pH ON OLSEN- AND WATER-EXTRACTABLE P VALUES

5.1 Introduction

Ground limestone ($CaCO_3$) is applied to many agricultural soils throughout the world with a view to overcoming soil acidity. The resulting increase in soil pH can affect the availability of several plant nutrients, including P. In some situations, lime has been reported to decrease the availability of soil P (e.g., Pearson, 1975), whereas in others it is thought that liming can increase P availability (e.g., Lambert and Grant, 1980; Haynes and Ludecke, 1981; Haynes, 1982). This increased availability has been attributed to a reduction in P sorption due to an increase in pH (Hsu and Rennie, 1962; Murrmann and Peech, 1969a; Dalal, 1977; Otabbong, 1981) and also to an increased rate of mineralisation of organic P (Halstead et al., 1963; Dalal, 1977; Otabbong, 1981).

Confusion in the literature concerning the effects of lime on soil P is partly due to the experimental difficulties involved in such assessments. Direct measurements can easily be made of plant yield, P content, and thus P uptake, but all of these parameters can also be influenced by factors which are not related to the chemistry or availability of soil P. For example, with very acid soils, liming often increases P uptake of plants by decreasing Al toxicity rather than by increasing the actual P availability (Ryan and Smillie, 1975; Vickers and Zak, 1978; Haynes and Ludecke, 1981). Attempts to characterise the effect of lime on available soil P by the use of chemical extractants have also given contradictory results (e.g., Griffin, 1971; Amarasiri and Olsen, 1973; Sumner, 1979; Haynes and Ludecke, 1981; Thomson, 1981). This can be attributed to the variation in extractants used by various workers and also to the differences in the range of soil pH values considered.

In New Zealand, the Olsen P test (0.5M $NaHCO_3$, pH 8.5, Olsen et al., 1954a) has been used as a routine soil-testing procedure since 1976. It was developed originally for calcareous soils but was later used successfully on acid and neutral soils (Barrow and Shaw, 1976). Recently, it has been suggested that the interpretation of the Olsen test is influenced by soil pH, at least with one particular soil group, namely the yellow-grey earth group (Saunders, 1981). He obtained the following relationship:

Relative yield = 21.2 ln (Olsen P) + 13.3 (Soil pH) - 44.8

which indicates that pasture production relative to maximum is dependent on soil pH as well as on the Olsen P test. It was suggested from this relationship that a soil with a pH of 5.5 would require an Olsen test of 19 to give 90% of maximum yield. In contrast, for a soil with a pH of 6.5, an Olsen test of 10 would be required to give the same level of production. A similar relationship was also obtained for a group of 20 soils used in the study described in Chapter 3 (i.e., Plant P uptake = -91.4 + 2.74 (Olsen-extractable P) - 0.44 (Phosphate retention) + 19.1 (Soil pH), Section 3.3.5). Soil pH had a positive effect on the prediction of plant-available P by the Olsen and PR tests. In other words, if the pH of a soil is increased by one unit the Olsen test required to predict the same level of plant-available P would decrease by seven units.

There are at least two possible explanations that may account for such a relationship: Firstly, it is possible that when soil pH is increased, plants can use soil P more efficiently and therefore they require lower soil P levels to maintain the same level of production (Edmeades and Crouchley, 1981). This is generally referred to as a phosphate-sparing effect of time (During et al., 1960). The second possibility is that the Olsen extraction procedure is itself pH-dependent and does not correctly indicate the amount of available soil P in high pH soils.

Evidence is accumulating to suggest that on some soils, the Olsen test gives lower values as the pH is increased and

that this decline in the Olsen test values is not supported by herbage data or by alternative soil tests (Allbrook and Stiefel, 1977; Lambert and Grant, 1980; Davis, 1981; Thomson, 1981; Holford, 1983). In other words, this anomaly may be a result of an artifact in the Olsen procedure. This has obvious implications to the interpretation of the Olsen P values of limed soils when used for making fertilizer P recommendation.

In this study, the suggested dependence of the Olsen test on soil pH was investigated by comparison with other estimates of available soil P, including water-extractable P. Attempts were made in laboratory experiments to study the origin of the effect of lime addition on Olsen P values. Also glasshouse and field experiments were carried out to evaluate the likely significance of the results obtained.

5.2 Materials and Methods

5.2.1 Soils

Two soils with contrasting P retention properties were used: an Egmont black loam with a high P retention capacity and a Tokomaru silt loam with a low P retention capacity. The soils were sampled to a depth of 7.5 cm from low fertility sites under pasture, air-dried, and sieved (<2 mm). They were first incubated with three rates of P (as solutions of KH_2PO_4, Table 5.1) for eight weeks. After being air-dried and sieved (<2 mm), the soils were re-incubated with four rates of lime (as $Ca(OH)_2$, Table 5.1) for a further eight weeks. The incubating soils were maintained at a moisture content corresponding to 80% field capacity and at a temperature of 20 ± 5°C. The moisture content at field capacity was determined at -50 cm pressure potential. At the end of the incubation period, the soils were air-dried and sieved (<2 mm). Soil pH was measured in distilled water as described in Section 3.2.2.

Table 5.1 Rates of P (KH_2PO_4) and lime ($Ca(OH)_2$ added in the incubation study

Treatment	Soil	
	Egmont	Tokomaru
Phosphate addition (μgP g^{-1} soil)		
Zero	0	0
Medium	200	75
High	400	150
Lime addition (kg ha^{-1})#		
L_0	0	0
L_1	2000	500
L_2	4000	1000
L_3	6000	2000

Rates of addition of $Ca(OH)_2$ were calculated on the basis of Ca equivalent to kg $CaCO_3$ ha^{-1}, assuming a soil depth of 7.5 cm and a bulk density of 810 and 1250 kg m^{-3} for the Egmont and Tokomaru soils, respectively.

5.2.2 Soil P analysis

Water- and Olsen-extractable P in soils were determined by the methods described in Sections 3.2.4.1 and 3.2.4.2.

Isotopically-exchangeable P was determined by pre-equilibrating 2 g of air-dried soil with 39 ml of distilled water for 5 h before adding 1 ml of carrier-free $H_3{}^{32}PO_4$ (providing 1 and 3 μCi ^{32}P per sample of the Tokomaru and Egmont soils, respectively) and shaking for 1 h. After centrifuging, the soil suspension was filtered through a membrane filter (Millipore, <450 nm), and the extract analysed for ^{31}P and ^{32}P, as described in Section 3.2.4.5.

5.2.3 Glasshouse study

The plant availability of P in each of the 24 soils (three rates of P x four rates of lime x two soils) which had been incubated with P and lime was determined in a pot experiment using the method of Stanford and DeMent (1957). This technique is designed to be highly exploitive for the nutrient under study. A 250-ml plastic container with the bottom removed was placed in a second intact container and filled with 300 g of washed river sand. Perennial ryegrass (Lolium perenne L., Grasslands "Nui") was used as the test plant and 30 seeds were sown, later thinned to 15 plants per pot. A complete nutrient solution (Middleton and Toxopeus, 1973) was applied regularly and moisture was maintained at field capacity by daily watering. After eight weeks, the roots of ryegrass had grown throughout the sand medium and formed a dense mat at the bottom of the pot. The plants were cut to a level of 2 cm above the soil surface. The inner pot (with roots) was then transferred onto another intact pot containing 20 g of incubated soil which had previously been moistened to field capacity. As a control treatment, the inner container was transferred onto 20 g of washed river sand. In the three weeks prior to the transfer, a nutrient solution free of P (Middleton and Toxopeus, 1973) was applied to the pots, replacing the complete nutrient solution, and this was continued until the completion of the experiment. The pots were watered daily to field capacity.

Two harvests were taken at 5 and 10 weeks after the plants were placed in contact with the soils. After the final harvest, the soil was separated from the sand, and the roots separated from the soil. Roots in the sand were washed and combined with those separated from the soil. The above-ground herbage and the root material were then analysed for P as described in Section 3.2.3.

5.2.4 Explanation of the effect of soil pH on Olsen-extractable P

5.2.4.1 Analysis of Olsen extracts

The pH of the Olsen extract after shaking with the soil was measured using a pH meter and combination electrode, and the Ca concentration determined using atomic absorption spectrophotometry.

5.2.4.2 Addition of Ca

To determine whether the decrease in Olsen-extractable P values was related to the increased level of Ca in limed soils, the concentration of Ca in unlimed soils was raised artificially by the addition of solid $CaCl_2$ immediately prior to the Olsen extraction. Solid $CaCl_2$ (supplying 3,240 $\mu gCa\ g^{-1}$ Egmont soil and 1,080 $\mu gCa\ g^{-1}$ Tokomaru soil) was thoroughly mixed with the soils that had previously been incubated with the medium rate of P (Table 5.1). The amounts of Ca added were equivalent to the highest rate of lime (L_3) in the incubation study. The soils were then extracted with the Olsen reagent and the extracts analysed for P, as described in Section 3.2.4.2.

The possibility that $CaCO_3$ could be precipitated in the Olsen extracts of limed soils and P be sorbed subsequently by the precipitate was explored as follows. The Olsen extractant (38 ml) was first shaken for 15 min with 1 ml of Ca solution (as $CaCl_2$). The concentrations of Ca in the solution were calculated to cover the range of Ca levels found in the Olsen extracts of limed soils. Then 1 ml of a solution of KH_2PO_4 (containing 30 $\mu gP\ ml^{-1}$) was added and the suspension shaken for a further 15 min. The extract was centrifuged, filtered through a membrane filter (Millipore,

<450 nm), and analysed for Ca and P as described in Sections 5.2.4.1 and 3.2.4.8, respectively.

5.2.5 Field study

To investigate the effect of lime addition on Olsen-extractable P under field conditions, an experiment was established on the site from which the Tokomaru soil was collected (soil pH = 5.5, Olsen-extractable P = 11 $\mu g\ g^{-1}$ soil). The site was under a permanent ryegrass-clover pasture. There were four treatments:

1. Control
2. Lime 1: 2,500 kg $CaCO_3$ ha^{-1}
3. Lime 2: 5,000 kg $CaCO_3$ ha^{-1}
4. Gypsum: $CaSO_4$ providing Ca equivalent to treatment 2 (Lime 1)

These were surface-applied to plots (10 x 10 m), in a completely randomised block layout with five replicates. A basal dressing of superphosphate (40 kgP ha^{-1}) was applied to all plots at the same time as the lime in March, 1982. Soil sampling was carried out at monthly intervals following lime application. At each soil sampling, 15 soil cores (0-7.5 cm depth and 2.5 cm diameter) were taken from each plot, and bulked. The soil was then air-dried and sieved (<2 mm). Subsamples of soils were taken for the determination of water- and Olsen-extractable P (Sections 3.2.4.1 and 3.2.4.2) and soil pH (Section 3.2.2). The trial was rotationally grazed by sheep, as required, to control pasture growth. In September, 1982, and February and April, 1983, yield cuts were taken prior to grazing. The herbage from mown strips was weighed and subsampled for P analysis (Section 3.2.3) and yield determination.

5.3 Results and Discussion

5.3.1 Extractable soil P

Addition of the highest rate of $Ca(OH)_2$ increased soil pH from 5.3 to 6.5 in the Egmont soil and from 5.0 to 6.2 in the Tokomaru soil (Table 5.2). The effects of $Ca(OH)_2$ addition on extractable soil P were variable (Table 5.3). Increasing soil pH caused a significant reduction ($P<0.01$) in Olsen-extractable P in both soils at all levels of P addition. The decrease was similar in both soils.

In contrast, there was a significant increase ($P<0.01$) with lime addition in the amounts of isotopically-exchangeable soil P. There was only a small increase in the amounts of water-extractable P as a result of liming. The increase was significant ($P<0.05$) only with the Egmont soil. This disagreement between the effect of lime on the Olsen test and that on alternative soil tests supports the work of Lambert and Grant (1980), Davis (1981), and Thomson (1981). In their studies, liming resulted in a decline in Olsen-extractable P but an increase in the Truog P test. In a long term field experiment, Allbrook and Stiefel (1977) recorded higher Truog P values in a limed soil than in the unlimed soil but when the Truog test was replaced by the Olsen test the reverse was obtained. A small effect of lime addition on water-extractable P was also reported by Mansell (1981), who found that when a yellow-brown earth and a yellow-brown loam were limed, Olsen-extractable P decreased while there was no change in water-extractable P. Edmeades and Crouchley (1981), however, did not observe any disagreement between soil P tests on a yellow-grey earth as a result of liming. They reported decreases in Olsen-, water-, and $CaCl_2$-extractable P. In a recent study, Wheeler and Edmeades (1984) reported that lime addition decreased Olsen P values by 50% on a yellow-brown loam. It appears that the effect of lime addition on extractable soil P may vary from soil to soil.

Table 5.2 pH values of soils incubated with P and lime

Soil	Rate of P addition	Rate of lime addition			
		L_0	L_1	L_2	L_3
Egmont	Zero	5.3	5.7	6.2	6.5
	Medium	5.3	5.7	6.1	6.5
	High	5.3	5.8	6.2	6.5
Tokomaru	Zero	5.0	5.2	5.4	6.2
	Medium	5.0	5.1	5.4	6.2
	High	5.0	5.2	5.4	6.2

Table 5.3 Amounts of Olsen- and water-extractable P, exchangeable P, and plant-available P in the Egmont and Tokomaru soils after incubation with P and lime (expressed as $\mu g\ P\ g^{-1}$ soil)

	Egmont				Tokomaru			
	Rate of lime addition				Rate of lime addition			
	L_0	L_1	L_2	L_3	L_0	L_1	L_2	L_3
Olsen-extractable P								
Zero P	10.8	9.3	8.4	8.3	10.2	10.0	8.7	8.0
Medium P	24.0	23.8	21.9	18.2	23.9	22.9	20.5	18.6
High P	32.8	29.2	26.1	25.6	39.5	38.0	35.1	32.8
	LSD (P<0.05) = 1.2				LSD (P<0.05) = 0.8			
	LSD (P<0.01) = 1.6				LSD (P<0.01) = 1.1			
Water-extractable P								
Zero P	0.4	0.4	0.4	0.4	2.8	2.8	2.8	2.8
Medium P	1.7	1.9	1.9	2.6	8.2	7.8	8.1	7.9
High P	3.5	3.6	3.5	3.6	15.8	15.7	15.6	15.8
	LSD (P<0.05) = 0.4				LSD (P<0.05) = 1.0			
	LSD (P<0.01) = 0.6				LSD (P<0.01) = 1.3			
Exchangeable P								
Zero P	26.1	24.9	28.8	33.8	6.4	6.9	6.9	9.3
Medium P	33.2	34.2	37.3	40.3	15.7	15.3	17.0	19.1
High P	48.6	49.3	53.4	54.3	22.4	24.9	23.4	26.5
	LSD (P<0.05) = 5.5				LSD (P<0.05) = 0.7			
	LSD (P<0.01) = 7.4				LSD (P<0.01) = 0.9			
Plant-available P#								
Zero P	41.6	47.2	29.7	33.3	15.8	18.0	16.1	21.9
Medium P	73.8	76.1	68.1	72.1	49.5	43.2	39.8	39.9
High P	105.5	96.9	74.9	83.6	70.5	82.6	86.2	83.8
	LSD (P<0.05) = 27.2				LSD (P<0.05) = 18.7			
	LSD (P<0.01) = 36.5				LSD (P<0.01) = 25.1			

Indicated by P uptake of ryegrass in 10 weeks.

5.3.2 Plant-available P

A significant ($P<0.01$) response to added P was obtained with both soils during the 10-week growth period, as assessed by both dry matter yield and P uptake by ryegrass (Table 5.3). Addition of lime, however, had no significant effect on either yield or P uptake by ryegrass. Certainly there was no consistent depressing effect of lime, which might have been implied by the decline in Olsen-extractable P values. This finding is in accord with the result reported by Davis (1981) for a yellow-brown earth subsoil, which showed that the decline in Olsen test following liming was not accompanied by a reduction in P uptake of white clover or lucerne.

The findings from this glasshouse study and the various extractions of soil P indicate that lime has an influence on the amounts of soil P extracted by the Olsen reagent which is not consistent with its effect on plant availability or the amounts of water-extractable and exchangeable P. This suggests that the decrease in Olsen-extractable P, with increasing soil pH, may be an artifact in the Olsen procedure which results in the removal of P from solution in the Olsen extraction rather than there being a smaller pool of available P in the soil itself.

5.3.3 Explanation of the effect of soil pH on Olsen-extractable P

5.3.3.1 Analysis of Olsen extracts

The pH of the Olsen extracts of soils that had been limed at different rates was essentially constant at 8.6 (Fig. 5.1), despite the marked differences in the original soil pH (Table 5.2). Thus it is unlikely that changes in final pH of the extracting solution are a dominant factor in the decline of Olsen-extractable P values of limed soils.

In contrast to pH, marked changes were obtained in the concentrations of Ca remaining in the Olsen extracts of limed soils (Fig. 5.1). As the rates of lime addition were increased, the Ca concentrations increased up to a certain

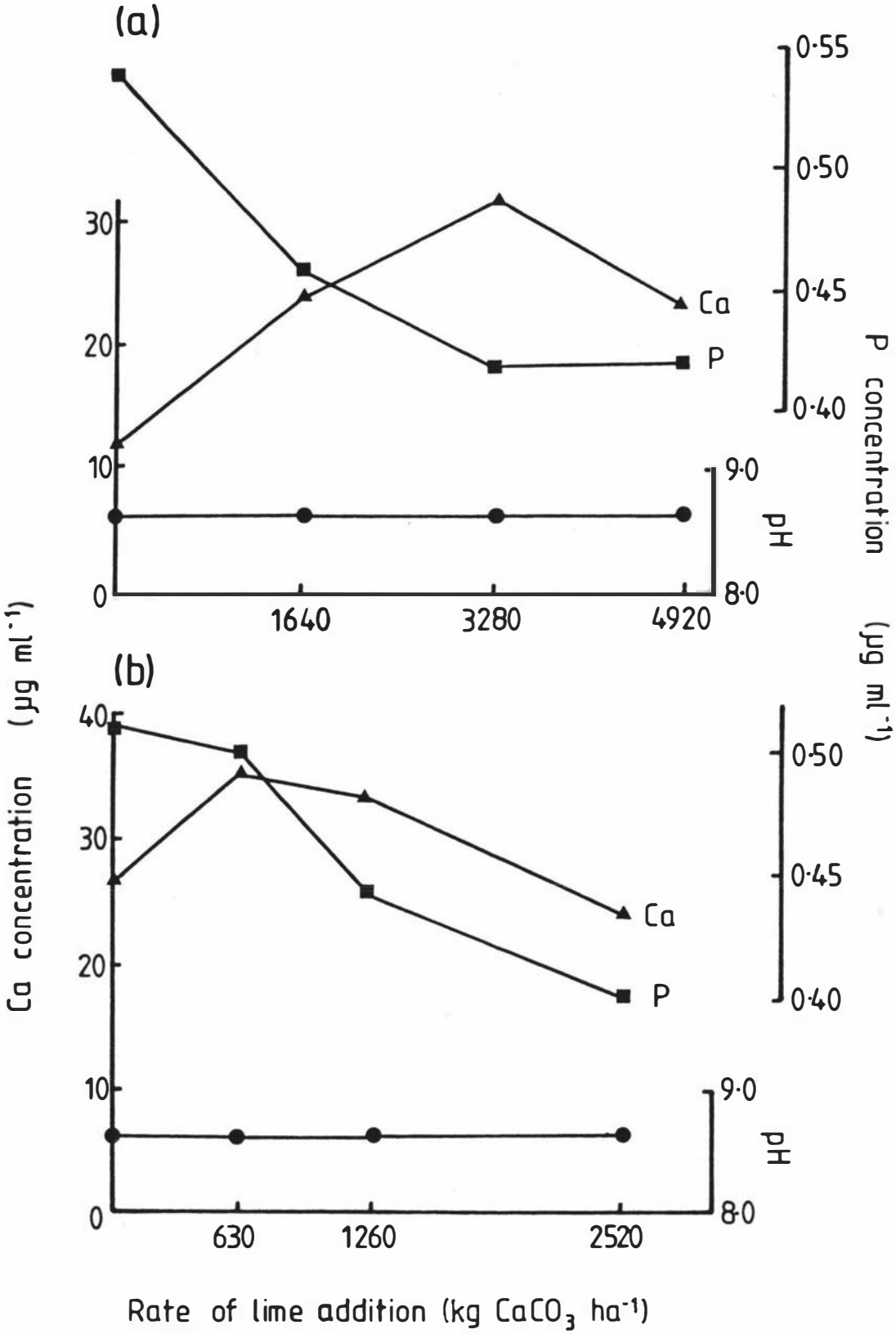

Figure 5.1 Concentration of Ca and P, and pH in Olsen extracts of Egmont (a) and Tokomaru (b) soils limed at different rates

* Least significant difference at 1 and 5% levels

level and then decreased. The sudden decrease in the Ca concentrations at high rates of lime addition suggests that precipitation of Ca has occurred. The decrease is also consistent with the reduction in P concentration in Olsen extracts.

