AN EVALUATION OF CHATHAM RISE PHOSPHORITE AS A DIRECT-APPLICATION PHOSPHATIC FERTILIZER

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Alec Donald Mackay

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ABSTRACT

Chatham Rise phosphorite (CRP) occurs as nodules on the sea floor some 800 km to the east of the South Island of New Zealand. The phosphate component is a carbonate fluorapatite and the material contains approximately 9% phosphorus (P) and 25% $CaCO_3$. Several lines of evidence suggest that CRP has potential as a direct-application phosphatic fertilizer for pasture.

In an initial evaluation in the glasshouse, CRP was found to be an effective source of P for ryegrass when compared to superphosphate over six harvests with four soils. The form (powdered or pelletised) and method (surface applied or incorporated) of application of CRP were found to have a marked effect on the agronomic effectiveness of this P source in the glasshouse. The effectiveness of CRP, when compared at 90% of the yield maxima obtained with superphosphate, which was assigned a value of 100, decreased in the order of powdered and incorporated (100 to 106) > powdered and surface applied (96 to 100) > pelletised and surface applied (85 to 104) > pelletised and incorporated (83 to 90).

Results from a comprehensive, long-term field evaluation of CRP at four contrasting sites under permanent pasture over 3 years confirmed and extended the findings of the preliminary glasshouse study with CRP. Apart from some initial differences, pelletised CRP was as effective as superphosphate at all four sites and at two of the hill-country sites (Ballantrae and Wanganui) it showed a marked residual effect in the third year. This was particularly pronounced in the clover component of the sward at these two sites. In fact at these two sites a single, initial application of 70 kgP ha^{-1} as CRP was agronomically as effective in the third year as three annual applications of 35 kgP ha^{-1} as superphosphate. This finding has implications to the strategy of fertilizer use. The origin of the marked residual effect shown by CRP at Ballantrae and Wanganui in the third year appears to result from the effect of $CaCO_3$ on the rate of release of P from CRP.

The findings that pelletised CRP was almost always as effective as both powdered CRP and superphosphate in the field contrasts with the results of the preliminary glasshouse study with four soils. This discrepancy probably results from the fact that in glasshouse studies a number of factors which can operate in the field and which may contribute to an increased effectiveness of a surface-applied, pelletised phosphate rock (PR) material are excluded (e.g. earthworms).

In a glasshouse study, earthworms increased the effectiveness of CRP as a source of P to ryegrass by 15 to 30% over seven harvests. Subsequent studies showed that both the burrowing and casting activity of earthworms indirectly increased the availability to ryegrass of P in the PR by improving the physical distribution and degree of contact of the PR particles with the soil. Interestingly, good agreement was found between the agronomic effectiveness of pelletised CRP in the field and in the glasshouse when earthworms were included as a treatment in the glasshouse. Consequently, care must be taken in extrapolating to the field situation, the results obtained with pelletised PR materials in the glasshouse in the absence of biological mixing.

In a comparison in the glasshouse, using six soils and both ryegrass and white clover as indicator species, CRP was as effective as North Carolina phosphate rock (NCPR) and Sechura phosphate rock (SPR), both of which are reactive PR materials. The agronomic data from this glasshouse study were used to evaluate a number of conventional, single chemical-extraction procedures used for assessing the likely agronomic effectiveness of PR materials. Of these, 2% formic acid appears to offer the most promise. However, sequential extraction appears to be necessary with PR materials which contain appreciable amounts of $CaCO_3$.

A procedure involving a single extraction with 0.5M NaOH was developed for measuring the extent of dissolution of a PR in soil. Because apatite minerals are largely insoluble in dilute NaOH and because this reagent extracts sorbed inorganic P, increases in 0.5M NaOH-extractable P in a soil to which a PR is added, provide a good estimate of the amount of P dissolved and retained on sorption sites. The extent of dissolution of SPR, measured by NaOH extraction, was found to vary from 22% of added P on the low P-sorbing Tokomaru soil to 48% on the high P-sorbing Egmont soil during incubation at $15^{o}C$ for 90 days. A high correlation ($r = 0.935^{**}$) was obtained for the relationship between the dissolution of SPR, measured by NaOH extraction, and the P-sorption capacity of the six soils used.

Whereas increasing the P status of the Wainui soil, by the addition of KH_2PO_4, had no measurable effect on the extent of dissolution of SPR, increasing addition of $Ca(OH)_2$ markedly decreased the dissolution of SPR in this soil. Of the decrease measured in the dissolution of SPR on liming the Wainui soil from pH 5.2 to 6.9, 75-79% of the decrease could be accounted for by the effect of Ca, which also increases on liming. Results with the Egmont soil indicate that a PR can dissolve at pH 6.5. This suggests that the effect of a higher pH on dissolution is decreased in a soil of high P-sorption capacity.

Although the extent of dissolution of SPR increased as the P-sorption capacity of the soils increased, the amounts of water-, Bray-, and bicarbonate-extractable P in the same soils decreased. Of these three estimates of plant-available P, both the Bray and bicarbonate procedures were found to be useful indicators of short-term, plant-available P when SPR and CRP were added to three contrasting soils. Of the two procedures, the Bray procedure accounted for more of the variability, possibly reflecting the difference in the mechanisms by which these two extractants remove P from soil. In contrast, a single water-extraction procedure grossly underestimated the amount of short-term, plant-available P in the soil to which a PR was added.

A simple model, based on a modified Mitscherlich equation, was developed to describe and predict the dissolution of SPR in soil. The model, which was developed and evaluated using contrasting soils, appears to have good practical application and should prove useful in future studies of the reactions of PR materials in soils.

Although not yet commercially available, CRP appears to have very good potential as a direct-application P fertilizer for pasture and, of particular relevance to hill country farming, it shows a good residual effect. A possible disadvantage is the relatively low P content.

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CHAPTER 1

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INTRODUCTION

New Zealand's predominantly agricultural economy relies heavily on phosphatic fertilizers. Since the establishment of the first superphosphate plant in 1882, superphosphate has been the principle phosphatic fertilizer used in New Zealand. Approximately 2 million tonnes of superphosphate have been used annually during the last 10 years (New Zealand Fertiliser Statistics, 1981).

In the absence of a suitable domestic phosphate rock (PR) resource, the PR requirements for superphosphate manufacture in New Zealand, which are of the order of 1 million tonnes each year, have been obtained in the past from Nauru and Ocean Islands in the West Pacific, and from Christmas Island in the East Indian Oceans. As a partner in the British Phosphate Commission, New Zealand has been in a position to exert some control over the marketing of PR from these islands and to obtain its supplies at advantageous prices. With the closure of the Ocean Island deposit and the limited life span of both the Nauru and Christmas Island deposits, 20 and 8 years, respectively, at present rates of production, uncertainty surrounds future supplies.

The huge Queensland PR deposits in Australia were regarded initially as the most likely alternative. However, because of the variable P_2O_5 content and the presence of significant amounts of Al_2O_3, Fe_2O_3, and SiO_2, the economic viability of mining these deposits is presently marginal. This has added to the uncertainty about future supplies of PR for the manufacture of superphosphate in New Zealand.

Very large deposits of PR occur elsewhere in the world. Some of the most extensive extend in a belt from Morocco, across North Africa, to Israel and Jordan. The current political instability of the Middle East limits the attraction of these alternatives. Other possible sources of PR for New Zealand are the extensive deposits of Florida, Peru, and Mexico. Significantly, some PR material has been imported from Peru and Florida in the last few years. In all these areas however, New Zealand would be obliged to compete on the world market and transport costs would be high. Thus, securing long-term supplies of high-grade PR for the manufacture of superphosphate has become of considerable importance to the future viability of New Zealand agriculture.

With the uncertainty surrounding future sources and costs of PR for the manufacture of superphosphate, interest has recently developed in New Zealand in the potential of the Chatham Rise phosphorite (CRP) deposit, which lies off the east coast of the South Island, on the Chatham Rise. Estimates of the size and extent of the CRP deposit vary. Cullen (1979) considered that 100 million tonnes of phosphorite occur on the central Chatham Rise. Because of the relatively low (20.5% P_2O_5) phosphorus content (Pasho, 1976), the very high content of calcium carbonate (23-29% $CaCO_3$), and associated high acid consumption during acidulation (Buckenham et al., 1971), it appears that CRP is unsuitable for the manufacture of superphosphate, unless it is first beneficated. Using the chemical reactivity scale developed by Hoffman and Breen (1964), however, Buckenham et al (1971) suggested that CRP may be suitable as a direct-application P fertilizer.

Before the present study was initiated, the agronomic evaluation of CRP as a direct-application P fertilizer had been confined to two glasshouse studies (Roberts and White, 1974; Andrews et al., 1978). In both these studies, the comparison with superphosphate had been restricted to one rate of P application and one soil type, and thus the evaluation was cursory. Nevertheless, the results obtained indicated that CRP was an effective source of P for both perennial ryegrass (Roberts and White, 1974) and white clover (Andrews et al., 1978).

The cost of superphosphate has increased dramatically in recent years; since 1978, the ex-works cost has tripled (New Zealand Fertiliser Statistics, 1981). Added to this there was a gradual decline in the quality of superphosphate between the mid 1960's and 1981, resulting from the increased use of Christmas Island 'A' grade PR in blends with Nauru (Quin, 1981). Also, there has been increasing concern about the effectiveness of superphosphate as a P fertilizer for all pastoral farming situations (During, 1972; Gregg, 1974; Syers, 1974). These factors have resulted in increasing interest in the potential of direct-application of P fertilizers in New Zealand pastoral farming and, specifically, in the likely role of CRP.

An evaluation of CRP as a direct-application P fertilizer forms the basis of this study. The agronomic effectiveness of CRP is evaluated in a series of glasshouse studies, using both perennial ryegrass and white clover, and at four contrasting field sites over three years. In addition to evaluating conventional chemical extraction procedures and new approaches for assessing the agronomic effectiveness of PR materials the reactions of PR materials in soil are also investigated in a series of incubation studies. An initial attempt is also made to develop a simple model to describe and predict the dissolution of PR materials in soils.

CHAPTER 2

CHAPTER 2

REVIEW OF LITERATURE

In this thesis, several aspects of the agronomic effectiveness of phosphate rock (PR) materials and their reactions in soils are considered. Because of the contrasting nature of these topics, literature relevant to each is reviewed in the appropriate Chapter. The brief review of literature in this Chapter is concerned with the forms, composition, and likely agronomic effectiveness of apatites in PR materials.

2.1 Forms of Phosphorus in Phosphate Rock Materials

Although over 150 naturally-occurring phosphate minerals are listed by Palache et al. (1951) only those of the apatite group occur in sufficient abundance and concentrations to serve as commercial sources of phosphate. These phosphate minerals have the generalised formula, $Ca_{10}\,(PO_4)_{6-x}\,(CO_3)_x\,(F,OH,Cl)_2$.

Apatite serves as a host for a great many minor substitutions. Small amounts of S^{6+}, Si^{4+}, As^{5+}, U^{5+}, and Cr^{6+}, in addition to carbonate substitute for phosphate, and minor amounts of Na^{+}, Sr^{2+}, Mn^{2+}, Mg^{2+}, K^{+}, U^{4+}, and rare earth (cerium, lanthanum and yttrium) substitute for Ca^{2+} (McKelvey et al., 1953). Degens (1965) lists fluorapatite, hydroxyapatite, chlorapatite, and carbonate fluorapatite as the four prominent end-members of the apatite family.

The term apatite is often used synonymously with fluorapatite ($Ca_{10}\,(PO_4)_6\,F_2$), because it is the most abundant and the most stable form (Deer et al., 1966), occurring as an ubiquitous, accessory mineral in igneous and metamorphic rocks. The very stable structure of fluorapatite, is attributed to the hexagonal network of Ca-O columns linked by PO_4^{3-} groups and to the arrangement of calcium and fluorine in the channels of the network (Landergren, 1962).

The structure of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is similar to fluorapatite. In contrast to fluorapatite, however, hydroxyapatite is usually regarded as occurring only rarely in nature (Smith and Lehr, 1966). Beevers and McIntyre (1946) suggested that the difference in the stability of these two apatites was due to the difference in the size and consequently the fit of the hydroxyl and fluoride ions in the lattice. Whereas the hydroxyl ion is 1.4 to 1.6 Å in diameter, the fluoride ion is 1.33 Å. Using x-ray and neutron diffraction techniques, Kay et al. (1964) have shown that the OH groups in hydroxyapatite are disordered about the mirror planes and that the hydroxyl direction always points away from the mirror plane. The rare occurrence of chlorapatite ($Ca_{10}(PO_4)_6\ Cl_2$) in nature is also probably because the lattice is more expanded than that of fluorapatite and hyrodxyapatite.

The literature on carbonate apatites, which are of secondary origin, is extensive, and has been reviewed by Silverman et al. (1952), Ames (1959), McConnell (1962), Smith and Lehr (1966), Lehr et al. (1967) and Elliot (1969). The structure of carbonate apatites has been debated for many years. It is now generally thought that a divalent planar carbonate group replaces a trivalent tetrahedral phosphate group in the apatite cell unit, with the vacant oxygen site occupied by fluoride preserving both the tetrahedral symmetry and the charge of the replaced phosphate group (Smith and Lehr, 1966). Smith and Lehr (1966) showed by x-ray diffraction studies that one phosphate group was replaced by one carbonate and one fluoride ion. The work of McClellan and Lehr (1969) confirms a practically one-for-one substitution of carbonate for phosphate. The name francolite had been used to describe an apatite containing appreciable carbonate but more than 1% of fluorine (McConnell, 1938) and the name dahllite has been used to describe an apatite containing abundant carbonate but a low concentration of fluorine (Deer et al., 1966).

2.2 Origin of Phosphate Rock Materials

Deposits of PR materials are found in a very wide range of geological environments and for the purpose of this review are classed into three broad groups, those apatites of igneous origin, marine phosphorites, and phosphatized rock derived from guano.

2.2.1 Apatite deposits of igneous origin

Three of the largest apatite deposits in the world are of igneous origin, namely the Khibina deposits on the Kola peninsula of U.S.S.R. (Fivey, 1937), the deposits of Eastern Uganda (Davies, 1947), and the Palabora deposits in East Transval of South Africa (Shand, 1932). These deposits are associated with intrusive complexes of alkalic rocks, and presently yield about 15% of the world's phosphate production (McKelvey, 1973). The P_2O_5 content is as high as 35% with fluorapatite, the principle P-bearing mineral, occurring in large, coarse crystalline units. Individual deposits contain millions of tonnes of potentially-recoverable apatite and a few may contain billions of tonnes.

2.2.2 Marine phosphorites

About 80% of the world's production of phosphate comes from those deposits of sedimentary origin, or more commonly referred to as marine phosphorites (McKelvey, 1973). There are two principle facies:

(i) The geosynclinal deposits, of which those of the western U.S.A. (McKelvey et al., 1953), North Africa (Cayeux, 1941), Kara-Tau of the Soviet Union (Vol'fkovich, 1945), and Sechura of Peru (Cheney et al., 1979) are the outstanding examples, consist of layers of phosphate pellets, generally less than 0.1 to 2 mm in diameter and containing 25 to 35% P_2O_5. They are generally associated with chert, black-carbonaceous shale and limestone. These deposits are found as blankets over thousands of square miles and account for the bulk of PR material of sedimentary origin.

(ii) The platform deposits are generally associated with limestone, glauconite, sandstone, and quartz, and occur as large nodules (2 to 10 mm) or pellets up to 50 mm, and contain 15 to 25% P_2O_5. They are generally sparsely disseminated in a matrix of non-phosphatic sediments. Examples of those include the glauconite marls of the Gulf Coastal Plains (Monroe, 1941), and the Tennessee 'blue rock' of the U.S.A. (Smith and Whitlatch, 1940). Although on a world scale this group is of minor commercial value, the inclusion of Chatham Rise phosphorite (CRP) in this group, makes it of considerable potential commercial value to New Zealand.

In contrast to the deposits of igneous origin, the principle P-bearing mineral in marine phosphorites is carbonate fluorapatite, found in microcrystalline (0.02 to 0.2 μm) structure. In addition to carbonate sustitution for phosphate, the substitution of fluoride by hydroxyl is also found in the Sechura phosphate rock (SPR) deposit of Peru. The P-bearing mineral in this deposit is a carbonate-hydroxy-fluorapatite (Chien and Hammond, 1978a; Cheney et al., 1979).

Debate still surrounds the mode of phosphorite deposition. Ames (1959) has summarized the different viewpoints with respect to the mineralogy and geochemical aspects of carbonate apatites. Possible modes of deposition include; chemical precipitates formed upon supersaturation of natural waters (Kazakov, 1937; McKelvey et al., 1953); a biogeochemical product, formed for example, by the action of microorganisms, or a simple replacement product, resulting from the introduction of phosphate units into pre-existing calcareous materials. The last of these phosphatization, is the most favoured, as conversion of calcite to carbonate apatite may take place at phosphate and calcium concentrations considerably below those required for precipitation. The inclusion of remnants, as in CRP, of foraminiforal tests of glauconite as both rounded grains and test fillings, and of a variety of detrital particles comparable with those in the surrounding sediments are consistent with a replacement origin (Pasho, 1976).

Ames (1959) considers that the essential environmental conditions required for the deposition of natural phosphate include, a pH >7, the presence of calcareous materials, and a system that is calcium saturated with respect to its bicarbonate content, phosphate concentrations >0.1 ppm, and a non-depositional environment. Redox potential apparently does not control the exchange rate to a significant extent, but it may effect the trace element assemblage of the carbonate-apatites (Arrhenius, 1963). An increase in temperature will speed up the reaction, while an increase in the grain size of the calcium carbonate precursor material will reduce the efficiency of phosphatization. Differences in the P_2O_5 content of CRP pellets provide an excellent example of the effect of the latter (Pasho, 1976). Degens (1965) suggests that if the diagenetic environment permits the chemical composition of a completely phosphatized limestone consisting of carbonate - apatite will gradually change in the direction of a "regular" apatite with a complete loss of carbonate.

2.2.3 Phosphatized rocks derived from guano

Although as a group, PR deposits of this origin are small on a world scale, they are of considerable commercial value, particularly to New Zealand. The mineralogy of the phosphatized rocks derived from guano depends on the composition of the underlying or host rock (Warin, 1968). Where limestone is present, as on many of the coral atolls, the phosphorite is apatite; where the underlying rock is silicate, as in islands of volcanic origin, the phosphate minerals contain Ca-Al-PO_4 and Al-Fe-PO_4. Most such deposits are of the order of only a few thousand or tens of thousand tonnes in size, but a few elevated islands are comparatively large deposits. Examples of these, the Nauru and Ocean Islands in the West Pacific (Hutchinson, 1950) and Christmas Island in the East Indian (deKeyer and Mcleod, 1968) Oceans. The principle P mineral in these three PR materials is a carbonate hydroxy-fluorapatite (Chien and McClellan, 1977), although the extent of carbonate substitution for phosphate in these PR materials is not as extensive as in SPR (Lehr et al., 1967). As will be shown later in this thesis these PR materials have widely different stabilities in soils. This points to the limitation of using only a description of mineralogical composition as a guide to likely agronomic effectiveness.

2.3 Composition of Apatite in Phosphate Rock Materials

Of the more than 25 elements that have been reported to occur in fluorapatite of igneous origin (Palache et al., 1951; Deer et al., 1966), most are present in insignificant amounts. Lehr et al. (1967) and McClellan and Lehr (1969) have shown that the composition of apatites in sedimentary PR materials can be closely approximated by their contents of CaO, Na_2O, MgO, P_2O_5, CO_2, and F. Smith and Lehr (1966) and Lehr et al. (1967) found that the extent of carbonate substitution for phosphate in the apatite structure can vary from 0.3 to 5.3% in sedimentary apatites. The electrostatic imbalance resulting from the substitution of planar carbonate for tetrahedral phosphate is only partially corrected by substitution of fluoride in vacant oxygen sites, so that a coupled monovalent cation substitution for calcium is necessary to maintain the electrostatic neutrality.

Using synthetic carbonate apatites, Ames (1959) found a coupled substitution in which sodium replaced about 10% of the calcium at the highest level of carbonate substitution for phosphate. This study was conducted in the absence of fluorine. In the presence of fluorine, Simpson (1964) reported sodium contents of 2 to 3% at the highest level of carbonate substitution (5 - 6% CO_2), but potassium showed little tendency to replace calcium, probably because the radius of the potassium ion is more than 30% larger than that of calcium, whereas sodium is 5% smaller than calcium. McClellan and Lehr (1969) also found that the sum of the magnesium and sodium contents of apatite increased as the degree of carbonate substitution increased.

The presence of carbonate, as well as sodium and magnesium, in the apatite structure inhibits crystal growth by limiting the number of repetitions than can occur before the statistical mismatch of structural units terminates growth of a crystallite. Newesly (1963) and Le Geros et al.,(1967), working with synthetic carbonate apatites, and Smith and Lehr (1966), Lehr et al. (1967), McClellan and Lehr (1969), and Lehr and McClellan (1972), working with apatites in commercial PR materials, found that as the extent of carbonate substitution for phosphate in the apatite structure increased, crystallite size of the apatite decreased. The net effect is a decrease in the mineral stability or conversely an increase in the "chemical reactivity" of the PR. As fluorapatite is more stable than hydroxyapatite (Landergren, 1954; Kay et al., 1964), substitution of fluorine by hydroxyl is likely to have a similar effect as carbonate substitution for phosphate in those PR materials containing carbonate-hydroxy-fluorapatite.

2.4 Effect of Apatite Composition on the Potential Agronomic Effectiveness of Phosphate Rock Materials

Until the study of Caro and Hill (1956), and in particular the more recent series of studies by Smith and Lehr (1966), Lehr et al. (1967) McClellan and Lehr (1969), and Lehr and McClellan (1972), differences in the composition of apatite in PR materials were thought to have little effect on the potential agronomic effectiveness of PR materials. The failure to recognize that differences exist in the agronomic effectiveness of PR materials, as a result of difference in apatite composition, explains to a large extent the variable agronomic results obtained with PR materials as direct-application P fertilizers throughout the world (Cottier, 1952; Cooke, 1956; Pimentel et al., 1962; Fassbender, 1965; Kramer and Lamberger, 1965; Ansorge, 1966; Barnes and Kamprath, 1975; Chien and Hammond, 1978a). It has now been established that as the degree of carbonate substitution for phosphate in the apatite structure increases so does the potential agronomic effectiveness of the PR. Caro and Hill (1956) found that the amount of "bound carbonate" in PR materials was closely correlated with their effectiveness as a P source for alfalfa in the studies reported by Armiger and Fried (1956). Engelstad et al. (1974) also found that the effectiveness of seven PR materials to flooded Nato rice increased as the degree of carbonate substitution for phosphate increased in the apatite structure. Similarly, the agronomic effectiveness of the PR materials evaluated by Chien and Hammond (1978a), increased as the degree of carbonate substitution for phosphate in the apatite structure, increased. Thus, the extent of carbonate substitution in the apatite structure provides a rational explanation for the differing agronomic effectiveness of PR materials.

CHAPTER 3

A PRELIMINARY EVALUATION OF CHATHAM RISE PHOSPHORITE AS A DIRECT-APPLICATION PHOSPHATIC FERTILIZER

3.1 Introduction

Chatham Rise phosphorite (CRP) is a sedimentary (marine) phosphorite which occurs on the Chatham Rise. This is a broad, elongate submarine ridge extending about 800 km east of the South Island of New Zealand. The geology and geomorphology of the Chatham Rise have been described in some detail by Norris (1964). Estimates of the size and extent of the CRP deposit vary; Cullen (1979) considers that 100 million tonnes of phosphorite occur as hard, dense, generally black nodules varying in size, shape, and chemical composition (Pasho, 1976), and in distribution (Cullen and Singleton, 1977). The P-bearing mineral in CRP, carbonate fluorapatite, occurs in microcrystalline units (Glasby and Summerhayes, 1975). A varying and sometimes appreciable amount of calcite is associated with the phosphatic material in the nodules.

The agronomic evaluation of CRP as a phosphatic fertilizer has been confined to a limited number of glasshouse studies. In the studies of both Roberts and White (1974) and Andrews et al. (1978), the comparison of CRP with superphosphate was restricted to one rate of application of P and one soil.

Roberts and White (1974) reported that powdered CRP was 70% as effective as superphosphate over six harvests when ryegrass was used as the indicator species. In contrast, Andrews et al. (1978), using white clover, found that powdered CRP outperformed (199%) monocalcium phosphate (the major form of P in single superphosphate) over the same number of harvests.

Although the study of Rajan (1981a) was also confined to one soil, CRP was compared to superphosphate at five rates of application. Whereas CRP was found to be as effective as superphosphate at 15 and 30 kgP ha^{-1} after four harvests, at the highest rate of application (240 kgP ha^{-1}) CRP was only 85% as effective as superphosphate after eight harvests. In an evaluation of the effect of mychorrizal fungi on the recovery of fertilizer P by plants, Powell (1979) and Powell et al. (1980) showed that CRP was an effective source of P for both ryegrass and white clover in the glasshouse.

The difference measured in the agronomic effectiveness of CRP in these studies probably reflects, in part, the choice of the indicator species, the number of harvests taken, and the rates of application at which the P sources were compared. In addition, the differences reported for the agronomic effectiveness of CRP may also reflect the form and method of application of CRP, which varied from a powdered form incorporated into the top 2cm of soil (Roberts and White, 1974; Andrews et al., 1978), to a powdered form mixed throughout the soil (Powell, 1979), to a minigranule (0.2 - 0.5mm) placed in the soil at a depth of 3mm (Rajan, 1981a), to a pelletised (0.4 - 1.4mm) form mixed throughout the soil (Powell et al., 1980). Both the form (Buchan et al., 1970; Stephens and Lipsett, 1975) and method (Alston and Chin, 1974; Wright, 1975) of application of PR have been shown to exert a marked effect on the agronomic effectiveness of PR under glasshouse conditions. However, because PR materials of limited agronomic effectiveness were used in many of these studies, use of these data in assessing the likely effect of form and method of application on the agronomic effectiveness of PR materials considered suitable for direct application under glasshouse conditions may be limited.

Although published data were predominantly obtained from the glasshouse (Terman et al., 1969; Buchan et al., 1970; Engelstad et al., 1974; Stephens and Lipsett, 1975; Powell et al., 1980), the work shows that pelletising, or granulation, generally results in a marked decrease in the availability of P from a PR. This is due to reduction of both the surface area exposed for dissolution and the physical distribution in the soil (Chien and Hammond, 1978b). To become commercially acceptable in terms of both handling and spreading, however, a finely-ground PR will have to be pelletised (Knight and Will, 1971; Chien and Hammond, 1978b) in a form which does not reduce its agronomic performance. To date, this appears from the published literature not to have been achieved.

In this Chapter, the agronomic effectiveness of finely-ground and pelletised CRP is compared to superphosphate at three rates of application and on four contrasting soils. In addition, the effect of form and method of application on the agronomic effectiveness of CRP in the glasshouse is also investigated.

3.2 Materials and Methods

3.2.1 Phosphate sources

A composite sample of CRP, representing seven sites on the Chatham Rise, was used in this glasshouse study and in subsequent studies. The location of individual sites is given in Table 3.1, as are values for total P and calcium carbonate ($CaCO_3$) content of samples from each site. Before use, all CRP was ground to pass through an 85-mesh sieve (180 μm). The particle-size distribution of the powdered CRP was obtained by the "end-point" sieving method (The Fertilisers Regulations, 1969). Over 80% of the powdered CRP passed through a 100-mesh sieve

Table 3.1 Location and total phosphorus and calcium carbonate contents of Chatham Rise phosphorite samples from individual sites on the Chatham Rise

Sample number	Location	Total P (%)	Total $CaCO_3$ (%)
N843	$43^{o}29.9'S$, $179^{o}20.0'E$	9.58	28.2
N844	$43^{o}30.5'S$, $179^{o}18.5'E$	8.92	29.8
N845	$43^{o}31.1'S$, $179^{o}17.2'E$	9.35	28.5
N846	$43^{o}32.2'S$, $179^{o}16.4'E$	9.53	25.2
N854	$43^{o}32.1'S$, $179^{o}32.7'E$	9.00	34.2
N857	$43^{o}32.6'S$, $179^{o}32.5'E$	8.31	32.3
N878	$43^{o}27.8'S$, $179^{o}16.6'E$	9.46	26.7

(Table 3.2). The present fertilizer regulations specify that, for registration as a P fertilizer, 80% of a PR material must pass through a 100-mesh sieve (150 μm). Exceptions are Sechura phosphate rock (SPR) and North Carolina phosphate rock (NCPR) where 60% must pass through a 100-mesh sieve for registration.

The pelletised CRP, prepared by a commercial firm from this powdered material using bentonite as the binding was very stable (mean pellet strength = 5.8N), of uniform size (80% >0.5mm to >2.0mm), and had excellent flow characteristics. The fresh pellets slaked readily in water and initial breakdown occurred rapidly on moist soil. The water stability of the pellets was evaluated as a function of time of storage at 80% relative humidity at 20°C. At each sampling (0, 30, 60, 90, 120, 153 and 183 days), 10g of the pellets were placed in the top of a tier of sieves (500, 250, and 125 μm fitted with a receiver) and carefully immersed in a container of distilled water mounted on an Endecott Mechanical Sieve Shaker. After a soaking period of 1 h, the shaker was switched on for 5 min. The amount of material retained on each sieve was determined by weighing.

To evaluate CRP as a source of P to plants, powdered and pelletised CRP was contrasted with 'granulated' single superphosphate obtained by combining samples from a number of stock-piles destined for aerial application.

Total P for all samples was determined using perchloric acid digestion (O'Connor and Syers, 1975). Values for water - (The Fertilisers Regulations, 1969), 2% citric acid - (AOAC, 1960), and neutral ammonium citrate - (AOAC, 1970) soluble P are summarized in Table 3.3, along with some physical characteristics of the two P sources.

Table 3.2 Particle-size distribution of powdered Chatham Rise phosphorite using the "end-point" method

Particle size (μm)	Particle-size distribution (%)
> 250	0
> 180	1.1
> 150	16.8
> 125	7.5
> 63	32.8
< 63	41.2

Table 3.3 Some physical and chemical characteristics of the phosphate sources

Phosphate source	Form	Particle size range (mm)			Total P	$CaCO_3$	P extracted by		
		1-2	0.5-1	< 0.5	(%)	(%)	Water	2% citric acid	Neutral ammonium citrate
							(% of total P)		
Superphosphate	Granules	43	27	30	8.5	-	45	79.5	75.0
CRP	Powder (<180 μm)	-	-	-	9.35	30.3	<0.01	20.7	5.6
CRP	Pellets	40	40	20	9.17	28.8	<0.01	20.7	5.6

3.2.2 Soils used in glasshouse study.

The four soils used in the preliminary glasshouse study were collected from sites where the four field trials evaluating the agronomic effectiveness of CRP (Chapter 4) were subsequently established. Detailed information on the location and past fertilizer history of each soil is given in the next Chapter (Table 4.1). Three of the soils, Kumeroa silt loam (Wanganui), Ramiha silt loam (Pahiatua Track), and Wainui silt loam (Woodville) are from hill country, while the fourth, the Tokomaru silt loam (Palmerston North), is located on a high river terrace.

All four soils were sampled to a depth of 10cm, air dried, and passed through a 6 mm sieve before use. The following chemical parameters were measured; soil pH, measured with a combination electrode pH meter after stirring 10g of soil in 25 ml of distilled water and leaving to stand overnight before reading; P sorption capacity (Saunders, 1965), determined after shaking 5g of soil for 16 h in a 25ml of 0.2M sodium acetate solution containing 1000 µgP ml^{-1} and adjusted to pH 4.65 with glacial acetic acid. P sorption capacity was calculated from the amount of P removed from solution by the soil, expressed as a percentage of the amount originally in solution; and estimates of plant-available P in the soil, using the bicarbonate method (shaking for 30 min at a solution:soil ratio of 20:1) of Olsen et al. (1954) and the double-water extraction method (two sequential 1-h extractions with distilled water at a solution:soil ratio of 40:1) of Ryden and Syers (1977). For all P extractions samples were shaken in 50-ml polycarbonate centrifuge tubes on an end-over-end shaker at 18 r.p.m. at 20°C. On the completion of shaking, the samples were centrifuged at 10,000 r.p.m. for 5 min in a Sorvall RC2-B refrigerated centrifuge (at 5°C) and the extracts filtered (<0.45 µm). Inorganic P in an aliquot of the extract was determined by the Watanabe and Olsen (1965) modification of the

Murphy and Riley (1962) method, except that the bicarbonate extracts were not neutralized prior to colour development. Absorbance was measured at 712 nm using a Pye Unicom SP 1800B spectrophotometer. Results from these analyses are given in Table 3.4.

3.2.3 Conduct of the glasshouse study

The air-dried and sieved (<6mm) soils were hand packed into pots measuring 10 x 10 x 9cm. The Wainui and Ramiha soils received seventeen treatments replicated three times, whereas the Kumeroa and Tokomaru received eleven and nine treatments, respectively, both replicated four times. Detailed information on each treatment is given in Table 3.5. The incorporated treatments were thoroughly mixed in the upper 2cm of soil. The trial was established in a randomised-block layout. Sulphur (S) was applied as gypsum to all treatments at the quantity of S added in the highest rate of superphosphate. Additional S was applied after the 3rd and 5th harvests. Nitrogen (N) as ammonium nitrate, potassium as potassium chloride, and the micronutrient solution of Middleton and Toxopeus (1973) were applied after each harvest.

Approximately 50 seeds of perennial ryegrass (*Lolium perenne*) were sown on the soil surface after the addition of fertilizer treatments and thinned to 30 seedlings at 3 weeks. Pots were watered to field capacity (0.40, 0.42, 0.46, and 0.58g of water g^{-1} of soil for the Tokomaru, Wainui, Kumeroa, and Ramiha soils, respectively) with distilled water throughout the trial, on a daily basis. A total of six harvests were taken at varying intervals (4 - 5 weeks). All herbage was removed and oven dried at $60^{o}C$ for 24 h before weighing. The concentrations of P and N in the ryegrass were determined, following Kjeldhal digestion, by the autoanalysis method of Twine and Williams (1971).

Table 3.4 Some characteristics of the soils

				Extractable P	
New Zealand Soil Group	Soil type	pH_{H_2O}	P-sorption capacity (%)	Bicarbonate ($\mu g\ g^{-1}$)	Water ($\mu g\ g^{-1}$)
Yellow-grey earth/ yellow-brown earth intergrade	Kumeroa silt loam	6.0	39	8.6	5.8
Yellow-grey earth/ yellow-brown earth intergrade	Wainui silt loam	5.0	36	10.7	5.8
Yellow-brown loam	Ramiha silt loam	5.6	87	8.9	1.6
Yellow-grey earth	Tokomaru silt loam	5.8	28	23.8	13.4

3.3 Results and Discussion

Total dry-matter yields are presented in Table 3.5. A significant ($P < 0.01$) response to applied P was found with all soils, but its size varied markedly between soils. The response to applied P increased with increasing rate of P for all soils. The type of P fertilizer, its physical form and the method of application also influenced the magnitude of the response. All soils were highly sulphur-responsive.

3.3.1 Effectiveness of powdered Chatham Rise phosphorite when compared to superphosphate

Overall, the effectiveness of surface-applied, powdered CRP was not significantly different from surface-applied superphosphate in increasing ryegrass yields (Table 3.5) with any soil or at any rate of P. On two soils (Wainui and Ramiha) for which incorporated, powdered CRP treatments were included, CRP outyielded surface-applied superphosphate at the highest rate.

To permit evaluation of CRP compared to superphosphate, response curves were drawn for the two P sources with each of the four soils. CRP was then compared at 90% of the yield maxima obtained from surface-applied superphosphate, which was assigned a value of 100. The relative yield values for surface-applied, powdered CRP were 96, 99, and 100 for the Ramiha, Kumeroa, and Wainui soils, respectively. For incorporated, powdered CRP, the relative yield values increased to 100 and 106 on the Ramiha and Wainui soils, respectively.

Total herbage P uptake data for the six harvests combined (Table 3.6) showed similar trends in the performance of powdered CRP in comparison with superphosphate, with one exception. On the basis of yield data, the incorporated, powdered CRP treatments were superior to the equivalent

Table 3.5 Total yield (g) in six harvests of perennial ryegrass as influenced by phosphate source, rate, and placement. Treatments 3 - 11 surface-applied, treatments 12 - 17 incorporated in upper 2 cm of soil

Treatment		Application rate (kgP ha^{-1})	Soil type			
			Wainui	Ramiha	Kumeroa	Tokomaru
1	Control	0	6.27 I[*]	3.72 J	3.67 D	8.20 D
2	Control + S[†]	0	8.09 H	5.38 I	9.52 E	17.08 C
3	Superphosphate	35	10.28 G	9.04 FG	12.92 D	17.01 C
4	"	70	13.55 DE	11.41 CD	15.38 C	18.96 AB
5	"	150	15.57 B	13.00 B	18.02 A	20.33 A
6	CRP (pelletised)	35	10.04 G	7.34 H	12.88 D	17.83 BC
7	"	70	12.57 F	9.68 E	14.58 C	19.13 AB
8	"	150	14.60 C	11.14 CD	17.09 B	19.43 A
9	CRP (powdered)	35	10.46 G	8.86 G	13.35 D	
10	"	70	13.24 E	10.99 D	15.26 C	
11	"	150	15.27 B	12.53 B	18.04 A	
12	Superphosphate	70	13.89 D	11.60 C		
13	"	150	15.78 AB	13.11 B		
14	CRP (pelletised)	70	12.16 F	9.47 EF		
15	"	150	13.97 D	10.87 D		
16	CRP (powdered)	70	14.07 CD	11.62 C		
17	"	150	16.21 A	13.94 A		

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[*] Capital letters denote Duncan's symbols for assessing significant differences; $P < 0.01$ for treatments within each soil.

[†] Sulphur

Table 3.6 Total phosphorus uptake (mg) in six harvests by perennial ryegrass as influenced by phosphate source, rate, and placement. Treatments and Duncan's symbols as in Table 3.5

	Soil type			
Treatment	Wainui	Ramiha	Kumeroa	Tokomaru
2	9.31 J	4.55 G	12.43 G	32.00 C
3	14.37 H	9.62 E	19.04 DE	33.41 C
4	19.65 DE	13.37 CD	24.05 C	40.77 B
5	26.69 A	16.73 B	31.86 A	49.76 A
6	11.86 I	7.49 F	17.37 F	33.63 C
7	17.13 GF	10.78 E	20.26 D	40.03 B
8	21.43 DC	13.14 D	23.92 C	43.08 B
9	15.62 GH	9.95 E	17.71 EF	
10	19.97 EDC	12.97 E	22.94 C	
11	23.85 B	15.98 B	27.13 B	
12	21.68 C	12.76 D		
13	26.75 A	16.45 B		
14	16.02 GH	9.96 E		
15	18.45 EF	12.13 D		
16	19.83 EDC	14.48 C		
17	24.73 B	19.49 A		

surface-applied treatments with the Wainui soil; the P uptake data reversed these treatment differences.

The effectiveness of powdered CRP, relative to surface-applied superphosphate in terms of cumulative yield differences over the six harvests, with the four soils is shown in Fig. 3.1. The curves represent the average effect of the rates within a fertilizer treatment, in contrast to the criteria used above to compare total yields. Throughout the trial, all soils showed an increasing responsiveness to P applied as powdered CRP. The initial difference between the surface-applied and incorporated CRP treatments gradually increased with the Wainui and Ramiha soils (Fig. 3.1a, b). In contrast, the initial difference between the two superphosphate treatments with these soils decreased over the trial period. The increasing effectiveness of powdered CRP with respect to superphosphate, particularly when incorporated, is clearly demonstrated.

The data for relative cumulative herbage P uptake over the six harvests (Fig. 3.2) support the ranking of the treatments established by the relative cumulative yield data, with the one exception mentioned earlier. The initial difference in availability of P between powdered CRP and superphosphate is more clearly reflected in the P uptake data than in the yield data. Whereas from the yield data (Fig. 3.1) initial differences were less than 15%, in terms of herbage P uptake (Fig. 3.2) these differences ranged from 12 to 30% at the first harvest. Herbage P concentrations for a number of treatments at the first and second harvests with the Ramiha, Wainui, and Kumeroa soils (Table 3.7) further demonstrate this initial difference. The low P concentration values, particularly on the Ramiha soil, demonstrate the demand imposed by glasshouse trials on available soil P. At the field site (Pahiatua Track) where the Ramiha soil was collected the P concentration of the mixed sward ranged from

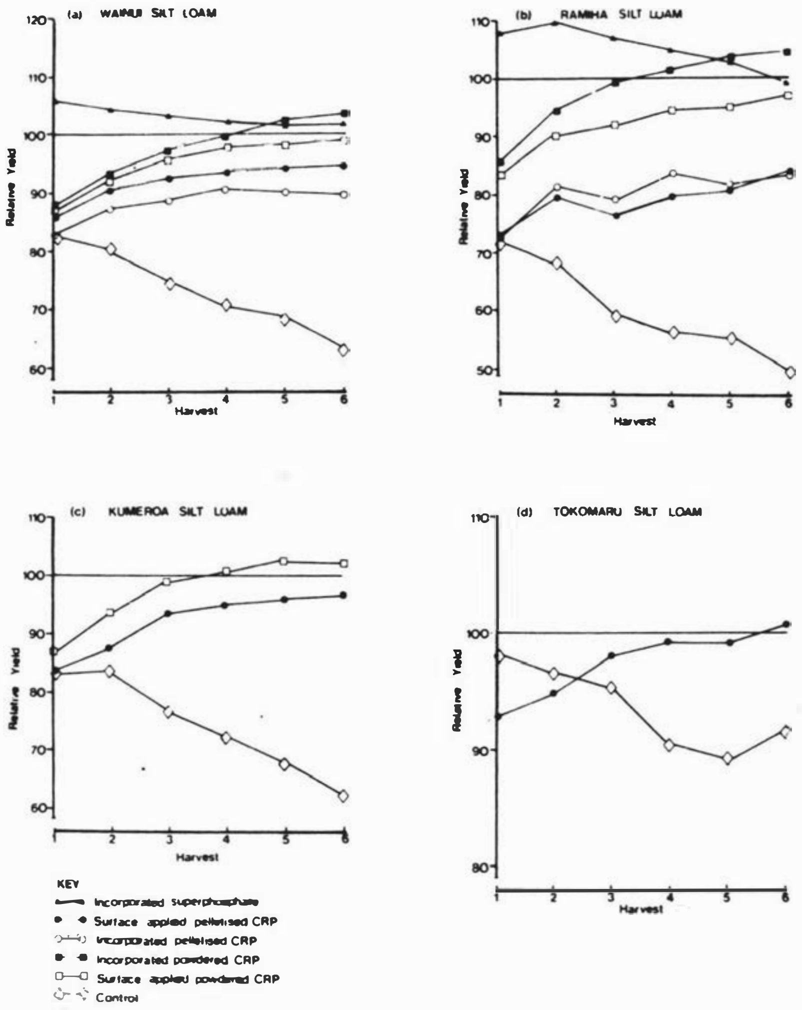

Figure 3.1 Relative cumulative yield data for six harvests with the four soils as influenced by phosphate source and placement (surface-applied superphosphate = 100). a = Wainui silt loam, b = Ramiha silt loam, c = Kumeroa silt loam, and d = Tokomaru silt loam.

Table 3.7 Phosphorus concentrations (mg g^{-1}) in perennial ryegrass as influenced by phosphate source and placement. Treatments as in Table 3.5.

		Harvest	
Soil type	Treatment	First	Second
Ramiha	2	1.09	1.09
	5	2.88	2.68
	8	1.52	1.66
	11	1.52	1.81
	15	1.24	1.45
	17	1.90	1.86
	LSD ($P < 0.01$):	0.74	0.63
Wainui	2	2.42	2.00
	5	3.95	3.65
	8	2.86	2.10
	11	2.85	2.25
	15	2.60	2.05
	17	2.56	2.20
	LSD ($P < 0.01$):	0.50	0.80
Kumeroa	2	2.50	2.03
	5	3.52	3.18
	8	2.39	2.42
	11	2.64	2.45
	LSD ($P < 0.01$):	0.29	0.26
Tokomaru	2	3.26	3.22
	5	4.13	4.47
	8	3.35	3.59
	LSD ($P < 0.01$):	0.55	0.63

only 0.16 to 0.18%, indicating the likelihood of P deficiency. With the exception of the data for incorporated, powdered CRP on the Ramiha soil (Fig. 3.2b) both superphosphate treatments were still superior to powdered CRP in supplying P to the plant at the sixth harvest. Relative P uptake decreased rapidly when superphosphate was incorporated, particularly on the Ramiha soil (Fig. 3.2b). This contrasts with the increasing availability of P from the powdered CRP treatments (Fig. 3.2).

3.3.2 Effectiveness of pelletised Chatham Rise phosphorite when compared to superphosphate

The water stability of the CRP pellets used in this preliminary glasshouse study, and in subsequent studies, increased over 183 days (Fig. 3.3). Whereas the <125-μm fraction decreased from 81 to 10% over 153 days, the 250 - 125-μm fraction increased from 19 to 74% over the same period. After 153 days, however, the 250 - 125-μm fraction also decreased. A corresponding increase was measured in the 250 - 125-μm fraction after 153 days. Increasing the soaking time before shaking to 1 h had little or no effect on the particle-size distribution.

Total ryegrass yields with surface-applied, pelletised CRP (Table 3.5) were lower than those with the equivalent surface-applied superphosphate treatment with the Wainui and Ramiha soils. Only at the highest rate of application to the Kumeroa soils however, was there any significant difference between these two P sources when surface-applied. No differences were found with the Tokomaru soil. The relative yield values of surface-applied pelletised CRP at 90% of the yield maxima for superphosphate were 85, 93, 93, and 104 with the Ramiha, Wainui, Kumeroa, and Tokomaru soils, respectively. These results contrast with those found for powdered CRP. Incorporation of the pelletised material into the upper 2cm of the soil resulted in a decrease in the relative yield value of CRP with the Ramiha (83) and Wainui (90) soils.

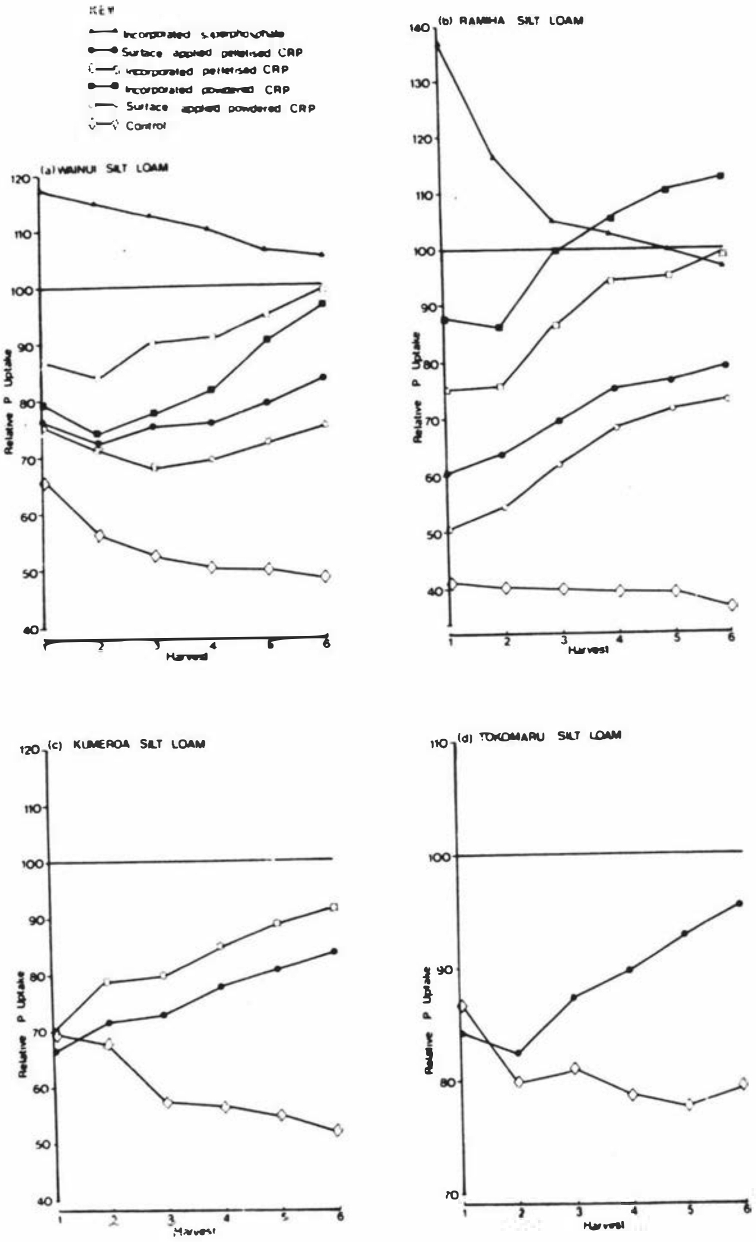

Figure 3.2 Relative cumulative herbage phosphorus uptake for six harvests with the four soils as influenced by phosphate source and placement (surface-applied superphosphate = 100). a = Wainui silt loam, b = Ramiha silt loam, c = Kumeroa silt loam, and d = Tokomaru silt loam.

Herbage P uptake by ryegrass over the six harvests from surface-applied, pelletised CRP with the Wainui, Ramiha, and Kumeroa soils was inferior to that from both superphosphate and CRP which was surface-applied in the powdered form (Table 3.6). Only at the highest rate of application was there any significant difference in the two P sources with the Tokomaru soil.

The effectiveness of pelletised CRP relative to surface-applied superphosphate in terms of cumulative yield differences for the four soils is shown in Fig. 3.1. Initially the difference between pelletised CRP and surface-applied superphosphate was 15-32%. As with powdered CRP, all soils showed increasing responsiveness to pelletised CRP throughout the trial. The initial differences between pelletised and powdered CRP slowly increased throughout the trial with the three soils for which this comparison was made. Whereas incorporation of powdered CRP or superphosphate increased their effectiveness, incorporation of the pelletised material (Fig. 3.1a, b) had no beneficial effect in either the short or the long term.

Pelletising reduced the initial availability of P in CRP, as indicated by the data for relative cumulative herbage P uptake (Fig. 3.2) for all four soils. Initially this varied from 51 to 81% of the figure for surface-applied superphosphate and from 79 to 104% of that for surface-applied, powdered CRP. Herbage P concentrations for the first and second harvests for all four soils (Table 3.7) further illustrate the effect of pelletising on the initial availability of P in CRP. Although in the glasshouse experiment PR gave rise to lower herbage P concentrations than superphosphate, in the field these differences were very much less pronounced (Chapter 4). The effect of incorporation on both the short-term and long-term availability of P in pelletised CRP is again clearly shown for both the Wainui and Ramiha soils (Fig. 3.2a, b).

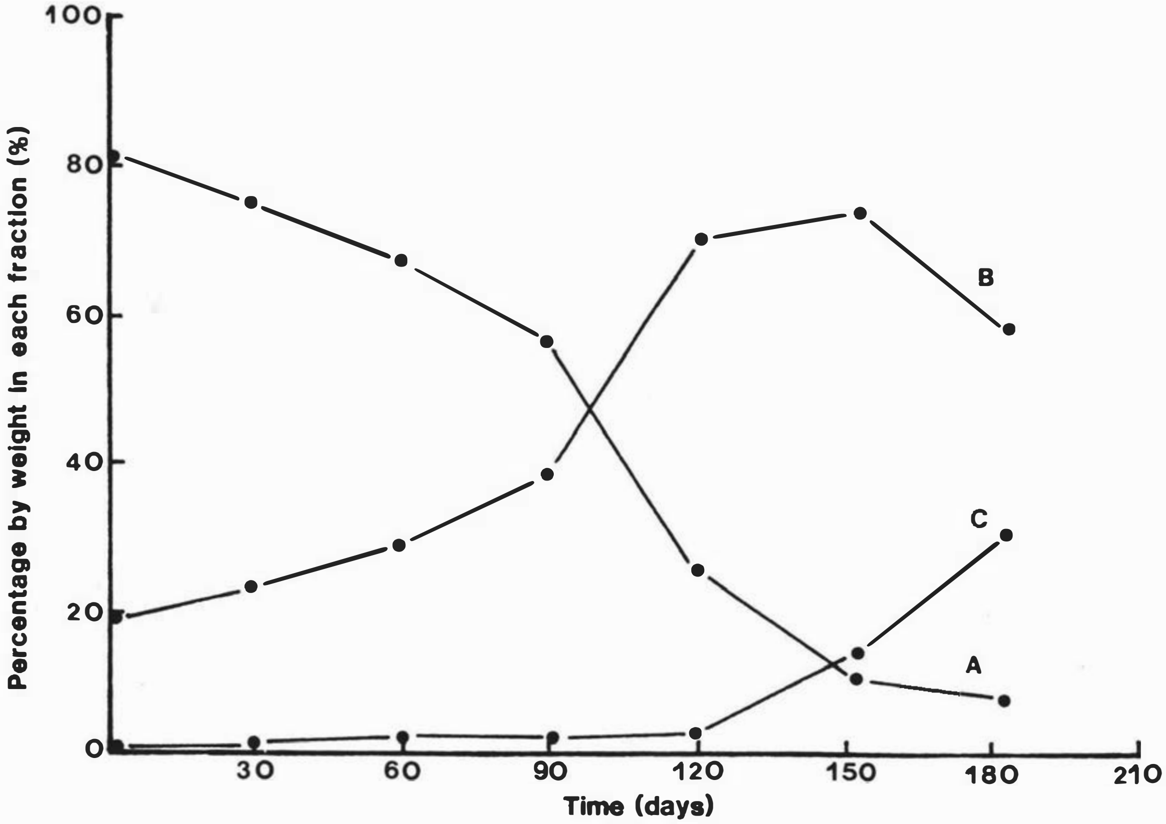

Figure 3.3 Changes in the particle-size distribution of pelletised Chatham Rise phosphorite as a function of time of storage at 80% relative humidity and 20°C.
A = <125-μm fraction, B = 250 - 125-μm fraction, and C = 500 - 250-μm fraction.

3.4 General Discussion

Over six harvests, CRP compared favourably with single superphosphate as a P source for perennial ryegrass grown in four soils in this initial glasshouse evaluation. The relative yield values for CRP ranged from 96 to 106 in the powdered form and from 83 to 104 in the pelletised form, when compared at 90% of the yield maxima for surface-applied superphosphate.

In the study of Roberts and White (1974) powdered CRP was only 70% as effective as single superphosphate applied at a rate of approximately 100 kgP ha^{-1} and incorporated into the surface 2 cm. This contrasts with the present findings. Using the same criteria for evaluating data as used by Roberts and White (1974), powdered CRP applied at 70 and 150 kgP ha^{-1} would be 102 and 107%, respectively, as effective as superphosphate when incorporated. This difference may, in part, reflect the quality of the superphosphate used in the respective experiments. That used by Roberts and White (1974) was 100% soluble in neutral ammonium citrate, whereas in the present glasshouse trial the equivalent value was only 65% (Table 3.3).

Good agreement was found, however, between the results of the present study for the high P-sorbing Ramiha soil and those reported by Rajan (1981a) for the high P-sorbing Morotui sandy loam, although the pelletised CRP used in the present study was larger (>0.5mm - <2mm) than the minigranules of CRP (0.4mm - 1.4mm) used by Rajan (1981a). On a relative basis, the pelletised CRP, when incorporated into the upper 2 cm of the Ramiha soil, was 82 and 84% as effective as superphosphate applied at 75 and 150 kgP ha^{-1}, respectively, in the present study. Rajan (1981a) found that minigranules of CRP placed in the soil at 3mm were 78 and 85% as effective as superphosphate applied at 60 and

120 kgP ha^{-1}, respectively. Interestingly, the superphosphate used in the study of Rajan (1981a) had 78% of total P soluble in 2% citric acid. This compares well with the 79.5% citric-soluble P value for the superphosphate used in the present study. This finding provides evidence to support the suggestion that the difference found in the effectiveness of CRP, when compared to superphosphate, in the study of Roberts and White (1974) and in the present study reflects the difference in the quality of superphosphate used in the respective studies.

The availability of P was generally lower from CRP than from superphosphate, on the basis of herbage P concentration and P uptake data. A number of workers have noted this in comparisons of PR with superphosphate (Peaslee et al., 1962; Barnes and Kamprath, 1975; Hagin et al., 1978a). The initial difference in availability between these two P sources is due to their varying solubilities and initial behaviour on contact with soils. Superphosphate dissolves immediately on contact with moist soils (Brown and Lehr, 1959) and the reaction products formed upon dissolution (iron and aluminium phosphates in acid and neutral soils) control, in the short term at least (McLaughlin and Syers, 1978), the availability of P. In contrast, the initial rate of dissolution of a PR is a function primarily of its solubility. In the present study this initial difference in availability of P between these two P sources, however, did not persist.

The similarity in both the yield and the P uptake data for the Wainui and Kumeroa soils indicates that pH values in the range 5 to 6 had little effect on the availability of P in CRP. This is consistent with the results of overseas glasshouse studies (Ellis et al., 1955; Barnes and Kamprath, 1975) evaluating PR fertilizers within a similar pH range. In a recent review, Khasawneh and Doll (1978) suggested that PR materials are ineffective in comparison with superphosphate as

P sources to plants on soils of moderate to high P status. The present results from the Tokomaru soil, and to a slightly lesser extent the Kumeroa and Wainui soils, do not support this viewpoint, but suggest that CRP has potential as a direct-use P fertiliser on soils of other than low P status.

A feature of the present results was the satisfactory performance of the surface-applied, pelletised CRP treatments in comparison with the equivalent powdered treatments. These results suggest that the freshly-made pelletised material breaks down readily on contact with moist soils, and that movement of the surface-applied, powdered CRP into the soil was sufficiently extensive. The increasing water stability of the pelletised CRP with time, indicated by the increases in the 250 - 125-μm fraction, however, suggests that some cementation reactions were occurring. This could lead, in the absence of biological mixing, to a decrease in the availability to the plant of P in a PR, by reducing the physical distribution of the PR in the soil.

The effectiveness of CRP, in the pelletised form, in the present study was found to vary somewhat between the soils tested. The relative yield values for surface-applied, pelletised CRP were 93, 93, and 100 for the Wainui, Kumeroa, and Tokomaru soils; for the Ramiha soil the relative yield value was 85. Although water uptake largely determines the initial breakdown of the pellet, subsequent movement of the CRP particles away from the site of application (in the glasshouse) is also influenced, in the absence of biological mixing, by the nature and configuration of the soil surface. With the Ramiha soil the surface configuration was uneven and broken, as a result of the stable structure, which is a particular characteristic of this soil. In contrast, the surface configuration of the Wainui, Kumeroa, and Tokomaru soils was even and continuous. As a consequence, movement of the CRP particles away from the site of application may have been reduced with the Ramiha soil. Use of CRP pellets with a smaller mean diameter may reduce this localisation effect on this particular soil by increasing the number of pellets per unit surface area.

As in the studies of Buchan et al. (1970), Alston and Chin (1974), Stephens and Lipsett (1975), Wright (1975), Powell et al., (1980) and Ledgard et al. (1981), both the form and method of application of the PR affected the agronomic effectiveness of CRP in the glasshouse. With one exception, the effectiveness of CRP, when compared to superphosphate, decreased in the order of powdered and incorporated > powdered and surface applied > pelletised and surface applied > pelletised and incorporated, particularly in initial harvest. Whereas incorporation of the powdered PR into the soil maximizes both the surface area exposed for dissolution and the physical distribution of the PR in the soil, surface application in either the powdered or pelletised form minimizes the physical distribution of the PR in the soil. Incorporation of the pellet into the soil also minimizes the surface area exposed for dissolution by effectively preventing the inital breakdown of the pellet. Because of the effect that both form and method of application have on the agronomic effectiveness of PR in the glasshouse, both become important considerations when comparing the findings of glasshouse studies in which PR materials are evaluated. For example, poor agreement is found between the results of the present study with powdered CRP and those reported by Rajan (1981a) with the minigranule of CRP.

The results obtained in this preliminary glasshouse evaluation show that finely-ground and pelletised CRP is an effective source of P to ryegrass. In the following Chapter, the agronomic evaluation of CRP as a direct-application P fertilizer is extended to the field.

CHAPTER 4

CHAPTER 4

FIELD EVALUATION OF CHATHAM RISE PHOSPHORITE

4.1 Introduction

In the past sixty years, numerous field studies have been conducted in New Zealand on the possible value of PR materials as direct-application phosphatic fertilizers. Possible worldwide shortages of elemental sulphur (S), threatening the manufacture of the traditional form of phosphatic fertilizer (superphosphate) used for correcting P deficiencies in New Zealand, prompted much of the early work.

The apparent failure to recognize the quite major differences that exist in the agronomic effectiveness of PR materials (Chapter 2.4), however, limits the usefulness of much of the data obtained in many of these studies. The PR materials traditionally used for the manufacture of superphosphate in New Zealand, namely Nauru phosphate rock (NPR) and to a lesser extent Christmas Island A grade phosphate rock, were used in many of these studies. Apart from a series of studies reported by Cottier (1952), which gave an encouraging result with NPR in pasture, the overwhelming evidence has shown that NPR is ineffective as a direct-application P fertilizer, even when finely ground (Lynch, 1951; Duncan, 1953; During, 1953; Hopkins, 1953; Scott, 1957; Karlovsky, 1961; Scott and Cullen, 1965; Grigg and Crouchley, 1980).

In contrast, when the North African, Gafsa phosphate rock (GPR) has been evaluated, favourable results have usually been obtained (Arnold, 1952; Cottier, 1952; During, 1953; Booth, 1956; Cullen, 1958; Karlovsky, 1958; Scott and Cullen, 1965), although the results of Lynch (1951) suggest that GPR is of limited agronomic effectiveness in drier (< 1000mm) rainfall areas. In fact the encouraging results obtained with GPR by Scott and Cullen (1965) prompted these workers to suggest that a more comprehensive evaluation of the possible role of PR materials in New Zealand was more than justified. However, apart from the recent publication of Grigg and Crouchley (1980), which reported work done in the 1960's, this research does not appear to have been followed up until very recently.

The results obtained with CRP in the preliminary glasshouse study (Chapter 3) suggest that this PR material has considerable potential as a direct-application P fertilizer. Also the results obtained with pelletised CRP suggest that the problems associated with the handling and spreading of a finely-ground PR material, which to date has largely restricted their use (During, 1972), can be overcome without seriously affecting the agronomic effectiveness of this material. However, further evaluation is required under field conditions.

The initial purpose of the field phase of the present study was to extend the evaluation of CRP, in both the powdered and pelletised forms, over a range of soil types under field conditions. In addition to generating basic agronomic data for the effectiveness of this PR, an additional objective was to evaluate the potential role of CRP as a direct application P fertilizer in two distinct pastoral farming systems.

Of the four field trials established, three were located in hill country, a farming area where PR materials are likely to have their greatest potential. In the North Island, hill country represents 4.5 million ha of the 13 million ha of pastoral land farmed, with stock numbers amounting to over 31 million. Hill-country farming is generally characterised by relatively low annual P inputs, with the principle aim of adding P being the successful establishment and maintenance of a vigorous clover component in the sward (Suckling, 1959). As a result of the poor competitive ability of clover for available P in the soil, when compared to grasses (Jackman and Mouat, 1972a), a P fertilizer needs to maintain a reasonably high level of available P in the soil for maximum effectiveness. Although superphosphate has traditionally been used for this purpose, it is possible that this P source may not be the most effective fertilizer for hill-country pastures. For instance, the initial high plant-availability of P in superphosphate (Rennes, 1978) may not always be utilized fully in hill country because of other limiting factors, including moisture, nitrogen, and temperature (Ball et al., 1976; Luscombe, 1980). The rapid decline in the short-term plant availability of P in superphosphate which follows application (Rennes, 1978), probably limits the effectiveness of this P source in the longer-term, particularly if applied in the Autumn, with most legume growth occurring during the following Spring and Summer period. Infrequent topdressing practices in hill country, due to fluctuating farm incomes, will lead to further variability in the amounts of plant-available P in the soil. Provided CRP is an effective source of P from the time of application, the P-release characteristics of a PR may make this P source as, if not more, effective than superphosphate as a P fertilizer for hill country.

The fourth trial was established on a high-producing dairy farm, where the P status of the soil was relatively high and only small seasonal responses to added P were likely. In contrast to hill country, the principle aim of topdressing at this site was to maintain rather than increase P status of the soil. With the major P losses occurring in the above-ground component of the P cycle in well-developed pastoral systems (Karlovsky, 1975), it was considered that unnecessary increases in the concentration of P in the pasture over and above both plant and animal requirements, are undesirable, leading to unnecessary losses of P by transfer. Again, provided CRP is an effective source of P from the time of application, then it might be satisfactory as a maintenance P fertilizer for well-developed pastoral farming situations.

4.2 Materials and Methods

4.2.1 Field-trial site selection and description

The location, farm type, and past fertilizer history of each of the four field-trial sites are given in Table 4.1. The selection of trial sites at each location was based on the evenness of the microtopography, uniformity of pasture composition, and range in soil pH and extractable P. Apart from the Ballantrae trial, which was located on a sloping (10 to 15^{o}) site, the remaining trials were established on flat sites. The Ballantrae and Wanganui sites are shown in Plates 4.1 and 4.2, respectively.

The New Zealand soil group and soil type, along with values for pH in water, organic carbon content (Bremner and Jenkinson, 1960), P-sorption capacity (Chapter 3.2.2) and estimates of plant-available P in the soil, measured by the bicarbonate (Chapter 3.2.2) and single-water (shaking for 1 h at a solution:soil ratio of 120:1), which correlates well (Currie, pers. comm.) with the double-water extraction of Ryden and Syers (1977), extraction methods for each soil at the commencement of the trials at each site are given in Table 4.2.

4.2.2 Phosphate sources used

Details of the collection and selection of both the superphosphate and CRP used in this study are given in the previous Chapter (3.2.1). Results for total P, determined by perchloric acid digestion (O'Connor and Syers, 1975); calcium carbonate content, determined by titration following carbon dioxide evolution; and water- (The Fertilisers Regulations, 1969) and citric- (The Fertilisers

Table 4.1 Location, farm type, and past fertilizer history of field trial sites

	Field trial site			
	Ballantrae	Wanganui	Pahiatua	Tokomaru
Location	10 km West of Woodville (Ruahine range)	20 km North East of Wanganui	20 km East of Palmerston North (Ruahine range)	5 km East of Palmerston North (High river terrace)
Farm type	Hill country Semi-intensive sheep	Hill country Intensive sheep and beef	Hill country Semi-intensive sheep	Intensive dairying
Pasture species	brown top (*Agrostis tenuis*), perennial ryegrass (*Lolium perenne*), white clover (*Trifolium repens*), subterranean clover (*Trifolium subterranean*)	browntop (*Agrostis tenuis*), danthonia (*Notadanthonia*), white clover (*Trifolium repens*), subterranean clover (*Trifolium subterranean*)	browntop (*Agrostis tenuis*), subterranean clover (*Trifolium subterranean*) lotus major (*Lotus pedunculatus*)	perennial ryegrass (*Lolium perenne*), white clover (*Trifolium repens*)
Past fertilizer history				
Superphosphate	Infrequent 250 kg $ha^{-1}yr^{-1}$ 1960 - 1978	Frequent 250 kg $ha^{-1}yr^{-1}$ 1960 - 1978	Infrequent 200 kg $ha^{-1}yr^{-1}$ 1970 - 1978	Frequent 350 to 400 kg $ha^{-1}yr^{-1}$ 1974 - 1978
Lime	None	2.5 tonnes ha^{-1} in Spring 1977	None	None

Plate 4.1 View of the Ballantrae field trial site.

Plate 4.2 View of the Wanganui field trial site.

Table 4.2 Several characteristics of the soils

	Field trial site			
	Ballantrae	Wanganui	Pahiatua	Tokomaru
New Zealand Soil Group	Yellow-grey earth/ yellow-brown earth intergrade	Yellow-grey earth/ yellow-brown earth intergrade	Yellow-brown loam	Yellow-grey earth
Soil type	Wainui silt loam	Kumeroa silt loam	Ramiha silt loam	Tokomaru silt loam
pH_{H_2O}	5.0	6.2	5.5	5.6
Organic carbon (%)	4.9	3.5	8.8	2.0
P-sorption capacity (%)	33	35	87	24
Extractable P in soil				
Bicarbonate ($\mu g\ g^{-1}$)	15.3 ± 6.5*	18.3 ± 2.1	9.8 ± 1.8	40.3 ± 5.2
Water ($\mu g\ g^{-1}$)	4.2 ± 2.4	7.8 ± 1.1	2.2 ± 0.8	20.3 ± 2.2

*Standard deviations.

Regulations, 1969) soluble P in the monocalcium phosphate (MCP), superphosphate, and powdered and pelletised CRP used in this study are presented in Table 4.3. The granule- and pellet-size range used for superphosphate and CRP, respectively, are greater than those used in the prelimary glasshouse study (Chapter 3.2.1). Sufficient superphosphate and powdered (100% < 180 μm) CRP was obtained at the outset of the study to supply all requirements over the three years. The pelletised CRP, produced from the powdered material, was used within one week of manufacture to eliminate any possible cementation effects (Chapter 3.3.2). The MCP was applied "as received" as a fine powder.

4.2.3 Fertilizer treatments

The effectiveness of pelletised CRP was compared to that of superphosphate on an equivalent P basis at two rates of application (35 and 70 kgP ha^{-1}). The field trials were designed to run for three years with the initial effectiveness of the P sources assessed in the first year and the residual effect assessed in the second and third years. To permit the evaluation of the residual effect of both superphosphate and CRP applied in the first year, one additional superphosphate treatment was included at all four trial sites; this was 35 kgP ha^{-1} as superphosphate, applied annually. A similar treatment, using CRP, was also included in the Tokomaru trial. To assess the effect of pelletising CRP, a powdered CRP treatment (35 kgP ha^{-1}) was included at the three hill-country sites. Both the S (applied as gypsum) and P (applied as MCP) responsiveness at each trial site was assessed in the first two years. Each trial consisted of nine treatments (Table 4.4).

4.2.4 Field-trial design and establishment

Each trial consisted of forty five plots made up of the nine treatments, replicated five times. Each plot was 3.5 m long and 2 m wide.