5.3.3.2 Addition of Ca

The addition of Ca (as solid $CaCl_2$) to the unlimed soils immediately prior to the Olsen extraction resulted in a decrease in Olsen-extractable P in both soils (Fig. 5.2). The decrease was more pronounced in the Egmont soil than in the Tokomaru soil. This finding supports the suggestion that the presence of high Ca concentrations in soil may be responsible for the removal of P from Olsen extracts.

The mechanisms involved in P removal from solution could include either the sorption of P by precipitated $CaCO_3$ or the co-precipitation of Ca with P. In an investigation of the first possibility, it was found that although $CaCO_3$ precipitated immediately following the addition of $CaCl_2$ to an Olsen extract, no detectable amount of added P was removed from solution if the addition of P took place after the $CaCO_3$ precipitate was formed. This suggests that it is unlikely that P is sorbed by $CaCO_3$ precipitates under the conditions of the Olsen extraction.

The second, and more likely possibility, is that the decrease in Olsen-extractable P values in limed soils occurs because of the formation of a precipitate containing Ca and P under the conditions of high Ca concentration and high pH. Once the solubility product of this precipitate has been reached, any further increase in Ca concentration will decrease the concentration of P remaining in solution.

5.3.4 Field study

The addition of two rates of lime increased soil pH at the Tokomaru site from 5.5 to 6.1 and 6.6, respectively (Fig. 5.3). The increases were obtained within one month of the lime application, and were still maintained after

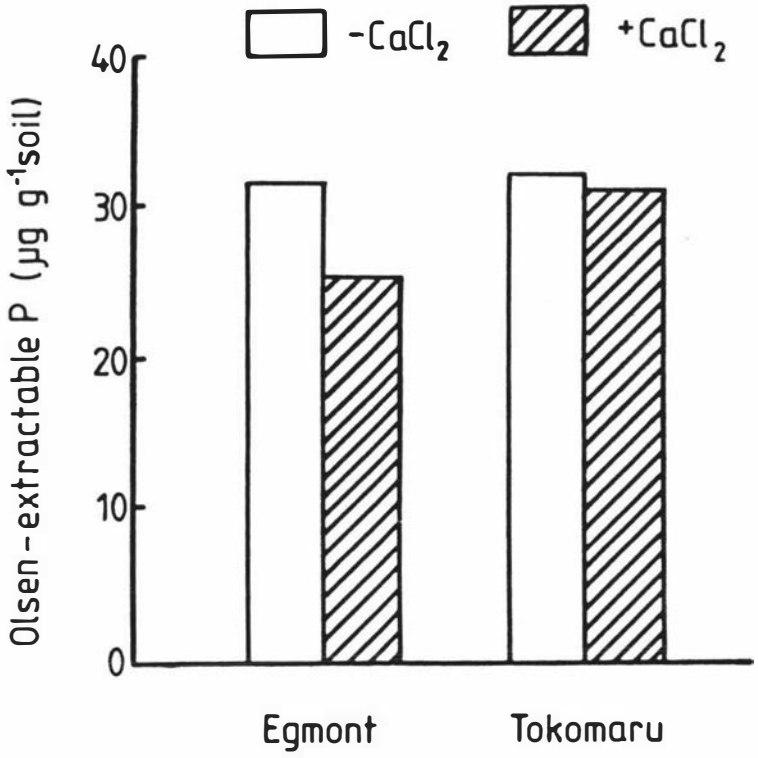

Figure 5.2 Olsen-extractable P values for the Egmont and Tokomaru soils with and without the addition of $CaCl_2$ immediately before the Olsen extraction

* Least significant difference at 1 and 5% levels

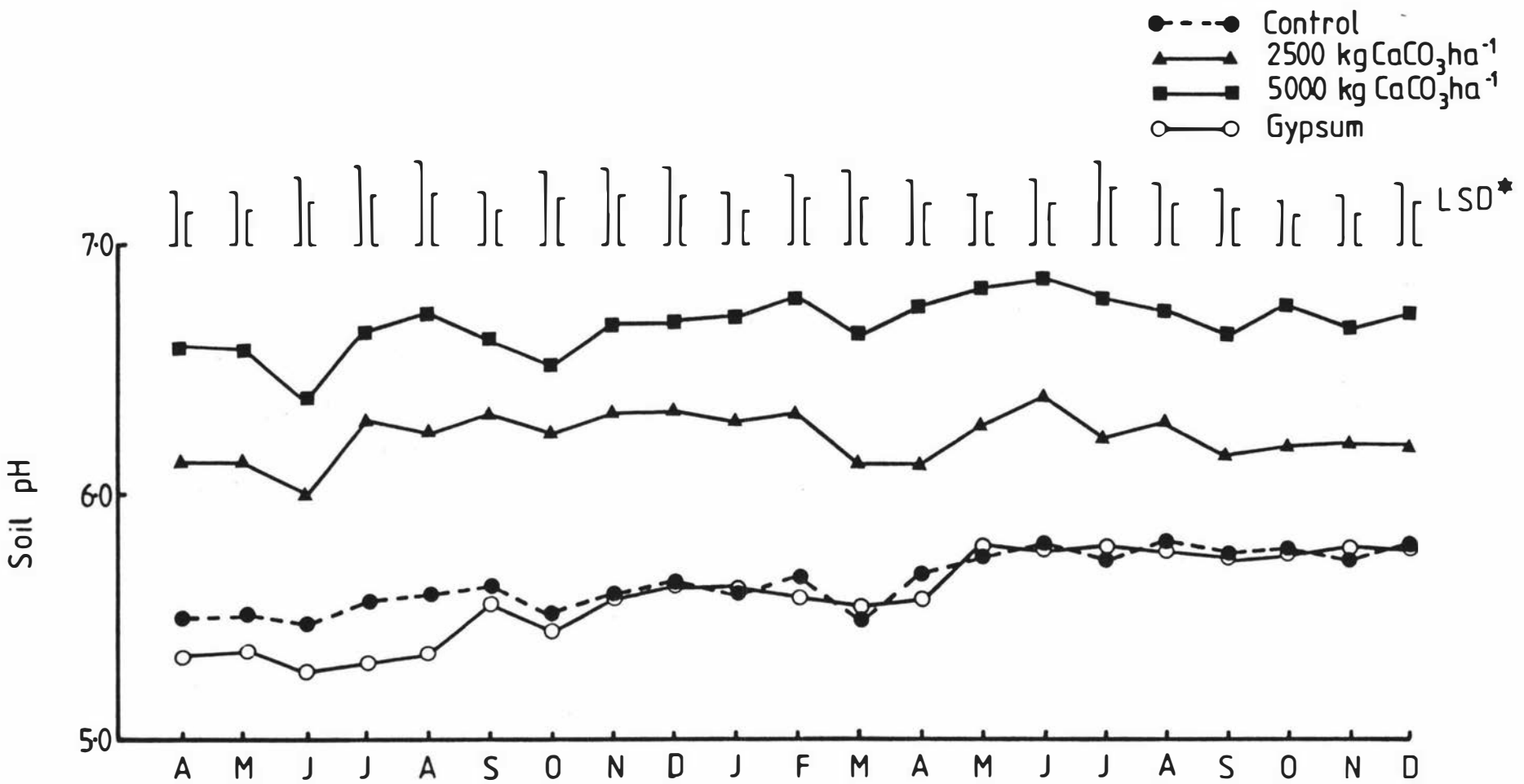

Figure 5.3 Changes in soil pH in the Tokomaru soil from the field study following the additions of 0, 2,500 and 5,000 kg $CaCO_3$ ha^{-1} and gypsum (as $CaSO_4$ providing Ca equivalent to 2,500 kg $CaCO_3$ ha^{-1})

* Least significant difference at 1 and 5% levels

21 months. However, there were no significant differences in Olsen-extractable P values between the control and the limed plots during the first five months after the application of lime (Fig. 5.4). After five months, Olsen-extractable P values of the limed plots started to decrease compared to those of the control plots. The decrease was slightly greater at the higher rate of lime addition. The 5-month delay in obtaining the observed decrease in Olsen-extractable P may be attributed to the slow rate of dissolution of surface-applied $CaCO_3$. In the measurement of soil pH, the soil sample was equilibrated with water for 24 h, and this condition may enhance the dissolution of $CaCO_3$ thereby increasing the soil pH immediately after the addition of lime. In contrast, the alkaline condition and the short extraction time of the Olsen procedure (see Section 3.2.4.2) are unlikely to alter the dissolution rate of $CaCO_3$.

The magnitude of the decrease in Olsen-extractable P values for the limed plots varied throughout the year. Greater reductions were observed during late spring and early summer, while smaller decreases occurred over the autumn and winter period. The levels of Olsen-extractable P on all plots were generally lower during the late autumn and winter period than during the spring and summer months. This seasonal pattern is consistent with that observed in another field study on the same soil described in Chapter 4.

After 21 months following lime application, the depressing effect of lime on Olsen-extractable P still persisted. At the final soil sampling in December, 1983, the Olsen-extractable P value at the highest rate of lime addition was 11.4 compared to 17.4 $\mu g\ g^{-1}$ soil on the control plots. This difference of 6.0 $\mu g\ g^{-1}$ soil represents a significant reduction ($P<0.01$) of 30% in the Olsen-extractable P value as a result of liming.

It is interesting to note that the addition of gypsum did not result in any significant reduction in Olsen-extractable P (Fig. 5.4). Although gypsum was applied at

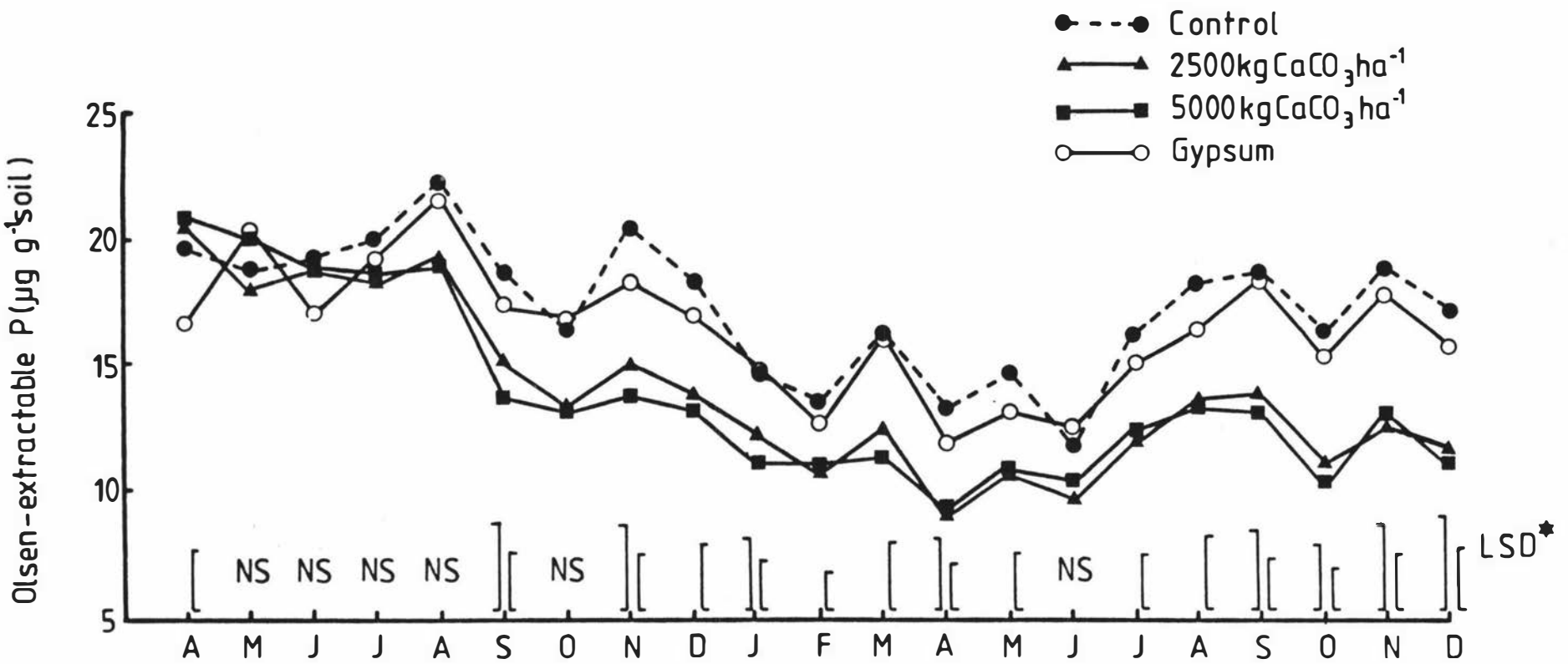

Figure 5.4 Changes in Olsen-extractable P in the Tokomaru soil from the field study following the additions of 0, 2,500, and 5,000 kg $CaCO_3$ ha^{-1} and gypsum (as $CaSO_4$ providing Ca equivalent to 2,500 kg $CaCO_3$ ha^{-1})

* Least significant difference at 1 and 5% levels

the rate which provided the same amount of Ca as the lowest rate of lime, it did not have the same effect on soil pH as did the lime addition. Soil pH values for the plots that had received gypsum were initially slightly lower than those for the control plots but after six months there was no difference between the two treatments (Fig. 5.3). It is unlikely that the difference in soil pH would account for the absence of the depressing effect on Olsen-extractable P because it was found earlier (Section 5.3.3.1) that the initial soil pH had no effect on the final pH of the Olsen extract.

The effect of the addition of lime on water-extractable P was markedly different from the effect on Olsen-extractable P. In contrast to the Olsen test, the amounts of water-extractable P on the plots that had received 5,000 kg lime ha^{-1} were slightly higher than those of the control plots (Fig. 5.5), although the overall increases were not statistically significant. This is consistent with the study of Bailey et al. (1976), who also reported increases in water-soluble P in the Dannevirke, Kiwitea, and Marton silt loams following the addition of lime. The increase in water-extractable P in the limed soils is likely to be a result of the increased mineralisation of soil organic P. Herbage data from the three cuts (Fig. 5.6) revealed that neither the yield nor P content of pasture showed any adverse effect of lime addition. This field trial result confirms the similar finding obtained from the glasshouse experiment (Section 5.3.2).

5.4 Conclusions

Liming a soil to increase its pH can result in a significant decrease in Olsen-extractable P which is not supported by alternative soil tests or plant data. The decline is thought to be the result of an artifact in the Olsen procedure by which calcium phosphates may be precipitated under the conditions of high Ca concentration and high pH. The high concentration of Ca in limed soils appears to be the dominant factor.

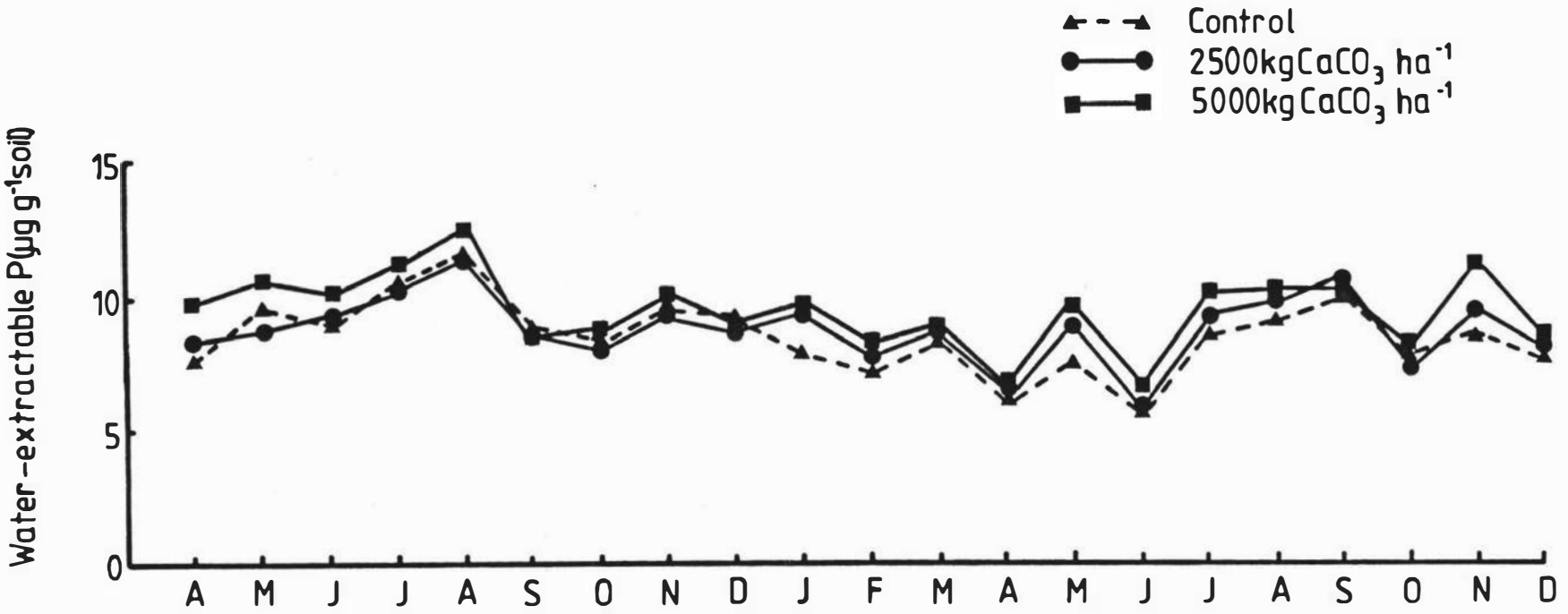

Figure 5.5 Changes in water-extractable P in the Tokomaru soil from the field study following the additions of 0, 2,500, and 5,000 kg $CaCO_3$ ha^{-1}

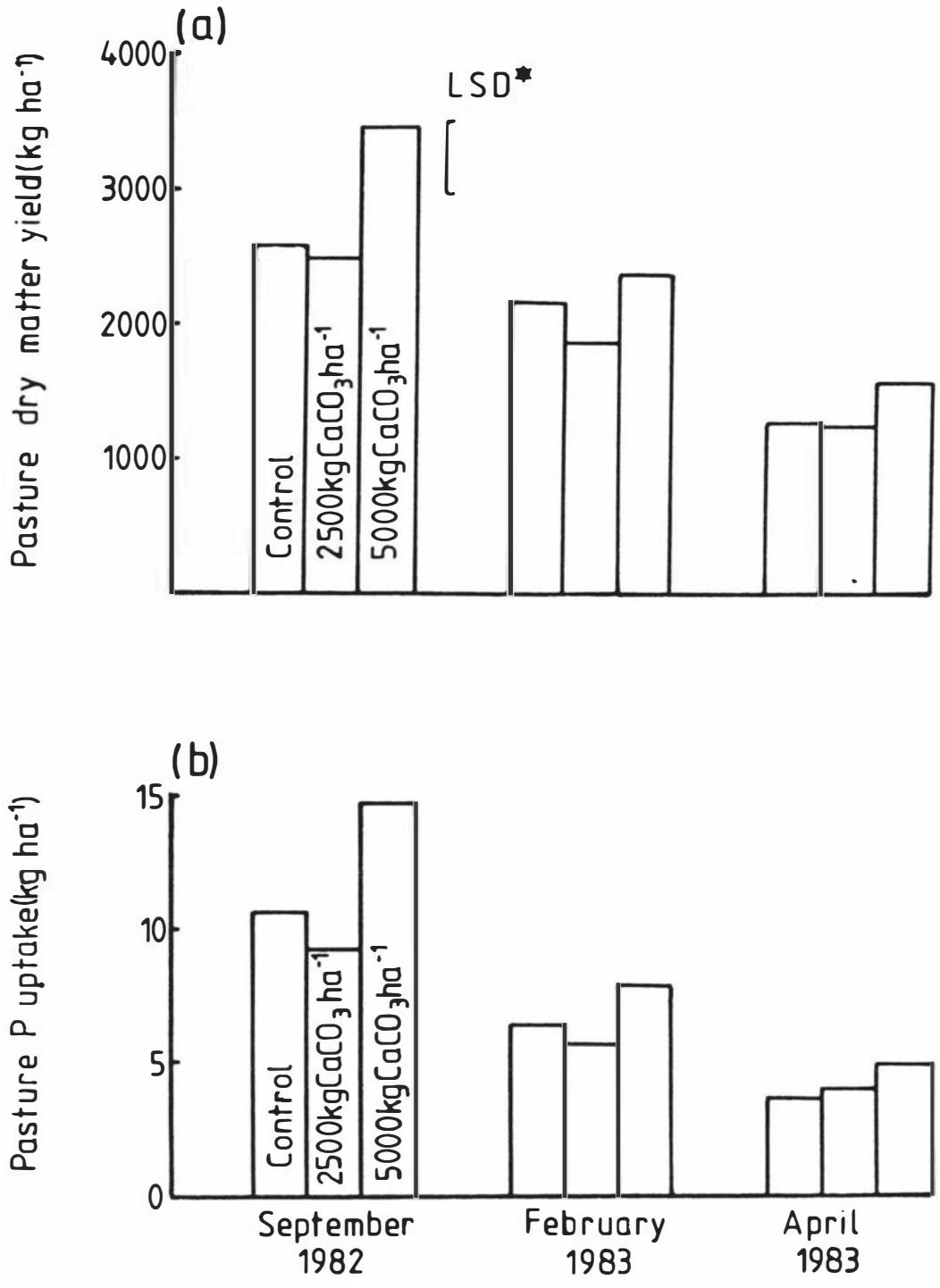

Figure 5.6 Dry matter yield (a) and P uptake (b) of pasture on the Tokomaru soil following the additions of 0, 2,500, and 5,000 kg $CaCO_3$ ha^{-1} in March, 1982

* Least significant difference at 1 and 5% levels

The fact that liming caused a decrease in Olsen-extractable P under field conditions, without any adverse effect on pasture production, strongly suggests that care should be taken in interpreting Olsen test values of limed soils when making recommendations for the use of fertilizer P. In this regard, the water-extraction procedure has an advantage over the Olsen test as a soil P test because water-extractable P values are much less influenced by soil pH.