Table 4.3 Several physical and chemical characteristics of superphosphate, monocalcium phosphate (MCP), and Chatham Rise phosphorite (CRP)

Phosphate source	Form	Particle size range (mm)				Total P (%)	Total $CaCO_3$ (%)	P extracted by (% of total P)	
		4-2	1-2	0.5-1	<0.5			Water	2% citric acid
MCP	powder					25.2	-	91	-
Superphosphate	granule	44	27	16	13	8.5		45	79.5
CRP	powder (<180 µm)					9.4	30.3	<0.01	20.7
CRP	pellet	30	40	24	6	9.2	28.8	<0.01	20.7

Table 4.4 Fertilizer treatments used at Ballantrae, Wanganui, and Pahiatua (1-9 in each case) and at Tokomaru (1-8 and 10)

		Rate of application					
		First year		Second year		Third year	
	Fertilizer treatment	sulphur	phosphorus	sulphur	phosphorus	sulphur	phosphorus
		(kg ha^{-1})		(kg ha^{-1})		(kg ha^{-1})	
1	Control	0	0	0	0	0	0
2	Gypsum	70	0	100	0	100	0
3	Monocalcium phosphate	0	35	0	0	0	0
4	Superphosphate	70	35	100	0	100	0
5	Superphosphate	70	70	100	0	100	0
6	Superphosphate	70	35	100	35	100	35
7	CRP, pelletised	70	35	100	0	100	0
8	CRP, pelletised	70	70	100	0	100	0
9	CRP, powdered	70	35	100	0	100	0
10	CRP, pelletised	70	35	100	35	100	35

Replicates were separated by a border strip of 0.5 m at Wanganui, Pahiatua, and Tokomaru to ease mowing. This was extended to 1 m at Ballantrae to reduce the possibility of any surface movement of fertilizer material downslope. The trials were fenced to exclude the grazing animal and a mowing with clippings removed harvesting technique was used throughout the 3 years at all sites.

Fertilizer treatments were applied on 10/4/78 at Ballantrae, 9/4/78 at Wanganui, 23/4/78 at Pahiatua, and 9/4/78 at Tokomaru. A randomised block design was used. Sulphur, as gypsum, was applied initially at the same rate as that applied in the highest superphosphate addition (70 kgS ha^{-1}) to all plots except the controls and those plots topdressed with MCP. Additional S (50 kg ha^{-1}), as gypsum, was applied the following Autumn and then at 6-monthly intervals for the remainder of the 3 years. All sites received a basal dressing of potassium (K) as KCl (50 kgK ha^{-1}) and molybdenum (Mo) as sodium molybdate (250 gMo ha^{-1}) in both the Autumn and Spring throughout the 3 years.

4.2.5 Sampling techniques

At each harvest both the total pasture dry matter production and botanical composition were assessed. The frequency of harvesting varied markedly, both within and between sites over the 3 years. A harvest was taken when approximately 12cm of pasture was present on a trial, rather than over defined time periods. Weather caused some variation in cutting frequency over the 3 years.

4.2.5.1 Assessment of pasture production

At each site pasture production was assessed by taking two mown strips (0.53 m wide x 2.44 m long) from each plot, using a rotary mower after first mowing and discarding clippings from one mown strip

(0.53 m) from the top and bottom of each plot. Cutting height was set to leave approximately 1.5cm of pasture on the plots. After recording the weight of clippings from each plot, which was taken as the difference between catcher weight before and after mowing each plot using a top loading balance with an accuracy of ± 10g, a subsample (approximately 100g) was taken for dry-matter assessment. These subsamples were weighed on return to the laboratory and then oven dried at 60°C for 24 h. After reweighing, dry matter percentages were calculated and these were converted to total pasture dry-matter production per hectare. Subsequently, in this thesis all pasture production data are expressed on a dry-matter basis.

4.2.5.2 Assessment of botanical composition

Along with total pasture production, botanical composition was assessed at each harvest. Approximately 100g of pasture was removed by clippings from the area between the two mown strips on each plot, before the trial was trimmed. After thoroughly mixing the pasture sample, botanical composition was determined on a dry matter basis after dissection of approximately half the sample into grasses (mainly perennial ryegrass, *Lolium perenne*; browntop, *Agrostis tenius*, with some annual poa, *Poa annua*; sweet vernal grass, *Anthoxanthum odoratum*; danthonia, *Notadanthonia clavata*; cocksfoot, *Dactylis glomerata*; Yorkshire fog, *Holcus lanatus*; timothy, *Phleum pratense*); and clover (mainly white clover, *Trifolium repens*; subterranean clover, *Trifolium subterranean*, with some red clover, *Trifolium pratense*; suckling clover, *Trifolium dubium*; and lotus major, *Lotus pedunculatus*). The remaining 50 g was placed into a separate bag and also air dried at 60°C for 24 h. This composite pasture sample was used for chemical analysis after grinding.

After drying separately at 60°C for 24 h, the grass and clover dissections were weighed separately. Clover content was expressed as a percentage of total dry weight of grass and clover combined, and total clover production was then calculated from pasture production using this percentage. Some grass-clover dissections from selected treatments for all sites over the 3 years were retained and used for chemical analysis.

4.2.5.3 Earthworm populations

An assessment was made of the earthworm species and numbers present at each site in the Autumn of 1981. Thirty, 15-cm diameter cores to a depth of 20 cm were taken at each site. Cores were also taken from outside each trial area to assess any possible effect of mowing with clippings removed on the earthworms species present and their biomass. Extraction of earthworms was by hand, with both the numbers and freshweight of each species determined.

4.2.5.4 Soil sampling

In addition to soil sampling before the field trials were commenced, soil samples were taken in both Spring and Autumn (before re-topdressing) from all plots at each site over the 3 years. At each sampling, 5, 2-cm diameter soil cores to a depth of 4 cm were taken from each plot. By restricting sampling depth to 4 cm it was considered that any differences between treatments would be detected more readily. After air drying in a glasshouse, all soil samples were ground to pass through a 2-mm sieve, bagged, and stored for analysis.

4.2.6 Soil and plant analysis

4.2.6.1 Soil analysis

Soil samples collected in both the Spring and Autumn from all sites over the 3 years were analysed for changes in pH, sorbed inorganic P measured by 0.5M NaOH extraction (solution:soil ratio of 100:1 and a 16-h shaking period with a prewash with 0.1M NaCl for 30 min); and plant-available P estimated by the single water (see 4.2.1), bicarbonate (Chapter 3.2.2), and the Bray (0.03 M NH_4F and 0.025M HCl at a solution: soil ratio of 7:1 and 5-min shaking period), of Bray and Kurtz (1945), extraction methods. Water-extractable P in soil samples was determined within 6 weeks of collection, because of possible changes in this soil P fraction with storage (Smith, 1979).

4.2.6.2 Plant analysis

Total P and N in composite pasture samples were determined following Kjeldahl digestion. Uptake of P and N by pasture was calculated from concentration and pasture production data. Selected grass and clover samples were periodically analysed for all macro- and micro-nutrients, with emphasis on S and Mo.

4.3 Results and Discussion

4.3.1 Sulphur and phosphorus responses

4.3.1.1 Pasture production

Annual pasture production varied from 3,420 to 10,000 kgDM ha^{-1} at Pahiatua and Tokomaru, respectively, reflecting differences in soil P status, amongst other factors. There were also appreciable differences within sites. For instance at Ballantrae, pasture production varied from 4,460 to 7,330 kgDM ha^{-1} over the 3 years, reflecting the varying climatic conditions. Above average pasture growth, due to wet summer conditions, resulted in increased pasture production at Pahiatua and Tokomaru in the first year and at Ballantrae in the second, whereas dry summer conditions at Ballantrae in the first and at Wanganui in the

Table 4.5 Pasture production at the four sites in the first and second years as influenced by phosphorus and sulphur addition

Fertilizer treatment	Application rate		Pasture production			
	Sulphur	Phosphorus	Ballantrae	Wanganui	Pahiatua	Tokomaru
	(kg ha^{-1})		(kgDM ha^{-1})			
First year						
Control	0	0	3978 Aa	5871 Bb	4767 Bb	10289 Aa
Sulphur (gypsum)	70	0	4570 Aa	6056 ABb	4886 Bb	10140 Aa
Phosphorus (MCP)	0	35	4246 Aa	6389 ABab	5971 Aa	10546 Aa
Superphosphate	70	35	4460 Aa	6810 Aa	5950 Aa	10272 Aa
Second year						
Control	0	0	5091 Bb	5819 Aa	2654 Ab	7374 Aa
Sulphur (gypsum)	170	0	5976 ABab	5581 Aa	2912 Aab	7407 Aa
Phosphorus (MCP)	0	35	6305 ABa	6032 Aa	2929 Aab	7883 Aa
Superphosphate	170	35	6852 Aa	6510 Aa	2980 Aa	7526 Aa

A Significant at the 1% level.

a Significant at the 5% level.

second year, probably decreased pasture production. In contrast to varying summer pasture production at each site, winter and spring pasture production was remarkably uniform at each site over the three years, a finding consistent with the work of Suckling (1975). Spring (1st September to 30th November) and Summer (1st December to 1st March) growth represented over 65% of pasture production at the three hill-country sites and 55% at Tokomaru.

In the absence of P, no significant increases were measured in pasture production to S applied as gypsum in either the first or second year at any of the four sites (Table 4.5). Small ($P < 0.05$) seasonal S responses, however, were measured at Tokomaru in the Autumn of the first year, at Wanganui in the Spring of the first and in the Autumn of the second year, and at Ballantrae in the Spring of the first and second year. The high P-sorption capacity of the Ramiha silt loam at Pahiatua probably explains the lack of any S response at this site. The large number of sites available for sulphate sorption would minimise the leaching of S.

Apart from a response ($P < 0.01$) to MCP at Pahiatua in the first year, no significant increases were measured in pasture production when P was added in the absence of S, in either the first or second years at any of the field sites (Table 4.5).

Large increases in pasture production were measured at Wanganui ($P < 0.01$) and Pahiatua ($P < 0.01$) in the first year, and at Ballantrae ($P < 0.01$) and Pahiatua ($P < 0.05$) in the second year when both S and P were applied as superphosphate (Table 4.5). Although no response was measured at Ballantrae to superphosphate in the first year, due probably to dry summer conditions, a response ($P < 0.01$) to superphosphate was measured in the spring harvests of the first year. The dry conditions over the Summer and the earlier Autumn at Wanganui probably explain the absence of a response to superphosphate in the second year (Table 4.5).

Responses ($P < 0.05$) to superphosphate were restricted to autumn harvests in the second year at Tokomaru, reflecting the high P status of this site at establishment.

The combined effect of P and S as superphosphate on total pasture dry matter production at Wanganui in the first year and at Ballantrae in the second year demonstrates the importance of meeting the swards requirements for both these macro-nutrients.

4.3.1.2 Clover production

As with annual pasture production, clover production varied markedly, not only between, but also within sites over the 3 years of this study. Over 75% of clover production was obtained in the late Spring and Summer at the three hill-country sites and 65% at Tokomaru. Total clover production, however, contributed less than 25% of total pasture dry matter production in any one year at each site.

Apart from a response ($P < 0.01$) to gypsum at Ballantrae in the second year, no responses to S in the absence of P were measured in clover production in either the first or second year at any of the four sites (Table 4.6). In the absence of S, clover responses to P applied as MCP were obtained at Wanganui ($P < 0.01$) and Pahiatua ($P < 0.01$) in the first year and at Ballantrae ($P < 0.01$) and Pahiatua ($P < 0.01$) in the second year (Table 4.6).

Addition of both S and P as superphosphate resulted in large increases in total clover production at both Ballantrae ($P < 0.01$) and Pahiatua ($P < 0.01$) in both the first and second years, and at Wanganui ($P < 0.01$) and Tokomaru ($P < 0.05$) in the first year (Table 4.6). Again this demonstrates the importance of supplying both these macro-nutrients for maximum pasture production.

In the remainder of this Chapter, the effectiveness of superphosphate and CRP as sources of P are compared in the presence of added S.

Table 4.6 Clover production at the four sites in the first and second years as influenced by phosphorus and sulphur addition

Fertilizer treatment	Application rate		Pasture production			
	Sulphur	Phosphorus	Ballantrae	Wanganui	Pahiatua	Tokomaru
	(kg ha^{-1})		(kgDM ha^{-1})			
First year						
Control	0	0	173 Bb	973 Bb	705 Bb	2435 Ab
Sulphur (gypsum)	70	0	260 ABb	1037 Bb	738 Bb	2414 Ab
Phosphorus (MCP)	0	35	235 ABb	1367 Aa	1431 Aa	2924 Aab
Superphosphate	70	35	452 Aa	1438 Aa	1595 Aa	3018 Aa
Second year						
Control	0	0	429 Cc	751 Aa	269 Bb	1236 Aa
Sulphur (gypsum)	170	0	691 Bb	712 Aa	363 ABb	1349 Aa
Phosphorus (MCP)	0	35	850 Bb	981 Aa	497 Aa	1602 Aa
Superphosphate	170	35	1288 Aa	985 Aa	458 Aa	1585 Aa

A Significant at the 1% level.

a Significant at the 5% level.

4.3.2 Effect of pelletising Chatham Rise phosphorite

4.3.2.1 Pasture and clover production

No difference was found in pasture production when P was supplied as powdered or pelletised CRP at a rate of 35 kgP ha^{-1} in either the first (Fig. 4.1a) or second (Fig. 4.1b) year at any of the three hill-country sites, although no P response was measured at Ballantrae in the first, or at Wanganui in the second year. Also in the spring harvests at Ballantrae in the first year, when a P response ($P < 0.01$) was measured, no difference was found between the two forms. Both forms of CRP were as effective as superphosphate from the time of application.

This result contrasts with the finding of the preliminary glasshouse study (Chapter 3), where pelletising reduced the agronomic effectiveness of CRP, particularly in initial harvests. A more detailed analysis of individual harvests in the first eight months of each of these three trials, when differences between powdered and pelletised CRP are likely to be the more pronounced, also failed to show any differences, even though the mean pellet size used (>0.5 mm to <4.0 mm) was greater than that used in the preliminary glasshouse study (>0.5 mm to <2.0 mm).

Also no differences were found in clover production from either powdered or pelletised CRP or superphosphate in either the first (Fig. 4.1a) or second (Fig. 4.1b) years at any of the three hill-country sites.

Visual observations in the field immediately following the application of pelletised CRP, indicated that the breakdown of the pellets occurred rapidly, with heavy dew providing sufficient moisture to achieve this. Results from the glasshouse (Chapter 3) also indicate that the surface-applied pellet breaks down rapidly, as this treatment performed

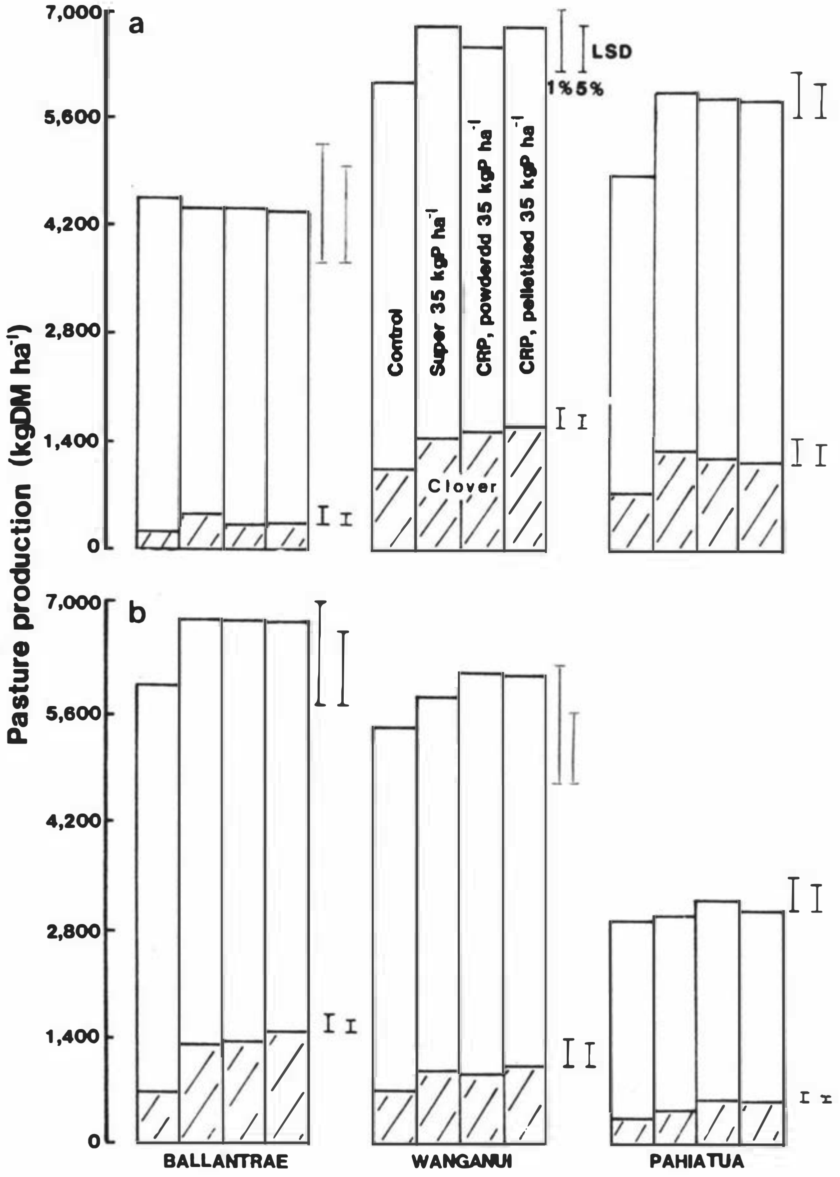

Figure 4.1 Clover and pasture production in the first (a) and second (b) year at the three hill-country sites as influenced by phosphate source. Least sifnificant difference (LSD) at the 1% and 5% level.

similarly to the surface-applied, powdered CRP. In initial harvests in the glasshouse the surface-applied, pelletised CRP and to a lesser extent the surface-applied, powdered CRP were both less effective than powdered CRP incorporated into the upper 2 cm of soil and also than superphosphate. This suggests that movement of the CRP particles from the soil surface down into the soil profile was restricted in the glasshouse. In contrast, in the field the initial differences between the two forms of CRP and superphosphate were far less pronounced, suggesting that after the breakdown of the surface-applied pellet, the particles of CRP moved sufficiently rapidly into the soil profile which would promote dissolution.

The number of earthworms at the trial sites were assessed in Autumn of 1981. The numbers of Lumbricus rubellus (Hoff) and Allolobophora caliginosa (Savigny) were greater in the trial areas than in the paddocks immediately surrounding each of the trials (Table 4.7). In general, the differences were more pronounced with L. rubellus. This difference possibly reflects the close grazing in the paddocks surrounding each trial, limiting litter return. The severe pugging which occurred in the paddock around the Tokomaru site in the previous year may be responsible for the marked difference found at this site.

4.3.2.2 Phosphorus concentration in pasture and phosphorus uptake by pasture

In contrast to the results obtained at Wanganui and Pahiatua, a difference was found in the pasture P concentration between the powdered and pelletised CRP treatments in the first two harvests at Ballantrae in the first year (Table 4.8). However, this difference was small and from an agronomic standpoint probably of little significance. It does suggest, however, that pelletising a PR can lead to some localization, in the short term, under certain field conditions. In a commercial operation

Table 4.7 Numbers of *L. rubellus* and *A. caliginosa* at the four sites and in the surrounding pastures in the Autumn of 1981

Earthworm species	Field trial site Ballantrae	 Wanganui	 Pahiatua	 Tokomaru
		(No. m^{-2})		
Field trial				
L. rubellus	127 ± 20* (47)†	150 ± 15 (30)	94 ± 20 (12)	350 ± 30 (29)
A. caliginosa	145 ± 21 (53)	350 ± 40 (70)	675 ± 50 (88)	855 ± 80 (71)
Combined population	271	500	769	1205
Surrounding pasture				
L. rubellus	77 ± 20 (32)	70 ± 18 (19)	79 ± 22 (12)	50 ± 25 (13)
A. calignosa	165 ± 30 (68)	300 ± 40 (81)	594 ± 65 (88)	324 ± 55 (87)
Combined population	242	370	673	374

*Standard error.

†Percentage of total earthworm population.

Table 4.8 Phosphorus concentration in pasture in initial harvests of the first year at the three hill-country sites as influenced by phosphate source

Treatment	Application rate (kgP ha^{-1})	Phosphorus concentration in pasture at harvest date (% P)			
Ballantrae		1-10-78	6-11-78	26-12-78	
Control	0	0.28 Cc	0.28 Ab	0.29 Bc	
CRP, powdered	35	0.36 Aa	0.36 Aa	0.35 Aa	
CRP, pelletised	35	0.33 Bb	0.32 Ab	0.31 Ab	
Superphosphate	35	0.36 Aa	0.37 Aa	0.35 Aa	
Wanganui		19-5-78	17-7-78	20-9-78	31-10-78
Control	0	0.40 Aa	0.29 Bb	0.45 Aa	0.33 Bb
CRP, powdered	35	0.43 Aa	0.36 Aa	0.47 Aa	0.41 Aa
CRP, pelletised	35	0.41 Aa	0.34 Aa	0.47 Aa	0.40 Aa
Superphosphate	35	0.42 Aa	0.38 Aa	0.49 Aa	0.38 Aa
Pahiatua		19-9-78	4-12-78		
Control	0	0.22 Cc	0.20 Bb		
CRP, powdered	35	0.29 Bb	0.24 Aa		
CRP, pelletised	35	0.28 Bb	0.23 Aa		
Superphosphate	35	0.34 Aa	0.24 Aa		

A Significant at the 1% level.

B Significant at the 5% level.

where the pellet-size range is not so strictly controlled and where damage of the pellet would probably occur during handling, transport, and spreading, a far wider range of pellet sizes would probably be present, reducing and probably eliminating the small differences found at Ballantrae in the first eight months.

Although this difference between powdered and pelletised CRP at Ballantrae was also reflected in initial P uptake data from this site no difference was found in total P uptake by pasture between the two forms of CRP in either the first (Fig. 4.2a) or second (Fig. 4.2b) years at any of the three hill-country sites. As was the case for annual pasture production, no differences were found between these two forms of CRP and superphosphate in either the first (Fig. 4.2a) or second (Fig. 4.2b) year at any of the sites. This result again contrasts sharply with the findings of the glasshouse study (Chapter 3), where differences between both powdered and pelletised CRP, and powdered CRP and superphosphate were far more pronounced when P uptake data were used. In addition to possibly reflecting the effect of using a single species indicator plant in glasshouse studies, these differences suggest that a number of factors which may operate in the field and contribute to an increased effectiveness of a PR, are generally excluded from glasshouse studies.

4.3.3 Initial effectiveness of Chatham Rise phosphorite

The discussion on the agronomic effectiveness of CRP will be divided into the initial and residual effects of this PR when compared to superphosphate. These two terms are used loosely, with first-year results representing the initial effectiveness of the two P sources and the residual effects of P sources assessed by their performance in the second and third year.

4.3.3.1 Pasture production

Responses ($P < 0.01$) to superphosphate and CRP were only

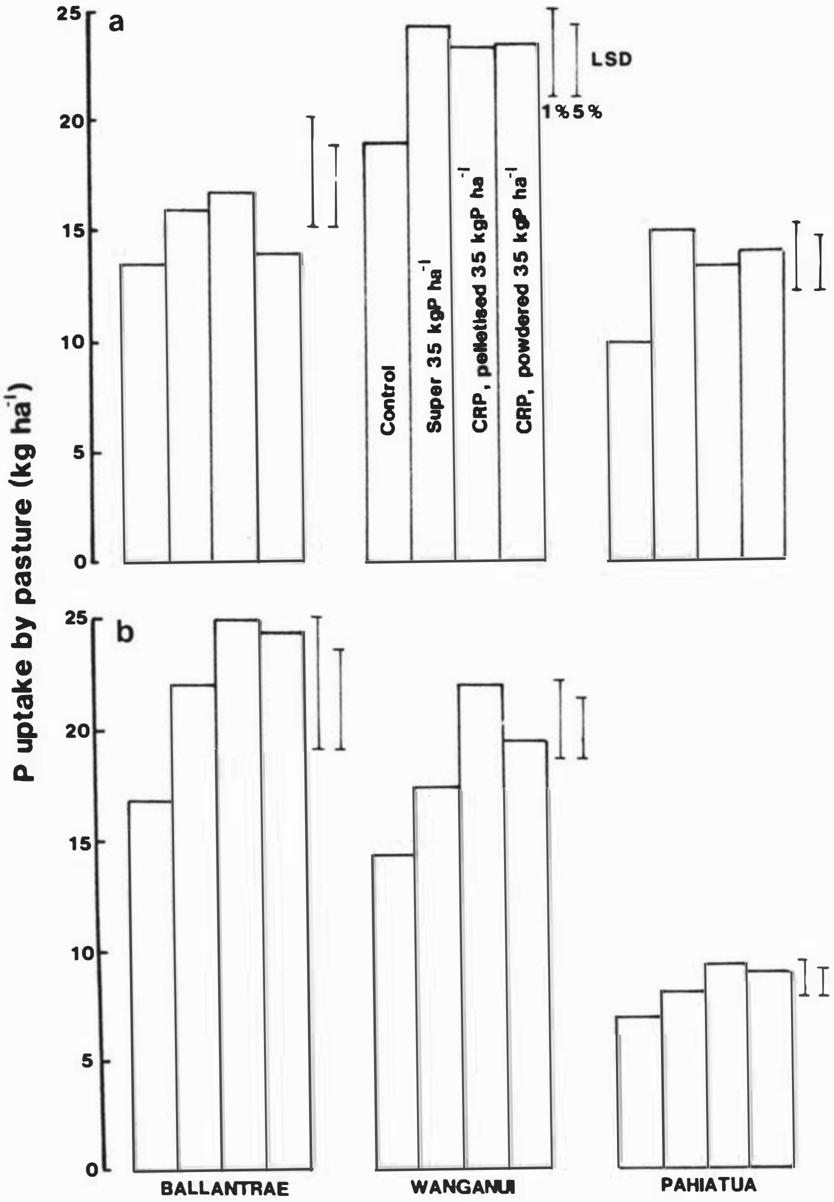

Figure 4.2 Phosphorus uptake by pasture in the fist (a) and second (b) year at the three hill-country sites as influenced by phosphate source. Least significant difference (LSD) at the 1% and 5% level.

obtained at Wanganui and Pahiatua in the first year (Fig. 4.3). No difference ($P < 0.01$) was found between superphosphate and CRP at either application rate at Wanganui (Fig. 4.3b). Application of 70 kgP ha^{-1} as CRP outyielded both superphosphate and CRP applied at 35 kgP ha^{-1} at Pahiatua which, in turn, outyielded the control plots (Fig. 4.3c). Although not shown in the two spring harvests at Ballantrae in the first year, both P sources increased ($P < 0.01$) pasture production to a similar extent. In fact by the end of the first year this site was showing a 20% response to added P.

On a relative basis, the increases in pasture production from superphosphate and CRP were 10 and 12%, respectively, at Wanganui and 27 and 35%, respectively, at Pahiatua.

A more detailed analysis of individual harvests in the first year also failed to show any significant differences in the effectiveness of CRP and superphosphate as sources of P to pasture. This suggests that the rate of dissolution of CRP was sufficiently rapid to meet the P requirements of the sward from the time of application. The slow rate of autumn and winter growth in the first year at Pahiatua, due to climatic conditions, may have favoured the lower water solubility of CRP, although at Wanganui both superphosphate and CRP increased ($P < 0.05$) growth by 10% at the first harvest in the Autumn. Significantly the relatively high pH (6.2) of the Wanganui site appears to have had no detrimental effect on the initial agronomic effectiveness of CRP.

4.3.3.2 Botanical composition of the sward and clover production

The legume species varied from predominantly white clover at Tokomaru, to a mixture of white and subterranean clover at Ballantrae and Wanganui, to subterranean clover and lotus major at Pahiatua. With the poorer competitive ability of legumes than grasses for soil P

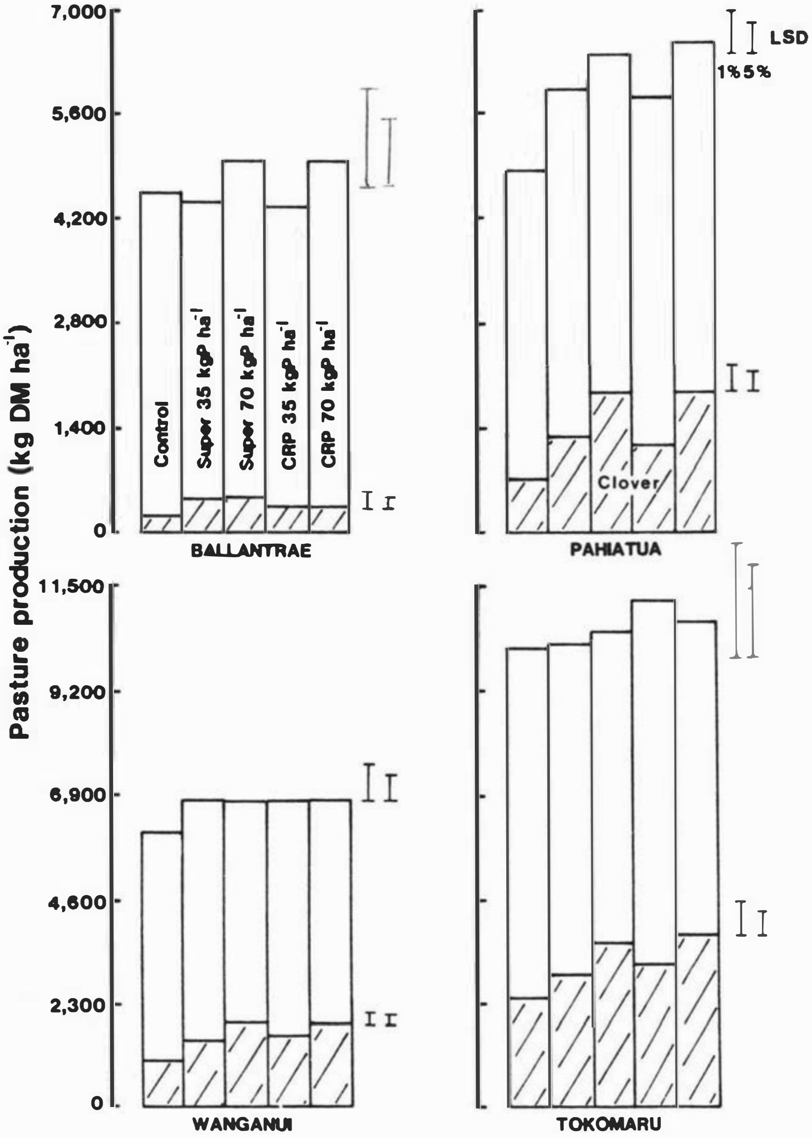

Figure 4.3 Clover and pasture production in the first year at the four sites as influenced by phosphate source. Least significant difference (LSD) at the 1% and 5% level.

(Jackman and Mouat,1972a), any differences in the initial effectiveness of the two P sources should be reflected in the clover component of the sward.

Apart from initial differences at Ballantrae ($P < 0.05$) and Pahiatua ($P < 0.01$), both P sources increased ($P < 0.01$) clover production markedly at both rates of application and at all trial sites including and surprisingly, Tokomaru (Fig. 4.3b). The wet summer conditions at this site in the first year may have been a factor contributing to increased clover growth (Hunt and Wagner, 1963; Boswell, 1977). Clover production nearly tripled at Pahiatua in the first year (Fig. 4.3c) in response to added P. This increase in clover production was also reflected in increased N uptake by the mixed sward at all sites (Table 4.9). Although the mixed pasture species were used for N determinations, the increases in N uptake at the hill-country sites, are of the same magnitude as those measured by Grant and Lambert (1979).

4.3.3.3 Phosphorus concentration in pasture and phosphorus uptake by pasture

The P concentration in the pasture resulting from superphosphate application was initially greater than that resulting from CRP application at all four trial sites in the first year, particularly when applied at 70 kgP ha^{-1} (Table 4.10). Whereas addition of increasing amounts of superphosphate led to increasing P concentrations in the sward in initial harvests, the initial P concentration in the sward following addition of CRP did not increase as the rate of addition increased (Table 4.10). This difference, which probably reflects the initial difference in the behaviour of the two P sources on contact with soil (Chapter 7.3.1), was not reflected in increased pasture production with superphosphate in the first year (Fig. 4.3). The fact that the initial P concentrations in the sward did not increase with increasing

Table 4.9 Nitrogen uptake by pasture in the first year at the four sites as influenced by phosphate source

Treatment	Application rate (kgP ha^{-1})	Nitrogen uptake by pasture (kg ha^{-1}) Ballantrae	Wanganui	Pahiatua	Tokomaru
Control	0	94 Ab	185 Bb	102 Bb	292 Bb
Superphosphate	70	109 Aa	225 Aa	164 Aa	340 Aa
CRP	70	112 Aa	230 Aa	165 Aa	335 Aa

A Significant at 1% level.

a Significant at 5% level.

Table 4.10 Phosphorus concentration in pasture in initial harvests of the first year at the four sites as influenced by phosphate source

Treatment	Application rate (kgP ha^{-1})	Phosphorus concentration in pasture at harvest date (% P)			
Ballantrae		1-10-78	6-11-78	26-12-78	
Control	0	0.28 D	0.28 A	0.29 B	
Superphosphate	35	0.36 B	0.37 AB	0.35 AB	
Superphosphate	70	0.46 A	0.40 A	0.38 A	
CRP	35	0.33 C	0.33 B	0.31 AB	
CRP	70	0.40 B	0.36 AB	0.35 AB	
Wanganui		19-5-78	17-7-78	20-9-78	31-10-78
Control	0	0.40 B	0.29 D	0.45 C	0.33 B
Superphosphate	35	0.42 B	0.38 AB	0.49 abc	0.38 A
Superphosphate	70	0.51 A	0.41 A	0.53 a	0.42 A
CRP	35	0.42 B	0.34 C	0.47 bc	0.40 A
CRP	70	0.42 B	0.34 C	0.51 ab	0.39 A
Pahiatua		19-9-78	4-12-78		
Control	0	0.22 D	0.20 C		
Superphosphate	35	0.34 B	0.24 B		
Superphosphate	70	0.38 A	0.29 A		
CRP	35	0.28 C	0.24 B		
CRP	70	0.29 C	0.23 B		
Tokomaru		22-5-78	3-7-78	17-9-78	3-11-78
Control	0	0.43	0.47	0.47	0.41
Superphosphate	35	0.50	0.52	0.52	0.43
Superphosphate	70	0.50	0.55	0.60	0.47
CRP	35	0.46	0.49	0.49	0.43
CRP	70	0.45	0.49	0.53	0.43

A Significant at 1% level.
a Significant at 5% level.

additions of CRP has some important implications to the efficiency of the P cycle in a grazed sward (see 4.3.5).

Although differences ($P < 0.05$), in favour of superphosphate, were found in P uptake by the pasture in initial harvests at both Ballantrae and Pahiatua, no differences were found between the two P sources in terms of total P uptake at either rate of application at any of the four sites in the first year (Fig. 4.4).

Calculation of apparent P recoveries, expressed as the percentage difference between a fertilizer treatment and control in relation to P applied, of the two P sources varied from 3.8 to 16% with superphosphate and 2.9 to 13.6% with CRP (Table 4.16).

4.3.3.4 Estimates of plant-available phosphorus in soil

Estimates of plant-available P in the soil to which either superphosphate or CRP was added, were obtained by three chemical-extraction methods, namely bicarbonate, single water and Bray extractions. The increases in bicarbonate-extractable P in the soil at all four sites 5 months after the application of 70 kgP ha^{-1} as superphosphate, was greater ($P < 0.01$) than that from an application of 70 kgP ha^{-1} as CRP (Table 4.11). This apparent difference, however, was not reflected in either clover or pasture production (Fig. 4.3) or in total P uptake (Fig. 4.4) in the first year at any of the four sites. This suggests that the effectiveness of the bicarbonate method as an estimate of plant-available P in the soil is influenced by the P source, at least in the short term. Although removing less P than the bicarbonate method, water extraction also removed far less P from those plots receiving CRP than superphosphate, suggesting that this method, also underestimates the amount of short-term, plant-available P in a soil to which a PR has been added.

With the exception of the results from Ballantrae, which possibly

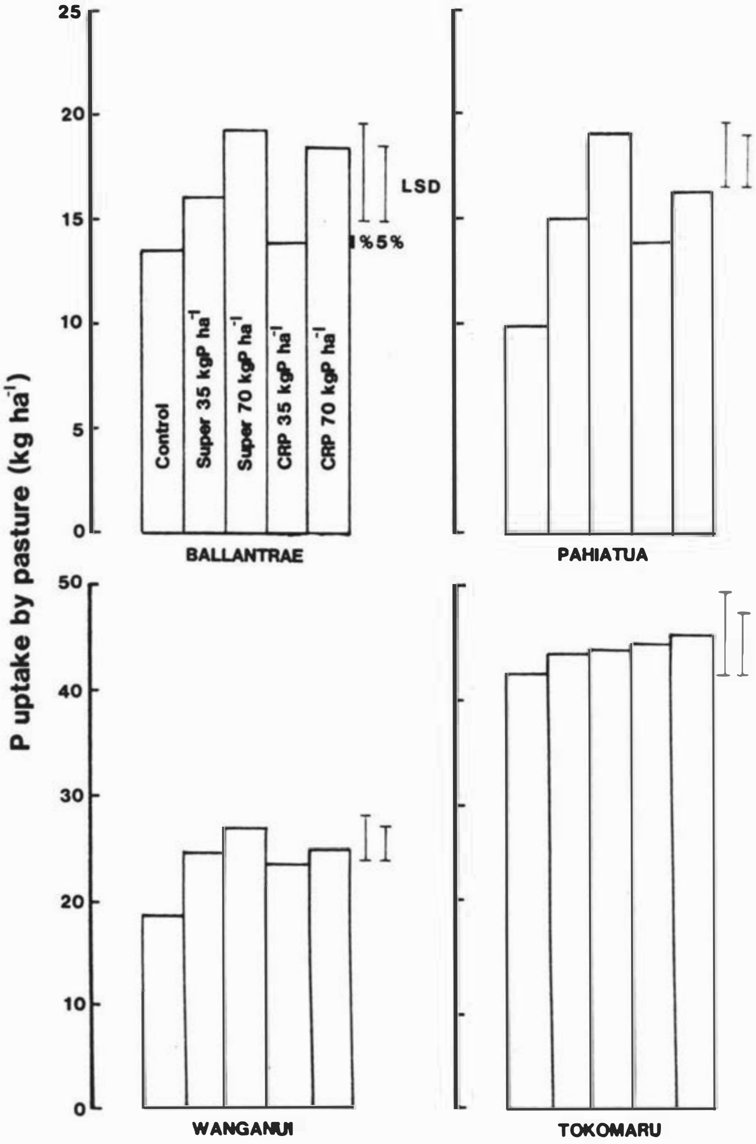

Figure 4.4 Phosphorus uptake by pasture in the first year at the four sites as influenced by phosphate source. Least significant difference (LSD) at the 1% and 5% level.

Table 4.11 Bicarbonate- and Bray-extractable phosphorus in the soil five months after the addition of either superphosphate or Chatham Rise phosphorite (CRP) at the four sites

Treatment	Application rate ($kgP\ ha^{-1}$)	Extractable phosphorus in soil ($\mu g\ g^{-1}$) Ballantrae	Wanganui	Pahiatua	Tokomaru
Bicarbonate					
Control	0	19.8 C	13.6 B	12.6 C	39.8 C
Superphosphate	35	22.3 C	14.7 B	15.5 B	45.5 B
Superphosphate	70	34.1 A	22.3 A	23.0 A	49.6 A
CRP	35	19.5 C	13.9 B	14.2 BC	41.8 C
CRP	70	27.3 B	14.9 B	15.4 B	41.3 C
Bray					
Control	0	26.2 C	13.8 C	8.8 C	41.3 C
Superphosphate	35	30.4 B	16.5 B	12.3 B	45.2 B
Superphosphate	70	39.1 A	26.0 A	18.8 A	55.1 A
CRP	35	30.2 B	16.8 B	13.2 B	44.3 BC
CRP	70	38.4 A	22.4 A	16.6 A	48.3 B

A Significant at 1% level.

reflect the lower pH of the soil at this site, bicarbonate-extractable P levels did not increase as the addition of CRP to soil increased from 35 to 70 kgP ha^{-1} (Table 4.11). In contrast, the Bray method extracted increasing amounts of P as the rate of addition of CRP increased at all four sites (Table 4.11). This difference probably reflects the difference in the pH of the two extractants. Whereas the pH of the Bray reagent is acidic (pH = 2), the pH of the bicarbonate solution is adjusted to 8.5, before use. This would result in a differing ability of these two extractants to dissolve P from any unreacted PR in the soil. The initial difference in bicarbonate-extractable P with the two P sources (Table 4.11). were far less pronounced than those obtained with the Bray method (Table 4.11). This is in line with the yield (Fig. 4.3) and P uptake (Fig. 4.4) data, suggesting that a proportion of the P in the unreacted PR and extracted by the Bray reagent becomes available to the plant, in the short term.

For an initial evaluation of these three extractants, the relationship between P uptake by pasture in the first year (Fig. 4.4) and estimates of plant-available P in soil to which either superphosphate or CRP was added (Table 4.11), was established by linear regression analysis (Table 4.12). Data from the Tokomaru site were not considered in the analysis, because of the small differences found between treatments in the first year (Fig. 4.4, Table 4.11). The slope of the regression lines and intercepts were found to vary, not only with the extraction method and soil type, but also with P source (Table 4.12). With the addition of superphosphate, all three extractants appeared to give a relatively good positive relationship (Table 4.12). In contrast to superphosphate, all three extraction methods, particularly water, gave inconsistent results with CRP (Table 4.12). Results from Ballantrae and Wanganui suggest that, with CRP, soil pH is one factor which affects these relationships, as

Table 4.12 Regression equations and correlation coefficients between phosphorus uptake by pasture in the first year and either Bray-, bicarbonate-, or water-extractable phosphorus in soil five months after the addition of either superphosphate or Chatham Rise phosphorite at the three hill-country sites

Extraction method	Regression equations and correlation coefficients		
	Ballantrae	Wanganui	Pahiatua
Superphosphate			
Bray	$y = 0.27x + 5.00$ $r^2 = 0.555^{**}$	$y = 0.48x + 14.50$ $r^2 = 0.626^{**}$	$y = 0.89x + 4.90$ $r^2 = 0.783^{**}$
Bicarbonate	$y = 0.31x + 7.13$ $r^2 = 0.571^{**}$	$y = 0.54x + 14.43$ $r^2 = 0.555^{**}$	$y = 0.84x + 0.14$ $r^2 = 0.819^{**}$
Water	$y = 0.77x + 3.84$ $r^2 = 0.489^{*}$	$y = 0.87x + 11.59$ $r^2 = 0.681^{**}$	$y = 1.33x + 5.65$ $r^2 = 0.725^{**}$
Chatham Rise phosphorite			
Bray	$y = 0.51x - 2.62$ $r^2 = 0.578^{**}$	$y = 0.16x + 19.63$ $r^2 = 0.081$	$y = 1.44x + 0.12$ $r^2 = 0.892^{**}$
Bicarbonate	$y = 0.38x + 6.35$ $r^2 = 0.384$	$y = 0.19x + 19.22$ $r^2 = 0.164$	$y = 1.82x - 14.5$ $r^2 = 0.693^{**}$
Water	$y = 0.76x + 2.45$ $r^2 = 0.434^{*}$	$y = 22.14 - 0.92x$ $r^2 = - 0.041$	$y = 4.1x - 9.2$ $r^2 = 0.772^{**}$

** Significant at 1% level.

* Significant at 5% level.

indicated by the correlation coefficients (Table 4.12).

By the end of the first year, differences in bicarbonate-extractable P in the soil to which either superphosphate or CRP was added were small (Table 4.13). Whereas bicarbonate-extractable P in the soil to which CRP was added had remained relatively constant from the initial sampling (Table 4.11), with superphosphate it had generally declined (Table 4.13). Differences between the two P sources in terms of both water- and Bray-extractable P were also small.

At the end of the first year, the Wainui silt loam at Ballantrae was showing a large (20%) response to added P. Bicarbonate-extractable P was 20 μg g^{-1} of soil on the control. In contrast, only a small (<10%) response to added P was measured on the Kumeroa silt loam at Wanganui. At this site bicarbonate-extractable P had decreased from 18 at the beginning of the trial to 12 μg g^{-1} of soil at the end of the first year. Interestingly, one of the few differences between the soils at these two sites is soil pH, which has been shown recently by Lambert and Grant (1980) to have a marked effect on the amount of P extracted by the bicarbonate method. These workers found that bicarbonate-extractable P decreased in the soil as pH increased with lime addition. More recent work at Massey University (P. Sorn-Srivichai, pers. comm.) suggests that although bicarbonate-extractable P may decrease on liming, available P, as assessed by plant uptake, is largely unaffected.

4.3.4 Residual effect of Chatham Rise phosphorite

4.3.4.1 Pasture production

Throughout most of the second year at Ballantrae, superphosphate and CRP increased total pasture production to a similar extent (Fig. 4.5). By the end of the second year, a single application at the start of the experiment of 70 kgP ha^{-1} as CRP was producing considerably

Table 4.13 Bicarbonate-extractable phosphorus in the soil at the end of the first year at the four sites as influenced by phosphate source

Treatment	Application rate ($kgP\ ha^{-1}$)	Bicarbonate-extractable phosphorus in soil ($\mu g\ g^{-1}$) Ballantrae	Wanganui	Pahiatua	Tokomaru
Control	0	20.4 Ab	11.7 Ab	10.3 Bc	24.1 Ac
Superphosphate	35	22.2 Ab	12.1 Ab	13.6 ABb	28.5 Ab
	70	25.8 Aa	16.0 Aa	17.8 Aa	35.1 Aa
CRP	35	22.3 Ab	13.4 Aab	13.5 ABb	28.7 Ab
	70	25.7 Aa	14.0 Aab	17.0 Aa	31.3 Ab

A Significant at the 1% level.

a Significant at the 5% level.

more pasture than superphosphate applied as either one application or two annual applications of 35 kgP ha^{-1} (Fig. 4.5). By the third year this difference between superphosphate and CRP was significant ($P < 0.01$) at Ballantrae (Fig. 4.6). The greater residual effect of CRP was also shown when these two P sources were compared at 35 kgP ha^{-1} at this site. In fact a single initial application of 70 kgP ha^{-1} as CRP was producing a similar amount of pasture to superphosphate applied in three annual applications (105 kgP ha^{-1}) in the third year (Fig. 4.6). Although, at the end of the 3 years the comparison favours CRP, results from the last harvest in the third year indicated that both P sources were behaving similarly.

As was the case at Ballantrae, CRP applied at 70 kgP ha^{-1} showed a marked residual effect at Wanganui, outproducing ($P < 0.05$) the equivalent superphosphate treatment in the third year and producing a similar pasture yield to the three annual applications of superphosphate (Fig. 4.6). At Wanganui, this difference between the P sources was not apparent at the lower application rate (Fig. 4.6).

No differences were found between the two P sources at Pahiatua in the second year (Fig. 4.5). The trial at Pahiatua was discontinued after 6 months into the third year, because of poor growth, probably due largely to the greater than normal growth at this site in the first year (Fig. 4.3) which exhausted available P. Until this trial was terminated, no differences were found in the residual effect of these two P sources (Fig. 4.6). This contrasts with the results obtained at both Ballantrae and Wanganui where CRP exhibited a greater residual effect than superphosphate (Fig. 4.6).

At both Ballantrae and Wanganui, the soils have a low P-sorption capacity, whereas at Pahiatua the soil has a high P-sorption capacity. This suggests that at the applications used and with the criteria used

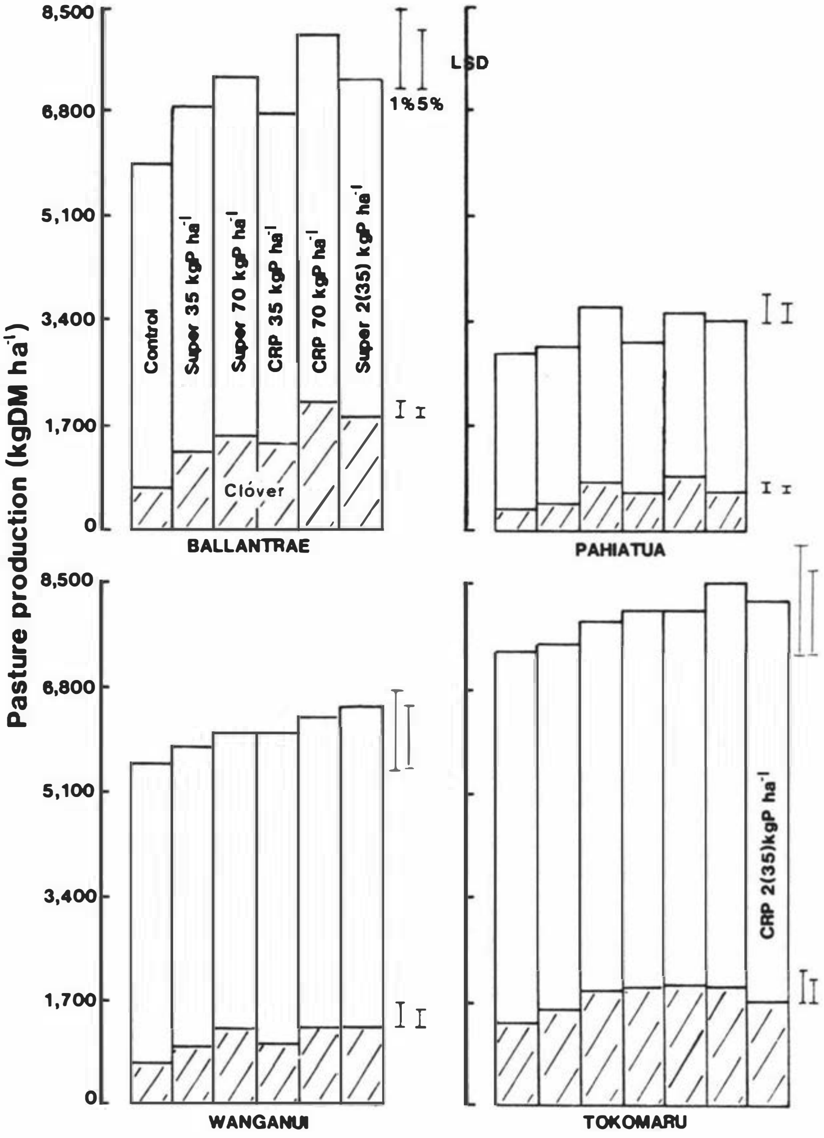

Figure 4.5 Clover and pasture production in the second year at the four sites as influenced by phosphate source. Least significant difference (LSD) at the 1% and 5% level.

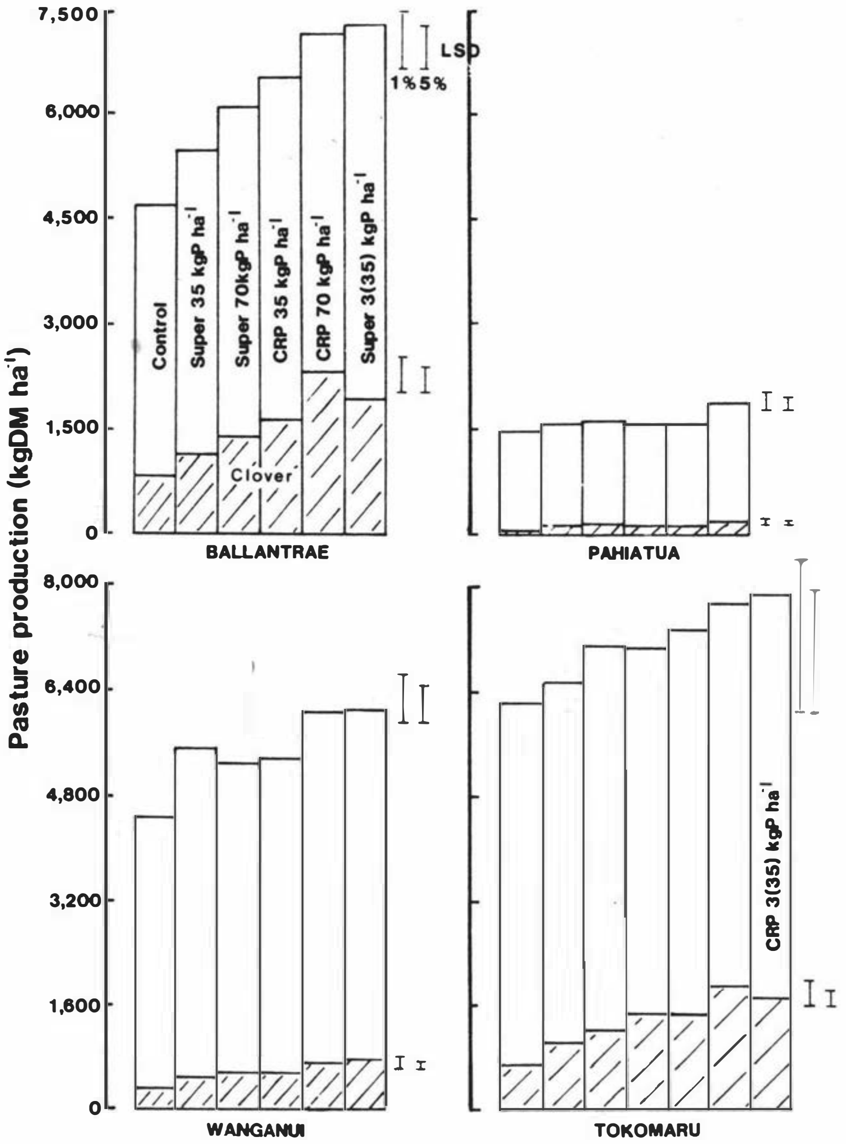

Figure 4.6 Clover and pasture production in the third year at the four sites as influenced by phosphate source. Least significant difference (LSD) at the 1% and 5% level.

to separate initial and residual effects, the residual effect of CRP is dependent on soil type.

An overall P response was not measured at Tokomaru in either the second (Fig. 4.5) or third (Fig. 4.6) year, but P responses ($P < 0.05$) were measured in the last two harvests of both the second and third years. No differences were found between the two P sources in these harvests. The small P responses measured at this site highlight the difficulties involved in evaluating P sources on soils of relatively high P status. The harvesting technique of mowing with clippings removed was used instead of mowing with clippings returned in an attempt to increase the P responsiveness of the site. This latter technique is probably more applicable at this site (Elliot and Lynch, 1958).

4.3.4.2 Botanical composition of the sward and clover production

By the second year, differences in clover vigour and content between those plots receiving P fertilizer, particularly at the highest rate of application, and those receiving no added P, were visible at all trial sites, including Tokomaru. Differences in the clover content of the sward, averaged from the spring and summer harvest at all four sites, in the second (Table 4.14), and third (Table 4.14) years, illustrate the effect of both the form and amount of added P. It is during this period that the bulk of clover growth occurs (see 4.3.1.2). Although CRP was more effective ($P < 0.01$) at 70 kgP ha^{-1} than superphosphate at Ballantrae, in general both P sources increased the clover content of the swards to a similar extent at all sites (Fig. 4.14) in the second year. By the third year, the effectiveness of the single initial application of 70 kgP ha^{-1} as CRP was more effective ($P < 0.01$) at three of the four field-trial sites (Table 4.14).

Table 4.14 Average clover content of the sward in the spring and summer harvests of the second and third years at the four sites as influenced by phosphate source

Treatment	Application rate (kgP ha^{-1})	Clover content of the sward (%)			
		Ballantrae	Wangaui	Pahiatua	Tokomaru
Second year					
Control	0	12 Cc	13 Cc	12 Cc	15 Bb
Superphosphate	35	22 Bb	17 Bb	18 Bb	21 Aa
Superphosphate	70	24 Bb	21 Aa	23 Aa	24 Aa
Superphosphate	2(35)*	28 Aa	20 Aa	20 Bb	23 Aa
CRP	35	24 Bb	17 Bb	20 Bb	23 Aa
CRP	70	29 Aa	20 Aa	24 Aa	25 Aa
CRP	2(35)				23 Aa
Third year					
Control	0	16 D	8 C	5 Aa	16 Dd
Superphosphate	35	20 CD	10 C	7 Aa	23 Cc
Superphosphate	70	22 BC	9 C	8 Aa	23 Cc
Superphosphate	3(35)	25 B	16 A	9 Aa	30 Aa
CRP	35	24 BC	11 BC	6 Aa	27 Bb
CRP	70	31 A	14 AB	9 Aa	26 Bb
CRP	3(35)				30 Aa

A Significant at the 1% level. a Significant at the 5% level. * Annual application of 35 kgP ha^{-1}.

The difference observed in the clover content of the swards was also reflected in total clover production in both the second (Fig. 4.5) and third (Fig. 4.6) years. Whereas both P sources produced similar yields at Wanganui, Pahiatua, and Tokomaru in the second year, at Ballantrae clover growth from the addition of 70 kgP ha^{-1} as CRP was greater ($P < 0.01$) than from the equivalent superphosphate treatment.

In the third year, CRP was showing a marked residual effect at both Ballantrae and Wanganui, outproducing superphosphate at 70 kgP ha^{-1} and maintaining a similar level of clover production to superphosphate applied at 35 kgP ha^{-1} in each of the 3 years (Fig. 4.6). This suggests that a single application of CRP was sustaining a sufficiently high concentration of P in the soil solution to give near maximum clover growth at both these sites for the 3 years.

The differences found in N uptake by the sward in both the second (Table 4.15) and third (Table 4.15) years between those plots receiving 70 kgP ha^{-1} and those receiving no added P at the three hill-country sites are again of a similar magnitude to those measured by Grant and Lambert (1979), where N fixation was found to be roughly proportional to clover growth. This measurement, however, probably underestimates the total amount of N fixed by the clover component. The long intervals between harvests, particularly at the hill-country sites, probably allow some recycling within the sward and the contribution of N from above-ground clover parts below the cutting height, and from under ground parts (nodules); these were not measured in the present study.

Surprisingly, the marked increases measured in the clover content of the swards and expressed in increased clover production, were not subsequently measured in increased production from the grass component of the sward, particularly in the third year. This may reflect the harvesting technique used, which largely eliminates the above-ground

Table 4.15 Nitrogen uptake by pasture in the second and third year at the three hill-country sites as influenced by phosphate source

		Nitrogen uptake by pasture		
Treatment	Application rate (kgP ha^{-1})	Ballantrae	Wanganui (kg ha^{-1})	Pahiatua
Second year				
Control	0	153 C	120 B	65 B
Superphosphate	70	212 AB	156 A	88 A
CRP	70	227 A	161 A	87 A
Superphosphate	2(35)*	208 B	150 A	82 A
Third year				
Control	0	140 C	80 C	30 C
Superphosphate	70	185 B	94 B	52 B
CRP	70	230 A	112 A	53 B
Superphosphate	3(35)	208 B	123 A	64 A

A Significant at the 1% level.

* Annual application of 35 kgP ha^{-1}.

recycling of nutrients, particularly N. The exhaustive nature of this technique was reflected in a general decline in the vigour of the swards at all sites, during the 3 years of the study, particularly in the third years.

In addition to the loss of biologically-fixed N in clippings, further losses of the remaining N by immobilization into the soil organic fraction, may have led to further reductions in the transfer of N to the grass component. The topsoils at two of the hill-country sites, Ballantrae and Pahiatua, were characterised by the presence of an organic mat. Walker et al. (1959) found that the ratio of C to N in the topsoil organic matter of a central North Island site, decreased, from 33:1 to 11:1 over 25 years following pasture development from scrub, with soil N accumulation occurring at an average annual rate of 110 kgN ha^{-1}. Therefore until the C:N ratio of the organic matter in the topsoil is near the desired level, approximately 10:1, only small annual increases in pasture production (i.e., grass production) may be expected (Suckling, 1975).

4.3.4.3 Phosphorus concentration in pasture and phosphorus uptake by pasture

As with the clover content of the sward, the P concentration in the pasture proved to be a sensitive indicator of the changes in plant-available P from these two P sources in the second and third years. Changes in the P concentration following the addition of superphosphate and CRP at 70 kgP ha^{-1}, and superphosphate in three annual applications of 35 kgP ha^{-1} at the hill-country sites over the 3 years (Fig. 4.7) reflected closely the changes in the clover content of the sward (Table 4.14) and clover production (Fig. 4.5; Fig. 4.6). For completeness, the P concentration in the pasture in the first year are included in each Figure.

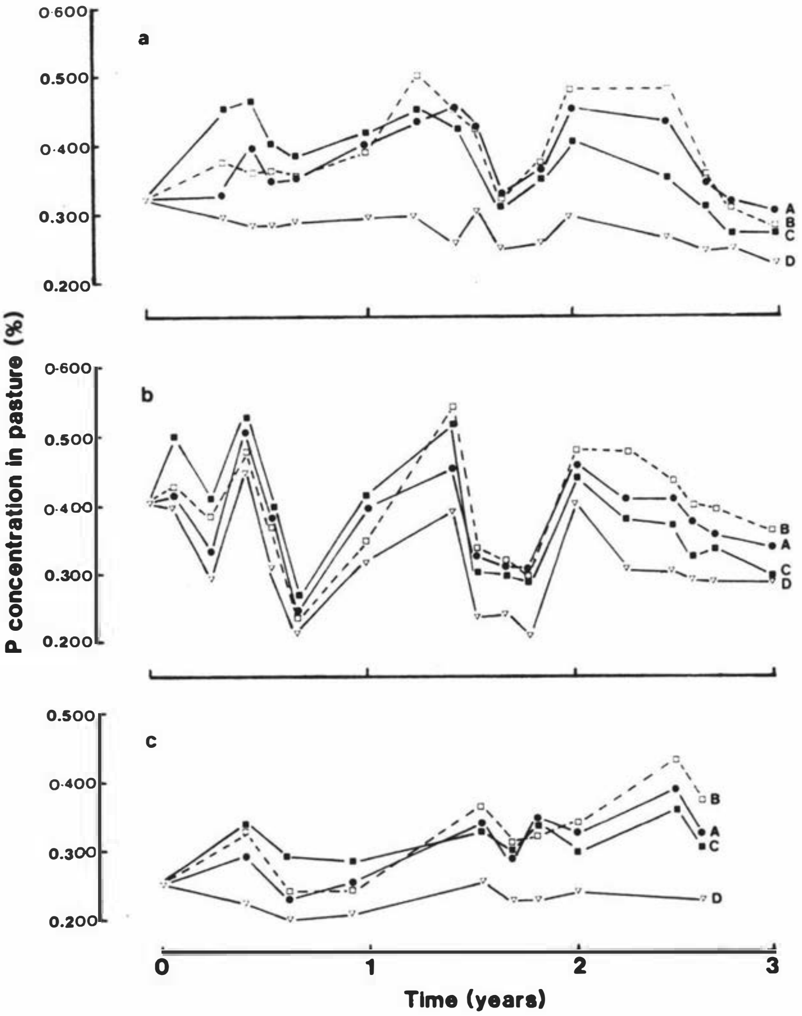

Figure 4.7 Changes in the phosphorus concentration in pasture over three years at the three hill-country sites as influenced by phosphate source. A = single initial application of 70 kgP ha^{-1} as Chatham Rise phosphorite, B = annual application of 35 kgP ha^{-1} as superphosphate, C = single initial application of 70 kgP ha^{-1} as superphosphate, and D = control. a = Ballantrae, b = Wanganui, and c = Pahiatua.

By the end of the first year, the differences in concentration in the sward with the two P sources was small at all three hill-country sites (Fig. 4.7). By the end of the second and throughout the third year, CRP was giving a higher P concentration in the sward than superphosphate at both Ballantrae (Fig. 4.7a) and Wanganui (Fig. 4.7b). In fact at Ballantrae (Fig. 4.7a), CRP was giving a similar P concentration to superphosphate applied in three annual applications, providing further evidence that a single application of CRP was able to maintain the concentration of P in the soil solution at a sufficiently high level for near maximum pasture production at this site over 3 years.

The increases in P concentrations in the pasture at Tokomaru were relatively small (Fig. 4.8a) and no differences were found between the two P sources when added as a single initial application in either the second or third years. In contrast to the first year P concentration data (Table 4.10), an annual application of 35 kgP ha^{-1} as CRP gave a similar P concentration in the sward as an annual application of 35 kgP ha^{-1} as superphosphate in the second and third years at Tokomaru (Fig. 4.8b). This suggests that the initial difference found between CRP and superphosphate may reflect, in part, past fertilizer history of the site, which until the commencement of the present trial had received only annual applications of superphosphate.

The grass and clover components of the swards in all four trials were sampled periodically over the 3 years, to monitor the concentration of essential macro- and micro-nutrients in the herbage. Apart from P and N, the concentrations of nutrients were more than adequate for maximum pasture growth. An exception, was one sampling at Wanganui during the dry summer of the second year, where Mo concentrations in clover were found to be relatively low (0.20 - 0.40 μgMo g^{-1}). With the basal application of Mo (250g ha^{-1} 0.5 yr^{-1}) at Wanganui, coupled with relatively

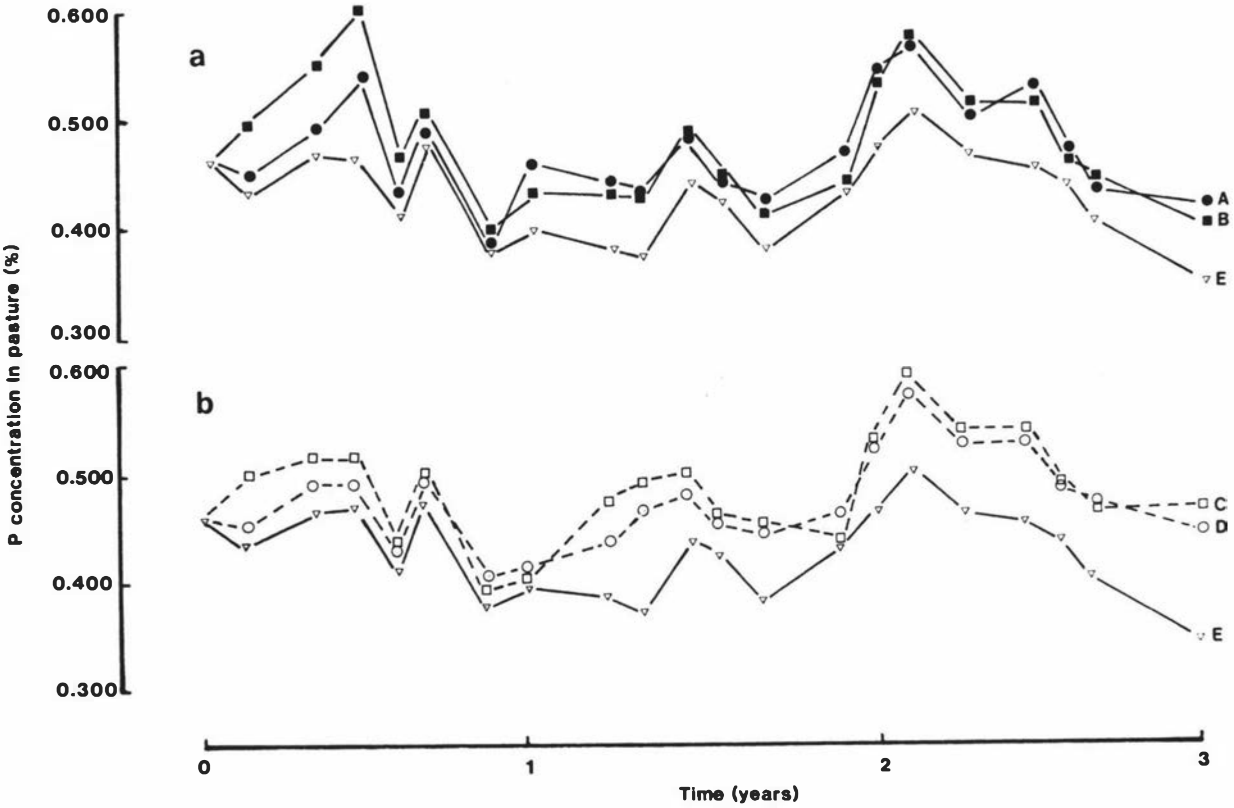

Figure 4.8 Changes in the phosphorus concentration in pasture over three years at Tokomaru as influenced by phosphate source. A = single initial application of 70 kgP ha^{-1} as Chatham Rise phosphorite, B = single initial application of 70 kgP ha^{-1} as superphosphate, C = annual application of 35 kgP ha^{-1} as superphosphate, D = annual application of 35 kgP ha^{-1} as Chatham Rise phosphorite, and E = control. a = single initial application of 70 kgP ha^{-1}, and b = annual application of 35 kgP ha^{-1}.

high pH (6.2) of this site, the low Mo concentration in the clover is rather surprising. Dry summer conditions may have provided an atypical sample for analysis.

No difference in total P uptake by the pasture was found between superphosphate and CRP applied at either 35 or 70 kgP ha^{-1}, as was the case for clover and pasture production (Fig. 4.5) in the second year at each of the four sites (Fig. 4.9). At Ballantrae and Wanganui, P uptake data suggest that CRP was supplying more P to the sward than superphosphate. These differences were significant ($P < 0.01$) in the third year when the two P sources were compared at 70 kgP ha^{-1} (Fig. 4.10). In fact, a single application of CRP at 70 kgP ha^{-1} increased P uptake in the third year at both Ballantrae and Wanganui to a similar extent to superphosphate applied in three annual applications (Fig. 4.10).

In contrast, no difference was found in the residual effect of CRP and superphosphate in either the second (Fig. 4.9) or third (Fig. 4.10) year at Pahiatua, using P uptake data as the basis for comparison. This provides further evidence to suggest that at the application rates used, the residual effect of CRP is dependent on soil type.

Data for apparent P recovery by pasture over 3 years further suggest that there is no difference in the long-term effectiveness of superphosphate and CRP on the high P-sorbing soil at Pahiatua (Table 4.16). At the other three sites, the apparent recovery of added P by pasture from CRP was greater than that from superphosphate at both rates of application (Table 4.16). This was particularly pronounced in the third year. The high apparent recovery of added P from CRP by the pasture at Tokomaru further supports the view that CPR is an effective P source on a soil of relatively high P status, even when applied annually.