In this study, the effect of soil pH on Olsen-extractable P was investigated using two soils. A more extensive study is needed to assess the extent of such an effect on a wider range of soils.

CHAPTER 6

CHAPTER 6

MODELLING CHANGES IN WATER-EXTRACTABLE P IN SOILS FOLLOWING FERTILIZER P ADDITION

6.1 Introduction

The results from field studies, discussed in Chapter 4, showed that water-extractable P levels in soils were significantly influenced by fertilizer P application. It appeared that the water-extraction procedure was more sensitive to fertilizer P application than was the Olsen procedure. Consequently, the water-extraction procedure may be a more useful soil test for the new fertilizer recommendation scheme recently introduced in New Zealand. The scheme is based on a model (Cornforth and Sinclair, 1982) which is used to calculate the maintenance P requirements of grazed pasture. In a maintenance situation, the amounts of fertilizer P applied are intended to replace P losses, thereby maintaining the existing level of available soil P. If an excessive amount of fertilizer P is applied, an appropriate soil P test should be sufficiently sensitive to reflect this situation. This requires a knowledge of the relationship between changes in the soil P test and the amounts of fertilizer P added.

Several models have been developed by different researchers in attempts to describe or predict such a relationship (e.g., Mansell et al., 1977; Russell, 1977; Barrow and Carter, 1978; Cox et al., 1981). One of the difficulties encountered in the development and evaluation of these models concerns the division of the sorbed P into conceptual compartments having varying degrees of availability. Ideally, this division should be based upon concepts of physical chemistry (Mansell and Selim, 1981). Because such an approach was used by Ryden et al. (1977a), their model of P sorption will be discussed here. Ryden et

al. (1977a) suggested that the P sorption data for contrasting soils and hydrous ferric oxide gel over a wide range of P concentrations could be described by three distinct, Langmuir-type sorption isotherms. Supporting data for the charge and pH relationships of sorption, and the effects of pH, other ions, and ionic strength on sorption (e.g., Ryden and Syers, 1975, 1977a, b; Ryden et al., 1977a, b), were used to develop two chemisorption mechanisms at equilibrium solution P concentrations of less than 200 $\mu g\ l^{-1}$. Above this concentration, a third mechanism became operational; this was described as 'more-physical sorption'. Subsequently, Ryden et al. (1977a) proposed that P could be sorbed at three distinct populations or regions of sites, each conforming to a particular Langmuir equation.

The Langmuir approach used by Ryden et al. (1977a) to describe P sorption assumes that solution P tends towards an equilibrium with the potential for P to be sorbed in three regions. In each region the rate of the forward reaction (P sorption at vacant sites) is controlled by solution P concentration, a rate factor (KF), and the number of vacant sites. This may be written as:

$$\text{KF} \times \text{Soln [P]} \times \text{vacant sites}$$

$$\text{Solution P} \longrightarrow \text{Sorbed P} \qquad (6.1)$$

Similarly, the rate of the reverse reaction (P desorption from occupied sites) may be written as

$$\text{KR} \times \text{occupied sites}$$

$$\text{Sorbed P} \longrightarrow \text{Solution P} \qquad (6.2)$$

where KR = a reverse rate factor or constant.

At equilibrium the forward reaction (eq. 6.1) is balanced by the reverse reaction (eq. 6.2) and this relationship can be rearranged to the linear form

$$1/x = 1/Kbc + 1/b \qquad (6.3)$$

where x = amount of P sorbed, c = equilibrium concentration of solution P, b = sorption maximum, and K = constant related to the sorption energy. Estimates of K and b can be derived from this equation (eq. 6.3). Ryden et al. (1977a) found that most soils appear to have similar sorption energies (K) for P but widely differing sorption maxima, or the amount of P required to completely saturate the sorbing surface (b).

There have been several criticisms of the validity of using the Langmuir equation to describe P sorption (see Section 2.2.1.3). It has been argued that the estimates of K and b, as calculated from the Langmuir isotherm, have no significant meaning. However, despite these criticisms, the Langmuir equation has proved useful in describing several aspects of P sorption by soils. The Langmuir-type model of P sorption has some advantages over other models (e.g., Bowden et al., 1977; Barrow, 1983a) in that it requires relatively little input of parameters and it can be applied to P sorption over a wide range of P concentrations.

Ryden et al. (1977a) found a close relationship between estimates of more-physically sorbed P, as obtained from the Langmuir isotherms, and the amounts of P removed by the water-extraction procedure. Using the approach of Ryden et al. (1977a), Rennes (1978) later developed a computer model to predict the amount of water-extractable P in soils after fertilizer P addition. He obtained a very close agreement between the values predicted by the model and those measured in three incubated soils which differed widely in their P sorption capacity.

The objective of this study was to further evaluate and validate the model of Rennes (1978) by laboratory incubation studies on a wider range of soils. The intention was to develop a working model which predicts the relationship between water-extractable P and fertilizer P addition for a wide range of soils.

6.2 Materials and Methods

6.2.1 Development and structure of the P sorption model of Rennes (1978)

The model of Rennes (1978) is based on the concept of P sorption proposed by Ryden et al. (1977a) (Section 2.2.1.3), which describes sorption of P at three distinct populations or regions of sites. The operation of the model allowed for concurrent P sorption from solution in all three regions. The proposed reaction mechanisms involved in P sorption and desorption in the model are shown on Fig. 6.1.

The equilibrium constant of the reaction in each region is equal to the ratio of the forward rate constant (KF) to the reverse rate constant (KR). It is also equal to the value of K obtained from the linear form of the Langmuir equation (Graham, 1953; Shapiro and Fried, 1959), i.e.,:

$$K_I = KF1/KR1 \quad (6.4)$$

$$K_{II} = KF2/KR2 \quad (6.5)$$

$$K_{III} = KF3/KR3 \quad (6.6)$$

Thus the rate equations of sorption and desorption used in the overall kinetic model of P sorption are as follows:

Region I

$$\text{Sorption} = KF1 \times \text{solution[P]} \times \text{time} \times \text{vacant sites} \quad (6.7)$$

$$\text{Desorption} = KR1 \times \text{time} \times \text{occupied sites} \quad (6.8)$$

Region II

$$\text{Sorption} = KF2 \times \text{solution[P]} \times \text{time} \times \text{vacant sites} \quad (6.9)$$

$$\text{Desorption} = KR2 \times \text{time} \times \text{occupied sites} \quad (6.10)$$

Region III

$$\text{Sorption} = KF3 \times \text{solution[P]} \times \text{time} \times \text{vacant sites} \quad (6.11)$$

$$\text{Desorption} = KR3 \times \text{time} \times \text{occupied sites} \quad (6.12)$$

The estimated rate constants for region III are generally higher than those for region II, and both are

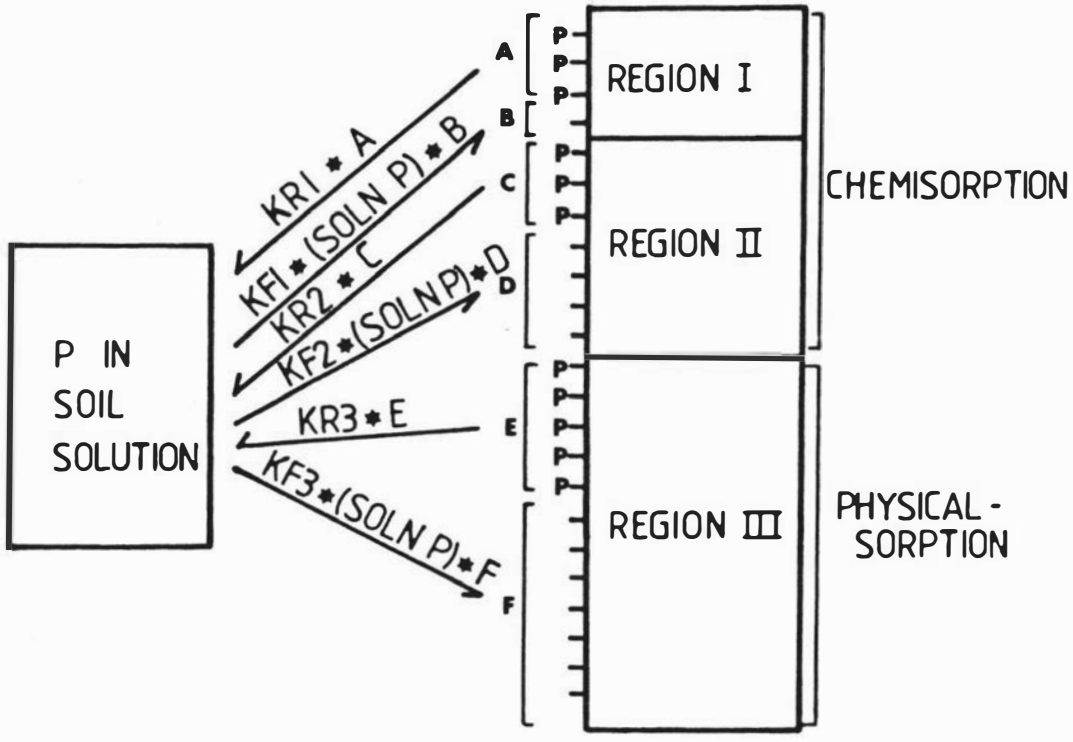

Figure 6.1 Schematic representation of the mechanisms involved in P sorption and desorption in the model of Rennes (1978)

higher than those for region I (Rennes, 1978). This progression of rate constant values is based on the work of McLaughlin et al. (1977) who showed that P sorption in region III by hydrous ferric oxide gel was initially rapid but was followed by a redistribution of sorbed P and slower, continuing sorption in regions II and I. Similar observations with soils were also reported by Ryden et al. (1977a).

The model of Rennes (1978) was used to simulate the sorption of P by soils following fertilizer P addition, the subsequent distribution of sorbed P in the three regions, and the amount of water-extractable P in soils. The overall model was operated as a FORTRAN programme with the double precision option (i.e., 12 significant decimal places), and executed on a computer. Such precision was necessary because the very small time interval (0.0002 day) set in the programme would produce an infinitesimally small change in the P concentration of the soil solution.

To simulate the sorption of P by soils during incubation with fertilizer P, the initial soil solution P concentration (at the beginning of incubation, i.e., at time = 0) was calculated from the rate of fertilizer P addition and the soil water content. The programme was then allowed to run for the appropriate incubation period.

Because the model of Rennes (1978) can also describe the desorption of P as well as sorption, it was then used to simulate the desorption of P during the water-extraction procedure. To determine the amount of water-extractable P at the end of the incubation period, the programme was stopped at the simulated time corresponding to the incubation period, the soil:solution ratio adjusted to 1:120, solution P concentration to zero, and the programme run for the simulated time of one hour (i.e., the extraction time of the water-extraction procedure). The final amount of P present in 120 ml of water after one hour was expressed as $\mu g\ g^{-1}$ soil extracted. Examples of the programme and the print-out showing distribution of sorbed P in each region and the concentrations of soil solution P are given in Appendix V.

Although the desorption of P normally continues for longer than one hour, Ryden et al. (1977a) adopted an arbitrary period of one hour for the water-extraction procedure. Rennes (1978), therefore, used the model to simulate P desorption for one hour during water extraction. Considering that the rate of reaction would proceed faster in a shaken system during the water-extraction procedure, he also increased all rate constants during the desorption procedure by a factor of 10. This assumption is questionable because it was not based on experimental data. In this study, varying rate constants were incorporated in the model and the predicted desorption curve for P compared to those obtained experimentally (Fig. 3.1). By trial and error, the closest prediction of desorption was obtained when the rate constants for both desorption and adsorption were left the same (data not presented here).

6.2.2 Changes in water-extractable P following fertilizer P addition to two soils

6.2.2.1 Incubation studies

Two topsoils (0-7.5 cm depth) with contrasting P retention properties were used: an Egmont black loam with a high P sorption capacity (PR = 82%) and a Tokomaru silt loam with a low P sorption capacity (PR = 20%). The soils were sampled from low fertility sites under pasture, air-dried, and sieved (<2 mm). They were brought to low, medium, and high P status by incubating with three rates of P (added as solutions of KH_2PO_4, Table 6.1) for eight weeks. The incubating soils were maintained at a moisture content of 80% of field capacity and at a temperature of 20±5°C. At the end of the incubation period, the soils were air-dried, sieved (<2 mm), and analysed for water-extractable P (Section 3.2.4.1), Olsen-extractable P (Section 3.2.4.2), and pH (Section 3.2.2). The results of these determinations are given in Table 6.2.

The previously-incubated soil was then divided into three subsamples and three more rates of P added (Table 6.1), giving a total of 9 soils which had varying rates of P added. The soil was re-incubated at 80% of field capacity

Table 6.1 Rates of P (as KH_2PO_4) addition to the Egmont and Tokomaru soils in the incubation studies

Soil		Rate of P addition ($\mu g\ g^{-1}$ soil)
Egmont	-P0	0
	-P1	200
	-P2	400
Tokomaru	-P0	0
	-P1	75
	-P2	150

Table 6.2 Measurement of water- and Olsen-extractable P and soil pH in the Egmont and Tokomaru soils after the first incubation with P

Soil		Water-extractable P	Olsen-extractable P	Soil pH
		($\mu g\ g^{-1}$ soil)		
Egmont	-low P	0.9	12.0	5.55
	-medium P	3.9	33.5	5.58
	-high P	9.0	51.7	5.63
Tokomaru	-low P	2.3	11.9	4.90
	-medium P	7.1	29.3	4.90
	-high P	13.4	49.3	4.98

for 14 more days. During the second incubation, samples were taken at 8 h, and 1, 2, 4, 8, 11, and 14 days after P addition and analysed for water-extractable P (Section 3.2.4.1).

The 14-day period was used in the study of Rennes (1978) who considered that the soil would be at or near equilibrium following P addition. However, it is possible that water-extractable P in soils after a 14-day incubation period with P might not be at equilibrium. To account for this possibility, the soils in this study were re-incubated for a further year. During this time, wetting/drying cycles were imposed in order to accelerate the reactions of soil P.

6.2.2.2 Model simulation

The model was used to predict the levels of water-extractable P in the Egmont and Tokomaru soils following fertilizer P additions, as described in Section 6.2.2.1. Two variables are required in the model: the sorption energy constants (K) and the sorption maxima (b). The average values of K for each region (derived from the Langmuir equations) in published data were used to calculate the forward (KF) and reverse (KR) rate constants. From the survey of literature, there are published data of K values for 17 New Zealand soils (Appendix VI), including some subsoils. In this study the average values of K for each region of nine topsoils (soils 1-9, Appendix VI) were used to derive KF and KR values (Table 6.3).

The values for the sorption maxima (b) for the Egmont soil (Table 6.4) were those of Rennes (1978). The Tokomaru soil was not included in the study of Rennes (1978), so it was decided to use the b values of the Ruamai soil from the study of Rennes (1978) for the Tokomaru soil in this study, because both soils have similar PR values (i.e., 23 and 20% for the Ruamai and Tokomaru soils, respectively).

Most field soils normally contain some P on their sorption surfaces. In other words, some P would already be present on sorption sites in each region. In this study,

Table 6.3 Sorption energy constants (K) (average of soils 1-9 in Appendix VI) and the estimated rate factors for forward (KF) and reverse (KR) reactions in each of three (I, II, and III) regions of P sorption used in the model

Region	K value	KF	KR
		(ml g^{-1})	
I	162	0.044	0.00027
II	2.882	0.115	0.04
III	0.093	0.098	1.05

Table 6.4 Sorption maxima (b) for each region of P sorption used in the model for the Egmont and Tokomaru soils

Soil	Reference	b_I	b_{II}	b_{III}
		($\mu gP\ g^{-1}$)		
Egmont	Egmont (Rennes, 1978)	870	1515	2220
Tokomaru	Ruamai (Rennes, 1978)	89	286	520

the amounts of P initially present on sites in each region (i.e., the number of occupied sites) were chosen so that the model would give the values of water-extractable P corresponding to the initial values before the incubation for each soil (Table 6.2).

It was intended to use the model to predict the relationships between the levels of water-extractable P and the addition of P. Consequently, it was considered that a prediction at equilibrium of water-extractable P in soils receiving added P would be of more value than a short-term prediction (e.g., 14 days following P addition). The model was therefore used to predict the amount of water-extractable P at 14 days following P addition as well as at equilibrium. To simulate the equilibrium situation, the programme of the model was allowed to run until there were no further changes in sorption and distribution of sorbed P in each region.

The significance of K and b values in the predictive ability of the model was investigated by varying the values of K_I, K_{II}, and K_{III} or b_I, b_{II}, and b_{III} (selected from published data shown in Appendix VI) in the model and examining the effect on the predicted values.

6.2.3 Changes in water-extractable P following fertilizer P addition to 16 soils

6.2.3.1 Incubation studies

Preliminary results from incubation studies of the Egmont and Tokomaru soils following additions of P (Section 6.3.1) showed that the model of Rennes (1978) may have potential in predicting water-extractable P values in soils which have received moderate amounts of P. The highest rates of P added (150 and 400 $\mu g\ g^{-1}$ soil for the Tokomaru and Egmont soils, respectively) in those incubation studies were probably well above the rate of fertilizer P normally applied in practice. Therefore, lower rates of P addition were used in the present incubation study in an attempt to reflect the normal situation more closely.

Sixteen soils with low to medium P status and selected from the 20 soils described in Chapter 3 (Section 3.2.1) were used. Soils with a PR test lower than 50 were incubated with solutions of KH_2PO_4 containing 0, 40, and 80 $\mu gP\ g^{-1}$ soil, and those with a PR test higher than 50 were incubated with solutions of KH_2PO_4 containing 0, 80, and 160 $\mu gP\ g^{-1}$ soil (Table 6.5). The soils were incubated at 60% of field capacity at 25±5°C for 40 days. Soils were not incubated at 80% of field capacity as before (Section 6.2.2.1) because this was found to cause too much wetness and this hampered proper mixing of the soil samples. At the end of the incubation, the soils were air-dried and analysed for water-extractable P (Section 3.2.4.1). Values of water-extractable P for these soils provided a base against which the modelling of soil P reactions could be tested.

6.2.3.2 Model simulation

The model of Rennes (1978) requires estimates of K and b values derived from sorption isotherm studies which involve accurate and time-consuming procedures. A model that will be useful for routine fertilizer recommendation purposes must be based on estimates which can be obtained by simple procedures. In this study, the working model proposed is intended for a general application to all soils, therefore a common set of K values was assumed for the model. These were estimated from average values of all published data for New Zealand soils (17 soils in Appendix VI). The forward (KF) and reverse (KR) rate factors were then derived from K values in the same manner as that used by Rennes (1978). These estimates are shown in Table 6.6.

It was proposed that estimates of b could be derived from values of the PR test (Saunders, 1965). Because the PR test procedure involves the determination of P sorption after the addition of a large amount of P to a soil, it should therefore approximate the total sorption maximum (b) of that soil. It is observed from the published data of 17 New Zealand soils (Appendix VI) that the ratios of $b_I:b_{II}:b_{III}$ did not vary greatly. The sum total of b values estimated from the PR test was then partitioned

Table 6.5 Water-extractable P and phosphate retention (PR) values for the 16 soils with their rates of P addition

Soil	Water-extractable P ($\mu g\ g^{-1}$ soil)	Phosphate retention %	Rate of P addition ($\mu g\ g^{-1}$ soil)
1. Carnarvon	3.8	45	0, 40, 80
2. Kiwitea	3.7	40	"
3. Konini	4.4	43	"
4. Kumeroa-low P	5.7	30	"
5. Manawatu	5.1	19	"
6. Okaihau	5.6	45	"
7. Tokomaru-low P	6.7	19	"
8. Wainui	4.9	36	"
9. Dannevirke	3.1	91	0, 80, 160
10. Egmont-low P	1.8	82	"
11. Hamilton	3.2	66	"
12. Patua	2.2	98	"
13. Ramiha-low P	1.2	88	"
14. Ramiha-high P	6.7	55	"
15. Taupo-low P	3.0	53	"
16. Taupo-high P	7.8	67	"

Table 6.6 Sorption energy constants (K) (average of 17 soils in Appendix VI) and the rate factors for forward (KF) and reverse (KR) reactions in each of three (I, II, and III) regions of P sorption used in the model to predict changes in water-extractable P following P additions in 16 soils

Region	K value	KF	KR
		(ml g^{-1})	
I	341	0.092	0.00027
II	4.50	0.115	0.04
III	0.136	0.098	1.05

into b_I, b_{II}, and b_{III} using the average ratio of $b_I:b_{II}:b_{III}$ from the 17 soils in Appendix VI. Estimates of the b values for the 16 soils used in this study are given in Table 6.7. The K and b values were then incorporated into the modified model of Rennes (1978) to predict the amounts of water-extractable P in each of the 16 soils following the addition of P. Comparisons were made between the values predicted by the model and the measured values of the 16 soils in the incubation studies (Section 2.3.2.1).

6.3 Results and Discussion

6.3.1 Decline in water-extractable P following fertilizer P addition to two contrasting soils

The decline in water-extractable P in both the Egmont and Tokomaru soils following the addition of P showed a similar pattern for different rates of P addition (Fig. 6.2 and 6.3). A rapid decrease in water-extractable P during the first 2-3 days was followed by a gradual decline towards the end of the 14-day incubation period. This finding is consistent with the general pattern of the reaction of P added to soils (e.g., Evans and Syers, 1971; Barrow and Shaw, 1975a; Parfitt, 1978; Rennes, 1978; White, 1980). In the present study, the initial rate of decline was faster at the higher rate of P addition but the rate of the subsequent gradual decline was comparable at both rates of P addition (Fig. 6.2 and 6.3).

After one year, the amounts of water-extractable P in the Egmont soils decreased markedly (Table 6.8), thereby confirming the suggestion that the soils were not at equilibrium at 14 days following P addition. In contrast, values of water-extractable P in the Tokomaru soils were not markedly different between 14 days and one year following P addition (Table 6.8). This result again suggests that sorption reactions of added P continue for a much shorter period in a low P-sorbing soil than in a high P-sorbing soil.

Table 6.7 Estimates of sorption maxima for the three regions (b_I, b_{II}, and b_{III}) for the 16 soils

	Soil	b_I	b_{II}	b_{III}
		($\mu gP\ g^{-1}$ soil)		
1.	Carnarvon	265	662	1323
2.	Kiwitea	235	588	1177
3.	Konini	253	632	1265
4.	Kumeroa-low P	177	441	882
5.	Manawatu	112	279	559
6.	Okaihau	265	662	1323
7.	Tokomaru-low P	112	279	559
8.	Wainui	212	529	1059
9.	Dannevirke	535	1338	2677
10.	Egmont-low P	482	1206	2412
11.	Hamilton	388	971	1941
12.	Patua	577	1441	2882
13.	Ramiha-low P	518	1294	2588
14.	Ramiha-high P	324	809	1617
15.	Taupo-low P	312	779	1559
16.	Taupo-high P	394	985	1971

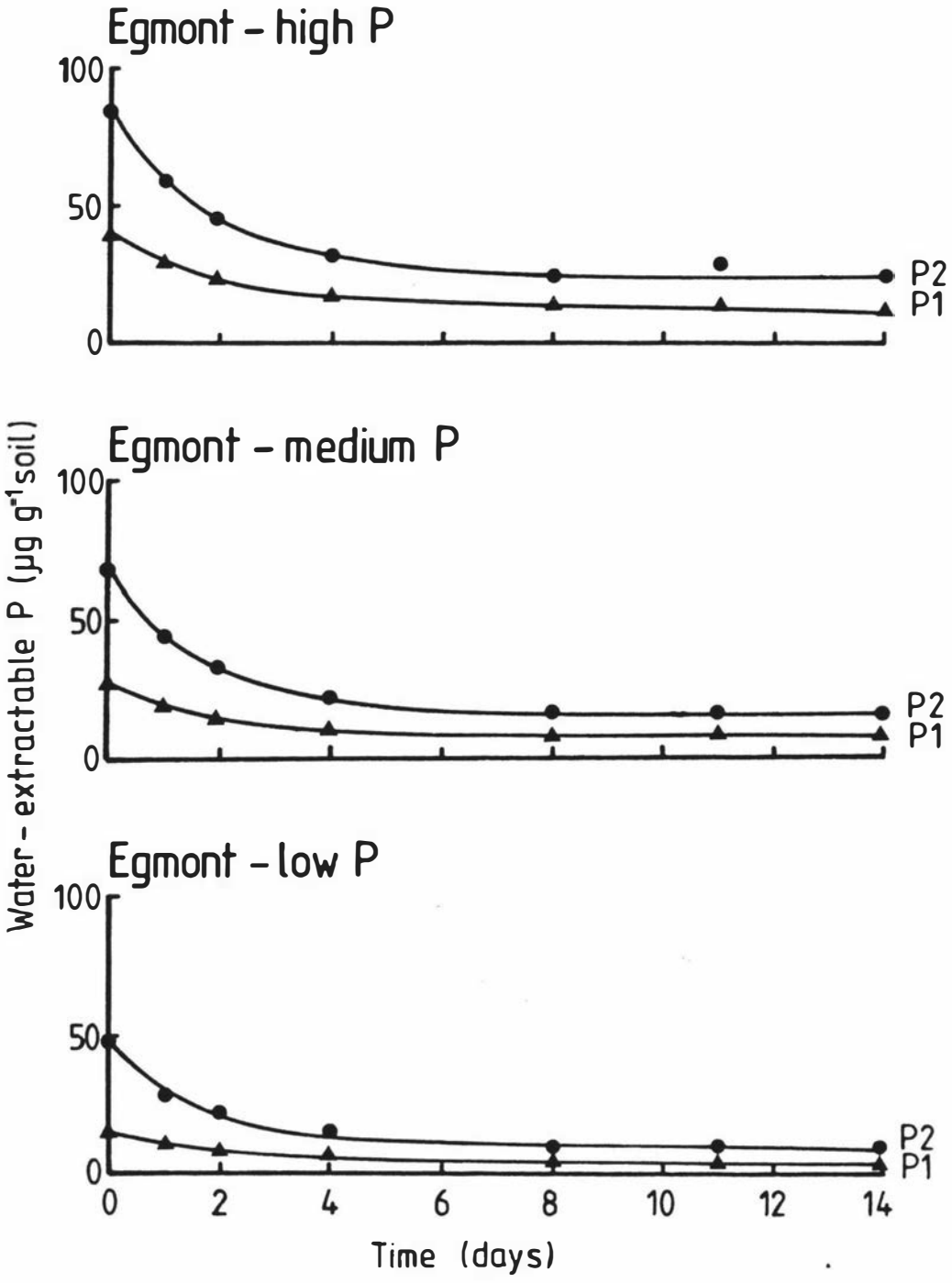

Figure 6.2 Decline in water-extractable P in three Egmont soils (low, medium, and high P) following the additions of 200 (P1) and 400 (P2) µgP g^{-1} soil (as solutions of KH_2PO_4)

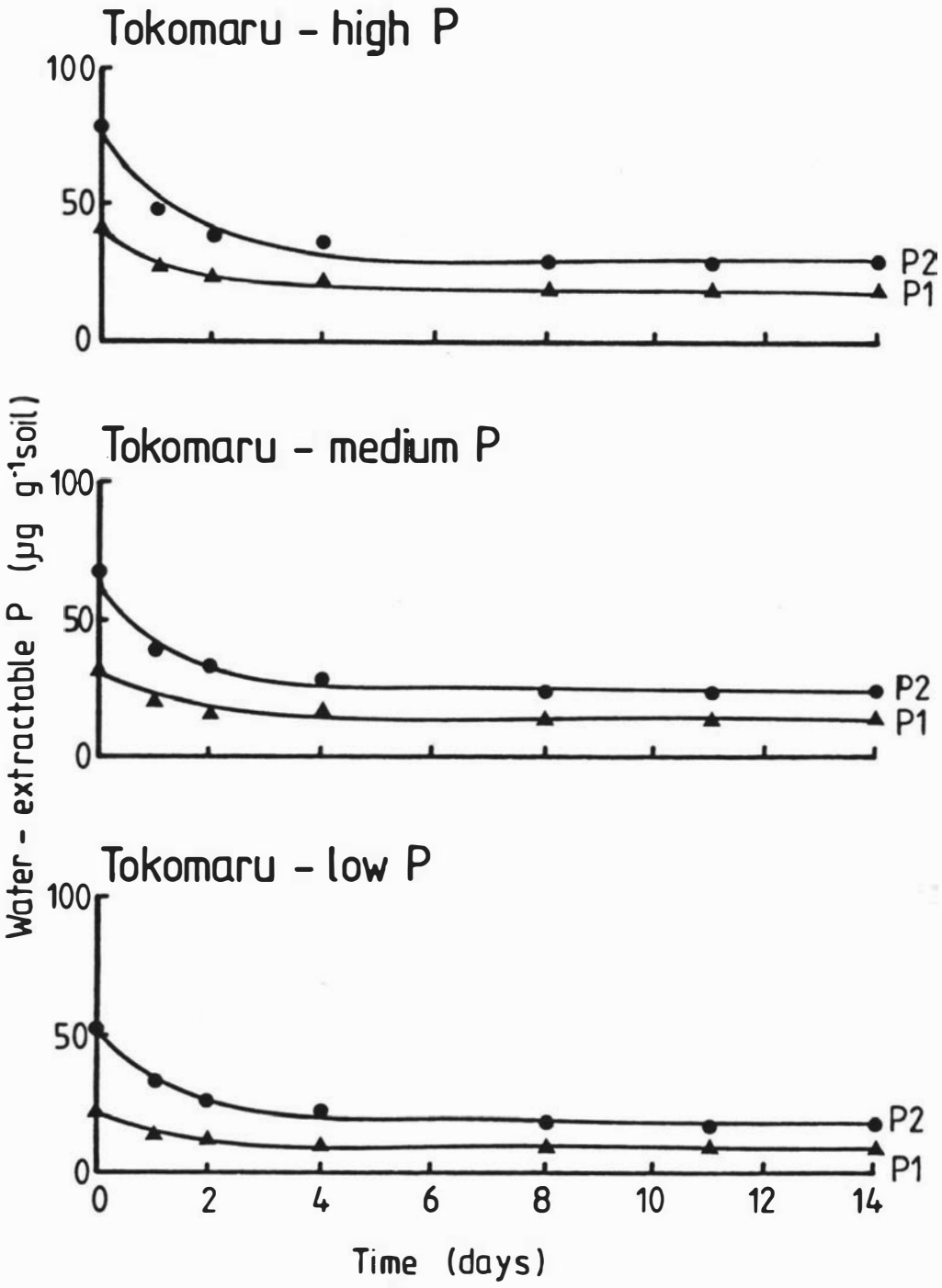

Figure 6.3 Decline in water-extractable P in three Tokomaru soils (low, medium, and high P) following the additions of 75 (P1) and 150 (P2) µgP g^{-1} soil (as solutions of KH_2PO_4)

Table 6.8 Predicted and measured amounts of water-extractable P in the Egmont and Tokomaru soils at 14 days and 1 year after incubation with P (as solutions of KH_2PO_4)

Soil	P addition ($\mu gP\ g^{-1}$)	Water-extractable P ($\mu g\ g^{-1}$ soil)			
		Measured		Predicted from model of Rennes (1978)(14 days)	Predicted from modified model (1 year)
		14 days	1 year		
Egmont -low P	0, 0	0.8	0.3	0.9	0.3
	0, 200	3.9	1.0	2.0	0.8
	0, 400	9.0	1.1	4.8	2.5
-medium P	200, 0	2.4	1.0	2.0	1.0
	200, 200	8.2	1.5	4.4	3.2
	200, 400	15.7	3.0	9.8	7.6
-high P	400, 0	4.7	1.7	4.8	1.7
	400, 200	11.8	3.2	9.6	5.0
	400, 400	25.0	5.0	18.0	10.2
Tokomaru -low P	0, 0	2.5	2.9	2.3	2.9
	0, 75	9.4	6.9	11.5	9.2
	0, 150	17.6	13.3	28.1	20.1
-medium P	75, 0	7.4	6.2	11.5	6.2
	75, 75	14.9	11.9	28.1	14.9
	75, 150	22.1	18.6	52.4	29.0
-high P	150, 0	11.8	11.2	28.1	11.2
	150, 75	19.4	17.1	52.4	23.1
	150, 150	28.0	23.1	85.5	40.2

6.3.2 Assessment of the model in predicting changes in water-extractable P following fertilizer P addition

6.3.2.1 Prediction of water-extractable P at 14 days following P addition

The model was found to underestimate the amounts of water-extractable P in the Egmont soils following the addition of P, except in three cases where the soils were initially incubated with P for eight weeks and did not receive any P prior to the second incubation (Table 6.8). In such cases good agreement was obtained between the predicted and measured values. This finding suggests that the water-extractable P values, measured at 14 days after P addition in the second incubation, may not have reached equilibrium.

In contrast, the predicted values for the Tokomaru soils were found to overestimate the experimental data (Table 6.8). The prediction worsened as the rate of added P was increased. It is possible that the estimates of sorption maxima (b) for the Ruamai soil, which were assumed to be the same as for the Tokomaru soil in this study, may not be appropriate. If the b values were too low, the sorption sites would be saturated with added P too rapidly resulting in excessive estimates of water-extractable P. However, this is unlikely because the Ruamai soil has a slightly higher PR test than the Tokomaru soil, so the b values for the Ruamai soil are unlikely to be too low for the Tokomaru soil. It is more likely that precipitation of added P occurs in soil after receiving large amounts of water-soluble P. The highest rates of P addition (Table 6.1), in particular, were much greater than the rate of fertilizer P normally added in practice. The influence of estimates of b values on the predictive ability of the model will be discussed in more detail in Section 6.3.2.3.

6.3.2.2 Prediction of equilibrium value of water-extractable P following P addition

Because the levels of water-extractable P were still changing in the incubated soils after 14 days of P addition, as well as in the soils which had received no P, it is likely that the values of water-extractable P, measured after the first incubation (i.e., low, medium, and high P soils in Table 6.2) were still changing and not at equilibrium. Instead, the equilibrium values would be those measured after one year in soils which had received a single P addition during the first incubation only. These values (0.3, 1.0, and 1.7 $\mu gP\ g^{-1}$ soil for the Egmont soils; 2.9, 6.2, and 11.2 $\mu gP\ g^{-1}$ soil for the Tokomaru soils) were used in a modified model as P for the low, medium, and high P soils at the beginning of the second incubation (replacing the values shown in Table 6.2). A modified model, based on these equilibrium values, was then used to predict equilibrium levels of water-extractable P following the second addition of P.

Closer agreement between predicted and actual values of water-extractable P in both Egmont and Tokomaru soils was obtained from the modified model (Table 6.8) than that from the original model of Rennes (1978). The predicted values, however, were still larger than the measured values, particularly at high rates of P addition.

6.3.2.3 Importance of estimates of sorption energy constants and sorption maxima

The two important variables required in the model of Rennes (1978) are sorption energy constants (K) and sorption maxima (b), both of which are obtained from the resolution of the linear form of the Langmuir sorption equation. It has been suggested that major differences exist between K_I and K_{II} values or K_{II} and K_{III} values within the soil but that the K values for each region of P sorption (K_I, K_{II}, and K_{III}) are similar for different soils (Rennes, 1978). Published data for K values, however, indicate that some variations exist among different soils (Appendix VI). It is possible that errors in the estimates

of K values used in the model will affect the predictive ability of the model.

Ryden et al. (1977a) suggested that differences in the rate and extent of P sorption in soils are dependent essentially upon the number of vacant sites and the distribution of vacant sites between the three regions. Differences in the P-sorption capacity of soils are related to the sorption maxima (b) values. There is a wide variation in the values of b in soils, as illustrated in Appendix VI. It was observed that the model overestimated the amounts of water-extractable P in the Tokomaru soils following P addition (see Section 6.3.2.1). The model also revealed that region I was essentially saturated with sorbed P and this could contribute to the excessive estimates of water-extractable P. Estimates of b values could, therefore, influence the prediction of water-extractable P by the model.

Different combinations of K and b values were used in the model to establish how sensitive the model was to variations in these estimates. It was found that variations in the K values had a more significant influence on the predicted values than variations in the b values in the Egmont soil (Table 6.9). This may be due to the fact that the b values for the Egmont soil were so large that P sorption was unlikely to reach saturation and hence be affected by b values. Variations in the K values, however, produced some significant differences in the predicted values, as shown in Table 6.9.

In contrast, the predicted values for the Tokomaru soils were found to be influenced more by variations in the b values than by variations in the K values (Table 6.10). It appears that in the low P-sorbing Tokomaru soil, the three regions (particularly region I) are quickly saturated because of the relatively small b values. Consequently, any increases or decreases in the b values would have a marked influence on the predicted values of water-extractable P.

Table 6.9 Amounts of water-extractable P in the Egmont soils following P additions predicted by the modified model using various estimates of sorption energy constants (K) and sorption maxima (b)

P addition ($\mu g\ g^{-1}$ soil)	Predicted water-extractable P using K and b values indicated below ($\mu g\ g^{-1}$ soil)			
0, 0	0.9	0.9	0.9	0.9
0, 200	2.0	1.6	2.0	1.9
0, 400	4.8	3.4	5.0	4.8
200, 0	2.0	1.6	2.0	2.0
200, 200	4.4	2.7	4.3	4.2
200, 400	9.8	5.5	11.2	9.2
400, 0	4.8	3.4	5.0	4.8
400, 200	9.6	5.1	10.3	9.0
400, 400	18.0	9.4	22.0	17.0
Sorption energy constants (K)	Average of soils 1-9 in Appendix VI	Average of soils 1-10 in Appendix VI	Egmont (Rennes, 1978)	Average of soils 1-9 in Appendix VI
Forward rate constants ($ml\ g^{-1}$)				
KF1	0.044	0.046	0.035	0.044
KF2	0.115	0.130	0.042	0.115
KF3	0.098	0.116	0.057	0.098
Sorption maxima ($\mu gP\ g^{-1}$)	Egmont (Rennes, 1978)	Egmont (Rennes, 1978)	Egmont (Rennes, 1978)	Egmont (Ryden and Syers, 1975)
b_I	870	870	870	1217
b_{II}	1515	1515	1515	1505
b_{III}	2220	2220	2220	3221

Table 6.10 Amounts of water-extractable P in the Tokomaru soils following P additions predicted by the modified model using various estimates of sorption energy constants (K) and sorption maxima (b)

P addition ($\mu g\ g^{-1}$ soil)	Predicted water-extractable P using K and b values indicated below ($\mu g\ g^{-1}$ soil)			
0, 0	2.3	2.3	2.3	2.3
0, 75	11.5	26.7	6.8	6.9
0, 150	28.1	71.7	17.3	17.1
75, 0	11.5	26.7	6.8	6.9
75, 75	28.1	63.3	13.6	13.6
75, 150	52.4	116.1	28.6	27.2
150, 0	28.1	71.7	17.3	17.1
150, 75	52.4	110.5	26.6	25.1
150, 150	85.5	153.3	40.6	43.3
Sorption energy constants (K)	Average of soils 1-9 in Appendix VI	Average of soils 1-10 in Appendix VI	Average of soils 1-10 in Appendix VI	Tokomaru (Hope, 1978)
Forward rate constants ($ml\ g^{-1}$)				
KF1	0.044	0.046	0.046	0.030
KF2	0.115	0.130	0.130	0.093
KF3	0.098	0.116	0.116	0.204
Sorption maxima ($\mu gP\ g^{-1}$)	Ruamai (Rennes, 1978)	Tokomaru (Hope, 1978)	Porirua (Ryden and Syers, 1975)	Porirua (Ryden and Syers, 1975)
b_I	90	52	130	130
b_{II}	285	74	285	285
b_{III}	520	172	530	530

6.3.3 Modelling changes in water-extractable P in 16 soils following fertilizer P additions using a modified model

Close agreement was found between the predicted and actual values of water-extractable P in soils with a high P-sorbing capacity (soils 9-16, Table 6.11). Predicted equilibrium values for soils with a low P-sorbing capacity, however, were generally lower than the measured values. The deviations could be due to estimates of the b values in the model being too high. This overestimation may result from the fact that the PR test is conducted at a pH of 4.65 (Saunders, 1965). At this pH, P sorption will be considerably greater than at the pH of the natural soils. This would result in an overestimate of the extent of P sorption, particularly in region I, and hence a relatively low water-extractable P value.