The apparent recovery of P added as MCP was greater than that added as superphosphate (Table 4.16), particularly in the third year, even though

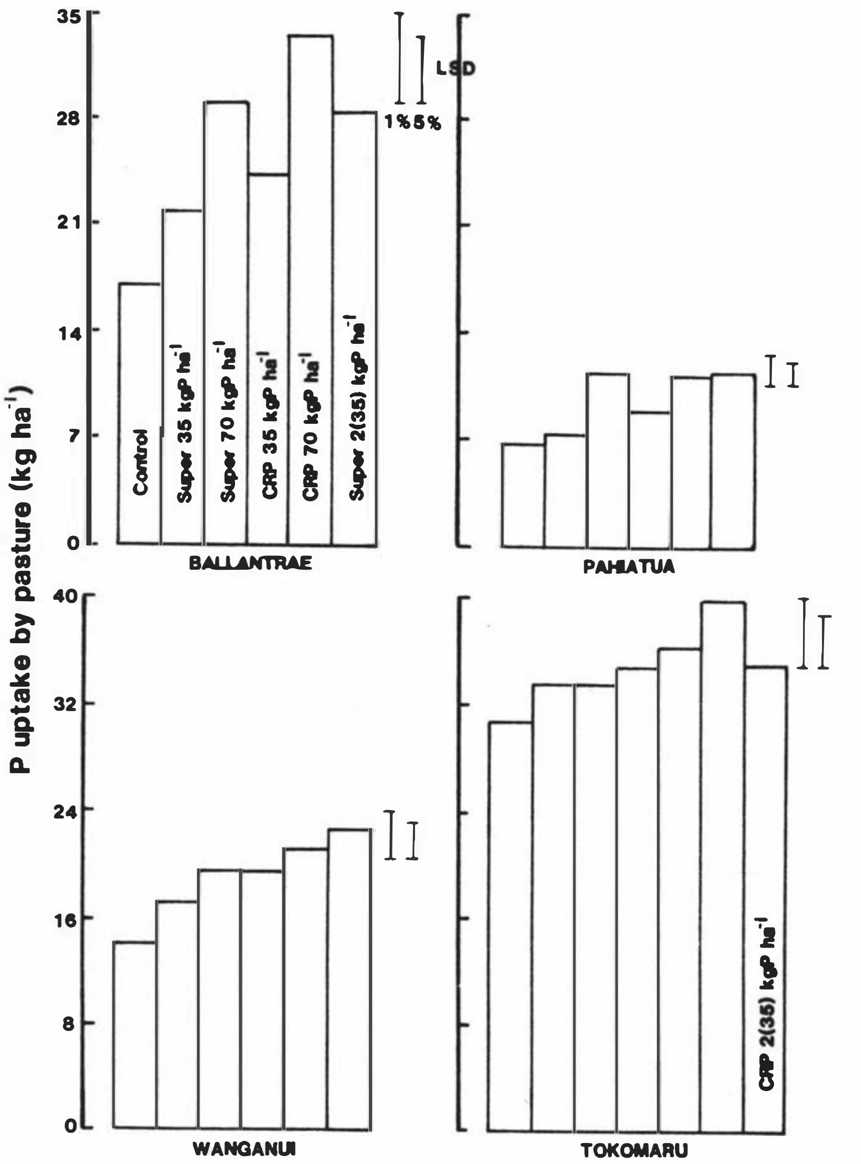

Figure 4.9 Phosphorus uptake by pasture in the second year at the four sites as influenced by phosphate source. Least significant difference (LSD) at the 1% and 5% level.

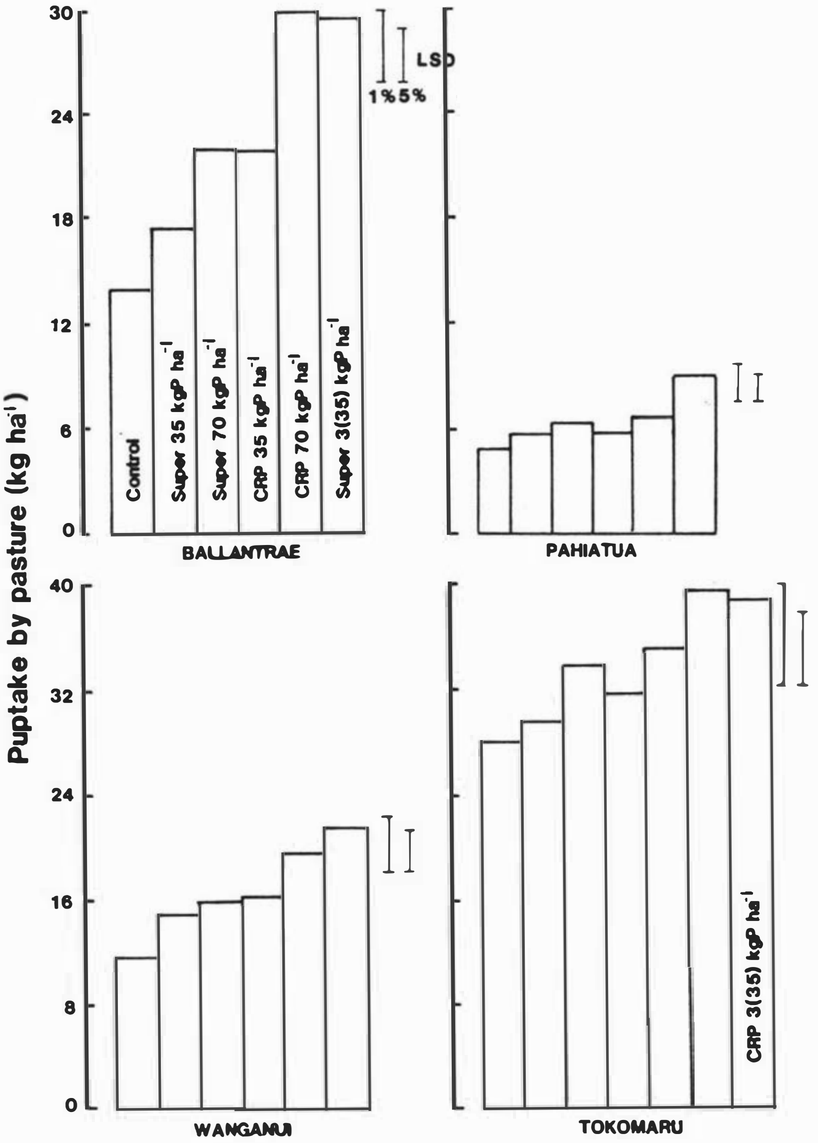

Figure 4.10 Phosphorus uptake by pasture in the third year at the four sites as influenced by phosphate source. Least significant difference (LSD) at the 1% and 5% level.

Table 4.16 Apparent recovery of phosphorus by pasture over two and a half years at Pahiatua and three years at Ballantrae, Wanganui, and Tokomaru as influenced by phosphate source

Treatment	Application rate (kgP ha^{-1})	Apparent recovery of phosphorus by pasture at															
		Ballantrae				Wanganui				Pahiatua				Tokomaru			
		1st	2nd	3rd	Total*	1st	2nd	3rd	Total	1st	2nd	3rd	Total	1st	2nd	3rd	Total
		(% of total P added)															
Superphosphate	35	7.0	14.6	8.2	29.8	14.9	8.7	9.6	33.2	14.2	3.2	1.8	19.2	6.0	8.0	4.4	18.4
CRP, powdered	35	9.0	23.3	18.6	50.9	12.4	13.5	13.0	38.9	9.3	6.5	1.3	17.1				
CRP, pelletised	35	2.9	21.1	17.5	41.5	12.6	14.7	13.8	41.1	11.3	5.9	2.3	19.5	8.6	11.9	10.4	30.9
MCP	35	22.0	18.0	3.4	43.4	22.6	12.6	8.2	43.4	19.3	3.0	0.8	23.1	11.9	17.4	6.3	35.6
Superphosphate	70	16.0	9.3	9.5	34.8	11.3	11.3	6.3	25.0	12.8	6.4	1.8	21.0	3.8	4.0	8.2	16.0
CRP, pelletised	70	13.6	16.0	19.4	49.0	8.4	8.4	11.4	29.7	8.9	6.2	2.1	17.2	5.6	8.1	10.1	23.8
Superphosphate	3(35)†				26.0				18.7				12.3				19.8
CRP pelletised	3(35)																17.2

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* Total P uptake for 3 years.

† Annual application of 35 kgP ha^{-1}.

in the absence of added S, the response to added P was not as pronounced (see 4.3.1). This difference between superphosphate and MCP may reflect the difference in the water solubility of these two P sources (Table 4.3). In contrast, the apparent recovery of added P by pasture over 3 years from MCP and CRP was very similar, although agronomically these two P sources behaved very differently, as shown by P uptake by pasture in the first and third years (Table 4.16).

4.3.4.4 Extractable phosphorus in soil

With the exception of some seasonal changes, bicarbonate- (Fig. 4.11, 4.12), water-, and Bray-extractable P in the soil continued to decline on the controls at all trial sites. This reflects, in part, the exhaustive nature of the technique of mowing with clippings removed.

By the end of the third year, the trials at the Wanganui and Ballantrae sites were showing a 25 and >40%, respectively, response to freshly-applied P with values for bicarbonate-extractable P on controls being 8 and 14 μgP g^{-1} of soil, respectively (Fig. 4.11). Although the responsiveness of the Wanganui site had increased from the first year, this apparent difference in the responsiveness of these two sites, is consistent with the observation that although bicarbonate-extractable P decreases on liming, the amount of plant-available P in the soil is largely unaffected.

Soil pH remained relatively constant at all sites over the 3 years. The application of 2.5 tonnes of lime at Wanganui maintained the soil pH above 6 throughout the 3 years, with the highest pH (6.35) being measured at the beginning of the second year. By the third year of this trial, soil pH was uniform (6.0 to 6.1) throughout the top (0 to 7.5cm) soil, indicating that the effect of the applied lime had not been restricted to the immediate surface (0 to 2cm) layer.

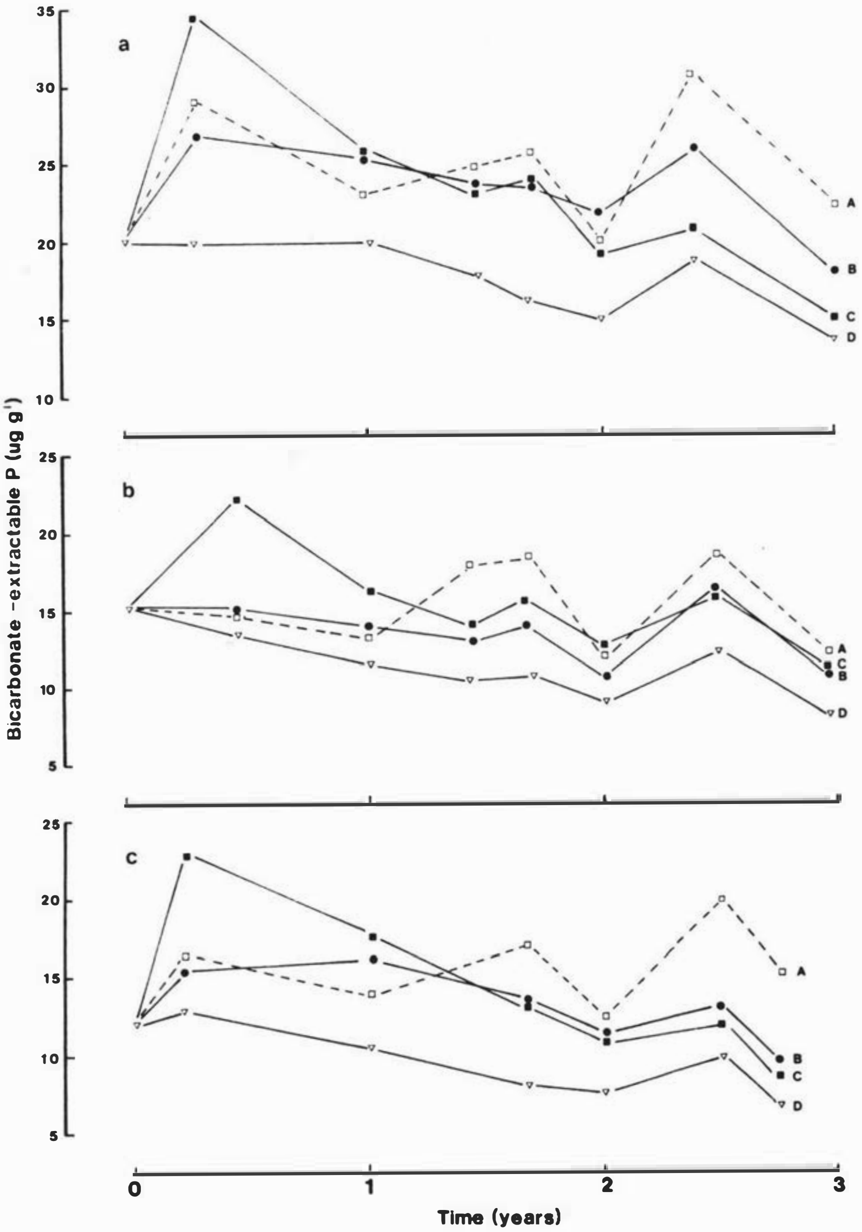


Figure 4.11 Changes in bicarbonate-extractable phosphorus in soil over the three years at the three hill-country sites as influenced by phosphate source. A = annual application of 35 kgP ha^{-1} as superphosphate, B = single initial application of 70 kgP ha^{-1} as Chatham Rise phosphorite, C = single initial application of 70 kgP ha^{-1} as superphosphate, and D = control. a = Ballantrae, b = Wanganui, and c = Pahiatua.

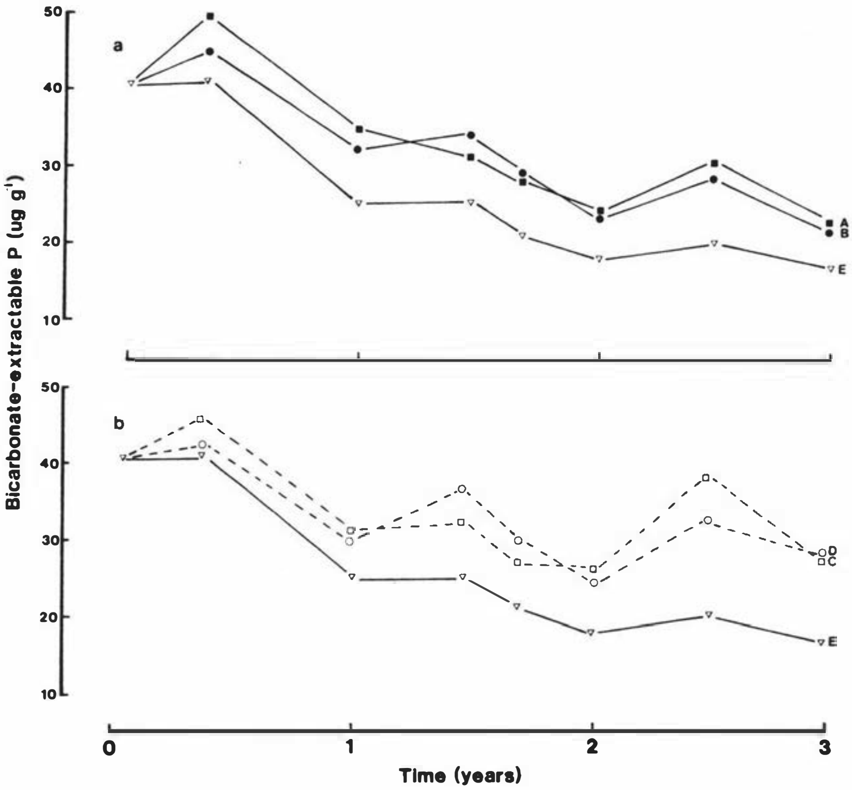


Figure 4.12 Changes in bicarbonate-extractable phosphorus in soil over the three years at Tokomaru as influenced by phosphate source. A = single initial application of 70 kgP ha^{-1} as superphosphate, B = single initial application of 70 kgP ha^{-1} as Chatham Rise phosphorite, C = annual application of 35 kgP ha^{-1} as superphosphate, D = annual application of 35 kgP ha^{-1} as Chatham Rise phosphorite, E = control. a = single initial application of 70 kgP ha^{-1}, and b = annual application of 35 kgP ha^{-1}.

Both the bicarbonate- (Fig. 4.11a) and Bray-extraction methods reflected the increased amounts of available P in the soil derived from CRP, compared to superphosphate, by the end of the second year and throughout the third year at Ballantrae. In contrast, the difference found in the residual effect of these two P sources at Wanganui was not reflected by either of these extractants (Fig. 4.11b). On the other hand, Bray-extractable P values indicated well the increased effectiveness of CRP, not only at Ballantrae but also at Wanganui in the third year. However, this difference at Wanganui was not as marked as it was at Ballantrae, suggesting that the Bray method may also be affected by the pH of the soil at this site. The Bray method, however, appears to be less sensitive to soil pH than the bicarbonate method.

The differing effect of P source on the relationship between P uptake by pasture and the amounts of plant-available P estimated by the three extractants, in both the second (Table 4.17) and third (Table 4.18) years, again justifies the evaluation of these three extractants, separately, as methods for estimating plant-available P with soils to which the two P sources were added.

The difference in the regression equations obtained with each P source decreased at all sites over the 3 years (Tables 4.12, 4.17, 4.18), suggesting that in the longer term, the mechanisms controlling plant-available P derived from the two P sources in soils are similar. Consequently, in the longer term, the effectiveness of these three extractants as estimates of plant-available P in the soil may be less dependent on P source.

The apparent recovery by pasture of P added as either superphosphate or CRP indicates that even at the highly P-responsive Ballantrae site, only about 50% of the total P added, was recovered during 3 years (Table 4.16). Although the apparent recovery of added P at Pahiatua,

Table 4.17 Regression equations and correlation coefficients between phosphorus uptake by pasture in the second year and either Bray-, bicarbonate-, or water-extractable phosphorus in the soil at the beginning of the second year to which either superphosphate or Chatham Rise phosphorite was added as a single application in the first year

	Regression equations and correlation coefficients			
Extraction method	Ballantrae	Wanganui	Pahiatua	Tokomaru
Superphosphate				
Bray	$y = 0.71x + 6.54$ $r^2 = 581^{**}$	$y = 0.83x + 7.93$ $r^2 = 0.686^{**}$	$y = 0.47x + 5.02$ $r^2 = 0.575^{**}$	$y = 0.37x + 32.69$ $r^2 = 0.056$
Bicarbonate	$y = 1.12x - 2.94$ $r^2 = 0.525^{*}$	$y = 0.24x + 14.75$ $r^2 = 0.188$	$y = 0.42x + 3.05$ $r^2 = 0.646^{**}$	$y = 0.29x + 26.97$ $r^2 = 0.270$
Water	$y = 2.53x - 10.37$ $r^2 = 0.844^{**}$	$y = 0.34x + 14.22$ $r^2 = 0.210$	$y = 0.60x + 5.06$ $r^2 = 0.547^{**}$	$y = 0.44x + 25.96$ $r^2 = 0.279$
Chatham Rise phosphorite				
Bray	$y = 0.93x + 2.66$ $r^2 = 0.639^{**}$	$y = 1.07x + 5.94$ $r^2 = 0.583^{**}$	$y = 0.74x + 2.97$ $r^2 = 0.641^{**}$	$y = 0.16x + 29.00$ $r^2 = 0.236$
Bicarbonate	$y = 0.96x + 1.07$ $r^2 = 0.458^{*}$	$y = 0.75x + 8.63$ $r^2 = 0.395$	$y = 0.43x + 2.57$ $r^2 = 0.754^{**}$	$y = 0.24x + 26.57$ $r^2 = 0.309$
Water	$y = 1.33x + 3.88$ $r^2 = 0.628^{**}$	$y = 0.98x + 7.27$ $r^2 = 0.558^{**}$	$y = 0.67x + 3.95$ $r^2 = 0.731^{**}$	$y = 0.49x + 25.37$ $r^2 = 0.318$

** Significant at 1% level.

* Significant at 5% level.

Table 4.18 Regression equations and correlation coefficients between phosphorus uptake by pasture in the third year and either Bray-, bicarbonate-, or water-extractable phosphorus in the soil at the beginning of the third year to which either superphosphate or Chatham Rise phosphorite was added as a single application in the first year

	Regression equations and correlation coefficients			
Extraction method	Ballantrae	Wanganui	Pahiatua	Tokomaru
Superphosphate				
Bray	$y = 0.76x + 4.02$ $r^2 = 0.672$**	$y = 1.1x + 4.90$ $r^2 = 0.799$**	$y = 1.26x + 0.75$ $r^2 = 0.908$**	$y = 0.69x + 16.76$ $r^2 = 0.496$*
Bicarbonate	$y = 0.77x + 2.86$ $r^2 = 0.519$*	$y = 1.03x + 4.98$ $r^2 = 0.593$**	$y = 0.73x - 0.69$ $r^2 = 0.805$**	$y = 0.46x + 21.79$ $r^2 = 0.368$
Water	$y = 0.94x + 7.21$ $r^2 = 0.419$*	$y = 1.67x + 3.51$ $r^2 = 0.737$**	$y = 1.21x + 2.69$ $r^2 = 0.374$	$y = 1.52x + 16.60$ $r^2 = 0.511$
Chatham Rise phosphorite				
Bray	$y = 0.86x + 3.05$ $r^2 = 0.739$**	$y = 1.08x + 5.40$ $r^2 = 0.651$**	$y = 0.35x + 3.23$ $r^2 = 0.572$**	$y = 0.59x + 18.99$ $r^2 = 0.584$**
Bicarbonate	$y = 1.32x - 5.64$ $r^2 = 0.754$**	$y = 1.27x + 3.18$ $r^2 = 0.523$*	$y = 0.31x + 1.74$ $r^2 = 0.683$**	$y = 0.39x + 23.99$ $r^2 = 0.364$
Water	$y = 0.54x + 11.60$ $r^2 = 0.194$	$y = 1.21x + 6.77$ $r^2 = 0.511$*	$y = 0.46x + 3.45$ $r^2 = 0.460$*	$y = 1.37x + 18.17$ $r^2 = 0.584$

** Significant at 1% level.

* Significant at 5% level.

(undeveloped), Ballantrae (moderately developed), and Wanganui (moderately to well developed), is high compared with much of the published literature for pasture swards during development (During, 1972), a relatively low recovery of added P (Karlovsky, 1966, 1975) was obtained at Tokomaru, which is a well-developed pasture near maintenance.

Because apatite minerals are insoluble in dilute NaOH and because this reagent extracts sorbed inorganic P (Williams et al., 1967), increases in the NaOH-extractable P fraction of a soil to which a PR has been added should provide a good estimate of the amount of P dissolved and retained in the soil inorganic P fraction on sorption sites (Chapter 7.2.4). However, because inorganic P can diffuse into short-range order hydrous ferric oxides in soil, leading to a progressive decrease in NaOH-extractable P with time (Ryden et al., 1977), the latter value represents a minimum for the amount of P added as PR which has dissolved in the soil but not yet been taken up by the plant. Similarly, NaOH extraction should provide a reasonable estimate of the P added as superphosphate which has dissolved and been retained on sorption sites accessible to NaOH.

By combining the amount of NaOH-extractable P with the P recovered by pasture (Table 4.16) an indication of the total P added as either CRP or superphosphate which has dissolved can be calculated. Conversely, an estimate of the P added which has yet to dissolve can be calculated by difference. This does not include any dissolved P which is immobilized as soil organic P. In the calculations given in Table 4.19 it was assumed that P added as either superphosphate or CRP reacted and remained in the top (4cm) soil. Of the total P added as superphosphate, 44 and 46% was recovered by NaOH extraction plus pasture, at Ballantrae and Wanganui, respectively, while 62% of total P added as CRP was recovered at Ballantrae, and 54% at Wanganui (Table 4.19).

On both the Wainui (Ballantrae) and Kumeroa (Wanganui) soils a far greater proportion of the total P added was recovered by pasture than by NaOH extraction (Table 4.19). Of the P added as CRP at Ballantrae and Wanganui, and recovered by either the sward or by NaOH extraction, only 23 and 46%, respectively, was recovered in the soil at the end of the third year. Although nearly 50% of the total P added as CRP was recovered in these two fractions at Pahiatua, a far greater proportion (65%) P was recovered by NaOH extraction, demonstrating the dominating effect that sorption reactions have on added P in this soil. These results demonstrate that, although dissolution of P from a PR is a prerequisite for P uptake by plants, an increase in the rate of dissolution does not necessarily imply an increase in the amount of plant-available P from the PR. A far greater proportion of the total P added as superphosphate and recovered was also in the soil inorganic P fraction at Pahiatua (Table 4.19), suggesting that in the longer-term the mechanisms controlling plant-available P from these two P sources are similar, at least on a high P-sorbing soil. The recovery of over 40% of the total P added as CRP by NaOH extraction and by the pasture at Tokomaru (Table 4.19) indicates that the dissolution of CRP was largely unaffected by the relatively high P status of the soil at this site.

4.3.5 Effectiveness of superphosphate and Chatham Rise phosphorite as phosphatic fertilizers

In the present study CRP showed considerable potential as a P fertilizer at all sites and showed a marked residual effect at two of the three hill-country sites. A comparison of P fertilizers based on differences in the apparent recovery of P by the pasture provides an initial evaluation of effectiveness. An evaluation of the potential

Table 4.19 Recovery of phosphorus by 0.5M NaOH at the end of the third year and apparent recovery of phosphorus by pasture during the two and a half years at Pahiatua and three years at Ballantrae, Wanganui and Tokomaru as influenced by phosphate source

	Estimate of dissolved fertilizer phosphorus			
	Ballantrae	Wanganui	Pahiatua	Tokomaru
	(μg g^{-1})			
Superphosphate				
Total P added	700	700	700	700
Recovery by sward	245 (35)*	175 (25)	147 (21)	112 (16)
Extracted by NaOH	64 (9)	150 (21)	206 (29)	140 (20)
Total recovered	309 (44)	325 (46)	353 (50)	252 (36)
Chatham Rise phosphorite				
Total P added	700	700	700	700
Recovery by sward	336 (48)	203 (29)	119 (17)	168 (24)
Extracted by NaOH	96 (14)	175 (25)	220 (31)	140 (20)
Total recovered	432 (62)	378 (54)	337 (48)	308 (44)

* Percentage of added phosphorus.

losses from the above-ground components of a grazed sward, however, offers a useful method for comparing the effectiveness of the two P fertilizers as sources of P by enabling an evaluation of the losses and recycled components of the sward.

Although the greatest proportion of total P in the P cycle of a grazed pasture is contained in the soil, at any one time it is the above-ground components of the P cycle that show the greatest scope for manipulation. Consequently, changes in the above-ground components have the greatest effect, not only on the efficiency of the P cycle (Karlovsky, 1975), but also on the efficiency of applied P. To compare the efficiency of superphosphate and CRP as P fertilizers in grazed hill country, the results from the present study are evaluated by using the P cycle constructed by Gillingham (1978).

In the P cycle of Gillingham (1978), measurements were made of P uptake by pasture and P returned in pasture litter and dung for differing paddock strata on two intensively-grazed, north- and south-facing paddocks in steep hill country soils of moderate to high P status. A net P balance was derived for each of the three paddock strata. Gillingham (1978) found a large net annual gain of P on easy slopes, including campsites (50 and 120 kgP ha^{-1} on North and South aspects, respectively), which was more than sufficient for annual pasture requirements. A considerable net P loss occurred from both 25^{o} slopes (20 and 10 kgP ha^{-1} on North and South aspects, respectively) and 45^{o} slopes (15 and 14 kgP ha^{-1} on North and South aspects, respectively). This net loss of P from slopes was equivalent to 29 - 71% of the annual P uptake by pasture at these sites.

Gillingham (1978) suggested that the significant transfer of P from slopes by the grazing anumal may explain the slow rate of pasture improvement noted in many hill-country situations (During, 1972; Brougham et al., 1973). Although subdivision offers a method for reducing the losses of P by transfer to campsites and selective topdressing can assist in reducing the total requirements for P by avoiding campsite areas (Mauger, 1977), both these options are of only limited practical value, as the topography of hill country is often quite variable over short distances.

Using a mathematical model based on field data from the north-facing paddock and validated against results from the south-facing paddock, Gillingham (1978) predicted that the quantity of P transfer from slopes was directly related to the P concentration in the pasture. In fact, using this model, Gillingham (1978) calculated that a decrease in the average P concentration from 0.45 to 0.35% would result in a direct reduction of 22% in the net P balance of each strata over one year. Therefore P concentrations which are higher than those required for optimum pasture production and animal requirements will result in unnecessarily high losses of P by transfer from slopes. The net effect is a reduction in the efficiency of applied P. As the P concentration in the sward is directly influenced not only by the rate of application of P (Table 4.10) but also, and of greatest interest here, by the source of P (Fig. 4.8), there appears to be scope for reducing the losses of P by transfer to campsites and thus increasing the efficiency of applied P.

In the present study the addition of increasing amounts of superphosphate in the initial harvest of the first year gave increasing P concentrations in the sward at all three hill-country sites (Table 4.10). These initial increases were not reflected in increased pasture production (see 4.3.3.1). In contrast, the addition of increasing amounts of CRP did not lead to increasing P concentrations in the sward in initial harvests of the first year (Table 4.10), although it did sustain a similar level of pasture production to superphosphate (see 4.3.3.1). To illustrate these differences in the P concentrations of the sward, resulting from the use of CRP and superphosphate under a single and annual topdressing strategy, the results from Ballantrae are reproduced in Fig. 4.13. The magnitude of any reductions in the annual losses of P by transfer from using CRP will be dependent on the level of pasture production during the period.

A large proportion of pasture production in hill country occurs in the Spring and Summer (see 4.3.1.1; Suckling, 1959, 1975), rather than during the Autumn and Winter when differences in P uptake by the pasture from superphosphate and CRP were found to be greatest. Consequently, even under optimal growth rate conditions in Autumn and Winter, the potential reductions in the annual losses of P by transfer from using CRP, in an Autumn topdressing strategy, would be small. Using the mathematical model of Gillingham (1978), the reduction in P losses, by transfer, at Ballantrae from the use of CRP, instead of superphosphate are less than 10%. On the other hand, under a spring or summer topdressing strategy, when the bulk of growth and thus P uptake occurs, the potential reduction in the losses of P by transfer, resulting from using CRP, may be of greater significance.

4.4 General Discussion

The results obtained in the field trials started in 1978 confirm and extend the findings of the preliminary glasshouse study (Chapter 3) in which CRP was found to be an effective source of P for perennial ryegrass. Except for glasshouse studies (Roberts and White, 1974; Andrews et al., 1978; Powell, 1979; Powell et al., 1980; Rajan, 1981a), the evaluation of CRP as a P fertilizer has been restricted to the studies of Quin (1981) started in 1979, and Rajan (1981b) started in 1980. Although only interim

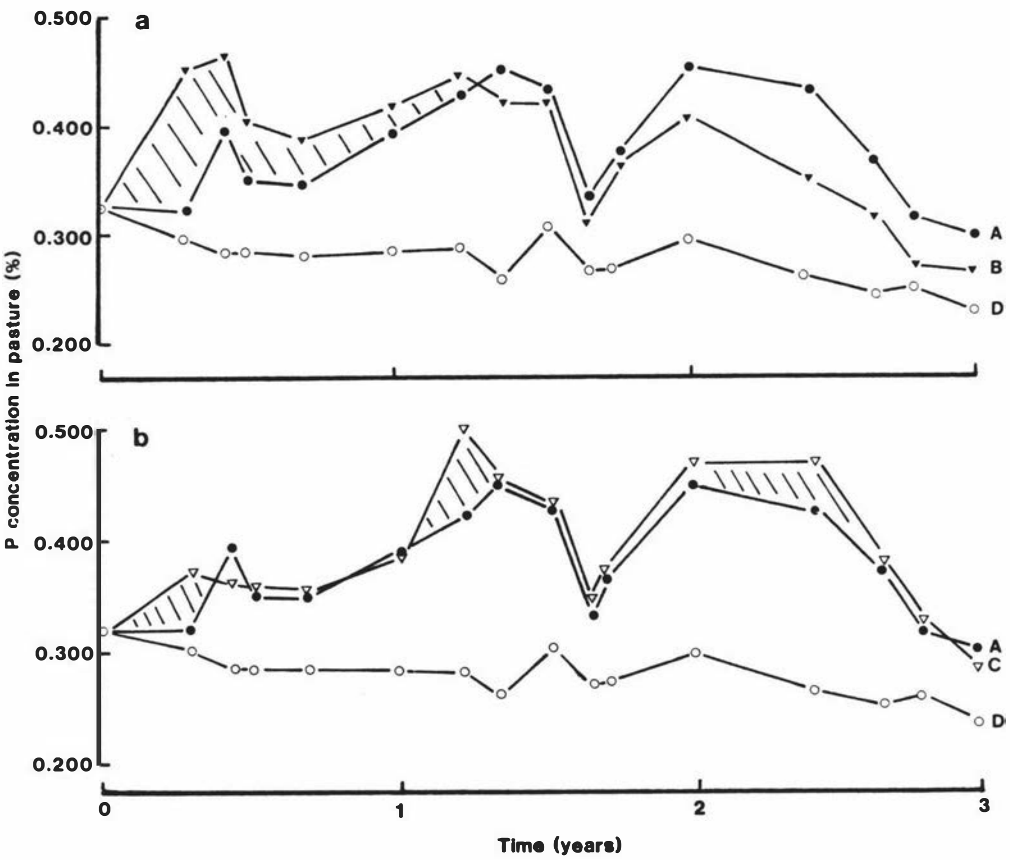


Figure 4.13 Changes in phosphorus concentration in pasture over three years at Ballantrae as influenced by phosphate source and topdressing strategy. A = single initial application of 70 kgP ha^{-1} as Chatham Rise phosphorite, B = single initial application of 70 kgP ha^{-1} as superphosphate, C = annual application of 35 kgP ha^{-1} as superphosphate, and D = control. a = single initial application, and b = single versus annual application.

results were reported in these studies, CRP was found to be an effective source of P for pasture when compared to superphosphate. Consequently, the results of the present field study provide the first comprehensive, long-term evaluation of CRP as a P fertilizer on several soil types and under a range of climatic conditions.

The finding that pelletised CRP was as effective as powdered CRP and superphosphate at the three hill-country sites, except for some initial differences at Ballantrae, contrasts with the results of the preliminary glasshouse study (Chapter 3), where pelletised CRP was less effective than the powdered material, and with the bulk of the literature (Terman et al., 1969; Buchan et al., 1970; Engelstad et al., 1972; Stephens and Lipsett, 1975; Powell et al., 1980), the results of which are also derived from glasshouse studies. This discrepancy probably results in part from the fact that in glasshouse studies a number of factors which operate in the field and which may contribute to an increased effectiveness of a PR material, are usually excluded. Of these earthworms are probably the most important (Chapter 5). Consequently, conclusions drawn from the glasshouse for the effectiveness of pelletised PR materials are not applicable to the field in the absence of biological mixing, based on the results of the present study.

Early differences in the agronomic effectiveness of superphosphate and CRP in the present study were restricted to the initial harvests of the first year. There is overwhelming evidence in the literature (Cooke, 1956; Cullen, 1958; Engelstad et al., 1974; Archer, 1978; Chien and Hammond, 1978b; Mokwunye, 1979) to show that, in the short-term PR materials are less effective than superphosphate. This reflects the marked difference in the initial behaviour of these two P sources on contact with soil. Whereas the initial plant availability of P in the soil to which largely water-soluble superphosphate is added is high and decreases with time (Rennes, 1978), the dissolution (Chapter 7.3.3.1) and subsequent plant availability of P from a PR (Chapter (7.3.2) increases on addition to soil. A difference between superphosphate and CRP was only found initially in terms of clover production and P uptake by mixed pasture. Quin (1981), also found only small differences in the initial effectiveness of CRP and superphosphate with pasture. As in the present study, this difference was short lived.