Experimental evidence has shown that the desorption of P in water continued for more than one hour (Fig. 3.1). This was also predicted by the model simulating the desorption of P in soil. Both types of evidence indicate that P desorption was rapid during the first few hours, followed by slower changes, and approached equilibrium after 24 h. It is therefore possible that predictions based on 1-h water extraction are subject to errors and the amount of soil P removed during a 24-h extraction may be more reliable. The amounts of water-extractable P in the 16 soils were then estimated after a 24-h shaking period. It was found that predicted equilibrium values of 24-h water-extractable P showed good agreement with the experimental values (Table 6.12). The correlation coefficient for the relationship between the predicted and measured values was significantly improved from 0.84 in the 1-h extraction to 0.91 in the 24-h extraction. In addition, the slope of the regression line obtained for the 24-h water extraction is almost equal to one (Fig. 6.4(b), slope = 0.98), indicating that the model predicted the amount of water-extractable P remarkably well. This is in contrast to the small slope of the regression line obtained for the 1-h

Table 6.11 Predicted and actual amounts of water-extractable P (1 h) for the 16 soils following the additions of P (as solutions of KH_2PO_4)

Soil	Rate of P addition (µg g^{-1} soil)						
	0	40		80		160	
	Actual	Actual	Predicted	Actual	Predicted	Actual	Predicted
1. Carnarvon	3.8	7.8	4.8	12.0	5.9		
2. Kiwitea	3.7	8.5	4.8	13.8	6.0		
3. Konini	4.4	11.9	5.5	15.5	6.7		
4. Kumeroa-low P	5.7	10.0	7.4	16.3	9.5		
5. Manawatu	5.1	15.1	7.5	23.4	10.9		
6. Okaihau	5.6	6.6	6.8	10.8	8.1		
7. Tokomaru-low P	6.7	16.0	9.7	25.0	13.8		
8. Wainui	4.9	14.4	6.2	21.5	7.8		
9. Dannevirke	3.1			3.7	4.5	5.0	6.1
10. Egmont-low P	1.8			2.8	3.0	4.3	4.5
11. Hamilton	3.2			6.3	4.8	11.7	6.5
12. Patua	2.2			3.0	3.5	4.2	5.1
13. Ramiha-low P	1.2			2.1	2.0	4.0	3.1
14. Ramiha-high P	6.7			16.1	9.5	24.3	13.2
15. Taupo-low P	3.0			9.2	4.7	16.8	6.8
16. Taupo-high P	7.8			11.1	10.2	16.2	13.2

Table 6.12 Predicted and actual amounts of water-extractable P (24 h) for the 16 soils following the additions of P (as solutions of KH_2PO_4)

Soil	Rate of P addition (μg g^{-1} soil)						
	0	40		80		160	
	Actual	Actual	Predicted	Actual	Predicted	Actual	Predicted
1. Carnarvon	5.0	11.6	12.0	19.3	15.0		
2. Kiwitea	5.3	11.2	13.1	19.7	16.6		
3. Konini	7.4	16.4	14.4	26.9	17.9		
4. Kumeroa-low P	7.1	16.9	24.6	28.8	31.5		
5. Manawatu	15.6	28.4	31.5	41.3	44.4		
6. Okaihau	9.6	12.9	17.4	18.9	21.1		
7. Tokomaru-low P	9.7	27.7	39.7	40.6	54.7		
8. Wainui	8.9	18.7	18.5	27.7	23.1		
9. Dannevirke	4.1			5.9	7.2	6.8	9.9
10. Egmont-low P	2.9			3.6	5.0	4.4	7.6
11. Hamilton	2.6			5.7	9.4	10.6	12.9
12. Patua	1.7			2.3	5.3	2.6	7.8
13. Ramiha-low P	0.7			1.9	3.2	2.4	5.0
14. Ramiha-high P	12.0			23.1	21.7	36.2	30.3
15. Taupo-low P	4.4			9.5	10.6	18.1	15.7
16. Taupo-high P	10.4			12.1	20.5	17.1	26.8

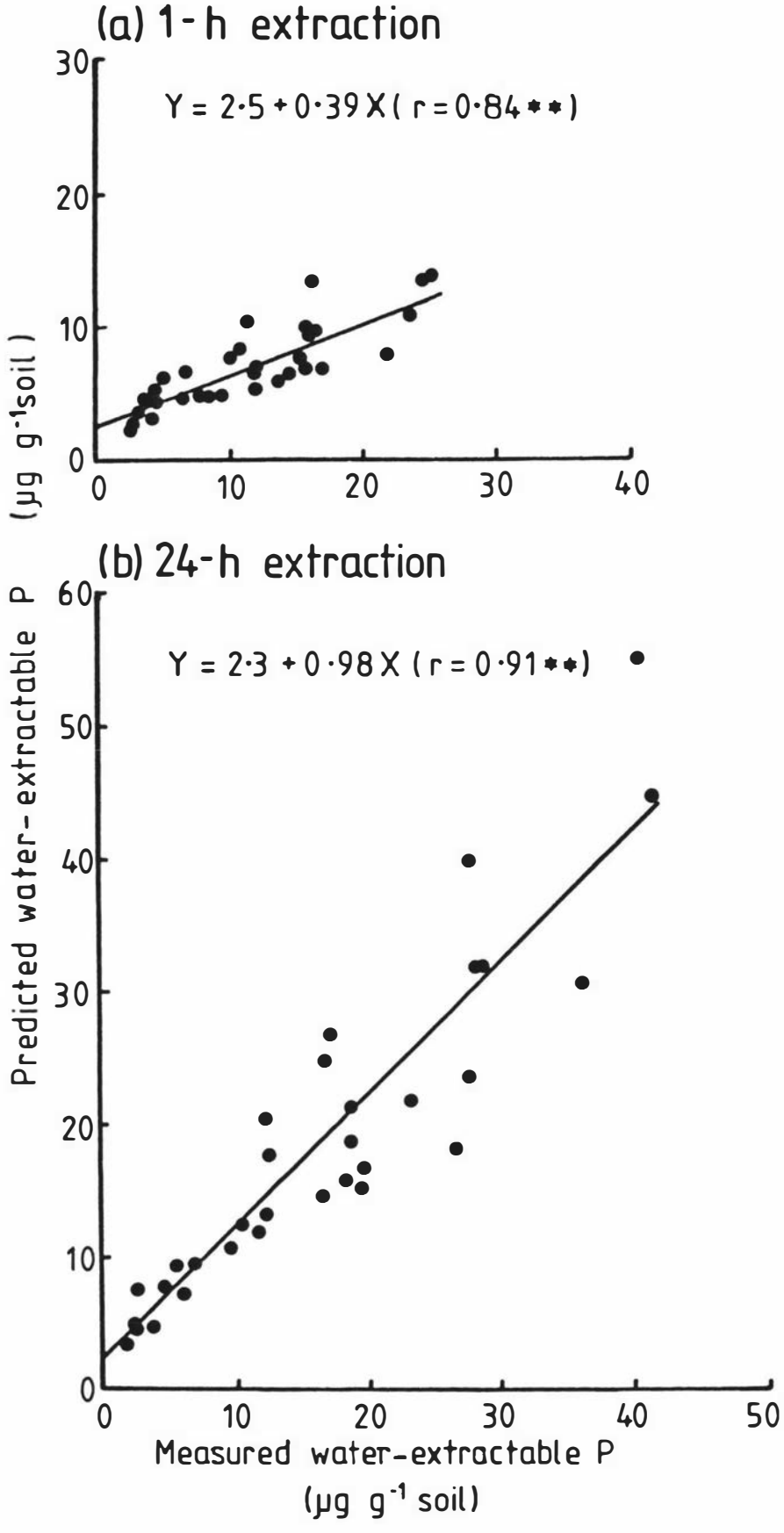

Figure 6.4 Regression between predicted and measured amounts of water-extractable P during 1-h (a) and 24-h (b) extraction periods in the 16 soils following the additions of P

water extraction (Fig. 6.4(a), slope = 0.39). Predictions obtained from 1-h water extraction data tended to underestimate the amounts of water-extractable P in soils following P additions.

It appears that values of water-extractable P in soils obtained from the 24-h extraction period are more reliable than those obtained from the 1-h extraction period. If the period used in the water extraction was 24 h, the model closely predicted the equilibrium values of water-extractable P in the 16 soils following P additions. This aspect requires further investigation.

6.4 Conclusions

When soils were incubated with fertilizer P, the changes in water-extractable P followed a similar pattern in all soils studied. Initially, there was a rapid decline which was followed by a gradual decrease. For a given soil, the initial rate of decline was faster at higher rates of P addition.

The model of Rennes (1978), based on the Langmuir isotherm, was used to simulate changes in water-extractable P in the Egmont and Tokomaru soils following different rates of P addition. Predictions were satisfactory for the high P-sorbing Egmont soils. The model, however, overestimated the levels of water-extractable P in the low P-sorbing Tokomaru soils. Further investigation revealed that the predictive ability of the model was strongly influenced by the estimates of sorption energy constants (K) in high P-sorbing soils. For low P-sorbing soils, the model was more sensitive to estimates of sorption maxima (b) than to estimates of K values.

A working model was developed to predict changes in water-extractable P in soils following fertilizer P addition. Estimates of b were derived from the routine PR test. Values for K were obtained from the average of 17 soils in previously-published studies. When the model

was tested on 16 soils, satisfactory prediction was found for soils with high P sorption capacity. The predicted values for soils with low to medium P sorption capacity were smaller than the measured values. The deviations could be due to overestimates of b values in the model which gave rise to low values of water-extractable P.

Experimental evidence from the desorption study reported earlier (Section 3.3.4) and predictions from the model showed that the desorption of P from soil was rapid during the first few hours, but after 24 h the change became significantly slower. More satisfactory predictions were obtained with the water-extraction period of 24 h compared to the 1-h period.

It has been shown in this study that the model of Rennes (1978) may be used to predict the long-term effect of fertilizer P addition on the level of water-extractable P in soils. The implication is that it may be possible to use the water-extraction procedure not only to determine whether or not fertilizer application rates are in excess of maintenance requirements but also to quantify this estimate.

CHAPTER 7

CHAPTER 7

CHARACTERISATION OF THE SHORT-TERM PLANT AVAILABILITY OF SOIL P USING A DOUBLE-LABELLING TECHNIQUE

7.1 Introduction

Soil P supply has frequently been evaluated by empirical methods that have been correlated with plant uptake. Such techniques can provide a good prediction of soil P availability when suitably calibrated using the plant species of interest.

It is well established that plants differ widely in their ability to use soil P (McLachlan, 1976; Barber, 1984). For example, there is good evidence that, when present with grasses, clovers are the poorer competitor for soil P (e.g., Mouat and Walker, 1959; Jackman and Mouat, 1972a,b; Haynes, 1980). This poorer competitive ability of clovers for soil P has been attributed to one or more of the following factors (see review by Haynes, 1980);

(i) root morphology,

(ii) threshold concentration of P below which plant uptake is reduced,

(iii) root cation exchange capacity, and

(iv) root exudates

These aspects have been reviewed in detail in Section 2.2.4.

Furthermore, it has also been suggested that the differing ability of plant species to recover soil P may be due to their ability to exploit different pools of soil P (Barber, 1980; Smith, 1983). However, there has been no conclusive evidence to support such a suggestion (Keay et

al., 1970; Probert, 1972; Caradus, 1980). This is possibly due to the difficulty in quantifying the pools of soil P which are being used by plants. Estimates of the plant-available pool of soil P have been obtained by calculating the levels of isotopically-exchangeable P (or labile P) using the L value (Larsen, 1952) and A value (Fried and Dean, 1952) techniques. However, these techniques appear to be unable to detect small differences in the soil P pools used by different species.

Recently, double-labelling techniques involving ^{32}P and ^{33}P, have been used to follow short-term uptake (Gillingham, 1978) and transport (Sasaki et al., 1982) of P, which previously was difficult to detect because of the extremely small amounts of P involved. The technique used by Gillingham (1978) involves labelling of soil with both ^{32}P and ^{33}P for differing durations and subsequently comparing the isotope ratios in soil extracts and plants grown on the labelled soil. Differences in the isotope ratios between plant species would indicate uptake of P from different soil pools.

The isotope ratios in soil extracts may also be used to help explain the P sorption reactions in soil. It is generally agreed (Hingston et al., 1972; Rajan and Fox, 1972; Parfitt, 1977; Ryden et al., 1977a) that soil P may be sorbed onto a range of sites varying in their sorption energies. Ryden et al. (1977a) proposed a concept of P sorption involving three regions or populations of sites. This was later used by Rennes (1978) to develop a model to predict P sorption in soils following P addition (see Chapter 6). Although the assumption of three distinct regions for P sorption may be questionable, the model developed by Rennes (1978) successfully predicted the fate of fertilizer P added to soils and thus may have practical application.

A double-labelling technique was used in this study to characterise the short-term uptake of P by ryegrass and white clover, and to determine whether the alleged superior

ability of ryegrass to use soil P can be attributed to its ability to recover P from different soil pools. Ryegrass and white clover were grown separately and together in order to examine the effect of competition on P uptake. Two soils with contrasting P-sorption capacities, and each of low and medium P status, were used in the study. The experiments were carried out in two soil moisture regimes.

7.2 Materials and Methods

The double-labelling technique involves placing growing plants in contact with soil that has been incubated with essentially carrier-free ^{33}P for a relatively long period of time and subsequently also with ^{32}P for a short period of time. After a given period of growth, plant uptake of ^{32}P and ^{33}P is measured.

The experiment was of a factorial design with two soils, each at two P levels, two soil moisture regimes, and two plant species, with four replicates of each treatment. An additional treatment involving mixed species was included with soils of low P status.

7.2.1 Preparation of plants

Ryegrass (Lolium perenne L., Grasslands "Nui") and white clover (Trifolium repens, Grasslands "Huia") were grown in a glasshouse using a technique based on that developed by Stanford and DeMent (1957). The procedures involved were similar to those described in Section 5.2.3. In this study, approximately 30 seeds were sown and later thinned to 15 and 20 plants per pot for ryegrass and white clover respectively. In the mixed species treatment, ryegrass and white clover were thinned to 10 plants each per pot. A complete nutrient solution including P (Middleton and Toxopeus, 1973) was applied regularly for six weeks and then replaced with a minus-P nutrient solution for a further two weeks. By this time plant roots had explored the full depth of sand, particularly in the case of ryegrass which had started to form a root mat at the bottom of the pot (Plate 7.1). Prior to being placed on labelled soils, the

Plate 7.1 Comparison of growth and root development in ryegrass, white clover, and ryegrass/ white clover mix prior to the placement on labelled soils

pots were leached with approximately 500 ml of distilled water to remove any excess nutrients which had accumulated.

7.2.2 Preparation of soil

The soils used were samples of Egmont and Tokomaru soils which had been collected from low fertility sites and brought to low and medium P status, as described in Chapter 5 (Section 5.2.1). Some chemical characteristics of the soils are given in Table 7.1. The Olsen P values were reasonably similar for each soil at the comparable P status. The air-dried soils were incubated for 47 days with solutions of essentially carrier-free ^{33}P at 20±5 C and approximately 60% field capacity (corresponding to gravimetric water contents of 0.26 and 0.41 for the Tokomaru and Egmont soils, respectively). On day 47, essentially carrier-free ^{32}P was added to the incubated soils and allowed to stand until day 51. The soils were then air-dried, each divided into two subsamples, and rewetted to achieve water potentials of -0.2 and -1.0 bar. These moisture regimes (M1 and M2) correspond to gravimetric water contents of 0.32 and 0.20 for the Tokomaru soil, and 0.45 and 0.31 for the Egmont soil, respectively. A sample of the remoistened soil (equivalent to 20g air-dried soil) was placed in a 250-ml plastic container identical to those used to grow the plants.

The above incubation periods were selected so that ^{33}P would exchange with most of the labile P in the soil while ^{32}P would only exchange, in the short time period used, with the more readily-available soil P. The five-day ^{32}P incubation period ensured that the initial rapid exchange was largely complete and the subsequent rate of exchange would be relatively slow (Gillingham, 1978).

7.2.3 Measurements of plant uptake of P

On day 52 (from the beginning of the incubation) the inner pot containing plants, with exposed roots at the bottom of the pot (Section 7.2.1), was transferred onto the pot containing the pre-moistened, labelled soil (Section 7.2.2) and left for six days. In this study, the six-day

Table 7.1 Chemical characteristics of the Egmont and Tokomaru soils used in the study

Soil	pH_{water}	P retention[#] (%)	Water-extractable P ($\mu g\ g^{-1}$)	Olsen-extractable P ($\mu g\ g^{-1}$)
Egmont -low P	5.6	82	0.9	11.4
-medium P	5.6	80	2.1	25.4
Tokomaru -low P	4.9	20	3.8	12.8
-medium P	4.9	17	8.1	27.5

Determined by the method of Saunders (1965).

contact period between plant and soil was chosen to ensure reasonable root penetration into the labelled soil and thus measureable isotope uptake by both species. Over the contact period, the soil moisture levels were maintained by supplying water between the rims of the nested pots.

After a growth period of six days, all above-ground growth was harvested and the mixed herbage was separated into ryegrass and white clover. The herbage was oven-dried, ground, digested, and analysed for ^{31}P, as described in Section 3.2.3. Total ^{32}P and ^{33}P activities in the herbage digests were measured separately due to the extremely low activity of ^{32}P. A Cerenkov counting method (Brown, 1971) was used to determine the ^{32}P activity of the samples. The efficiency of Cerenkov counting was determined by spiking the samples with a known amount of ^{32}P and recounting. The activity of ^{33}P was determined by liquid scintillation counting using a Triton-toluene based scintillation cocktail (Patterson and Greene, 1965).

7.2.4 Soil analysis

Soil samples were taken both before (day 52) and after (day 58) plant uptake of P in order to measure any changes in isotope ratio occurring in the soil extracts over this period. Water and Olsen extracts were obtained using the procedures described in Sections 3.2.4.1 and 3.2.4.2, respectively. Total ^{32}P and ^{33}P activities in the extracts were measured as described above (Section 7.2.3).

7.3 Results and Discussion

7.3.1 ^{31}P concentrations

7.3.1.1 Relationship between ^{31}P concentrations in Olsen and water extracts

Although for each P status (low or medium) the Olsen P values in the two soils were very similar, there was a considerable variation in the amounts of water-extractable P between the two soils (Table 7.1). The amounts of ^{31}P in the Olsen extracts of the Egmont soils were approximately 12 times larger than those in the water extracts, while the

difference was only three-fold for the Tokomaru soils. There was also a considerable variation in the ratio of Olsen-extractable P to water-extractable P (Table 7.2) in the 16 soils described in Chapter 6 and, once again, the higher ratios usually occurred in soils with high P retention.

To further investigate this effect, the P sorption model of Rennes (1978) was used. A detailed description of the model is presented in Chapter 6. In brief, the model assumes that when P is added to the soil solution, it can potentially be sorbed concurrently onto three regions of sites (Fig. 6.1). These three regions differ principally in the strength with which the P is bound to the surface. The P is held most strongly in region I and least strongly in region III.

When the model was applied to the 16 soils described in Chapter 6 and the four soils used in this study, it was apparent that in high P-sorbing soils of moderate P status, such as the Egmont soil, most sorbed P is present in regions I and II, and only a small proportion is present in region III; whereas in low P-sorbing soils, such as the Tokomaru soil, a relatively higher proportion of sorbed P is present in region III (Table 7.2).

The amounts of water-extractable P in the four soils used in this study and the 16 soils used in Chapter 6 were closely related ($r = 0.99^{**}$) to the amounts of P in region III in the model. This is consistent with the finding of Ryden and Syers (1977b) who suggested that water extraction largely removes more-physically sorbed P (region III). In contrast, a much weaker correlation was found between the amounts of Olsen-extractable P and those of P in region III in the model ($r = 0.61^{**}$), but the relationship was improved ($r = 0.75^{**}$) if the amounts of P in regions I and II were added to that in region III. These results suggest that the Olsen reagent is able to desorb some of the more tightly-bound P, presumably because of its relatively high hydroxyl ion concentration. It appears that the ratio of water-

Table 7.2 Amounts of water- and Olsen-extractable P, ratio of Olsen- to water-extractable P, P retention values, and amounts of P sorbed in the three regions (I, II, and III) predicted by the model of Rennes (1978) for the Egmont and Tokomaru soils used in this study and the 16 soils used in Chapter 6

Soil	Water-extractable P	Olsen-extractable P	Ratio of Olsen- to water-extractable P	P retention	Sorbed P in region		
	($\mu g\ g^{-1}$ soil)			(%)	I	II	III
					($\mu g\ g^{-1}$ soil)		
Egmont-low P	0.9	11.4	12.7	82	380	57	4
-medium P	2.1	25.4	12.1	80	434	129	9
Tokomaru-low P	3.8	12.8	3.4	20	110	130	14
-medium P	8.1	27.5	3.4	17	111	191	34
Soils from Chapter 6							
Carnarvon	3.8	8.9	2.3	45	256	185	15
Dannevirke	4.6	22.7	4.9	91	496	193	14
Egmont-low P	1.8	8.1	4.5	82	427	113	8
Hamilton	3.2	13.6	4.3	66	367	184	14
Kiwitea	3.7	10.7	2.9	40	228	172	15
Konini	4.4	12.3	2.8	43	246	203	18
Kumeroa-low P	5.7	9.0	1.6	30	174	208	23
Manawatu	5.1	25.4	5.0	19	111	154	20
Okaihau	5.6	20.6	3.7	45	259	245	23
Patua	2.2	11.8	5.4	98	513	139	9
Ramiha-low P	1.2	6.2	5.2	88	437	86	6
Ramiha-high P	6.7	25.7	3.8	55	316	287	26
Taupo-low P	3.0	18.0	6.0	53	297	158	12
Taupo-high P	7.8	40.0	5.1	67	385	365	34
Tokomaru-low P	6.7	16.3	2.4	19	111	177	28
Wainui	4.9	12.7	2.6	36	208	206	20

extractable P to Olsen-extractable P in a soil reflects the ratio of loosely-held P to more tightly-held P and that this ratio is strongly dependent on the P sorption capacity of the soil.

7.3.1.2 Relationship between ^{31}P concentrations in soil extracts and plants

The amounts of ^{31}P in both water and Olsen extracts usually declined slightly during plant growth (Table 7.3). Decreases were generally larger in the Tokomaru than in the Egmont soils, particularly in the high P status soils. There was a tendency for soil ^{31}P levels to be lower after the growth of ryegrass than after the growth of white clover in the Tokomaru soils, suggesting that ryegrass removed larger amounts of P from soil than did clover. This was confirmed by the uptake of ^{31}P, ^{32}P, and ^{33}P by plants, which indicated a greater uptake of P by ryegrass than by white clover (Tables 7.4 and 7.5).

The ^{31}P concentrations in both white clover and ryegrass at the end of the experiment ranged from 0.947×10^3 to 2.428×10^3 $\mu gP\ g^{-1}$ (Table 7.4). These are considered to be at a deficient level (McNaught, 1970). Although the growing plants were in contact with the soils for only six days, the ^{31}P concentrations of both ryegrass and of white clover were significantly affected by soil type and also by P status within a soil type (Table 7.4). The significant differences in ^{31}P concentration between plants grown on the two soils are interesting because the soils had been chosen so as to have similar Olsen P levels. The ^{31}P concentration in both ryegrass and white clover increased in a similar order to the amounts of ^{31}P in the water extracts of the soils (Table 7.1), although the differences in the plants were smaller than those apparent in the soil extracts.

Soil moisture had no effect on the amounts of ^{31}P in the soil extracts after growing either ryegrass or white clover (Table 7.3). Similarly, there was no effect of soil moisture on the ^{31}P concentrations of the plants growing on these soils (Table 7.4).

Table 7.3 ^{31}P concentrations in water and Olsen extracts of the Egmont and Tokomaru soils before and after plant uptake ($\mu g\ g^{-1}$)

Soil	^{31}P in water extract					^{31}P in Olsen extract				
	Before plant uptake	After plant uptake			LSD* (5%)	Before plant uptake	After plant uptake			LSD* (5%)
		Ryegrass	White	Mixed			Ryegrass	White clover	Mixed	
Egmont										
low P -M1#	0.9	1.0	0.8	1.0	NS	11.4	11.1	11.2	10.5	0.5
-M2	0.9	0.9	0.7	0.9	0.1	11.4	11.5	11.4	11.1	NS
medium P -M1	2.1	2.1	1.7	-	0.1	25.4	22.9	21.1	-	1.7
-M2	2.1	2.1	2.0	-	NS	25.4	21.9	22.7	-	1.4
Tokomaru										
low P -M1	3.8	3.5	3.2	3.3	0.4	12.8	10.9	12.9	11.3	0.7
-M2	3.8	3.2	3.5	3.3	0.2	12.8	10.5	12.4	10.4	0.4
medium P -M1	8.1	6.0	7.7	-	1.0	27.5	20.1	26.7	-	1.2
-M2	8.1	5.2	7.8	-	1.2	27.5	19.0	26.0	-	1.6

Moisture levels M1 and M2 (Section 7.2.2).

* For comparison between columns.

Table 7.4 Mean plant ^{31}P concentrations of ryegrass and white clover grown on the Egmont and Tokomaru soils (10^3 µg g^{-1})

Soil	Ryegrass		White clover	
	Pure	Mixed	Pure	Mixed
Egmont				
low P - M1#	1.406	1.488	0.937	1.292
- M2	1.375	1.683	1.024	1.097
medium P - M1	1.977	-	1.333	-
- M2	2.065	-	1.392	-
Tokomaru				
low P - M1	1.959	1.902	1.313	1.276
- M2	2.012	2.271	1.201	1.165
medium P - M1	2.361	-	1.738	-
- M2	2.428	-	1.896	-

Moisture levels M1 and M2 (Section 7.2.2).

Least significant differences (5% level)

Effect	
Soils	0.167
Soil P level: within soil	0.103
: all soils	0.167
Moisture: within soil	NS
: all soils	NS
Species: within soil	0.121
: all soils	0.167

Table 7.5 Total ^{32}P and ^{33}P activities (10^3 dpm g^{-1}) and dry matter yield (g pot^{-1}) of ryegrass and white clover grown on the Egmont and Tokomaru soils

Soil	^{32}P				^{33}P				Yield			
	Ryegrass		White clover		Ryegrass		White clover		Ryegrass		White clover	
	Pure	Mixed	Pure	Mixed	Pure	Mixed	Pure	Mixed	Pure	Mixed	Pure	Mixed
Egmont												
low P - M1#	3.781	4.186	1.456	2.187	6.886	7.774	2.290	4.412	2.83	1.79	1.23	0.19
- M2	4.333	5.155	1.803	2.402	7.035	10.323	3.058	3.882	2.85	2.04	1.21	0.23
medium P - M1	11.426	-	1.837	-	24.463	-	3.213	-	2.60	-	1.20	-
- M2	15.447	-	2.230	-	34.146	-	4.363	-	2.62	-	1.17	-
Tokomaru												
low P - M1	8.735	6.221	2.486	2.135	23.544	17.940	6.303	4.296	2.72	2.06	1.16	0.20
- M2	9.721	12.046	2.623	1.793	27.711	34.170	5.855	3.997	2.70	2.06	1.16	0.20
medium P - M1	12.964	-	3.239	-	45.344	-	9.934	-	2.84	-	1.17	-
- M2	17.602	-	3.089	-	56.705	-	9.625	-	2.81	-	1.26	-

Moisture levels M1 and M2 (Section 7.2.2).

Least significant differences (5% level)

Effect	^{32}P		^{33}P		Yield	
	Egmont	Tokomaru	Egmont	Tokomaru	Egmont	Tokomaru
Soil P level	1.204	0.910	2.586	2.878	NS	NS
Moisture : low P soils	0.484	0.741	NS	1.874	NS	NS
: all soils	1.204	0.910	2.586	2.878	NS	NS
Species : low P soils	0.685	1.048	1.228	2.651	0.17	0.16
: all soils	1.204	0.910	2.586	2.878	0.14	0.14

7.3.2 ^{32}P:^{33}P ratios

7.3.2.1 ^{32}P:^{33}P ratios in soil extracts

Because ^{32}P was added to the soil for a relatively short time (five days), compared to ^{33}P (47 days), the ^{32}P would probably not have equilibrated to the same extent with the less labile pool of soil P. Consequently, the ratios of ^{32}P:^{33}P in soil extracts should decrease if less labile P was being extracted. This is well demonstrated by the isotope ratios in the water and Olsen extracts from the Tokomaru soil (Table 7.6). The ^{32}P:^{33}P ratio in the Olsen extract was always lower than that in the water extract, which is thought to remove more loosely-held P (Ryden et al., 1977a). Surprisingly, the reverse trend was observed in the Egmont soil (Table 7.6). Lower ^{32}P:^{33}P ratios were obtained in the water extracts than in the Olsen extracts of the Egmont soil. Although this conflicting result is unexpected, a possible explanation is offered below to account for such a contradiction.

When ^{32}P is added to a soil, most of the ^{32}P will initially be in the soil solution and this will gradually exchange with the labile P on the surface. Because ^{33}P was added to the soil for a long period of time, it can be assumed to have exchanged with much of the native ^{31}P in soils. The ^{32}P:^{33}P ratio will initially be highest in the soil solution and will decrease as more ^{32}P is exchanged with the surface P. It is suggested that the most readily-exchangeable soil P pools will equilibrate with the soil solution, and that exchange with the more tightly-bound P will occur more slowly. As this process continues, the net movement of ^{32}P from the solution to the surface will slow down and ^{32}P will begin to be re-distributed amongst the various surface groups.

At this stage the ratio of ^{32}P:^{33}P in the soil solution and the very rapidly-exchangeable pool will decrease to a value intermediate between that existing in the P pools which had previously reached equilibrium with the soil solution and that existing in the less highly-labelled pools to which the ^{32}P is now migrating. In such a situation it

Table 7.6 $^{32}P:^{33}P$ ratios in water and Olsen extracts of the Egmont and Tokomaru soils before and after plant uptake

Soil	$^{32}P:^{33}P$ in water extract					$^{32}P:^{33}P$ in Olsen extract				
	Before plant uptake	After plant uptake			LSD* (5%)	Before plant uptake	After plant uptake			LSD* (5%)
		Ryegrass	White clover	Mixed			Ryegrass	White clover	Mixed	
Egmont										
low P -M1 #	0.21	0.21	0.14	0.20	0.03	0.30	0.28	0.29	0.30	NS
-M2	0.21	0.19	0.16	0.16	0.03	0.30	0.29	0.29	0.29	NS
medium P -M1	0.20	0.21	0.18	-	NS	0.30	0.28	0.30	-	NS
-M2	0.20	0.21	0.21	-	NS	0.30	0.27	0.28	-	NS
Tokomaru										
low P -M1	0.28	0.27	0.26	0.31	NS	0.21	0.21	0.23	0.21	NS
-M2	0.28	0.25	0.26	0.28	NS	0.21	0.20	0.22	0.20	NS
medium P -M1	0.23	0.23	0.24	-	NS	0.18	0.18	0.22	-	NS
-M2	0.23	0.24	0.25	-	NS	0.18	0.18	0.22	-	NS
LSD (5%)	0.04	0.03	0.02	0.04		0.03	0.03	0.02	0.01	

Moisture levels M1 and M2 (Section 7.2.2).

* For comparison between columns.

is possible that an extractant, such as water, which removes only the soil solution P together with a small quantity of readily-exchangeable P, will have a lower ^{32}P:^{33}P ratio than the Olsen extractant which appears to remove some less readily-exchangeable P.

This effect would be most marked in soils with the largest difference in the amounts of P extracted by water and the Olsen reagent. As explained in Section 7.3.1.1, such soils usually have a high P sorption capacity. This is consistent with the observation described above, that for the high P-sorbing Egmont soil the ^{32}P:^{33}P ratios in the water extracts were lower than those in the Olsen extracts.

In a similar study using a double-labelling technique with an Egmont soil, Gillingham (1978) reported a higher ^{32}P:^{33}P ratio in the water extracts at a 40:1 solution:soil ratio than in water extracts at a 20:1 ratio. Although commenting that the result was unusual as it would be anticipated that the 40:1 extraction would remove less-labile P, with an expected lower rather than a higher isotope ratio, Gillingham (1978) offered no explanation for this observation. However, if it is assumed that increasing the solution:soil ratio would result in more P being desorbed from less readily-exchangeable pools, which contain a relatively high proportion of ^{32}P as described above, then higher ^{32}P:^{33}P ratios might be obtained in the 40:1 than in the 20:1 extraction.

7.3.2.2 ^{32}P:^{33}P ratios in plants

As ^{33}P had been incubated with the soil for a long time prior to the placement of the plants it should have achieved near-equilibrium with the native soil ^{31}P. Total plant uptake of ^{33}P should therefore be a good indicator of total P uptake from the soil. As long as comparisons are restricted to between species within a soil at a given moisture content, total plant uptake of ^{33}P is likely to be more accurate than estimates of ^{31}P uptake, as these will be relatively small compared to the large quantity of ^{31}P already present in the plant prior to the placement on the soil.

Ryegrass always took up very much larger quantities of ^{33}P than did white clover (Table 7.7). This is consistent with the much more vigorous proliferation of ryegrass roots and the larger decrease in soil ^{31}P levels (Table 7.3) observed after ryegrass growth.

The effects of increasing soil moisture was generally to increase the uptake of ^{33}P by ryegrass, with the effect being more apparent in the medium P status soils, and in the mixed species treatments on the low P status soils (Table 7.7). These observations can be explained by considering the rate of diffusion of soil P to the plant roots. This diffusion rate will increase with increasing soil moisture content (Nye and Tinker, 1977) and should result in increasing plant P uptake. The relatively small effect noted when ryegrass is grown alone on the low P status soils is probably because the plants had already completely depleted the pool of readily-available P. In the mixed species treatments there were fewer ryegrass plants per pot and presumably also a lower root density. This severely restricted P uptake at low soil moisture levels but could be overcome at higher moisture contents when the P was able to diffuse to the more widely-spaced roots. It is significant that at high moisture contents the ^{33}P uptake by the 10 ryegrass plants in the mixed species treatment was very similar to that by the 15 plants in the ryegrass alone treatment (Table 7.7).

Similarly, as the medium P status soils had more than sufficient P to last for the whole growth period, the increased rate of diffusion at higher moisture contents resulted in significantly greater uptake by the ryegrass plants (Table 7.7).

Differences in soil moisture content had no consistent effect on the uptake of ^{33}P by white clover. This difference between ryegrass and white clover is difficult to explain.

The ^{32}:^{33}P ratio in ryegrass was always significantly lower than that in white clover when each species was grown

Table 7.7 Total ^{33}P uptake (10^3 dpm pot^{-1}) by ryegrass and white clover grown on the Egmont and Tokomaru soils

Soil	Ryegrass alone	White clover alone	Mixed species		
			Ryegrass	White clover	Total
Egmont					
low P - M1#	19.518	2.791	13.888	0.836	14.724
- M2	24.475	3.675	21.055	0.875	21.930
medium P - M1	63.918	3.769	-	-	-
- M2	88.787	5.134	-	-	-
Tokomaru					
low P - M1	63.017	7.307	35.162	0.836	35.998
- M2	74.708	6.702	70.135	0.794	70.929
medium P - M1	127.760	11.557	-	-	-
- M2	158.742	11.783	-	-	-

Moisture levels M1 and M2 (Section 7.2.2).

Least significant differences (5% level)

Effect	Egmont	Tokomaru
Soil P level	7.170	5.831
Moisture : low P soils	2.946	3.392
: all soils	7.170	5.831
Species : low P soils	4.167	4.797
: all soils	7.170	5.831

alone (Table 7.8). This suggests that ryegrass was removing P from less readily-exchangeable soil P pools than was white clover. If less-labile P is becoming available for uptake by ryegrass this may occur simply because of the larger depletion of soil P which occurred with ryegrass, or it may be due to the ability of ryegrass to exploit soil P pools which are not available to white clover. It is interesting to note that in all but one case, the ^{32}P:^{33}P ratios in both ryegrass and white clover when grown together did not change greatly from when they were grown separately. This was despite the fact that up to 10 times the amount of ^{33}P was being taken up from the mixed species pots than was removed from pots with white clover alone (Table 7.7). This suggests that even when ryegrass and white clover are growing in the same pot, they continue to draw on different pools of soil P in a highly depletive system.

The present results are contrary to those obtained in a similar double-labelling study by Gillingham (1978) who found no difference in the isotope ratios in white clover and ryegrass. In the latter study, plants were grown on soils with a very high P status and under moisture conditions which would maximise uptake of P. Such conditions would be less suitable for distinguishing between plant species as to their efficiency in the utilisation of soil P. In the present study, the soils used did not have a very high P status. Hence it is likely that the supply of P would be more limiting, particularly in the Egmont soils which have a high P sorption capacity (Table 7.1).

The ability of ryegrass to recover P from a less-labile pool may be associated with its ability to lower the concentration of P in solution at root surfaces, thus promoting desorption from less-labile P in the soil (Barrow, 1975a). Parfitt et al. (1982) have reported that the concentration of P in the soil solution required for near optimum growth is lower for ryegrass (0.06 $\mu g\ l^{-1}$) than for clover (0.31 $\mu gP\ l^{-1}$). They also found that ryegrass was able to desorb more P from soil than was clover. Similarly, the study of Barrow (1975b) indicated that, in comparison

Table 7.8 $^{32}P:^{33}P$ ratios in ryegrass and white clover grown on the Egmont and Tokomaru soils

	Ryegrass		White clover	
	Pure	Mixed	Pure	Mixed
Egmont				
low P - M1#	0.55	0.55	0.65	0.50
- M2	0.51	0.50	0.60	0.62
medium P - M1	0.47	-	0.60	-
- M2	0.46	-	0.51	-
Tokomaru				
low P - M1	0.37	0.35	0.47	0.50
- M2	0.35	0.35	0.43	0.45
medium P - M1	0.29	-	0.33	-
- M2	0.31	-	0.32	-

Moisture levels M1 and M2 (Section 7.2.2).

Least significant differences (5% level)

Effect	Egmont	Tokomaru
Soil P level	0.05	0.01
Moisture: low P soils	0.04	NS
: all soils	0.05	NS
Species: low P soils	0.06	0.04
: all soils	0.05	0.01

with clover, grass roots were able to take up more P because of the larger numbers of root hairs, as well as their ability to reduce the P concentration at the root surface to a lower level than did clover.

In one case (Egmont-low P at low soil moisture) the $^{32}P:^{33}P$ ratio (Table 7.8) in white clover grown together with ryegrass was much lower (0.50) than when the white clover was grown alone (0.65). Indeed, the $^{32}P:^{33}P$ ratio of the white clover was lower than that of the ryegrass growing in the same pot (0.55). This result is in contradiction to the others discussed above and is difficult to explain. Inspection of the individual replicates reveals very little variation and suggests that the effect was not a statistical anomaly. Further work is required to investigate this finding.

It is interesting to note that the amounts of ^{33}P removed by ryegrass (dpm g^{-1} soil) were not greatly different from those present in the water extracts (Table 7.9), suggesting that ryegrass took up soil P in amounts comparable to those removed by the water extraction. This is consistent with the earlier finding that the amounts of water-extractable P in soils correlate well with the amounts of plant-available P (see Chapter 3). However, the $^{32}P:^{33}P$ ratios in both Olsen and water extracts were always lower than those in the plants (Tables 7.6 and 7.8). It is difficult to draw any firm conclusions from this observation because the wide soil:solution ratio in the water extract is likely to speed up exchange and slightly lower the $^{32}P:^{33}P$ ratio in solution.

7.4 Conclusions

Although the soils used in this study had similar Olsen P levels, they varied considerably in their amounts of water-extractable P. The P sorption model of Rennes (1978) could be used to provide a possible explanation for such an observation. Although the assumptions implicit in such a multi-region approach to P sorption are open to inter-

Table 7.9 Amounts of ^{33}P (10^3 dpm g^{-1} soil) removed by water extraction and plant uptake by ryegrass and white clover grown on the Egmont and Tokomaru soils

Soil	^{33}P in water extract	^{33}P in herbage		
		Ryegrass	White clover	Mixed species
Egmont				
low P - M1#	1.451	0.976	0.140	0.736
- M2	1.451	1.224	0.184	1.097
medium P - M1	1.808	3.196	0.188	-
- M2	1.808	4.439	0.257	-
Tokomaru				
low P - M1	4.867	3.151	0.365	1.800
- M2	4.867	3.782	0.335	3.547
medium P - M1	6.892	6.401	0.578	-
- M2	6.892	7.937	0.589	-

Moisture levels at M1 and M2 (Section 7.2.2).

pretation, the model provided a plausible explanation for the differences in the ratio of water-extractable P to Olsen-extractable P among soils. It appears that the ratio of water- and Olsen-extractable P in a soil reflects the ratio of loosely-held to more tightly-held P and that this ratio is strongly dependent on the P sorption capacity of the soil.

Ratios of ^{32}P:^{33}P in the Olsen and water extracts of soils, obtained by a double-labelling technique, also showed a contrasting pattern between the low P-sorbing Tokomaru soil and the high P-sorbing Egmont soil. It is suggested that the lower ^{32}P:^{33}P ratio in the water extract of the Egmont soil, as compared to the ratio in the Olsen extract, is related to the large difference in the amounts of P extracted by water and the Olsen reagent.

The lower ^{32}P:^{33}P ratio in ryegrass, as compared to that in white clover, indicated that ryegrass was removing P from pools of less readily-exchangeable soil P than was white clover. Even when ryegrass and white clover were growing together in the same pot, they continued to draw on different pools of soil P in a highly depletive system. It is suggested that less-labile P becomes available for uptake by ryegrass both as a result of the ability of ryegrass to exploit soil P pools which are not available to white clover as well as the larger depletion of soil P by ryegrass.

In the present study, the double-labelling technique was successfully used to characterise the short-term plant availability of soil P and also to establish if different plant species have the ability to exploit different pools of soil P. Further evaluation of the double-labelling technique could usefully involve investigation of the intensity of P depletion, particularly the interaction between the number of plants, the amount of soil used, and the duration of contact between plants and soil. The concept of labelling a soil with two P isotopes for differing durations provides a means of distinguishing different pools of soil P, which can be useful in several

areas of investigation, including the characterisation of short-term plant availability of soil P, the ability of different plant species to exploit soil P from various pools, and the movement of soil P between different pools, particularly in relation to the transformations of soil organic P.