Interestingly, CRP applied annually was as effective as superphosphate applied annually in both the second and third years at Tokomaru. Quin (1981) also found that initial differences in the effectiveness of superphosphate and either Sechura phosphate rock (SPR) or CRP in the first year of application were not obtained in the second year of application. This suggests that the initial differences found between the two P sources in the first year in the present study, may partly reflect past fertilizer history of the site. It also suggests that in future comparisons of superphosphate and PR materials, less emphasis should be placed on any differences measured in the first year.

At Wanganui, CRP performed effectively as a P fertilizer from the time of application, even though this site had received 2.5 tonnes of lime ha^{-1} approximately 6 months before the start of the trial, and soil pH was 6.2. This finding conflicts with the bulk of the literature in New Zealand with GPR (Cullen, 1958; Karlovsky, 1958; Scott and Cullen, 1965; Grigg and Crouchley, 1980) where liming has generally resulted in marked decreases in the agronomic effectiveness of this PR. Both soil pH and exchangeable Ca, which increase on liming, have been shown to reduce the agronomic effectiveness of PR materials (Barnes and Kamprath, 1975; Khasawneh and Doll, 1978). In contrast to the present study, however, lime was applied along with GPR in each of the above studies. This may suggest that provided the initial reaction of the lime with the soil has occurred, then any detrimental effect that lime has on the agronomic effectiveness of a PR can be reduced. This conclusion is supported by the early field work of Roberts (1930) and Ames and Kitsuta (1932), who showed that the effect of lime on the ability of a PR to provide P for plant growth was reduced by adding the lime in advance.

Although the P response in the first year at Tokomaru was restricted to the clover component of the sward, CRP and superphosphate increased clover production to a similar extent, even though the initial P status of this site was relatively high. Rajan (1981b) also found that CRP and North Carolina phosphate rock (NCPR) performed effectively on a soil with a relatively high P status. This conflicts with the viewpoint held by Khasawneh and Doll (1978), but supports the conclusions reached earlier (Chapter 3.4) and agrees with results reported later (Chapter 7.3.3.2). The result from Tokomaru indicates that CRP would be an effective maintenance P fertilizer on soils of relatively high P status.

A feature of the results from the present field study was the marked residual effect exhibited by CRP when compared to superphosphate at Ballantrae and Wanganui. The residual effect was reflected not only in greater clover and total pasture production, but also in P uptake by the sward, particularly at these two sites in the third year. Surprisingly, except for the study by Scott and Cullen (1965) with GPR, little difference has generally been found in the residual effect of superphosphate and PR materials on permanent pasture under New Zealand conditions. Although predominantly derived from annual crops rather than permanent pasture, there is conflicting evidence in the overseas literature as to the residual effect of PR materials when compared to superphosphate (Cook, 1956; Mattingly, 1968; Engelstad et al., 1974; Archer, 1978; Chien and Hammond, 1978b; Mokwunye, 1979).

It is interesting to consider the reason for the origin of the marked residual effect exhibited by CRP in the present study. When 70 kgP ha^{-1} is added as CRP, approximately 200 kg$CaCO_3$ ha^{-1} is also added. Although this $CaCO_3$ had no measurable effect on soil pH, During (1972) has reported pasture dry matter responses on yellow-grey earth/yellow-brown earth intergrade soils to relatively small amounts (350 to 600 kg ha^{-1}) of lime. These responses could not always be attributed solely to the effect of added lime on plant-available Mo in the soil. A direct lime response, however, appears an unlikely explanation, as the residual effect shown by CRP was not restricted to Ballantrae but was also found at Wanganui. A positive lime-P interaction is also an unlikely mechanism, because of the relatively high pH (6.2) of the soil at Wanganui throughout the trial. The effect of the $CaCO_3$ in CRP on the availability of Mo in the soil is also an unlikely mechanism, as all trial sites were topdressed with Mo on a regular basis throughout the 3 years.

Because $CaCO_3$ is more soluble than phosphorite (Silverman et al., 1952), the presence of this $CaCO_3$ in close proximity to the phosphorite, would decrease the rate of dissolution of the phosphorite by increasing the pH and Ca concentration in the solution film immediately surrounding the phosphorite particle (Chapter 6.3.3.1). In fact in a later study (Chapter 7.3.3.1) it is reported that the rate of dissolution of CRP is slower than that of SPR, which contains a substantially lower amount of $CaCO_3$ (8.9%).

Evidence to support the suggestion that the origin of the residual effect exhibited by CRP at Ballantrae and Wanganui results from the influence of $CaCO_3$ on the rate of release of P from the phosphorite, is obtained from the results of two recent field trials evaluating the agronomic effectiveness of SPR, CRP, and superphosphate on two yellow-grey earth/yellow-brown earth integrade soils (Gregg et al., 1981). Results from the first year of these trials indicated that SPR was slightly more effective than CRP at both sites, a finding which is consistent with the glasshouse results (Chapter 6.3.1). However, in the second year these workers found that CRP was outyielding not only superphosphate, but also SPR. In fact no difference was found in the residual effect of superphosphate and SPR in the second year in either of these trials (Gregg et al., 1981).

Further indirect evidence to support the conclusion that the residual effect of CRP results simply from slow release, is obtained from the study of Scott and Cullen (1965) in which GPR showed a marked residual effect, when compared to superphosphate. In this study, 1250 kg ha^{-1} of lime was accidently applied over the no-lime plots at the start of the pasture production measurements. This may have reduced the rate of release of P from GPR in a similar manner to that found with CRP in this study (Chapter 7.3.3.1).

In marked contrast to the residual effect shown by CRP at Ballantrae and Wanganui, no measurable differences were found in the residual effect of CRP and superphosphate in the 2.5 years of study at Pahiatua. This suggests that at the application rates used in the present study and with the criterion used to separate initial and residual effects, that the residual effect of CRP is dependent on soil type. The absence of a residual effect from CRP on the high P-sorbing Ramiha silt loam at Pahiatua may reflect the dominating effect that P-sorption reactions have on added P in this soil. Evidence for this comes from the relatively high proportion of P added as CRP which was recovered by NaOH extraction from this soil as inorganic P at the end of 2.5 years. Of the P added as CRP and recovered from this soil by either the sward or by NaOH extraction, 65% was recovered by the latter. Similarly of the P added as superphosphate and recovered, 58% was recovered from the soil as inorganic P. However, of the P added as CRP at Ballantrae and Wanganui, and recovered by either the sward or by NaOH extraction, only 23 and 46%, respectively, was recovered in the soil at the end of the third year. There is conflicting evidence in the literature for the relative effectiveness of PR materials on high P-sorbing soils, although most of this has been obtained in the glasshouse. For instance, Wong Yun Cheong (1966) and Mclean and Logan (1970) found that the relative agronomic effectiveness of a PR material, when compared to superphosphate, increased as the P-sorption capacity of the soil increases. As in the present study, Juo and Kang (1978) found no real differences between the two P sources.

Another feature of the present study was the marked difference found in the response to added P of the grass and clover components of the sward. Whereas grass production remained relatively constant clover production varied markedly with the form and amount of P. Because of the importance of clover to the N economy of the sward, and because of the greater sensitivity of clover to changes in available P in the soil, when compared to grasses (Ozanne et al., 1969; Jackman and Mouat, 1972a; Barrow, 1975), due to their poor competitive ability for available P in the soil (Jackman and Mouat, 1972b), the effectiveness of a P fertilizer in stimulating the clover component of the sward is of special importance. In addition to any shortage of plant available N in the soil limiting grass production, the absence of any real response by the grass component of the sward when compared to clover, to added P, may simply reflect the difference in the sensitivity of these two plant species to available P levels in the soil (Jackman and Mouat, 1972a).

Apart from some initial differences in early harvests of the first year, CRP was as effective as superphosphate in increasing clover production at all sites. In fact, the residual effect exhibited by CRP was very pronounced in the clover component of the sward at both Ballantrae and Wanganui, particularly in the third year. Although legumes have a greater ability to utilize P from a PR than grasses (Deist et al., 1971), a single application of CRP was sustaining a similar level of bicarbonate-extractable P in the soil as annual applications of superphosphate (Fig. 4.11). In fact, this level was sufficiently high to achieve maximum clover growth at Ballantrae and Wanganui for 3 years, as no yield difference was found between those two treatments. This provides further evidence to support the suggestion that the origin of the residual effect exhibited by CRP results from slow release.

Quin (1981) partly attributed the increased effectiveness of SPR and CRP in the second year, when compared to superphosphate in a maintenance P trial, to the poor quality of superphosphate used. Only 62% of the total P in the superphosphate used by Quin, was soluble in 2% citric acid. Assuming that 2% citric acid gives a reasonable estimate of plant-available P in superphosphate, then of the 20 kg of P applied annually in the maintenance trial of Quin (1981) some 13 kg was potentially available to the plant. The superphosphate used in the present study contained a much higher proportion (80%) of total P soluble in 2% citric acid. At Pahiatua, where no S response was measured, there was no yield difference between superphosphate and MCP in either the first or second year, although apparent recovery of added P by pasture from MCP was greater than that from superphosphate at this, and the other three field trial sites.

Also no differences were found between superphosphate and CRP at this site, suggesting that the differences found between superphosphate and CRP at Ballantrae and Wanganui in the third year, represent a real difference in the residual effect of these two P sources.

Ultimately, the usefulness of the findings of the present study will depend on how applicable they are to a grazed sward. The harvesting technique used, of mowing with clippings removed, largely eliminates the above-ground recycling of nutrients, found in a grazed sward. In other studies (Elliott and Lynch, 1958; Wolten, 1963), this technique has led to a gradual deterioration in the vigour of the sward after repeated harvests. This is confirmed in the present study. This loss of vigour has been attributed largely to a depletion of N and K more than to a depletion of P (Elliott and Lynch, 1958; Wolten, 1963). The decline in bicarbonate extractable P in the soil on the controls (no added P) at all four trial sites in the present study, suggests that a decline in the P status also contributes to the loss of vigour.

From a comprehensive evaluation of various harvesting techniques, Elliot and Lynch (1958) concluded that mowing with clippings returned duplicated the pasture production measurements obtained with a grazed sward using small cages, more closely than did mowing with clippings removed, on easy country. The good agreement found suggests that no net loss of above-ground nutrients from either dung or urine occurred from the grazed sward in their study, and the return was relatively uniform. In hill country, however, in which three of the present trials were located, the return of dung and urine is highly modified by topography. Gillingham and During (1973) found that large quantities of P, N, and K were transferred in dung and urine by the grazing animal from steeper slopes, which made up 60% of the grazed area, to easy slopes and to campsites which represented less than 10% of the grazed area. In fact in a later, more comprehensive study Gillingham (1978) found that a large net loss of P occurred by transfer from both 25^{o} and 45^{o} slopes (29 to 71% of annual P uptake by pasture), with a large net gain of P occurring on easy slopes and campsites. The harvesting technique of mowing with clippings removed is therefore probably more applicable in hill country, where significant losses occur by nutrient transfer from a large proportion of the grazed area.

Based on the results of the studies by Hunt and Wagner (1963) and Boswell (1977), the mowing technique adopted in the present study probably overestimates the annual and seasonal pasture production of a grazed sward by stimulating plant growth. Boswell (1977) found that infrequent harvesting consistently led to higher yields than frequent cutting, especially in the Spring and Summer. During this period of maximum growth, cutting to 3 cm also consistently outyielded those plots on which 6 cm of herbage was left after cutting. Boswell (1977) also found that cutting height had a pronounced effect on clover production although unlike total pasture production, frequency of cutting was of less significance. Consequently, the pronounced increases in clover production measured at all four sites probably reflect, in addition to a response to added P, a response to the mowing regime adopted. Although clover and total pasture dry matter production may have been over-estimated in the present study, the results probably represent the maximum differences that would be found between these two P sources under field conditions.

CHAPTER 5

CHAPTER 5

THE EFFECT OF EARTHWORMS ON THE AVAILABILITY OF PHOSPHORUS IN A PHOSPHATE ROCK

5.1 Introduction

The results obtained in the preliminary glasshouse study (Chapter 3) for the effectiveness of pelletised CRP are not consistent with those obtained under field conditions (Chapter 4). The difference found between powdered and pelletised CRP in the glasshouse (Chapter 3) was not found in the field (Chapter 4). Muller (1970) also found that the results obtained in the glasshouse for the effectiveness of a pelletised PR were not directly applicable to those obtained in the field. He found that responses to pelletised Calciphos were greater under field conditions than in the glasshouse experiment reported by Buchan et al. (1970). This difference probably results in part from the fact that in glasshouse studies, a number of factors which operate in the field and which may affect the agronomic performance of a pelletised PR material, are usually excluded (Chapter 3). These include the impact of raindrops and treading by the grazing animal, as they affect the breakdown and distribution of a pelletised PR, and the influence of cracks and channels in the soil, along with the activity of fauna (particularly earthworms) as they influence the incorporation of the powdered material derived from the PR pellet into the soil.

The influence of earthworms on the physical and chemical properties of soil materials has been well documented since the pioneering work of Darwin (1881). The enrichment of earthworm casts in plant nutrients, such as P, N, K, Ca, and Mg (Parle, 1963; Graff, 1970; Sharpley and Syers, 1976; Dash and Patra, 1979) and the importance of earthworms in the cycling of P (Mansell et al., 1981) and N (Syers et al., 1979) in pasture ecosystems have been demonstrated. Also, the importance of earthworms in the incorporation of plant residues in both cropping and pasture systems (Barley and Kleinig, 1964; Stockdill, 1966), and in forest ecosystems (Edwards and Heath, 1963; Vimmerstedt and Finney, 1973) has been studied extensively. However, the role played by earthworms in the incorporation of surface-applied agricultural materials, such as fertilizers, lime, and pesticides and the effect this has on their subsequent performance has largely been overlooked.

In one of the very few studies on this topic in New Zealand, Stockdill (1966) attributed improved vertical distribution of lime in the field, resulting in increases in both soil pH and extractable Ca to a depth of 15 cm, to the feeding and burrowing activity of surface-casting earthworms. Stockdill (1966) also measured increases in the vertical distribution of D.D.T. and, as a result, an increase in its effectiveness in the control of grass grub in the field, where earthworms were active. Whether earthworms directly incorporate these materials into the soil through their feeding and burrowing activity or whether the presence of earthworm burrows, open to the surface, simply facilitates the downward movement of the surface-applied material, is unclear. In addition to the incorporating effect earthworms may have on surface-applied material, ingestion of these materials, particularly lime, by earthworms during feeding could lead to an increase in the degree of intimate contact of the lime with the soil during passage through the digestive tract. This intimate contact could promote dissolution of the lime, leading to further increases in both the pH and exchangeable Ca of the soil. Although evidence for this suggestion is lacking it is clear that earthworms play an important role in the field in the incorporation and mixing of surface-applied material. Thus their exclusion from glasshouse studies may decrease the agronomic effectiveness of a surface-applied, pelletised PR material.

The bulk of data for the performance of PR materials has been obtained in the glasshouse (Armiger and Fried, 1957; van der Paauw, 1965; Bengtson et al., 1974; Roberts and White, 1974; Chien and Hammond, 1978a), largely because of the fewer resources required to conduct glasshouse studies and the relatively short-time period required to obtain results. An understanding of the way in which earthworms affect the agronomic performance of a surface-applied PR material may be useful in the interpretation and extrapolation of results from the glasshouse to the field situation.

This Chapter reports the results from a glasshouse study in which the effect of earthworms on the plant availability of P in a pelletised PR is investigated. Subsequently, results from a series of studies in which the mechanisms of incorporation and possible effect of ingestion of PR particles by earthworms are evaluated in an attempt to explain the origin of the effect of earthworms on the agronomic effectiveness of PR materials.

5.2 Materials and Methods

Four studies were conducted. The first involved a glasshouse study to measure the effect of earthworms on the plant availability of P in superphosphate and pelletised PR; the second experiment involved a glasshouse trial with tillage treatments to investigate the mechanisms controlling incorporation; the third experiment involved an incubation study to evaluate the effect of the ingestion of PR particles by earthworms;

and the fourth experiment involved a series of soil-ingestion trials to estimate earthworm ingestion rates.

5.2.1 Soil used in experiment

The Tokomaru silt loam used in each of these four experiments was collected from three depths, 0-10, 10-15, and 10-20 cm. The following chemical parameters were measured; soil pH in water; organic carbon (Chapter 4.2.1); exchangeable Ca (total of 4, 10-min extractions with M ammonium acetate (pH 7) at a solution:soil ratio of 2.5:1); P-sorption capacity (Chapter 3.2.2); 0.5M NaOH-extractable P (Chapter 4.2.6.1); and estimates of plant-available soil P, the bicarbonate (Chapter 3.2.2), the Bray (Chapter 4.2.6.1) and single water (Chapter 4.2.1) methods. Results for these analyses are given in Table 5.1.

5.2.2 Glasshouse experiment involving earthworms

All soils were air dried and passed through a 6-mm sieve before potting. The soil was hand packed, in the two (0-10 and 10-15cm) depths, into pots measuring 30 x 30 x 18 cm to leave the soil surface 3 cm below the top of the pot. The weight of air-dried soil per pot was 9 kg.

Earthworms were collected in winter (July, 1978) from under permanent pasture adjacent to where the soil was sampled. A solution containing 1% formalin was used to extract the earthworms. This concentration extracted earthworms for use in the pots without undue damage. The earthworm population density was estimated using 16, 0.02 m^2 hand-sorted soil cores and 16, 0.02 m^2 cores immersed in 2% formalin solution (Springett, 1981). The population was approximately 50% Allolobophora caliginosa (Savigny) 50% Lumbricus rubellus Hoff. An earthworm population of 600 m^{-2} (54 pot^{-1}) was used in the glasshouse trial. Measurement of the N content of the mixed earthworm population was made following Kjeldahl digestion (Bremner, 1965). The population

Table 5.1 Some chemical characteristics of Tokomaru silt loam from three depths

Soil depth (cm)	pH_{H_2O}	Organic carbon (%)	Exchangeable Ca (meq %)	P-sorption capacity (%)	NaOH-extractable P in soil ($\mu g\ g^{-1}$)	Extractable-soil P		
						Bicarbonate	Bray ($\mu g\ g^{-1}$)	Water
0-10	5.7	2.29	6.6	24	72	8.4	8.9	3.9
10-15	5.7	-	-	26	-	6.2	-	3.2
10-20	5.5	1.06	5.3	26	45	4.2	5.6	3.1

density of Enchytraeidae was also measured in the field prior to soil collection. Sixteen soil cores (3.6 cm in diameter and 8 cm deep) were extracted in heated, wet funnels for 3 h (Table 5.2). Additional pots with earthworms were included for destructive sampling during the experiment to check on earthworm survival.

The PR used in the glasshouse experiment was Chatham Rise phosphorite (CRP). The pelletised CRP had a total P content of 9.2%, of which 20.7% was soluble in 2% citric acid, and the granulated single superphosphate contained 8.5% total P, of which 79.5% was soluble in 2% citric acid. Additional information on these two P sources is given in Chapter 3 (Table 3.3). The treatments are listed in Fig. 5.1. A complete randomised block design was used. Incorporated treatments were mixed into the upper 2 cm of soil. Sulphur (S) was applied as gypsum to all treatments at the quantity of S added in the highest rate of superphosphate. Additional S was applied after the 3rd and 5th harvests. Nitrogen (N) as ammonium nitrate, potassium as potassium chloride, and the micronutrient solution of Middleton and Toxopeus (1973) were applied after each harvest. Approximately 150 seeds of perennial ryegrass (Lolium perenne) were sown on the soil surface after the addition of earthworms and fertilizers.

A total of seven harvests were taken at varying intervals (8, 4, 4, 4, 4, 4, and 5 weeks). All herbage was removed and oven dried at 60°C for 24 h before weighing. The concentrations of P and N in the ryegrass were determined following Kjeldhal digestion. Three cores (2.5 cm in diameter) from selected treatments were also taken for soil chemical analysis at the end of the glasshouse trial.

5.2.3 Incorporation experiment involving tillage

Before potting, both the upper (0 to 10 cm) and lower (10 to 20 cm) soil horizons were air dried and passed through a 6-mm sieve. Soil from

Table 5.2 Changes in field populations of earthworms under permanent pasture from July 1978 to February 1979

	Earthworm population	
Parameter	July 1978	February 1979
Numbers (m^{-2})	672 ± 69*	333 ± 29.4
Biomass† ($g\ m^{-2}$)	127.8	28.7

* Standard errors

† Wet weights

the lower depth was hand packed to the field bulk density into the bottom 10 cm of pots having a diameter of 25 cm and a depth of 24 cm. Soil collected from the upper 10 cm in the field was then added and again hand packed to field bulk density to leave the soil surface 4 cm below the top of the pot.

The PR used in the glasshouse trial was Sechura phosphate rock (SPR) from the Sechura Desert area of northern Peru. Values for total P, determined following perchloric acid digestion (O'Connor and Syers, 1975) and water- (The Fertilisers Regulations, 1969) and 2% citric acid- (The Fertilisers Regulations, 1969) extractable P in the powdered and pelletised SPR, and of superphosphate are summarised in Table 5.3, as are some physical characteristics of the two P sources.

The individual treatments used in the experiment are given in Table 5.4. The pelletised SPR treatments were surface applied, while both powdered SPR and granulated (<2 mm) superphosphate treatments were incorporated into the upper 4 cm of soil to maximise effectiveness.

The tillage treatment was devised to simulate the number of earthworm burrows open to the soil surface at any one time. This was achieved by pressing metal needles into the soil. To standardise the procedure, 10 needles, of varying diameter (1.5 to 4.0 mm) and length (4 to 22 cm), were fixed to a board having the same diameter as the pots, and the board was pressed onto the soil surface. The 10 holes formed are equivalent to the number of burrows which would be open to the surface on a daily basis if an earthworm population of 30 pot^{-1} (600 m^{-2} in the field) was present (Springett, unpublished data). The tillage I treatment was applied every second day. The tillage II treatment relates to a field earthworm population of 1200 m^{-2}, with 20 burrows open to the surface.

Sulphur (S) was applied as gypsum to all treatments in the same

Table 5.3 Some physical and chemical characteristics of Sechura phosphate rock (SPR) and superphosphate

Phosphate source	Form	Total P (%)	Total $CaCO_3$ (%)	P extracted by Water (% of total P)	P extracted by 2% citric acid (% of total P)
Superphosphate	Granules	10.1	0	53.2	83.5
SPR	Powder (<180 μm)	13.7	8.9	<0.01	42.4
	Pellets (2-4 mm)	13.0	8.1	<0.01	42.4

Table 5.4 Total yield of ryegrass and phosphorus uptake by ryegrass over four harvests as influenced by tillage and the source, form, method, and rate of application of phosphate

Treatment	Application Rate ($kgP\ ha^{-1}$)	Yield (g)		P uptake (mg)	
Control	0	40.3	H*	126.9	F
Control, Tillage I	0	43.7	G	138.8	E
Control, Tillage II	0	47.8	F	146.1	E
Pelletised SPR	75	55.6	E	179.9	D
Pelletised SPR, Tillage I	75	58.1	D	197.0	C
Pelletised SPR, Tillage II	75	59.9	CD	202.4	C
Powdered SPR	75	64.2	B	222.5	B
Superphosphate	75	61.0	C	214.8	B
Superphosphate	150	70.4	A	272.4	A

* Capital letters denote Duncan's symbols for assessing significant ($P < 0.01$) differences.

quantity as the S added in the highest superphosphate treatment. Additional S was applied after the 3rd harvest. Nitrogen (N), potassium, and the micronutrient solution of Middleton and Toxopeus (1973) were applied after each harvest. Approximately 120 seeds of perennial (Ruanui) ryegrass (Lolium perenne) were sown on the soil surface after the addition of fertilizer. Pots were watered to field capacity (taken at 40-cm suction) on a daily basis. A total of 4 harvests were taken at varying intervals (7, 4, 4, and 5 weeks). All herbage was removed and oven dried at 60°C for 24 h before weighing. The concentration of P and N in the ryegrass was determined following Kjeldahl digestion. Three soil cores (2.5 cm in diameter) were taken from one replicate of each treatment at the first harvest and the remaining four replicates sampled at the fourth harvest, and used for soil analysis.

5.2.4 Incubation study with earthworms

Duplicate 4000-g samples of air-dried and sieved (< 6mm) Tokomaru silt loam (0 - 10 cm) with 50 g of organic matter added as finely-ground (<0.5 mm) herbage, were incubated in pots with SPR and superphosphate at an application rate to give 500 μgP g^{-1} of soil. The herbage contained 3.2% N, 0.41% P, and 0.95% Ca. Incubations were done in the presence and absence of earthworms at field capacity (42% water content and 20°C for 70 days). Thirty L. rubellus were added to each pot at the start of the experiment. Earthworms were also added to the above treatments in a separate set of pots 24 days after the start of the incubation.

The 50 g of organic matter was added to each pot as a food source for the earthworms. Because of possible interactions between earthworm activity and extractable-soil P levels, the effect of addition of various amounts of organic matter (0, 50, and 100 g per 4000 g of soil), was also monitored over 70 days in a separate study.

During the 70 days, a total of 12 samplings were conducted. At each sampling a duplicate 20-g soil sample was taken from each pot, sieved (<2 mm), and analysed. In addition to changes in bicarbonate-, Bray-, and 0.5M NaOH-extractable P in the soil, changes in pH and organic carbon content were also determined at each sampling. Earthworm casts, collected after 7 days from the SPR treatment, were incubated separately at 20°C and analysed for changes in 0.5M NaOH-extractable P at six time intervals.

Because of the difficulty of identifying CRP particles in the soil, SPR was used in the incubation study and a small optical and scanning electron microscopy study was included.

5.2.5 Soil ingestion trials with earthworms

Estimates of ingestion rates by earthworms were made using three methods:

(i) After weighing 50 earthworms (*L. rubellus*) which had been feeding in the Tokomaru silt loam for 48 h, the gut content was retrieved by stripping. The soil collected was weighed after drying at 60°C for 24 h.

(ii) Fifty earthworms (*L. rubellus*) were placed in the Tokomaru silt loam (a soil of light colour) for 48 h. These were then transferred to Manawatu silt loam (a soil of darker colour) for a further 24 h, then removed. The soil was then separated out and the readily-identifiable casts of the Tokomaru soil removed, oven dried at 60°C for 24 h, and then weighed.

(iii) The third method used for estimating earthworm ingestion rates used the frame technique developed by Springett (pers. comm.). Two earthworms of either *L. rubellus* or *A. caliginosa*, or one of each species, were placed in 200 g of sieved (<2 mm)

Tokomaru soil in frames measuring 20 x 10 cm (side) x 1 cm (width), with one glass side, watered to field capacity (42% water content), and kept in a growth cabinet at 16°C. There were ten replicates of each. Daily counts, over 19 days, were made on an area basis of the soil affected by earthworms either by casting or burrowing, using a grid placed over the glass side. Between counts the frames were kept in polythene boxes.

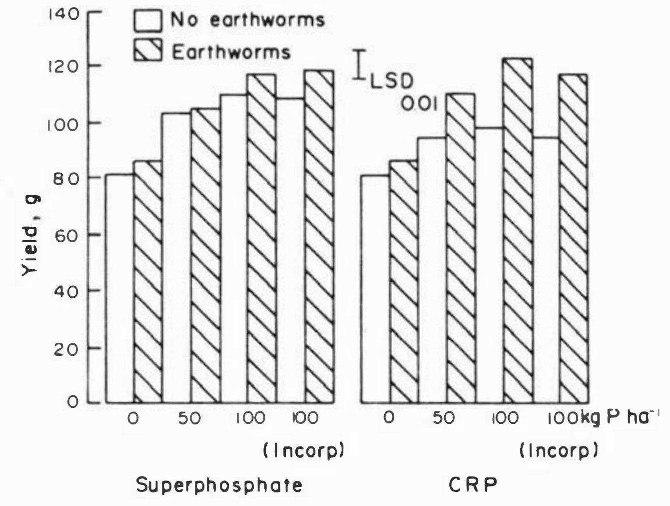
5.3 Results and Discussion

5.3.1 Effect of earthworms on the plant availability of phosphorus in superphosphate and Chatham Rise phosphorite

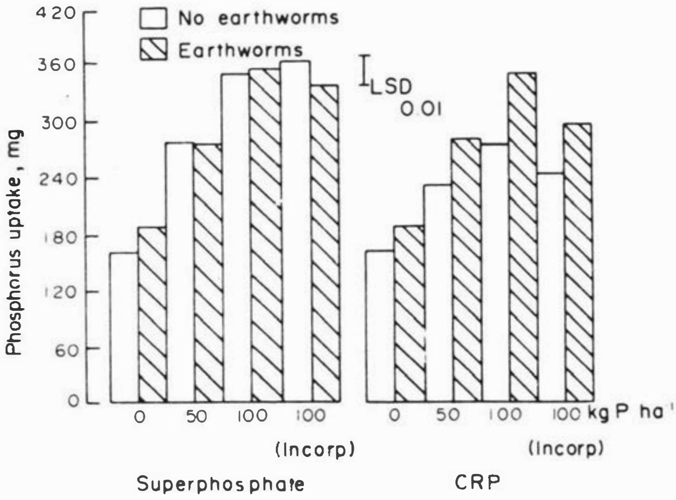
The mixed earthworm population affected both the yield of ryegrass and P uptake by ryegrass over seven harvests(Fig. 5.1). This effect, however, varied in magnitude with the source and rate and method of application of P. The effect of earthworms on the performance of superphosphate and pelletised CRP will be discussed separately.

5.3.1.1 Changes in earthworms population

The numbers and weights of earthworms per pot at the beginning and at the end of the experiment are shown in Table 5.5. The field population and biomass of earthworms over the same time period are shown in Table 5.2. Although the numbers of earthworms in the pots remained relatively constant throughout the trial period, total earthworm biomass per pot decreased markedly. As the N content of earthworms was 8.95%, the loss in biomass contributes, on average, an additional 17 μgN g^{-1} to the N pool in the soil. The survival of earthworms in the pots (Table 5.5) was greater than that of the field population (Table 5.2) during the same period. Mean earthworm weight was also greater



(a)



(b)

Figure 5.1 Yield of ryegrass (a) and phosphorus uptake by ryegrass (b) over seven harvests as influenced by earthworms and the source and method and rate of application of phosphate.

Table 5.5 Number and weight of earthworms present at the start (July 1978) and at the end (February 1979) of the experiment

Treatment	Application rate (kgP ha^{-1})	Earthworm numbers			
		July 1978		February 1978	
		Numbers (pot^{-1})	Weight* (g pot^{-1})	Numbers (pot^{-1})	Weight (g pot^{-1})
Control	0	54	26.08	48	8.71
Superphosphate	50	54	26.16	51	8.56
Superphosphate	100	54	25.20	52	8.32
Superphosphate	100 (Incorp.)	54	24.96	47	8.21
CRP	50	54	25.81	49	8.16
CRP	100	54	24.87	46	8.28
CRP	100 (Incorp.)	54	25.30	48	8.24
Mean earthworm weight (g)			0.465		0.171

* Wet weights.

in the glasshouse than in the field at the end of the experiment.

5.3.1.2 Effectiveness of superphosphate

Total ryegrass yields for the seven harvests were increased significantly ($P < 0.01$) by superphosphate addition at both the 50 and 100 kgP ha^{-1} application rates and in both the presence and absence of earthworms (Fig. 5.1a). No significant ($P < 0.01$) differences in ryegrass yields were found between superphosphate treatments in the presence and absence of earthworms. Total P uptake by the ryegrass over the seven harvests (Fig. 5.1b) also showed no significant ($P < 0.01$) differences between superphosphate treatments in the presence and absence of earthworms.

The relative cumulative yield data over seven harvests for superphosphate in the presence and absence of earthworms are shown graphically in Fig. 5.2a. Where there are two rates for a fertilizer treatment, the curve represents the average effect. The effectiveness of superphosphate was increased markedly in the presence of earthworms at the first (19 to 35%), second (19 to 33%), and to a lesser extent the third (10 to 19%) harvests. Incorporation increased the effectiveness of superphosphate in the presence of earthworms by 12% at the first harvest. The initial yield of the controls was also increased in the presence of earthworms. By the seventh harvest, the differences in the effectiveness of superphosphate in the presence and absence of earthworms had decreased to between 7 and 10%. The relative cumulative P uptake by ryegrass from superphosphate (Fig. 5.2b) was also initially greater (20 to 40%) in the presence of earthworms. Incorporation of superphosphate in the presence of earthworms increased its initial effectiveness by 20%. As with the relative yield data, however, these differences did not persist. Incorporation of superphosphate had no measurable effect on its effectiveness in the absence of earthworms.

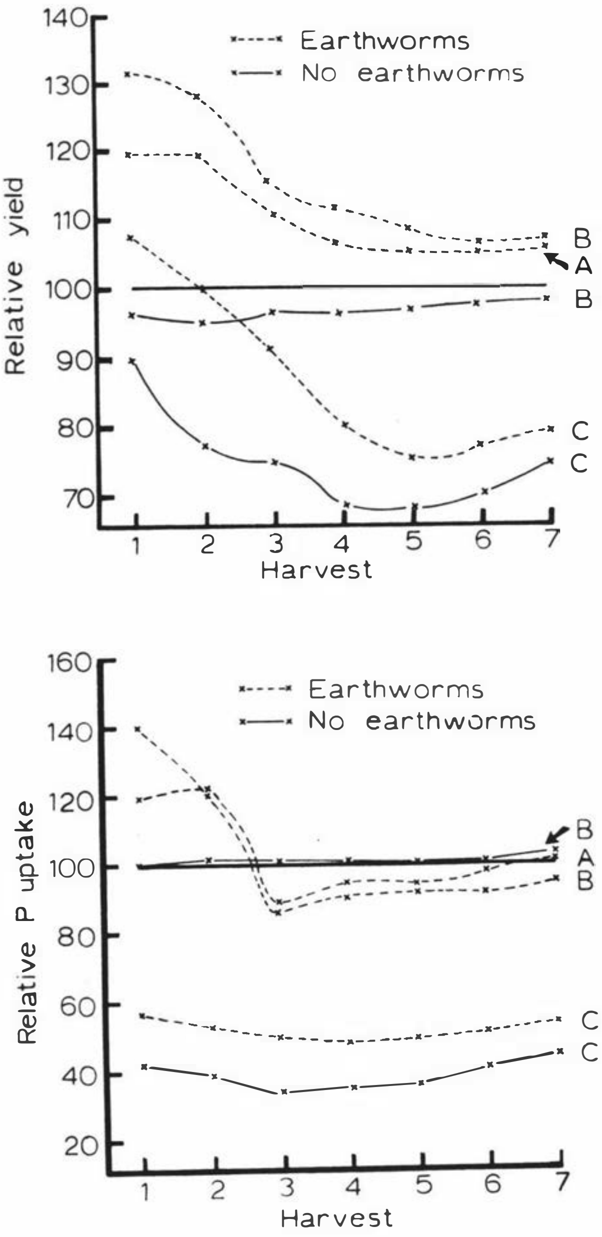


Figure 5.2 Relative cumulative yield of ryegrass (a) and phosphorus uptake by ryegrass (b) for seven harvests with superphosphate in the presence and absence of earthworms (surface-applied superphosphate in the absence of earthworms = 100). A = surface-applied superphosphate, B = superphosphate incorporated, and C = control.

In addition to significant differences in initial P uptake by ryegrass between superphosphate treatments in the presence and absence of earthworms, a significant ($P<0.01$) difference was also found in the concentration of N in ryegrass for the same treatments at the first harvest. In the absence of earthworms, the average N content of the ryegrass was 3.55%, whereas in the presence of earthworms the average N content of the ryegrass increased to 3.95% at the first harvest. As was the case for P uptake and yield differences, this difference did not persist. Average N contents of the ryegrass for the remainder of the trial ranged from 4.00 to 4.20%. With one exception, no differences were found in the amounts of water-extractable P (Fig. 5.3) in soils between superphosphate treatments in the presence and absence of earthworms at the three depths at the end of the experiment. The exception was for superphosphate treatments when incorporated at the 0-2 cm depth.

5.3.1.3 Effectiveness of Chatham Rise phosphorite

Total ryegrass yields with pelletised CRP for the seven harvests were significantly ($P < 0.01$) greater in the presence of earthworms at both rates of application (Fig. 5.1). On a relative basis, the increase in yield was 19 to 22% greater in the presence of earthworms. Incorporation reduced the performance of pelletised CRP, compared to the surface-applied treatment, by 5% in both the presence and absence of earthworms. As for total yield, total P uptake by ryegrass from pelletised CRP was also significantly ($P < 0.01$) greater in the presence of earthworms.

The overall difference between pelletised CRP in the presence and absence of earthworms (Fig. 5.1) existed from the first harvest, as shown by the relative cumulative yield data over the seven harvests (Fig. 5.4a). Again all treatments are compared to surface-applied superphosphate, in

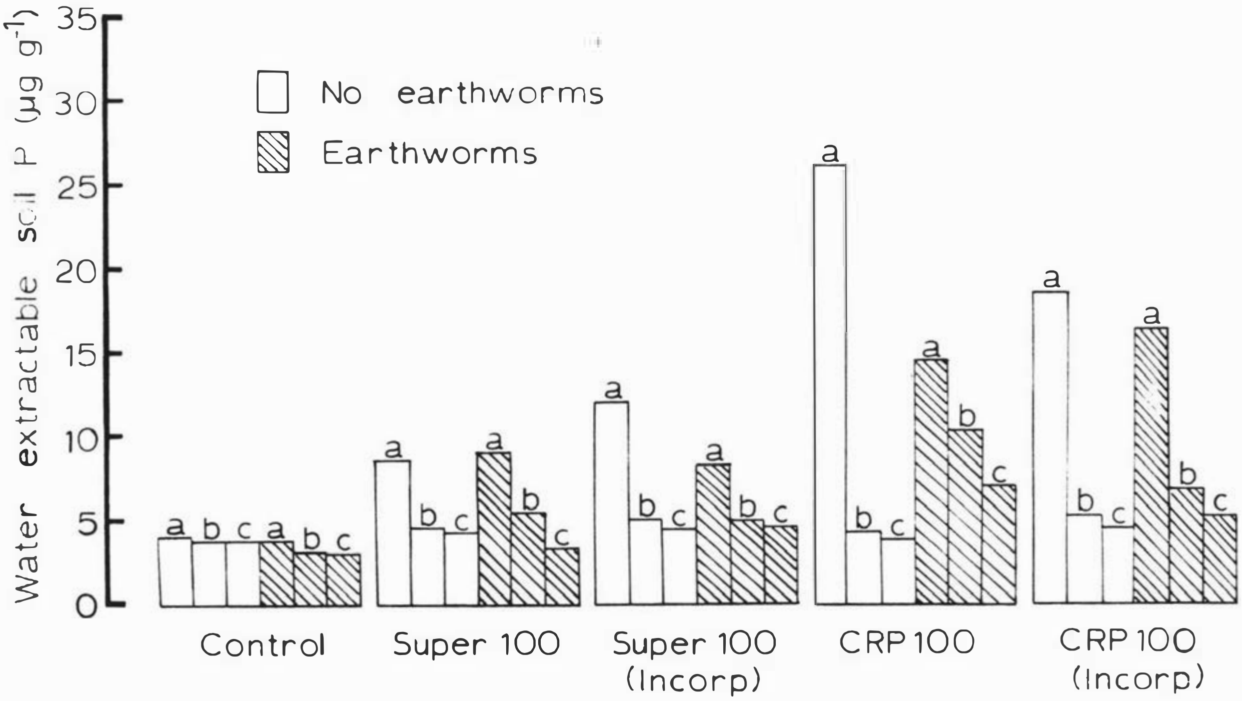


Figure 5.3 Amounts of water-extractable phosphorus in the soil from three depths as influenced by earthworms and the source and method of application of phosphate.
a = 0-2 cm, b = 2-4 cm, c = 4-6 cm.

the absence of earthworms. This difference in the effectiveness of pelletised CRP remained relatively constant throughout the trial, although the actual effectiveness of pelletised CRP increased with time in the presence of earthworms. By the seventh harvest, the yields with pelletised CRP in the presence of earthworms were 28 to 33% greater than the controls, whereas in the absence of earthworms the increases in yield were only 11 to 15% higher. Comparisons based on relative cumulative P uptake by ryegrass from pelletised CRP over seven harvests gave the same trends as the yield data, although at a lower level when compared to superphosphate (Fig. 5.4b). As with the superphosphate treatments, a significant ($P < 0.01$) difference was found in the concentration of N in the ryegrass between pelletised CRP treatments in the presence and absence of earthworms at the first harvest. In the absence of earthworms the average N content of the ryegrass was 3.62% whereas in the presence of earthworms the average N content increased to 3.89%. Again this difference in the concentration of N in the ryegrass did not persist. The N content of the ryegrass for the remainder of the trial was within the range reported earlier for superphosphate. The presence of earthworms had a smaller effect on P uptake (7 to 14%) at the first harvest than it had on ryegrass yield (16 to 20%). The effect of method of application on the plant availability of P in CRP is again clearly demonstrated.

Water-extractable P levels in soil from the surface-applied pelletised CRP treatment were greater at the lower two sampling depths in the presence of earthworms at the end of the experiment (Fig. 5.3). This result contrasts with that found for superphosphate. When the pelletised CRP was incorporated the differences in water-extractable P levels at the lower two depths were far smaller.

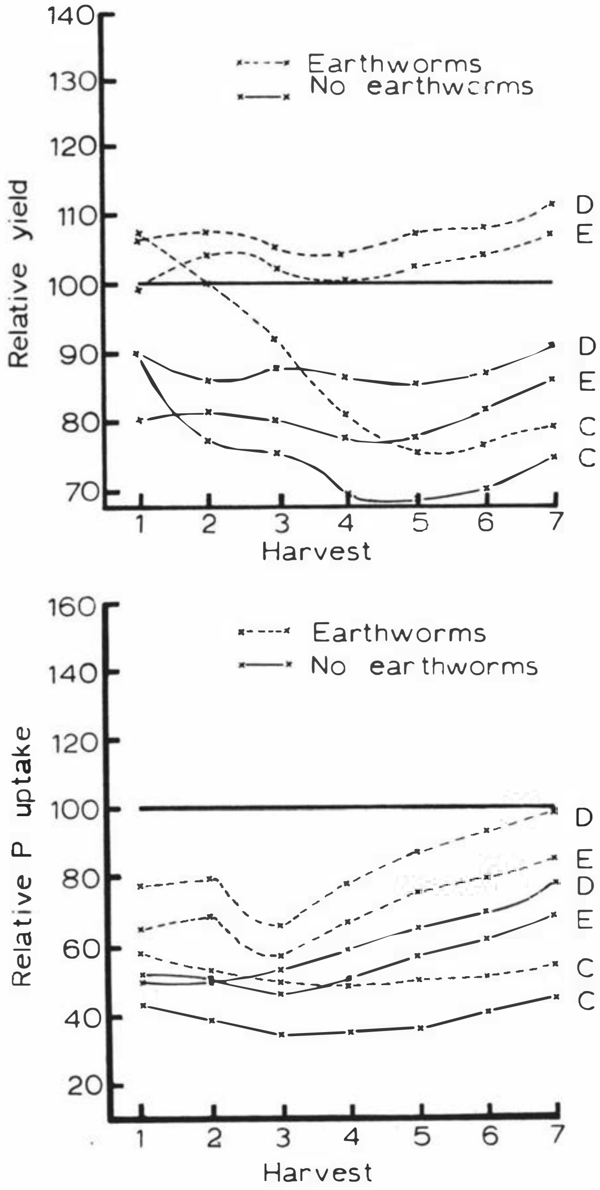


Figure 5.4 Relative cumulative yield of ryegrass (a) and phosphorus uptake by reygrass (b) for seven harvests with pelletised Chatham Rise phosphorite in the presence and absence of earthworms (surface-applied superphosphate in the absence of earthworms = 100). D = pelletised Chatham Rise phosphorite, E = pelletised Chatham Rise phosphorite incorporated, and C = control.

5.3.2 Possible mechanisms of incorporation and the possible effect of ingestion of phosphate rock particles by earthworms

5.3.2.1 Incorporation experiment involving tillage

Total ryegrass yield for the four harvests combined are given in Table 5.4. A significant ($P < 0.01$) P response was obtained with both superphosphate and SPR in both the powdered and pelletised forms. The soil also showed an increasing response to P with increasing rates of application. Whereas at 75 kgP ha^{-1} powdered SPR gave a greater ($P < 0.01$) yield of ryegrass than superphosphate, in the pelletised form SPR was less ($P < 0.01$) effective (Table 5.4). On a relative yield basis, powdered SPR was 105% as effective as superphosphate.

The two tillage treatments increased the yields of ryegrass in both the controls (9 to 19%) and with the pelletised SPR (4 to 7%). On a relative yield basis, ryegrass yields from pelletised SPR were increased from 91% of that obtained with superphosphate to 95 and 98% with the tillage I and II treatments, respectively.

No differences were found in total P uptake by ryegrass between superphosphate and powdered SPR although pelletising reduced the effectiveness of SPR (Table 5.4). Again, the two tillage treatments increased P uptake by the ryegrass in both the controls (9 to 15%) and pelletised SPR (10 to 13%) treatments. Although both the tillage treatments increased ($P < 0.01$) the effectiveness of pelletised SPR, these increases were still less ($P < 0.01$) than those with either superphosphate or powdered SPR (Table 5.3).

Water-extractable P in the top 4-cm soil depth in the pots increased at the first harvest when powdered SPR was incorporated (Fig. 5.5). Even after four harvests, the increases in water-extractable P were restricted to the upper 2 cm of soil in the pots when pelletised SPR was

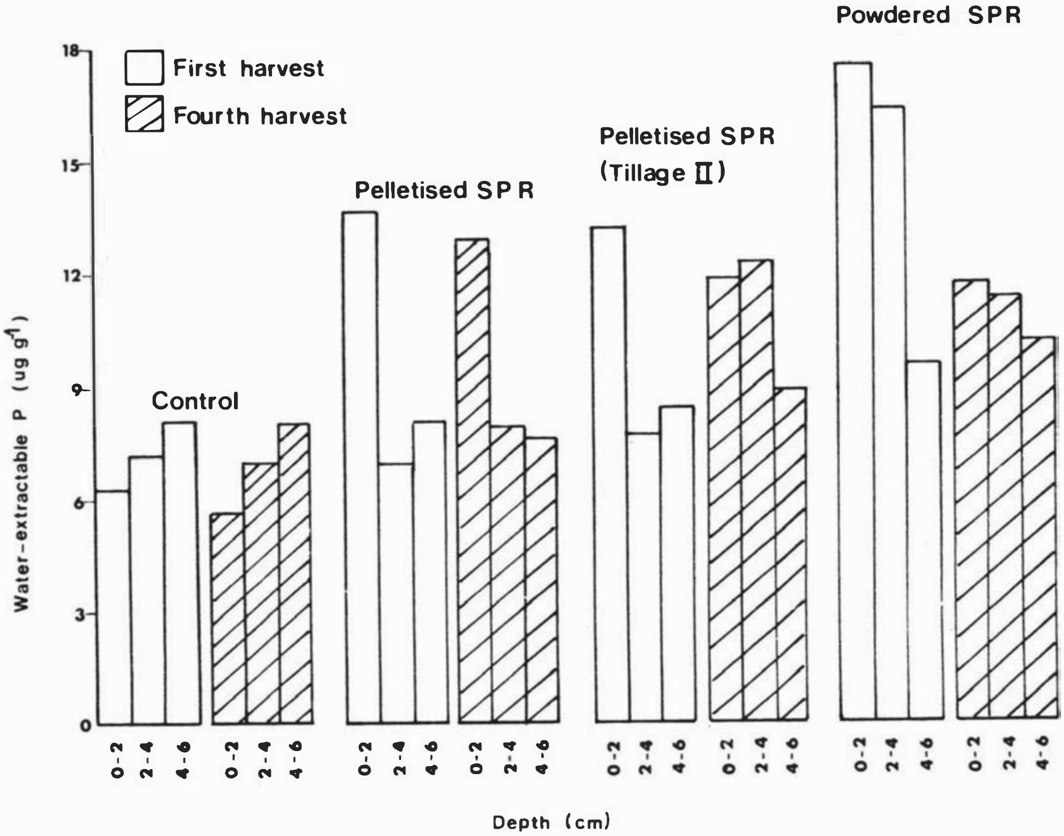


Figure 5.5 Amounts of water-extractable soil phosphorus at three depths (0-2, 2-4, and 4-6 cm) after the first and fourth harvests as influenced by tillage and the form of application of phosphate. Pelletised Sechura phosphate rock (SPR) treatments were surface applied and powdered Sechura phosphate rock was incorporated (0-4 cm).

surface applied. When the tillage treatments were used in conjunction with surface-applied, pelletised SPR, the amounts of water-extractable P increased in the 2 to 4 cm soil depth at the fourth harvest (Fig. 5.5).

5.3.2.2 Incubation studies with earthworms

In the first 20 days, no differences were found between earthworm and non-earthworm treatments but by day 38, earthworms had increased the Bray-extractable P in the soil to which SPR was added, by 32% (Fig. 5.6). Addition of earthworms after 24 days to soil incubated with SPR also resulted in an increase in Bray-extractable P, but this increase (16%) was not as pronounced.

The amounts of 0.5M NaOH-extractable inorganic P in the soil to which SPR was added, increased in both the presence and absence of earthworms over 70 days (Fig. 5.7). Because apatite minerals are insoluble in dilute NaOH and because this reagent extracts sorbed inorganic P (Williams et al., 1967), increases in the 0.5M NaOH-extractable P fraction of a soil to which a PR is added, provides a good estimate of the amount of P dissolved and retained by the soil. Validation of the use of the NaOH extraction to provide an estimate of the amount of PR dissolved in a soil is presented later (Chapter 7.2.4).

As with Bray-extractable P (Fig. 5.6), earthworms had no marked effect on 0.5M NaOH-extractable P in the soil to which SPR was added over the first 20 days. However, by 70 days 0.5M NaOH-extractable P had increased by 19% in the presence of earthworms (Fig. 5.7). Although these percentage increases are less than those reported for Bray-extractable P (Fig. 5.6), the actual increases in 0.5M NaOH-extractable P are far greater (40 μgP g^{-1} of soil). Earthworm casts collected from the soil to which SPR was added 7 days after the start of the study and incubated separately, showed a similar increase in 0.5M NaOH-extractable P to that in the soil with SPR in the presence of earthworms (Fig. 5.7).

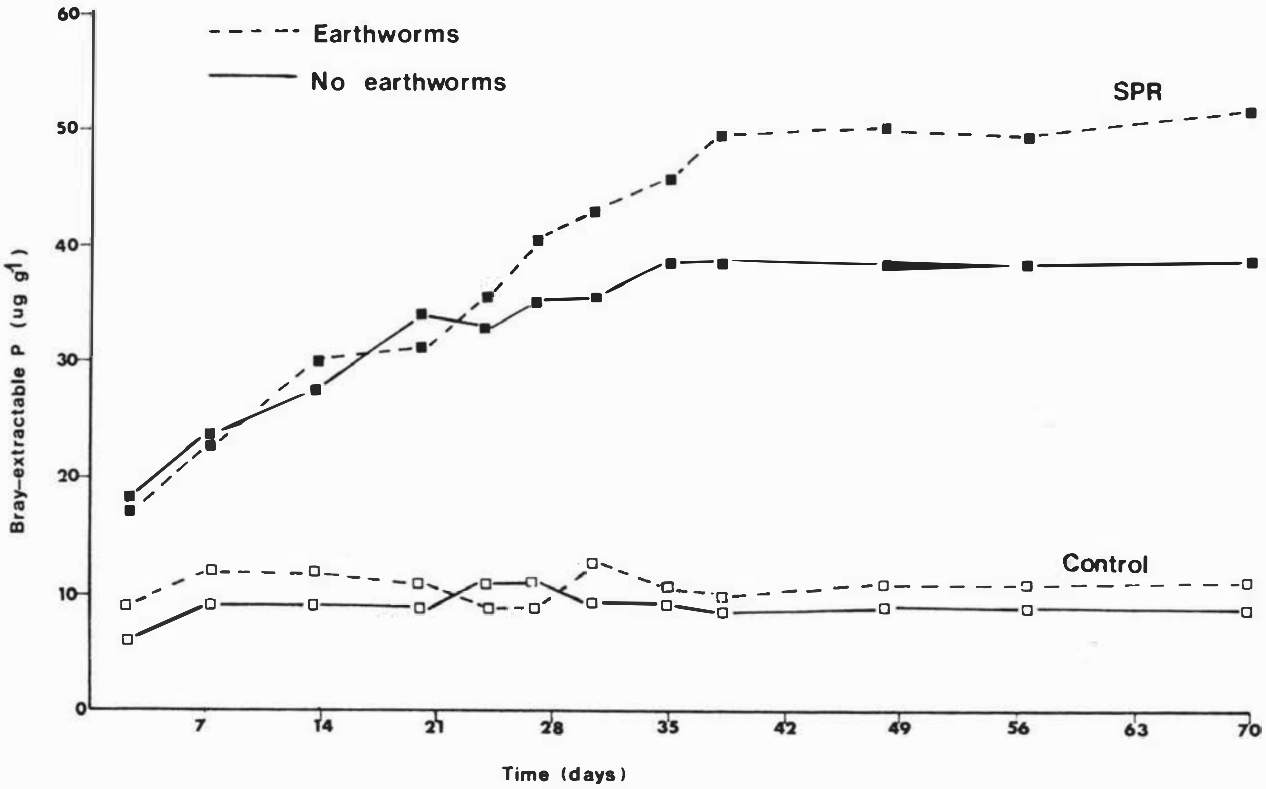


Figure 5.6 Amounts of Bray-extractable phosphorus as influenced by the addition of Sechura phosphate rock (SPR) in the presence and absence of earthworms over 70 days. Control = no added Sechura phosphate rock.

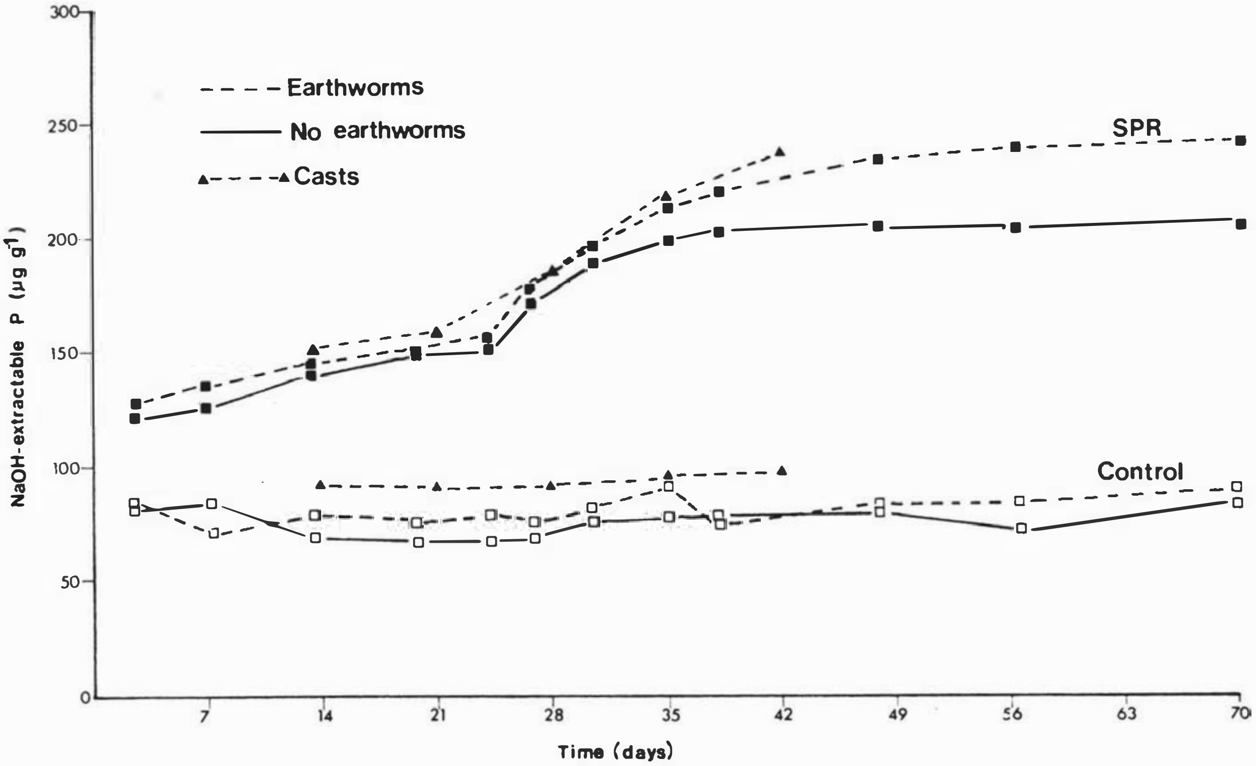


Figure 5.7 Amounts of 0.5M NaOH-extractable phosphorus in soil and casts (collected after 7 days) as influenced by the addition of Sechura phosphate rock (SPR) in the presence and absence of earthworms over 70 days. Control = no added Sechura phosphate rock.

Marked differences were observed by optical microscopy in the degree of intimate contact of SPR particles with soil in earthworm casts (Plate 5.1) compared to particles incubating in the soil (Plate 5.2). Whereas contact of the SPR particles with soil aggregates in the incubating soil was restricted to a few surfaces (Plate 5.1), the PR particles were in intimate contact with soil on all surfaces (Plate 5.2) in the earthworm casts.

A more detailed examination by scanning electron microscopy (SEM) however, showed no visible differences in the surface morphology of SPR particles following passage through the earthworms digestive tract (Plate 5.3), compared to that of particles incubated in the soil (Plate 5.4) and prior to incubation (Plate 5.5). Four earthworm species (A. caliginosa, L. rubellus, A. longa, and Octalasium cyaneum) and two soil types (Tokomaru silt loam and Stratford sandy loam) were included in this study.

When 50 g (supplying 51.3 μgP g^{-1} of soil) and 100 g (supplying 102.6 μgP g^{-1} of soil) of organic matter were added as finely-ground herbage to the Tokomaru silt loam, bicarbonate-extractable P in the soil increased, particularly in the presence of earthworms (Table 5.6). Increases in bicarbonate-extractable P in the soil to which SPR was added, were in fact very similar to those reported for Bray-extractable P (Fig. 5.6). After 70 days, marked increases were found, particularly at the highest organic matter addition, in bicarbonate-extractable P in the soil to which either SPR or superphosphate was added in the presence of earthworms (Table 5.6).

Measurements of soil pH showed no changes over 70 days in the soil alone and in the soil to which 50 g of organic matter was added in either the presence or absence of earthworms. In contrast, at the highest level of organic matter addition (100 g), soil pH decreased in the presence of earthworms from 5.45 initially, to 5.10 at 35 days, and to 4.82 at 70 days.

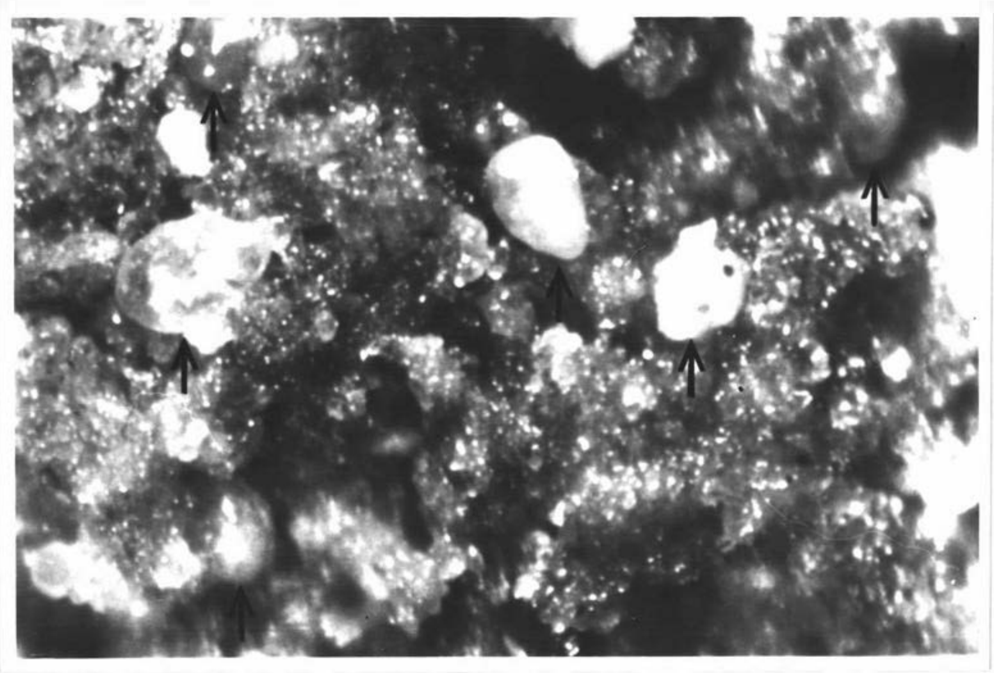


Plate 5.1 Nature and extent of the contact between Sechura phosphate rock particles when mixed with sieved (<2 mm) Tokomaru silt loam (magnification = 80).

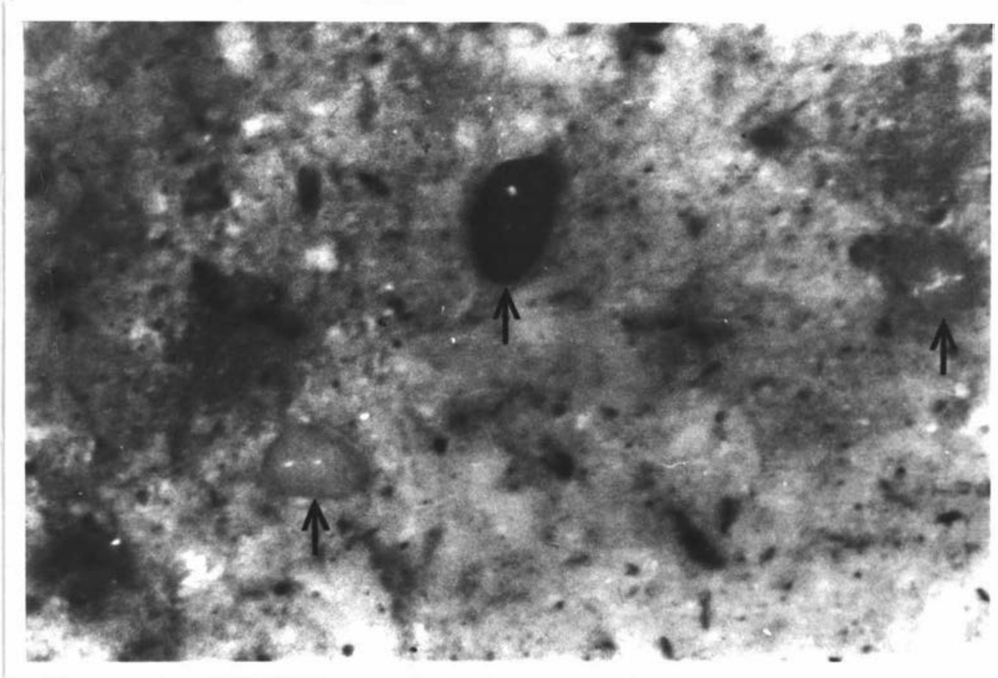


Plate 5.2 Nature and extent of the contact between Sechura phosphate rock particles and soil material in casts after passage through the earthworm's digestive tract (magnification = 80).

Plate 5.3 Scanning electron micrograph of a Sechura phosphate rock particle after passage through the earthworm's digestive tract (magnification = 400).

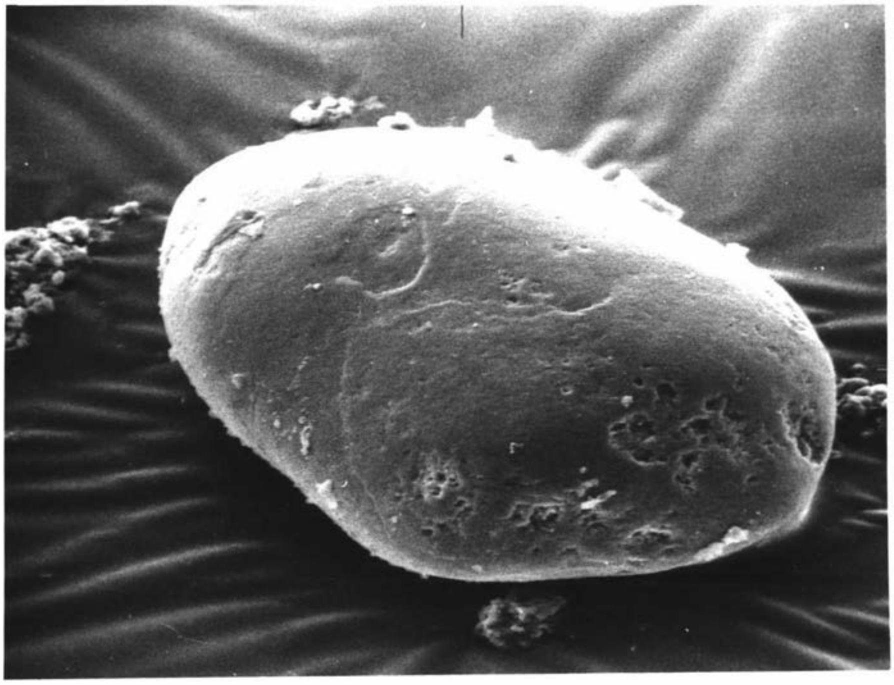


Plate 5.4 Scanning electron micrograph of a Sechura phosphate rock particle after incubation in sieved (<2 mm) Tokomaru silt loam (Magnification - 400).

Plate 5.5 Scanning electron micrograph of a Sechura phosphate rock particle prior to incubation (magnification = 400).

Table 5.6 Bicarbonate-extractable soil phosphorus (μg g^{-1}) values at 70 days as influenced by the source of phosphate, addition of organic matter, and earthworms. Treatments 1-3 earthworms absent; treatments 4-6 earthworms present

Differences between duplicates <1.5 μgP g^{-1}

Treatment	Application rate (μgP g^{-1})	Level of organic matter addition (g)		
		0	50	100
1 Control	0	6.0	8.4	12.6
2 SPR	500	26.4	30.6	32.2
3 Superphosphate	500	70.7	72.0	75.5
4 Control	0	7.8	9.6	15.6
5 SPR	500	34.2	42.6	48.0
6 Superphosphate	500	79.2	86.4	93.6

In the absence of earthworms, the decreases were far less pronounced; 5.38 at 35 days to 5.12 at 70 days. Organic carbon monitored throughout the study, however, remained constant, even in the earthworm treatments. Although not measured, addition of organic matter in the incubating soil could have increased exchangeable Ca levels by as much as 119 and 238 μg g^{-1} of soil as a result of the addition of 50 to 100 g of organic matter, respectively.

The average weight of 30 earthworms added at the start of the experiment was 0.33 g per earthworm. After 70 days, the average weight of earthworms was related closely to the level of added organic matter. With soil alone, the average weight per earthworm was 0.21 g, whereas with soil and 50 g and 100 g of added organic matter the average weight per earthworm was 0.27 g and 0.30 g, respectively, after 70 days, representing losses in biomass of 9 to 36%.

5.3.2.3 Soil ingestion trials with earthworms

The gut capacity of the earthworms, estimated by stripping, yielded 188 mg oven-dry soil per g of earthworm. Assuming that this amount is ingested once every 24 h, then the 30 earthworms in the incubating soil would have ingested only 131 g or 3.3% of the 4000 g of soil in 70 days.

Estimates derived by collection and weighing of casts gave 274 mg oven-dry soil per g of earthworm. Assuming that this amount is ingested once every 24 h, then the 30 earthworms in the incubating soil would have ingested 4.7% of the 4000 g of soil in 70 days.

Using the frame technique, the percentage of soil affected by the two earthworm species on an area basis, measured by both casts (Fig. 5.8a) and burrows (Fig. 5.8b), increased over 19 days. *A.caliginosa* casts accounted for approximately 44% of the soil area after 19 days, whereas

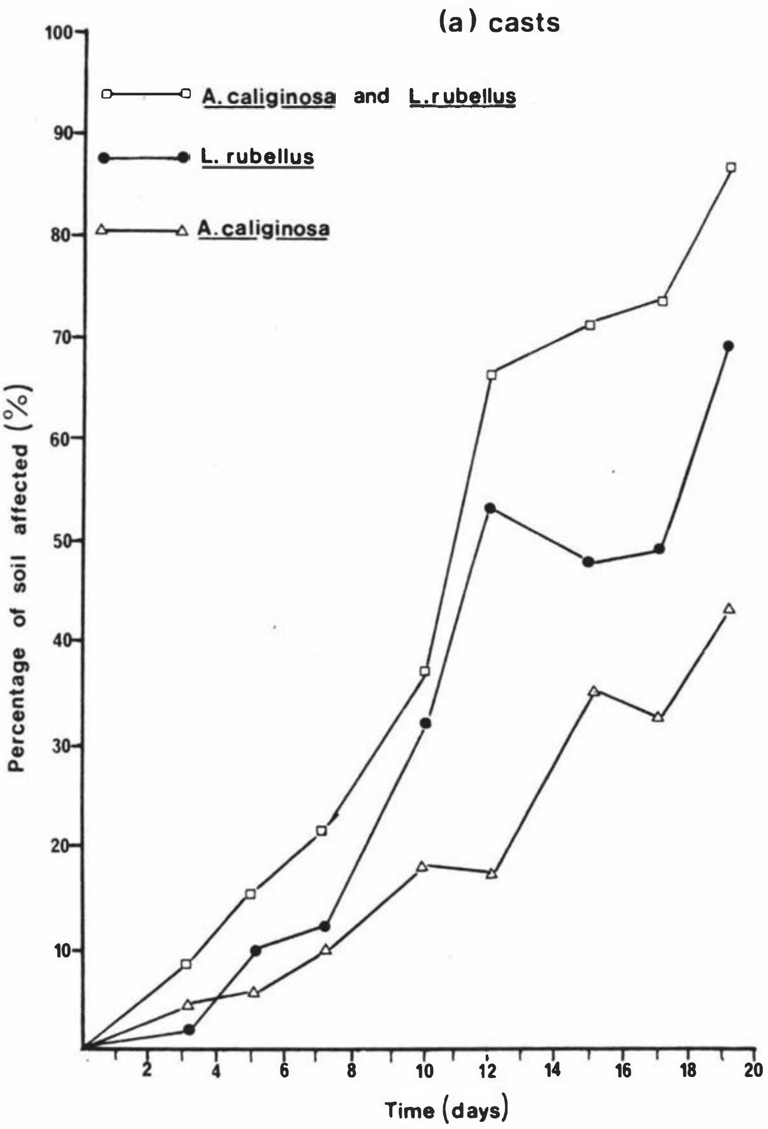


Figure 5.8 Percentage of soil affected by the activity of L. rubellus and A. caliginosa as measured by casts (a), burrows (b), and casts and burrows (c) on an area basis.