SUMMARY AND CONCLUSIONS

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The work presented in this thesis may be summarised as follows:

1. A review of the literature indicates that among the various processes controlling the concentration of P in the soil solution, sorption-desorption reactions are the most important, although the mechanisms involved are still not fully understood. There has also been an increasing recognition of the significance of soil organic and microbial P as sources of plant-available P in soils. Assessment of the availability of soil P to plants requires an understanding of the physico-chemical aspects of soil inorganic P, as well as the dynamics of organic P in soil.

2. In New Zealand, the fertilizer P requirements of well-developed pasture, maintained at a steady level of production, are calculated using a model developed by Cornforth and Sinclair (1982). The model is based on estimates of P losses with various combinations of stock and land type, and soil P losses due to immobilisation. A soil test is required in the model to assess whether the level of available soil P is appropriate for the proposed level of production and to subsequently monitor the effectiveness of the maintenance fertilizer P programme calculated by the model.

3. In an initial evaluation in the glasshouse using 20 soils, the amount of inorganic P removed by water extraction was highly correlated ($r = 0.90^{**}$) with plant-available P as indicated by plant uptake of P. Inclusion of an estimate of P buffering capacity (P retention value or the slope of the desorption isotherm) did not improve the prediction of plant-available P using water extraction, although the reverse was the case for the Olsen test. Water-

extractable P appears to reflect not only the intensity factor, as previously thought, but also the buffering capacity of soil P. Because the interpretation of water-extractable P data is not greatly influenced by the buffering capacity of soils and appears to be largely independent of soil type, the water-extraction procedure may have advantages over other procedures for assessing plant-available P in soils, provided adequate amounts of P are present for routine measurement.

4. Results over 12 months from field experiments at two contrasting sites under permanent pasture showed that the amounts of water-extractable P in the soils were always lower than those of Olsen-extractable P. For example, the average values of water-extractable P (0-7.5 cm depth) over the 12-month period were 1.8 and 4.9 $\mu g\ g^{-1}$ soil for the Ramiha and Tokomaru soils, respectively, while the corresponding values of Olsen-extractable P were 12.6 and 8.7 $\mu g\ g^{-1}$ soil, respectively. However, the variability associated with water-extractable P within each sampling was comparable with that for Olsen-extractable P.

5. Seasonal variations during the 12-month period of study were larger for water-extractable P (coefficient of variation = 15 and 23% for the Tokomaru and Ramiha soils, respectively) than for Olsen-extractable P (coefficient of variation = 12 and 16% for the Tokomaru and Ramiha soils, respectively). Seasonal fluctuations were related closely to the pattern of pasture P uptake. Low levels of water-extractable P were associated with autumn and spring flushes of pasture growth, while high values were obtained during periods of slow growth in winter. In the Ramiha soil, the value for water-extractable P was as low as 1.2 $g\ g^{-1}$ soil in May, then increased to 2.4 $g\ g^{-1}$ soil in July, and decreased again to 1.2 $g\ g^{-1}$ soil in October.

6. The amounts of water- and Olsen-extractable P in soils were higher in the 0-4.0 cm sampling depth than in the 0-7.5 cm depth. In the 0-7.5 cm sampling depth, the average values over the 12-month period for water- and Olsen-extractable P in the unfertilized Ramiha soil were 1.8 and 12.6 $\mu g\ g^{-1}$ soil, respectively. In contrast, the corresponding values at the 0-4.0 cm depth were 3.7 and 16.2 $\mu g\ g^{-1}$ soil, respectively. The effect of sampling depth on the variability of water-extractable P varied between soils.

7. When fertilizer P was added, increases in both Olsen- and water-extractable P in the 0-7.5 cm sampling depth were not as marked as those in the 0-4.0 cm depth. The increase in water-extractable P in the Tokomaru soil two weeks after the addition of 40 kgP ha^{-1} was 5.3 $\mu g\ g^{-1}$ in the 0-7.5 cm sampling depth, compared to an increase of 9.9 $\mu g\ g^{-1}$ in the 0-4.0 cm depth. In addition, the increase from fertilizer P addition in the 0-7.5 cm depth became undetectable within a few months of addition, although there was a continuing response of pasture to added P. In fact, the effect of fertilizer P addition on water-extractable P of both soils in the 0-4.0 cm sampling depth still persisted at 12 months following addition. Consequently, it appears that the effect of fertilizer P addition is better reflected by the water-extractable P value determined in the 0-4.0 rather than in the 0-7.5 cm sampling depth.

8. The value for water-extractable P (0-4.0 cm depth) in both soils two weeks following the addition of 40 kgP ha^{-1} was increased by more than 150%, whereas only 100% increases were obtained in Olsen-extractable P at the same sampling time. However, the initial increases in both water- and Olsen-extractable P were approximately proportional to the rate of fertilizer P added. The increases were approximately doubled when the rates of P addition were increased twofold. The effect of fertilizer P addition on water-extractable P

varied considerably with elapsed time after application and also with season. The increases were ,as expected, largest immediately following addition and became smaller with time. However, the increases again became larger in late winter, when the amounts of water-extractable P in soils were also generally higher than at other times of the year.

9. Seasonal variations in water-extractable P in unfertilized and fertilized soils were not related to changes in soil microbial biomass P. Significantly, seasonal fluctuations in microbial biomass P were also not related to P uptake by pasture. The lack of any relationships between seasonal variations in microbial biomass P and P uptake by plants suggests that microbial biomass P may be a less sensitive index of soil P availability than previously thought.

10. Results of laboratory and incubation studies on two soils with contrasting P sorption capacity indicated that liming caused a significant decrease in Olsen-extractable P which was not supported by alternative soil tests, such as water-extractable and isotopically-exchangeable P, or by plant uptake data. For example, Olsen-extractable P in the Tokomaru and Egmont soils of medium P status was decreased by 20% as a result of the addition of $Ca(OH)_2$ at rates equivalent to 2,000 and 6000 kg $CaCO_3$ ha^{-1}, respectively. The decline appears to be the result of an artifact in the Olsen procedure by which calcium phosphates may be precipitated under the conditions of high Ca concentration and high pH. Results from a field study also confirm the findings obtained from the glasshouse experiment. In fact, there was a significant reduction of 30% in Olsen-extractable P of the Tokomaru soil at 21 months following the application of 5,000 kg $CaCO_3$ ha^{-1}. Because water-extractable P values are much less influenced by soil pH, water extraction may have an advantage over the Olsen test as a soil-testing procedure for limed soils.

11. The model of Rennes (1978), based on the Langmuir adsorption equation, was used to simulate changes in water-extractable P in soils following fertilizer P addition. The predictions obtained were satisfactory for a soil with high P sorption capacity. The predictive ability of the model was strongly influenced by estimates of sorption energy constants (K) for a high P-sorbing Egmont soil, whereas for a low P-sorbing Tokomaru soil, estimates of sorption maxima (b) were more important. A working model was developed using phosphate retention (PR) test data as estimates of b. Very good predictions ($r = 0.84^{**}$) were obtained with the model for a group of 16 soils with a wide range of P sorption capacities. It was observed that the amounts of P extracted by water from some soils were still changing rapidly at 1 h, which is the extraction period in the original water-extraction procedure, but that the rate of change had become significantly smaller at 24 h. Significantly, the predictions by the model were further improved ($r = 0.91^{**}$) when a water-extraction period of 24 h was used. It may be possible to use the water-extraction procedure not only to determine whether fertilizer application rates are in excess of maintenance requirements but also to quantify this estimate.

12. In a study using a double-labelling technique designed to characterise soil P, the soil was incubated with ^{33}P for a relatively long period of time (51 days) and ^{32}P for a relatively short period of time (5 days). The ^{32}P:^{33}P ratios in the Olsen and water extracts of soils showed a contrasting pattern between the low P-sorbing Tokomaru soil and the high P-sorbing Egmont soil. In general, as the exchangeability of soil P decreases, so should the ratio of ^{32}P:^{33}P. The lower ^{32}P:^{33}P ratio in the water extract than in the Olsen extract appears to be associated with the high ratio of Olsen- to water-extractable P in this soil. This, in turn, reflects the ratio of more tightly-held P to loosely-

held P. When plants were grown on the labelled soils, the ^{32}P:^{33}P ratio in ryegrass was always lower than in white clover, indicating that ryegrass removed P from less readily-exchangeable soil P pools than white clover. This appears to be largely a result of the ability of ryegrass to exploit soil P pools which are less available to white clover as well as the larger depletion of soil P by ryegrass.

13. Because it is possible to model changes in water-extractable P in soils following fertilizer P addition, a water-extraction procedure may be the preferred soil test in the model of maintenance fertilizer P requirements (Cornforth and Sinclair, 1982). Similarly, water extraction may also be used to monitor the influence of other P inputs, such as litter, dung, and mineralisation, on the P fertility of the site. Because water-extractable P values in soils closely predict the amounts of plant-available P and because their interpretation appears to be independent of soil type, the water-extraction procedure may be useful as a practical soil test to assess the level of plant-available P over a wide range of soils.

14. Areas of further investigation could include application of the model of Rennes (1978) to predict changes in water-extractable P in field soils following fertilizer P additions. The suggestion that values of water-extractable P obtained after 24 h may be more reliable than those obtained after 1 h requires further investigation. More extensive field trials, involving a wide range of soil types and field conditions, are also needed to confirm the findings obtained in this study.

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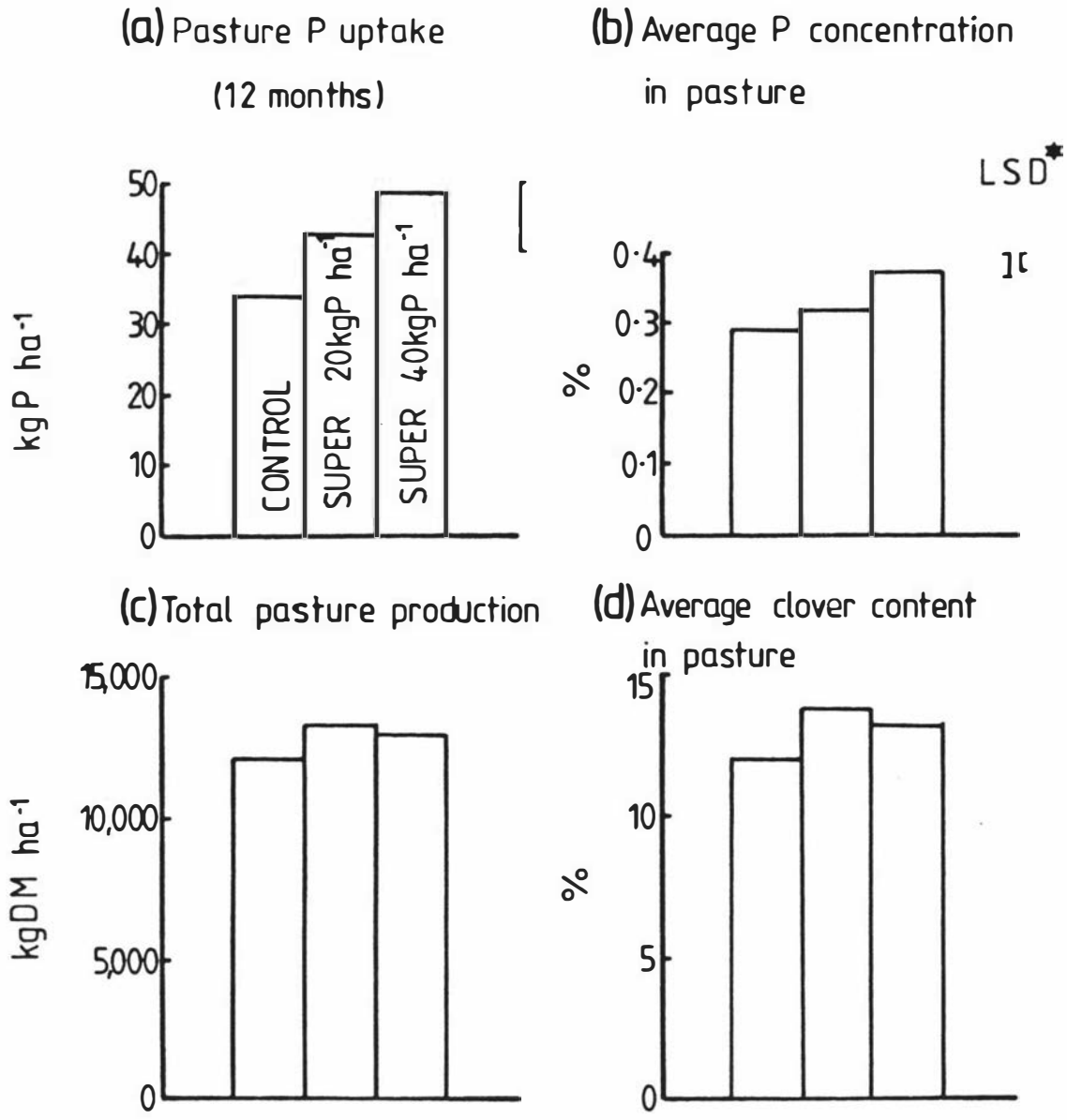
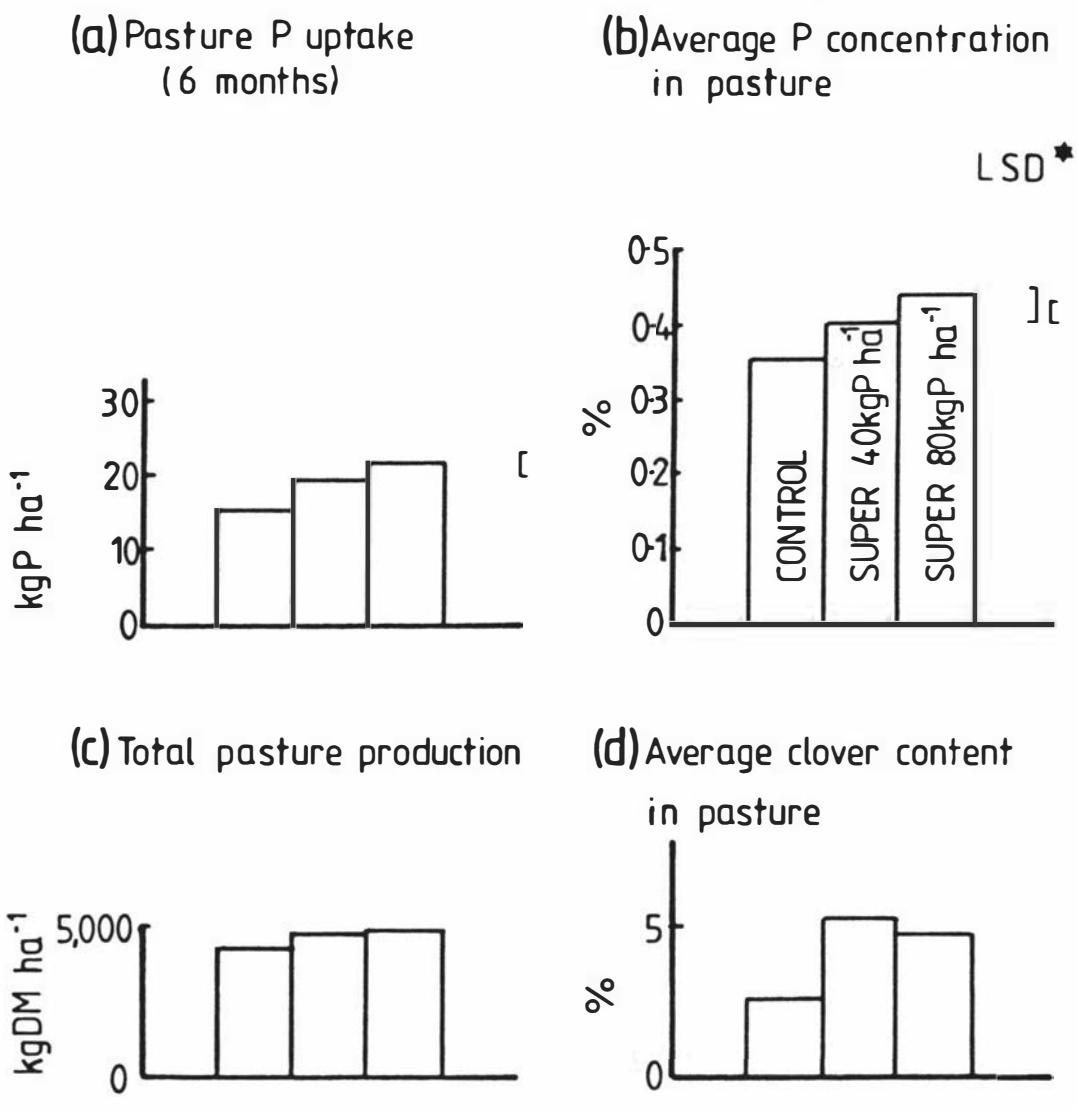
APPENDICES



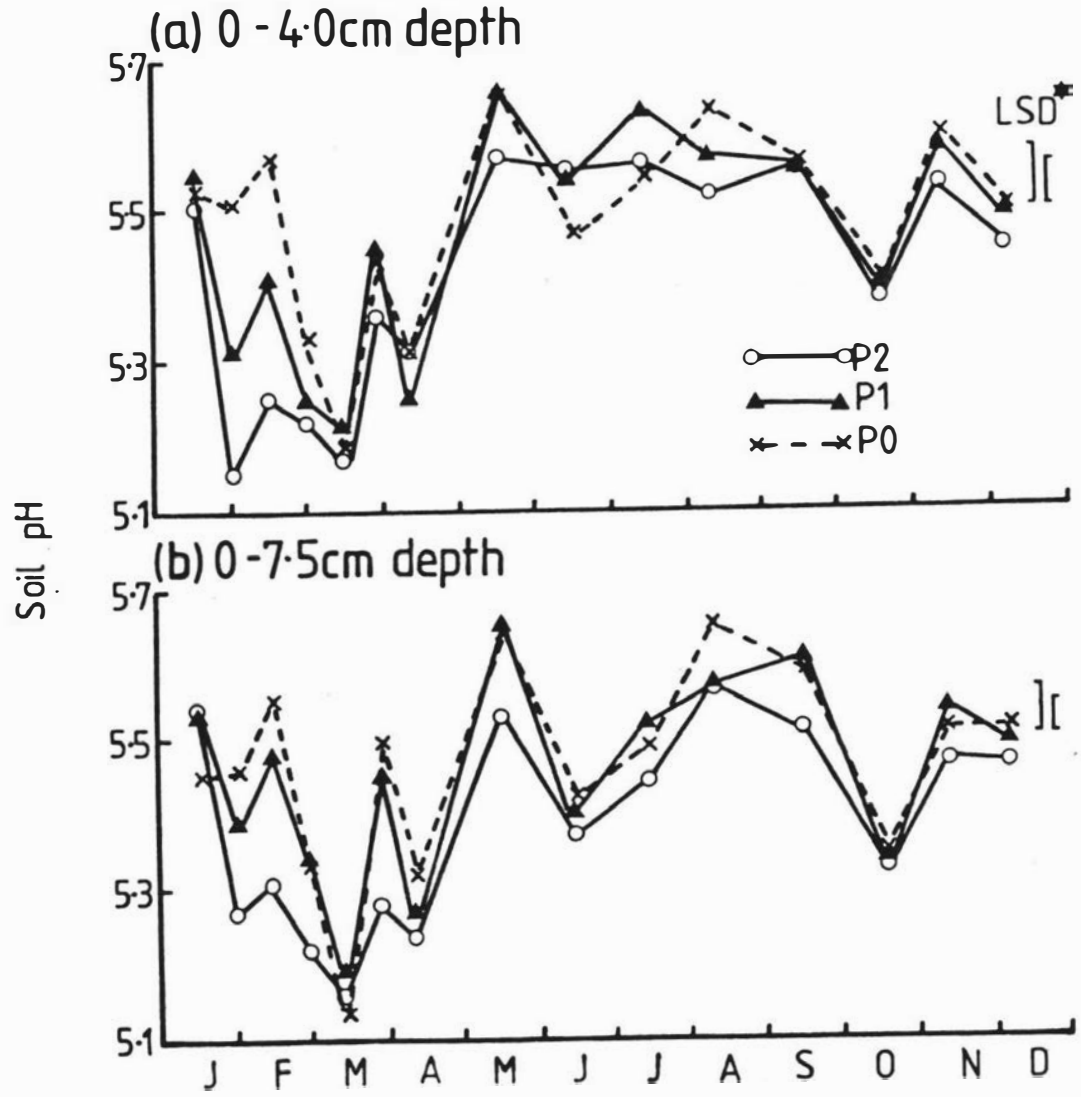
APPENDIX I Pasture P uptake (12 months) (a), average P concentration of pasture (b), total pasture production (c), and average clover content in pasture (d) on the Tokomaru soil following the additions of 0 (P0), 20 (P1), and 40 (P2) kgP ha^{-1} of superphosphate

* Least significant difference at 1 and 5% levels



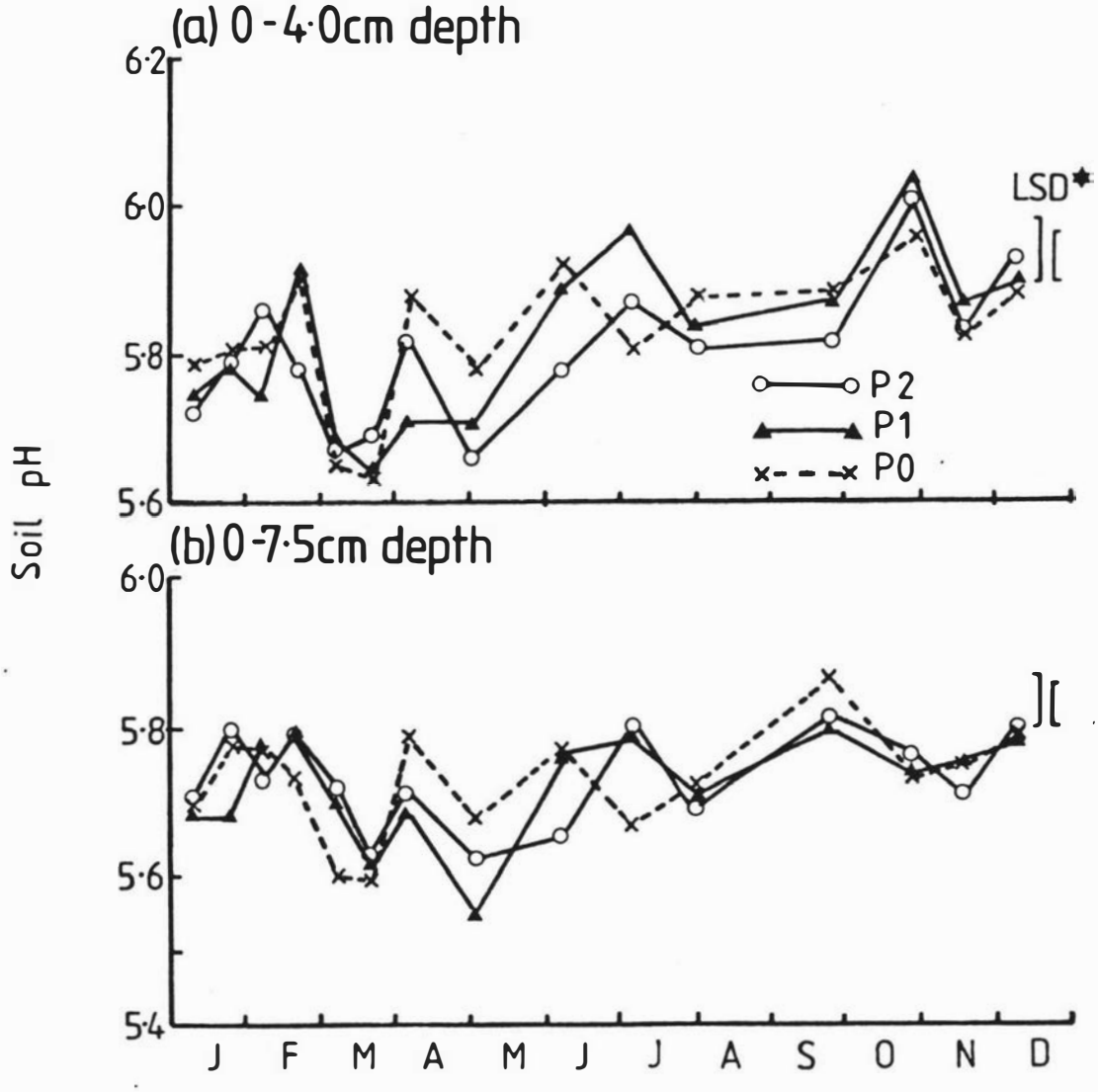
APPENDIX II Pasture P uptake (6 months) (a), average P concentration of pasture (b), total pasture production (c), and average clover content in pasture (d) on the Ramiha soil following the additions of 0 (P0), 40 (P1), and 80 (P2) kgP ha^{-1} of superphosphate

* Least significant difference at 1 and 5% levels



APPENDIX III Changes in soil pH in the 0-4.0 (a) and 0-7.5 (b) cm sampling depths in the Ramiha soil following the additions of 0 (P0), 40 (P1), and 80 (P2) kgP ha^{-1} of superphosphate

* Least significant difference at 1 and 5% levels



APPENDIX IV Changes in soil pH in the 0-4.0 (a) and 0-7.5 (b) cm sampling depths in the Tokomaru soil following the additions of 0 (P0), 20 (P1), and 40 (P2) kgP ha^{-1} of superphosphate

* Least significant difference at 1 and 5% levels

APPENDIX V EXAMPLES OF COMPUTER PROGRAMMES AND PRINT-OUTS FOR THE P MODEL

SS0736SRIVICHAI>PMODEL>INCUBATION.F77

```
0001       program pmodel
0002
0003 COMMENT    Langmuir sorption model for the Wainui soil
0004
0005 COMMENT    constants used in model
0006
0007 COMMENT    soln = soil solution concentration
0008
0009 COMMENT       a = amount of p in region 1
0010 COMMENT       c = amount of p in region 2
0011 COMMENT       e = amount of p in region 3
0012
0013 COMMENT    vac1 = number of vacant sites in region 1
0014 COMMENT    vac2 = number of vacant sites in region 2
0015 COMMENT    vac3 = number of vacant sites in region 3
0016
0017 COMMENT      i1 = increment of p sorbed onto region 1
0018 COMMENT      i2 = increment of p desorbed from region 1
0019 COMMENT      i3 = increment of p sorbed onto region 2
0020 COMMENT      i4 = increment of p desorbed from region 2
0021 COMMENT      i5 = increment of p sorbed onto region 3
0022 COMMENT      i6 = increment of p desorbed from region 3
0023
0024 COMMENT     meanings for kf1,kr1,kf2,kr2,kf3,kr3 are explained in text
0025
0026        external openfile, stop, title, ftn, ttya
0027        intrinsic mode
0028
0029        real*8 soln, a, c, e, isoln, ia, ic, ie,
0030       *       i1, i2, i3, i4, i5, i6,
0031       *       vac1, vac2, vac3,
0032       *       kf1, kf2, kf3, kr1, kr2, kr3,
0033       *       delt
0034
0035        real   l, m, fintim, prdel
0036
0037        call title (' PMODEL EMULATION')
0038
0039        call openfile(6,' ','write')
0040        call ftn(6)
0041
0042        call ttya(' Enter FINTIM: ')
```

```
0043        read(1,*) fintim
0044        call ttya('Enter DELT:     ')
0045        read(1,*) delt
0046        call ttya(' Enter PRDEL:   ')
0047        read(1,*) prdel
0048
0049        call ttya(' Enter SOLN:    ')
0050        read(1,*) soln
0051        call ttya(' Enter A:       ')
0052        read(1,*) a
0053        call ttya(' Enter C:       ')
0054        read(1,*) c
0055        call ttya(' Enter E:       ')
0056        read(1,*) e
0057
0058        call ttya(' Enter KF1:     ')
0059        read(1,*) kf1
0060        call ttya(' Enter KR1:     ')
0061        read(1,*) kr1
0062        call ttya(' Enter KF2:     ')
0063        read(1,*) kf2
0064        call ttya(' Enter KR2:     ')
0065        read(1,*) kr2
0066        call ttya(' Enter KF3:     ')
0067        read(1,*) kf3
0068        call ttya(' Enter KR3:     ')
0069        read(1,*) kr3
0070        write(1,*)
0071
0072        write(6,'(9A)')'           TIME',
0073       *                ,'           SOLN',
0074       *                ,'              A',
0075       *                ,'              C',
0076       *                ,'              E',
0077       *                ,'             IA',
0078       *                ,'             IC',
0079       *                ,'             IE',
0080       *                ,'          ISOLN',
0081
0082        write(6,'(F14.3,4D14.6)') 0.0, soln, a, c, e
0083
0084        do 20 l = prdel, fintim, prdel
0085
0086           do 10 m = delt, prdel, delt
0087
0088 COMMENT      vac1=212-a
0089              i1=kf1*soln*delt*(212-a)
0090              i2=kr1*delt*a
0091 COMMENT      vac2=529-c
0092              i3=kf2*soln*delt*(529-c)
```

```
0093                  i4=kr2*delt*c
0094 COMMENT          vac3=1059-e
0095                  i5=kf3*soln*delt*(1059-e)
0096                  i6=kr3*delt*e
0097
0098                  a=a+i1-i2
0099                  c=c+i3-i4
0100                  e=e+i5-i6
0101                  soln=soln+(i2+i4+i6-i1-i3-i5)/.34
0102
0103
0104    10            continue
0105
0106                  ia=i1-i2
0107                  ic=i3-i4
0108                  ie=i5-i6
0109                  isoln=(i2+i4+i6-i1-i3-i5)/.34
0110
0111               write(6,'(F14.3,8D14.6)') l, soln, a, c, e, ia, ic, ie, isoln
0112               call ttya('*')
0113    20        continue
0114
0115          call stop(0)
0116          end
```

SS0736SRIVICHAI>PMODEL>INCUBATION.COMI

```
0001        run77 incubation.seg
0002        wai5.out          NAME OF OUTPUT DATA FILE
0003        1000              FINTIM
0004           0.001          DELT
0005         100              PRDEL
0006         242.1            SOLN
0007         207.71           A
0008         206.20           C
0009          20.044          E
0010           0.092          KF1
0011           0.00027        KR1
0012           0.180          KF2
0013           0.04           KR2
0014           0.1427         KF3
0015           1.05           KR3
```

TIME	SOLN	A	C	E	IA	IC	IE	ISOLN
0.000	0.242100D+03	0.207710D+03	0.206200D+03	0.200440D+02				
100.000	0.238182D+00	0.209282D+03	0.273700D+03	0.332054D+02	0.305734D-05	-0.258717D-05	-0.469020D-06	-0.340122D-08
200.000	0.238046D+00	0.209403D+03	0.273597D+03	0.331868D+02	0.325674D-06	-0.275607D-06	-0.499437D-07	-0.362178D-09
300.000	0.238032D+00	0.209416D+03	0.273586D+03	0.331848D+02	0.347267D-07	-0.293881D-07	-0.532549D-08	-0.386198D-10
400.000	0.238030D+00	0.209418D+03	0.273585D+03	0.331846D+02	0.370399D-08	-0.313438D-08	-0.568209D-09	-0.412253D-11
500.000	0.238030D+00	0.209418D+03	0.273585D+03	0.331845D+02	0.395768D-09	-0.334709D-09	-0.609077D-10	-0.443991D-12
600.000	0.238030D+00	0.209418D+03	0.273585D+03	0.331845D+02	0.429834D-10	-0.361443D-10	-0.682210D-11	-0.498491D-13
700.000	0.238030D+00	0.209418D+03	0.273585D+03	0.331845D+02	0.535308D-11	-0.398515D-11	-0.136424D-11	-0.108586D-13
800.000	0.238030D+00	0.209418D+03	0.273585D+03	0.331845D+02	0.181898D-11	-0.176470D-11	-0.546230D-13	0.100129D-14
900.000	0.238030D+00	0.209418D+03	0.273585D+03	0.331845D+02	0.181898D-11	-0.176470D-11	-0.546230D-13	0.100129D-14
1000.000	0.238030D+00	0.209418D+03	0.273585D+03	0.331845D+02	0.181898D-11	-0.176470D-11	-0.546230D-13	0.100129D-14

SS0736SRIVICHAI>PMODEL>EXTRACTION.F77

```
0001       program pmodel
0002
0003 COMMENT    Langmuir sorption model for the Wainui soil
0004
0005 COMMENT    constants used in model
0006
0007 COMMENT    soln = soil solution concentration
0008
0009 COMMENT       a = amount of p in region 1
0010 COMMENT       c = amount of p in region 2
0011 COMMENT       e = amount of p in region 3
0012
0013 COMMENT    vac1 = number of vacant sites in region 1
0014 COMMENT    vac2 = number of vacant sites in region 2
0015 COMMENT    vac3 = number of vacant sites in region 3
0016
0017 COMMENT      i1 = increment of p sorbed onto region 1
0018 COMMENT      i2 = increment of p desorbed from region 1
0019 COMMENT      i3 = increment of p sorbed onto region 2
0020 COMMENT      i4 = increment of p desorbed from region 2
0021 COMMENT      i5 = increment of p sorbed onto region 3
0022 COMMENT      i6 = increment of p desorbed from region 3
0023
0024 COMMENT     meanings for kf1,kr1,kf2,kr2,kf3,kr3 are explained in text
0025
0026       external openfile, stop, title, ftn, ttya
0027       intrinsic mode
0028
0029       real*8 soln, a, c, e, isoln, pw
0030      *       i1, i2, i3, i4, i5, i6,
0031      *       vac1, vac2, vac3,
0032      *       kf1, kf2, kf3, kr1, kr2, kr3,
0033      *       delt
0034
0035       real   l, m, fintim, prdel
0036
0037       call title (' PMODEL EMULATION')
0038
0039       call openfile(6,' ','write')
0040       call ftn(6)
0041
0042       call ttya(' Enter FINTIM:  ')
0043       read(1,*) fintim
0044       call ttya('Enter DELT:     ')
0045       read(1,*) delt
0046       call ttya(' Enter PRDEL:   ')
0047       read(1,*) prdel
0048
```

```
0049        call ttya(' Enter SOLN:    ')
0050        read(1,*) soln
0051        call ttya(' Enter A:       ')
0052        read(1,*) a
0053        call ttya(' Enter C:       ')
0054        read(1,*) c
0055        call ttya(' Enter E:       ')
0056        read(1,*) e
0057
0058        call ttya(' Enter KF1:     ')
0059        read(1,*) kf1
0060        call ttya(' Enter KR1:     ')
0061        read(1,*) kr1
0062        call ttya(' Enter KF2:     ')
0063        read(1,*) kf2
0064        call ttya(' Enter KR2:     ')
0065        read(1,*) kr2
0066        call ttya(' Enter KF3:     ')
0067        read(1,*) kf3
0068        call ttya(' Enter KR3:     ')
0069        read(1,*) kr3
0070        write(1,*)
0071
0072        write(6,'(7A)')'           TIME',
0073       *               '           SOLN',
0074       *               '              A',
0075       *               '              C',
0076       *               '              E',
0077       *               '             PW',
0078       *               '          ISOLN',
0079
0080
0081
0082        write(6,'(F14.3,4D14.6)') 0.0, soln, a, c, e
0083
0084        do 20 l = prdel, fintim, prdel
0085
0086           do 10 m = delt, prdel, delt
0087
0088 COMMENT      vac1=212-a
0089              i1=kf1*soln*delt*(212-a)
0090              i2=kr1*delt*a
0091 COMMENT      vac2=529-c
0092              i3=kf2*soln*delt*(529-c)
0093              i4=kr2*delt*c
0094 COMMENT      vac3=1059-e
0095              i5=kf3*soln*delt*(1059-e)
0096              i6=kr3*delt*e
0097
0098              a=a+i1-i2
```

```
0099              c=c+i3-i4
0100              e=e+i5-i6
0101              soln=soln+(i2+i4+i6-i1-i3-i5)/120
0102              pw=soln*120*1.032
0103
0104              isoln=(i2+i4+i6-i1-i3-i5)/120
0105
0106    10        continue
0107
0108             write(6,'(F14.3,6D14.6)') 1, soln, a, c, e, pw, isoln
0109             call ttya('*')
0110    20      continue
0111
0112        call stop(0)
0113        end
```

SS0736SRIVICHAI>PMODEL>EXTRACTION.COMI

```
0001        run77 extraction.seg
0002        wai6.out          NAME OF OUTPUT DATA FILE
0003           5              FINTIM
0004           0.005          DELT
0005           0.208          PRDEL
0006           0.000674417    SOLN
0007         209.42           A
0008         273.59           C
0009          33.185          E
0010           0.092          KF1
0011           0.00027        KR1
0012           0.180          KF2
0013           0.04           KR2
0014           0.1427         KF3
0015           1.05           KR3
```

TIME	SOLN	A	C	E	PW	ISOLN
0.000	0.674417D-03	0.209420D+03	0.273590D+03	0.331850D+02		
0.208	0.626083D-01	0.209410D+03	0.271671D+03	0.276816D+02	0.775341D+01	0.117485D-02
0.416	0.100488D+00	0.209402D+03	0.270236D+03	0.245784D+02	0.124444D+02	0.722381D-03
0.624	0.123943D+00	0.209396D+03	0.269105D+03	0.229012D+02	0.153491D+02	0.451442D-03
0.832	0.138764D+00	0.209391D+03	0.268168D+03	0.220651D+02	0.171845D+02	0.289275D-03
1.040	0.148413D+00	0.209387D+03	0.267358D+03	0.217211D+02	0.183795D+02	0.192006D-03
1.248	0.154954D+00	0.209383D+03	0.266637D+03	0.216621D+02	0.191895D+02	0.133372D-03
1.456	0.159614D+00	0.209379D+03	0.265978D+03	0.217653D+02	0.197666D+02	0.977132D-04
1.664	0.163123D+00	0.209375D+03	0.265368D+03	0.219581D+02	0.202011D+02	0.757195D-04
1.872	0.165915D+00	0.209372D+03	0.264796D+03	0.221979D+02	0.205469D+02	0.618626D-04
2.080	0.168250D+00	0.209369D+03	0.264258D+03	0.224596D+02	0.208361D+02	0.528627D-04
2.288	0.170282D+00	0.209365D+03	0.263748D+03	0.227287D+02	0.210877D+02	0.467745D-04
2.496	0.172104D+00	0.209362D+03	0.263264D+03	0.229969D+02	0.213133D+02	0.424443D-04
2.704	0.173773D+00	0.209359D+03	0.262804D+03	0.232594D+02	0.215200D+02	0.391875D-04
2.912	0.175323D+00	0.209356D+03	0.262367D+03	0.235136D+02	0.217121D+02	0.365974D-04
3.120	0.176777D+00	0.209354D+03	0.261951D+03	0.237584D+02	0.218921D+02	0.344320D-04
3.328	0.178149D+00	0.209351D+03	0.261554D+03	0.239930D+02	0.220619D+02	0.325466D-04
3.536	0.179447D+00	0.209348D+03	0.261177D+03	0.242175D+02	0.222227D+02	0.308546D-04
3.744	0.180679D+00	0.209346D+03	0.260817D+03	0.244318D+02	0.223753D+02	0.293033D-04
3.952	0.181850D+00	0.209343D+03	0.260475D+03	0.246363D+02	0.225203D+02	0.278608D-04
4.160	0.182963D+00	0.209341D+03	0.260148D+03	0.248313D+02	0.226582D+02	0.265067D-04
4.368	0.184023D+00	0.209338D+03	0.259838D+03	0.250172D+02	0.227894D+02	0.252281D-04
4.576	0.185032D+00	0.209336D+03	0.259542D+03	0.251943D+02	0.229143D+02	0.240164D-04
4.784	0.185992D+00	0.209334D+03	0.259260D+03	0.253630D+02	0.230333D+02	0.228655D-04
4.992	0.186906D+00	0.209332D+03	0.258992D+03	0.255237D+02	0.231465D+02	0.217707D-04

APPENDIX VI Sorption energy constants (K) and sorption maxima (b) for each region of P sorption for various soils

	Soil	Reference	K_I	K_{II}	K_{III}	b_I	b_{II}	b_{III}
			ml g^{-1}			µg g^{-1}		
1.	Egmont	Rennes (1978)	131	1.06	0.054	870	1515	2220
2.	Ruamai	"	51	0.77	0.059	89	286	520
3.	Dannevirke	"	113	1.09	0.041	154	372	785
4.	Dannevirke	Hope (1978)	142	1.90	0.061	147	248	644
5.	Okaihau	"	432	5.65	0.139	153	517	1106
6.	Ramiha	"	182	3.84	0.142	304	954	1474
7.	Tokomaru	"	110	2.32	0.194	52	74	172
8.	Egmont	Ryden and Syers (1975)	190	4.61	0.167	1217	1505	3221
9.	Porirua	"	106	4.68	0.081	130	285	530
10.	Okaihau	"	238	6.71	0.162	663	1031	1731
11.	Waikakahi	"	96	5.10	0.287	43	81	325
12.	Egmont	Ryden (1975)	580	9.00	0.171	248	560	1160
13.	Okaihau	"	1470	4.80	0.110	130	455	694
14.	Dannevirke	Hope (1978)	397	5.88	0.113	173	471	1031
15.	Okaihau	"	746	10.20	0.220	188	780	1332
16.	Ramiha	"	323	5.46	0.226	517	1291	2261
17.	Tokomaru	"	494	3.45	0.084	72	155	443
	Average of 17 soils		341	4.50	0.136			