Figure 5.8 contd.

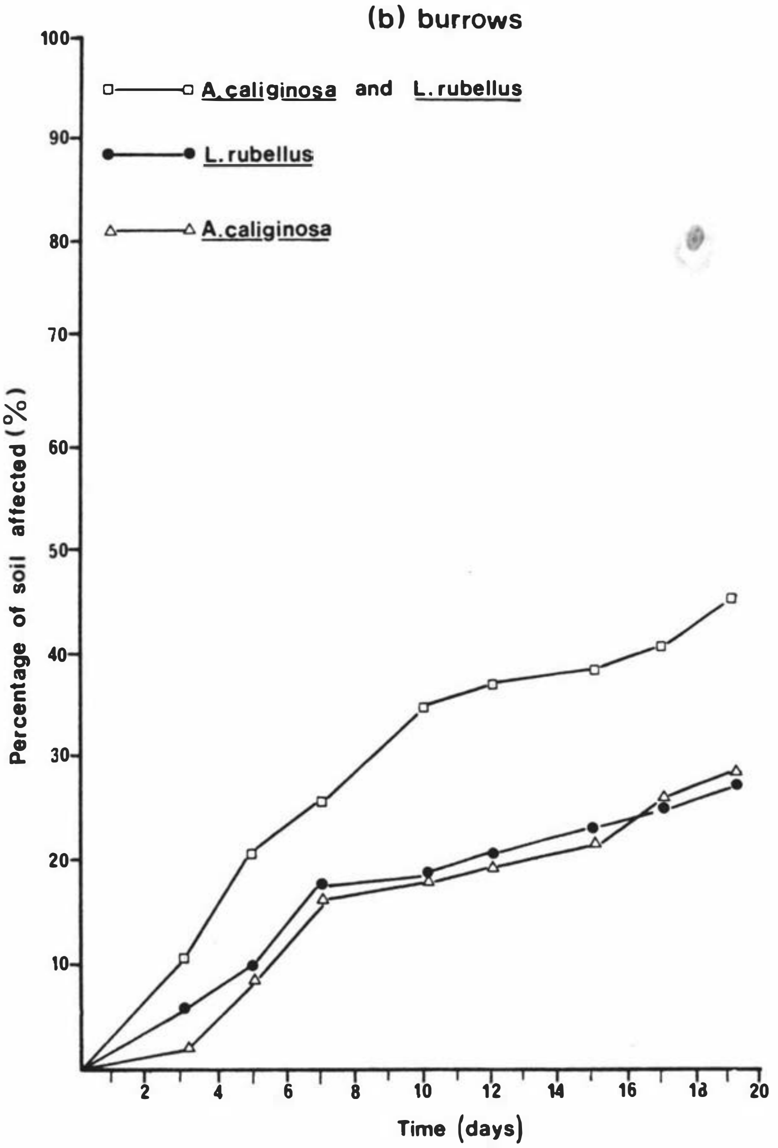
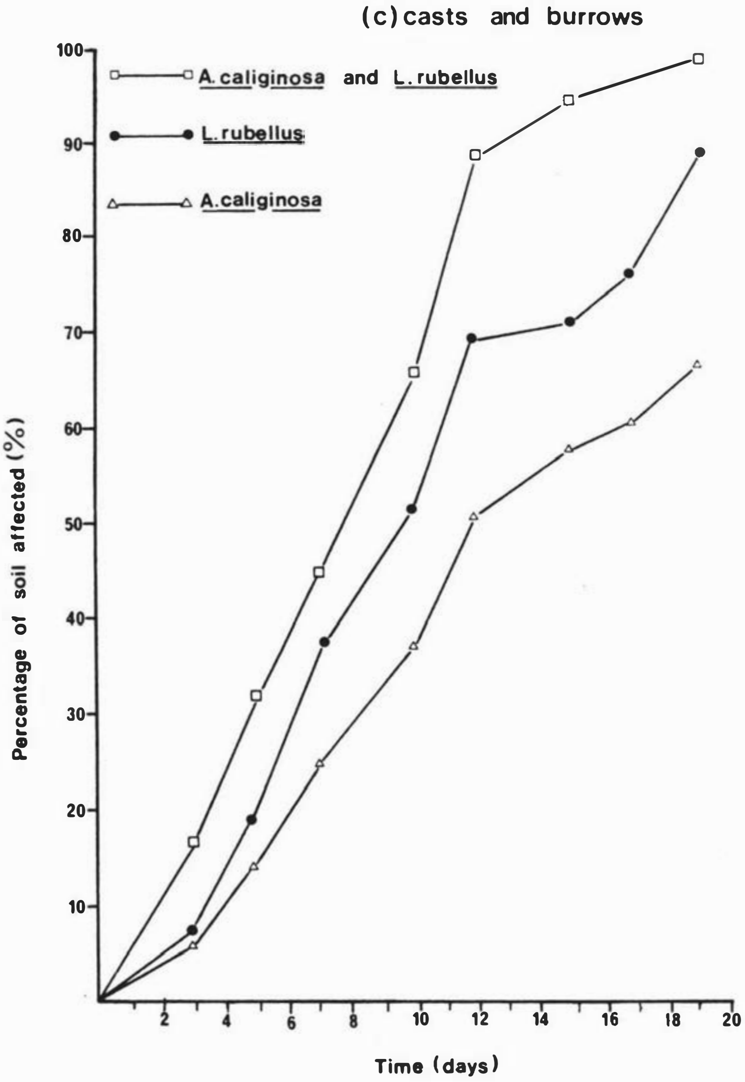


Figure 5.8 contd.



L. rubellus casts accounted for over 70% of the soil area (Fig. 5.8a) over the same period. A combination of the two species increased this to approximately 88% (Fig. 5.8a). No distinction was made between discrete casts and soil particles partially or completely coated with cast material. Burrows accounted for 28 and 27% of the soil area affected by A. caliginosa and L. rubellus, respectively, after 19 days (Fig. 5.8b). A combination of the two species increased this proportion. Combining casts and burrows gives an indication of the total area of the soil affected by the two earthworm species over the 19 days (Fig. 5.8c).

5.4 General Discussion

The effect of earthworms on the yield of ryegrass and P uptake by ryegrass in the present glasshouse experiment varied with the source, rate, and method of application of P, and with time. The increase in the yield of ryegrass in the presence of earthworms varied from 2 to 32%, while the increase in P uptake by ryegrass ranged from 0 to 40% over seven harvests. A number of other workers have reported that earthworms increase herbage yields, both in the glasshouse (Hopp and Slater, 1949; Waters, 1951; Nielson, 1953; Edwards and Lofty, 1978) and in the field (Nielson, 1953; Stockdill, 1959; Edwards and Lofty, 1980). Nielson (1953) found increases in production ranging from 30 to 110% from a sward containing both grasses and clover over 20 months in a pot experiment. Waters (1951) also obtained similar increases in the growth of ryegrass in the presence of earthworms in the glasshouse. Edwards and Lofty (1978) and (1980) found that the number of barley seedlings emerging, weight of barley roots, and height of barley plants were greater in direct-drilled soil in which earthworms were present.

In addition to a marked difference in the physical appearance of the soil in which earthworms were present, all earthworm treatments gave a significantly higher concentration of N in the herbage at the first harvest, which would account, in part, for the increased yield of ryegrass. The initial increase in N concentration of the ryegrass probably results from an increase in the amount of plant-available soil N. A number of workers have measured increases in the amounts of plant-available soil N as a result of the activity of earthworms in glasshouse studies (Russell, 1910; Hopp and Slater, 1949; Barley and Jennings, 1959). Several workers (Satchell, 1958; Edwards and Lofty, 1972) have suggested that earthworm mortality is the probable source of the increase in the plant-available soil N pool. Although over 85% of the earthworms were recovered from the pots at the end of the present glasshouse experiment, a marked decrease in their total biomass was measured (Table 55). Calculations indicate that the contribution of N from this source to the plant-available pool was relatively small (3.4%) in relation to the total added inorganic N. Differences in the concentration of N in the ryegrass did not persist after the first harvest.

There were similar changes in both the field and glasshouse populations of earthworms over the period of the experiment. This would suggest that measurements in the glasshouse are relevant to the field situation, as the loss in population biomass is not simply a result of the glasshouse technique.

Probably the most significant feature of the results obtained in the glasshouse experiment involving earthworms was the different effect earthworms had on the performance of the two P sources. With superphosphate, the initial increase in both ryegrass yields and P uptake by the ryegrass ranged from 20 to 40% at first harvest, to less than 10% by the seventh harvest. The effect of earthworms on the concentration of N in the ryegrass and on consequent yield probably explains the initial difference in the performance of superphosphate. In marked contrast, earthworms increased the performance of pelletised CRP by 15 to 30% throughout the whole trial period. In the absence of earthworms, however, pelletising reduced the effectiveness of CRP. In addition to any effect of increased short-term, plant-available soil-N levels on plant growth, the increased effectiveness of CRP in the presence of earthworms appears to have resulted, in part, from the incorporation into the soil of the surface-applied CRP material by the feeding and burrowing activity of the earthworm. Increases in the amounts of water-extractable P (Fig. 5.3) in the soil measured at the lower two depths indicate movement of CRP particles from the soil surface. It is not clear, from these results, however, whether the earthworms directly incorporated CRP particles into the soil at lower depths, through their feeding and burrowing activity, or whether the presence of burrows open to the surface simply facilitated the downward movement of the surface-applied PR particles during watering.

Although the agronomic data from the tillage experiment were inconclusive, increases in the amounts of water-extractable P at the 2 - 4 cm soil depth after four harvests, indicate movement of SPR particles, derived from the pelletised PR applied on the soil surface, into the soil under the tillage treatment (Fig. 5.5). In fact the increases in water-extractable P in the soil were very similar to those found in the soil used in the glasshouse study with pelletised CRP in the presence of earthworms (Fig. 5.3); suggesting that earthworms play neither an active nor a direct role in the incorporation of a surface-applied, pelletised PR. The presence of earthworm burrows open to the surface simply appears to facilitate the downward movement of PR particles from the site of application on watering. These increases in water-extractable P in the soil may have been reflected in increased plant growth, had the present glasshouse study been extended beyond four harvests.

The presence of earthworms in the incubating soil was found to increase the amounts of extractable P in the soil to which either SPR or superphosphate was added. Although a number of workers have noted increases in extractable P in earthworm casts compared to underlying soil (Sharpley and Syers, 1976, 1977; Mansell et al., 1981), and in soil with earthworms relative to soils without earthworms (Graff, 1970), the effect of earthworms on extractable P in the soil to which P fertilizers are added has not been reported. Addition of earthworms to the soil incubated with SPR resulted in a 32% increase in Bray-extractable P in the soil after 70 days in the present study (Fig. 5.6). Grigg (1968) has previously shown the Bray extractant to correlate well with plant-available soil P in New Zealand soils. The increase in extractability in the presence of earthworms appears to result, in part, from an increase in the degree of intimate contact of the SPR particles with soil surfaces during passage of the PR particles through the earthworms' digestive tract. A comparison of SPR particles in earthworm casts (Plate 5.2) and in the surrounding soil (Plate 5.1) clearly shows the difference in the degree of contact and also explains the increased dissolution, measured by 0.5M NaOH extraction of soil P derived from SPR in the presence of earthworms (Fig. 5.7). Although SPR was used in this study, earthworms are likely to affect other PR materials in a similar manner.

A closer examination of the surface morphology of SPR particles incubated in the soil (Plate 5.4) and after passage through the earthworms' digestive tract (Plate 5.3) showed no visible differences from these SPR particles, prior to incubation (Plate 5.5). Because of the porous nature of many PR materials, a high proportion of total surface area is comprised of internal surfaces (Hill et al., 1954). Consequently, a small increase in external surface area due to passage of a PR particle through the earthworm would have only a minor effect on the rate of dissolution; this would be too small to explain the increases measured in the present study. Possible attack of PR particles by acids during passage through the earthworms digestive tract, however, can not be ruled out.

As well as increasing bicarbonate-extractable soil P, the addition of increasing amounts of organic matter (as finely-ground herbage) to the soil, particularly in the presence of earthworms, also resulted in increases in bicarbonate-extractable P in the soil to which either SPR or superphosphate was added. In the presence of earthworms, bicarbonate-extractable P increased by 30, 39, and 44% with soil alone, soil with 50 g, and soil with 100 g of added organic matter, respectively, in the soil to which SPR was added. With superphosphate, however, the increases ranged from only 12 to 24%, reflecting the differing solubilities and behaviour of these two P sources in soil. Unlike superphosphate, where dissolution occurs immediately and is largely independent of direct soil contact (Brown and Lehr, 1959), the dissolution of PR occurs more gradually with time (Fig. 5.7), with the rate of dissolution being directly dependent on the degree of contact with soil surfaces (Chien and Hammond, 1978).

Loss in biomass of earthworms, which is not uncommon under both glasshouse (Table 5.5) and field (Table 5.2) conditions, was far less (9%) when 100 g of organic matter as finely-ground herbage was added, than in the soil with no added organic matter (36%). Reduction in earthworm activity, as a consequence of this weight loss, may have resulted in a decrease in the extent of intimate mixing of the SPR particles with the soil by the earthworms, although the relationship between earthworms biomass and activity is not well understood.

Associated with the addition of 100 g of organic matter to the

Tokomaru silt loam in the present study, was a decrease in soil pH, particularly in the presence of earthworms. The increased solubility of a PR, with a decrease in soil pH, has been demonstrated by several workers (Joos and Black, 1950; Peaslee et al., 1962). However, as no decrease in soil pH was measured when 50 g of organic matter was added in either the presence or absence of earthworms, it seems unlikely that soil pH can explain fully the increases measured in the extractability of SPR in this study. In contrast to the varying effect of soil pH, addition of 100 g of organic matter to the Tokomaru silt loam represents a possible increase of over 200 μgCa g^{-1} of soil to the exchangeable pool. Although few workers (Satchell, 1955) have attempted to evaluate the relative importance of soil pH, *per se*, and exchangeable Ca in influencing earthworm activity, results from the present study suggest that earthworms remain active at relatively low soil pH, provided adequate Ca is available.

Estimates of soil ingestion by *L. rubellus* using the stripping method yielded 188 mg oven-dry soil per g of earthworm per day while the cast-collection method gave 274 mg oven-dry soil per g of earthworm per day. With the stripping method the fore-gut is not emptied, leading to an under-estimation, whereas with the cast-collection method some soil contamination occurs. The values presented, however, are still within the range reported in the literature by a number of workers. For example, Barley (1961) calculated a soil ingestion rate of 290 mg dry weight per g of earthworm per day with *A. caliginosa* and Satchell (1967) a similar ingestion rate (200 to 300 mg dry weight per g of earthworm per day) with *L. terrestris*. In contrast, Crossley et al. (1971) calculated an ingestion rate of only 100 to 120 mg dry weight per g of earthworm per day with *Octalasium* spp. Taking the average of the two ingestion rates obtained in the present study, then after 70 days the earthworms would have ingested only 4% of the total soil.

In marked contrast, measurement of the proportion of soil affected by earthworms on an area basis using the frame technique ranged from 66% with A. caliginosa and 89% with L. rubellus after 19 days, to 100% for the two species combined after 19 days. The apparent increases in the effect of earthworms on the soil measured by this technique explains more fully the increases not only in Bray- and bicarbonate-extractable soil P, but also in NaOH-extractable P. In addition to counting both burrows and casts, the frame technique counts soil particles partially or completely coated with cast material as earthworms do not always cast discretely in soils. Because SPR particles were found in soil voids and on soil surfaces (Plate 5.1), deposition of cast material in these areas, would increase the degree of contact in a similar manner to that resulting from ingestion by earthworms. Calculation of ingestion rates, using stripping or casting data, shows that earthworms would have ingested only 4% of the soil in the 70 days. It is clear that soil particles coated partially or completely with cast material make up the bulk of cast material, per se, in the soil and thus direct ingestion by earthworms probably plays only a minor part in increasing extractable P from a PR. The absence of any differences in 0.5M NaOH-extractable P when SPR was added to soil containing earthworms and when earthworm casts collected from the soil to which SPR was added were incubated separately (Fig. 5.7), further indicates that measurement of the effect of earthworms in a soil, determined by the frame technique, approximates more closely the actual situation, than that indicated by the two ingestion methods. This suggests that traditional ingestion methods used for assessing earthworm effects on soils may require re-evaluation.

The results from the study investigating the mechanism of incorporation of a surface-applied PR into soil by earthworms and the two studies investigating the effect of ingestion of PR particles by earthworms, are summarized in Fig. 5.9. These suggest that both burrowing and casting indirectly increased the availability of P in the PR to ryegrass by improving the physical distribution and intimate contact of the PR with the soil.

The findings of the present study are important not only to the design and conduct of glasshouse trials, which evaluate P fertilizers varying widely in solubility, but also to the interpretation and extrapolation of the results obtained in the glasshouse to the field situation. Whereas good agreement has generally been found, on a relative basis, between glasshouse and field trial results comparing water-soluble P fertilizers (Hausenbuiller and Weaver,1960; Mackay et al., 1980), the results of Muller (1970) and the results of the preliminary glasshouse study (Chapter 3) indicate that differences exist between the glasshouse and field when evaluating pelletised PR materials. In the preliminary glasshouse study (Chapter 3) pelletised CRP was less effective than superphosphate. No difference was found between powdered CRP and superphosphate when incorporated into the upper 2 cm of the soil in the glasshouse. Unlike the results from the glasshouse, no difference was found between either pelletised or powdered CRP and superphosphate in the field (Chapter 4). In the present glasshouse study, pelletised CRP was found to be as effective as superphosphate in the presence of earthworms. Thus, in the absence of biological mixing, both the form and method of application of PR materials become an important consideration in their evaluation as a source of P to plants under glasshouse conditions.
In addition, when earthworms are excluded the form and method of application of a PR become important in the interpretation and extrapolation of glasshouse results to the field situation.

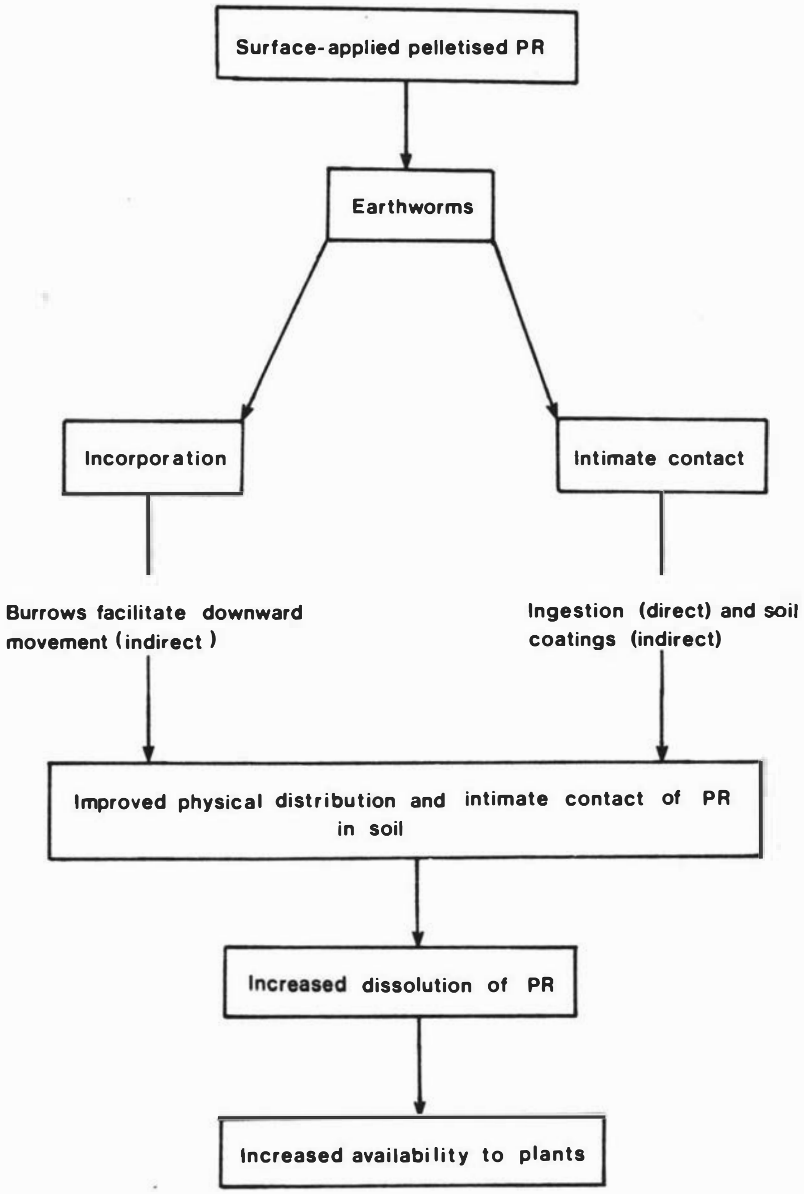


Figure 5.9 Schematic representation of the origin of the effects of earthworms on the availability of phosphorus in a phosphate rock (PR).

CHAPTER 6

CHAPTER 6

METHODS FOR ASSESSING AND PREDICTING THE AGRONOMIC EFFECTIVENESS OF PHOSPHATE ROCK MATERIALS

6.1 Introduction

The suitability of PR materials for direct application varies considerably. In general, the agronomic effectiveness of a PR material increases as the extent of carbonate substitution in the lattice increases (Lehr and McClellan, 1972). Of the methods available for assessing and predicting the agronomic effectiveness of PR materials, the glasshouse has been used the most extensively. The agronomic effectiveness of a large number of PR materials has been evaluated in glasshouse studies (Armiger and Fried, 1957; Bengtson et al. 1974; Engelstad et al., 1974; Chien and Hammond, 1978a).

Data for the agronomic performance of CRP in the glasshouse appear to be restricted to studies by Roberts and White (1974), comparing CRP with a range of calcined Christmas Island 'C' products; by Powell (1979), comparing CRP with five other PR materials in an experiment evaluating the importance of mycorrhizal fungi to ryegrass; and by Andrews et al. (1978), Powell et al. (1980), Rajan (1981), and the writer (Chapters 3 and 5) in comparisons with superphosphate. This permits only a provisional ranking of the agronomic effectiveness of CRP in relation to the range of PR materials available throughout the world.

In addition to extending the agronomic evaluation of CRP over a wider range of soils, the initial purpose of the work reported in this

Chapter was to compare the agronomic effectiveness of CRP with a range of other PR materials. These other materials include Sechura phosphate rock (SPR), North Carolina phosphate rock (NCPR), and Tennessee phosphate rock (TPR), of which the last two have been studied extensively (Engelstad et al., 1974; Chien and Hammond, 1978a; Khasawneh and Doll, 1978). Calcined Christmas Island C grade PR (Calciphos) was also included in the present study because of its contrasting mineralogy. Although of little agronomic value in the raw state, calcination at 500°C results in degradation of the mineral lattice, increasing the solubility and agronomic performance of this material. Calciphos has been evaluated extensively in both the glasshouse and the field in New Zealand and Australia (Doak et al., 1965; Buchan et al., 1970; Muller, 1970; Stephens and Lipsett, 1975; Wright, 1975; Gilkes and Palmer, 1979). The high energy inputs required for calcination, now makes the manufacture of Calciphos uneconomic under present conditions.

Although biological techniques provide the most reliable method for assessing the agronomic effectiveness of PR materials, the resources and facilities required, and the time delay in obtaining results, prevent rapid assessments. Of the indirect methods, chemical extraction procedures offer simple and rapid alternatives. Although numerous studies have evaluated chemical extraction procedures (Bengtson et al., 1974; Engelstad et al., 1974; Chien and Hammond, 1978a), the conclusions reached as to their suitability for predicting the agronomic effectiveness of PR materials vary widely. Whereas several workers (Terman et al., 1970; Bengtson et al., 1974; Engelstad et al., 1974; Fenster and Leon, 1978) have found neutral ammonium citrate (NAC) to be useful, Caro and Hill (1956) found that 2% citric acid was a better indicator of agronomic effectiveness. A similar conclusion was reached by Jacob and Ross (1932) and by Bartholomew and Jacob (1933), although Armiger and Fried (1957) found both reagents to be useful. In contrast, Cooke (1956) found that

2% citric acid and Bennett et al. (1957) and Hoffman and Breen (1964) found that NAC were poor indicators of the agronomic effectiveness of the PR materials which they evaluated. Amberger (1978) reported that 2% formic acid was a better indicator than 2% citric acid, as did Chien and Hammond (1978a) who, in addition, found ammonium citrate (pH = 3) to be a useful chemical extraction procedure.

Apart from two studies (Hoffman and Breen, 1964; Chien and Hammond, 1978a) only single chemical extractions have been used for predicting the likely agronomic effectiveness of PR materials. Hoffman and Breen (1964) suggested that the sum of four sequential extractions with NAC or 2% citric acid may be more useful as a method of assessing the agronomic effectiveness of PR materials than a single extraction. Chien and Hammond (1978a) found that the second extraction with NAC was more effective than the first in assessing agronomic effectiveness. However, Chien and Hammond (1978a) did not assess the potential of using the first and second extractions combined. This would be necessary if P sources of varying solubilities were to be compared. In addition to enabling a comparison of PR materials containing varying amounts of $CaCO_3$, a sequential extraction procedure may improve the predictive ability of conventional chemical extractants in other than the short-term by removing a greater proportion of total P. Both of these are limitations presently shown by single-extraction procedures (Bengtson et al., 1974; Chien and Hammond, 1978a).

On addition to soil, a PR material gradually dissolves releasing some P to the plant-available pool. An approach which attempts to characterize this pattern of P release may have advantages over conventional extraction techniques, which simply remove a fraction of total P from a PR. A further purpose of the work reported in this Chapter is to evaluate two such approaches, namely reaction with hydrous ferric oxide gel (Fe gel) and electro-ultrafiltration (EUF). Fe gel has been used widely for modelling P behaviour in soils (Hope, 1977; Mclaughlin et al., 1977; Ryden and Syers, 1977). To date, this approach has not been used to evaluate the P-release characteristics of PR materials. As Fe gel acts as a sink for P, in a similar manner to the P-sorbing components in a soil (Mclaughlin et al., 1977), removal of P from solution by Fe gel may be used to study the rate and extent of dissolution of a PR and may provide an indirect method for assessing the agronomic effectiveness of PR materials.

The EUF procedure is a combination of electrodialysis and ultrafiltration, and was developed for characterizing the availability of nutrients in soil (Nemeth, 1972). Unlike Fe gel, which acts as a sink for P, EUF continuously removes the reaction products from solution by ultrafiltration, during the electrodialysis process. This procedure also offers potential for assessing the dissolution of PR materials.

6.2 Materials and Methods

6.2.1 Phosphate sources used

Values for total P, determined by perchloric acid digestion (O'Connor and Syers, 1975) and the calcium carbonate content, determined by titration after carbon dioxide evolution, of the eight P sources used are presented in Table 6.1.

6.2.2 Conduct of glasshouse study

Values for soil pH (in water), organic carbon content (Chapter 4.2.1), P-sorption capacity (Chapter 3.2.2), and extractable P estimated by the bicarbonate- (Chapter 3.2.2) and single water- (Chapter 4.2.1) extraction methods for the six soils are presented in Table 6.2.

Before potting, soils were air dried, sieved (<6mm), and then

Table 6.1 Total phosphorus and calcium carbonate contents of the phosphate sources

Phosphate source	Abbreviated name	Total P (%)	Total $CaCO_3$ (%)
Superphosphate		10.1	-
North Carolina phosphate rock	NCPR	13.2	11.7
Sechura phosphate rock	SPR	13.7	8.9
Chatham Rise phosphorite	CRP	9.2	27.6
Calcined Christmas Island C grade phosphate rock	Calciphos	14.7	-
Tennessee phosphate rock	TPR	12.9	1.7
Nauru phosphate rock	NPR	15.8	-
Christmas Island A grade phosphate rock	CIAPR	14.6	-

Table 6.2 Some characteristics of the soils

New Zealand soil group	Soil type	Total carbon (%)	pH_{H_2O}	P-sorption capacity (%)	Extractable soil P	
					Bicarbonate	Water
					($\mu g\ g^{-1}$)	
Yellow-grey earth	Tokomaru silt loam	2.00	5.5	22	7.6	3.4
Yellow-grey earth/ yellow-brown earth intergrade	Wainui silt loam	3.85	5.0	32	15.6	6.3
Yellow-grey earth/ yellow-brown earth intergrade	Kumeroa silt loam	4.85	6.2	35	11.5	5.8
Yellow-brown earth	Maharahara sandy loam	5.20	5.7	41	7.9	2.9
Yellow-brown earth/ yellow-brown loam intergrade	Konini silt loam	5.85	5.5	54	6.8	3.0
Yellow-brown loam	Ramiha silt loam	9.43	5.6	87	5.2	1.4

hand packed (550 to 760 g) into pots measuring 10 x 10 x 10 cm.

In the first trial, the effectiveness of NCPR, SPR, CRP, TPR, and Calciphos was compared to single superphosphate at two rates of application (75 and 150 kgP ha^{-1}) on six soils using perennial ryegrass (*Lolium perenne*) as the indicator species. All the PR materials were ground to pass through a 180-μm sieve (85 B.S. mesh), before use. Superphosphate was surface applied as granules (<2 mm). The PR materials were surface applied in a pelletised form. The mean pellet size used (0.5 to 1.0 mm) was smaller than that used in the initial glasshouse evaluation of CRP (Chapter 3) and in the field (Chapter 4).

In the second trial, pelletised SPR, CRP, and TPR were compared with superphosphate at two rates of application (75 and 150 kgP ha^{-1}), on three soils (Wainui, Konini, and Ramiha), using Huia white clover (*Trifolium repens*) as the indicator species. All treatments were surface applied and replicated three times. A randomized block design was used in both trials.

Approximately 50 perennial ryegrass seeds were sown and then thinned to 30 seedlings per pot at 20 days. In the case of white clover, 30 seeds were sown and then thinned to 15 seedlings at 20 days. Inoculum (*Rhizobium trifolii*) was applied in suspension 3 days after thinning. Differences in the sulfur (S) content of the various treatments were adjusted by addition of gypsum. Both the nitrogen (N) and potassium (K) were applied in three split dressings during each growth period, along with the micronutrient solution of Middleton and Toxopeus (1973). For white clover, only a single dressing of N was applied after germination and immediately after each cut. With the exception of S, all nutrients were applied in solution. Pots were watered to field capacity (taken at 40-cm suction) daily.

In all, four harvests were taken at intervals of 7, 4, 5, and 6 weeks for perennial ryegrass and 10, 6, 7, and 7 weeks for white clover. At each harvest, herbage was cut 2 cm above the soil surface, removed, and oven dried at 60°C for 24 h before weighing. After grinding, total P and N were determined following Kjeldahl digestion.

6.2.3 Assessment of chemical extraction procedures

The solubility of the P sources (<180 μm) was investigated using seven chemical extraction procedures:

2% Formic acid A 0.4-g sample of each P source was extracted with 40 ml of 2% formic acid at 23°C for 1 h (Hoffman and Mager, 1953). The sample was then centrifuged at 10,000 rpm for 5 min, filtered (0.45 μm Millipore filter), and then the residue was extracted again with 40 ml of fresh formic acid. Soluble P was determined in individual filtrates, following dilution , by the Watanabe and Olsen (1965) modification of the Murphy and Riley (1962) method.

2% Citric acid A 0.4-g sample of each P source was extracted with 40 ml of 2% citric acid at 23°C for 1 h (AOAC, 1960) or 0.5 h (The Fertilisers Regulations, 1969). The sample was centrifuged, filtered, and the residue extracted again with 40 ml of fresh citric acid. This was repeated a third time.

Neutral ammonium citrate A 0.4-g sample of each P source was extracted with 40 ml of NAC solution at 65°C for 1 h (AOAC, 1970). Three further extractions were carried out on all samples. No interference from citrate in the determination of P was measured at the dilutions used in the present study.

Alkaline ammonium citrate A 0.2-g sample of each P source was extracted with 40 ml of the alkaline ammonium citrate (AAC) solution of Petermann at 65°C for 1.5 h (Boxma, 1977). Two further extractions were carried out.

5 and 15% Citric acid A 0.4-g sample of each P source was extracted with 40 ml of either 5 or 15% citric acid at 23°C for 1 h.

6.2.4 Outline of new approaches

6.2.4.1 Studies with hydrous ferric oxide gel

The Fe gel was prepared by adjusting a solution of 0.4M $Fe(NO_3)_3$ to pH 7, initially with 1M NaOH and subsequently by additions of 0.1M NaOH over a period of 1 h to maintain a pH of 7 during constant stirring. The neutralized solution was left overnight and the Fe gel recovered by centrifugation (2000 rpm, IEC UV Centrifuge). The precipitated gel was washed with distilled water until the gel ceased to flocculate during centrifugation. The volume of gel was adjusted to give a suitable working concentration (5 mg ml^{-1}). Information on some of the properties of the Fe gel prepared in this way has been given by Ryden et al. (1977).

In the first study, the dissolution of SPR, NCPR, CRP, Nauru phosphate rock (NPR), Christmas Island A grade phosphate rock (CIAPR), and superphosphate were evaluated by dialysing duplicate 0.2-g samples (125 - 63-μm fraction) of each against the Fe gel. The P sources were sealed in dialysis tubing (Union Carbide cellulose casing) and immersed in 400 ml of a suspension containing 2.0 g of Fe gel in 0.5M $NaClO_4$ contained in 500 cm^3 polypropylene containers. The pH of the suspension was adjusted to 6 and 4 μmol of $HgCl_2$ was added to inhibit microbial activity. The containers were shaken on a flat-bed shaker at 20°C. After 2, 4, 6, 8, 10, 14, and 17 days a suitable aliquot of the Fe gel suspension was removed from the container and shaken with 35 cm^3 of 0.25M NaOH. A separate study showed that this treatment removed at least 95% of the P sorbed by the Fe gel. Following centrifugation (10,000 rpm for 10 min) and filtration (0.45 µm Millipore filter), the P concentration in the supernatant liquid was determined after neutralization. In a separate study, the pH of the Fe gel was monitored over a similar period and at the end of 14 days, the pH and P and Ca concentration of the filtered suspension from the dialysis tubing was also determined.

Results from the first study indicated that there was a problem with pH control of the Fe gel. Therefore in subsequent studies the effect of varying the initial pH (3 to 6) of the Fe gel on the dissolution of SPR and TPR was evaluated. In addition to pH, the effect of introducing the cation exchange resin (CER) Chelex 100 (styrene lattice with iminodiacetic acid exchange groups), with a total capacity of 0.6 mmole $Cu(NH_3)_4^{+2}$ ml^{-1} resin bed in a sodium form and an actual wet-mesh range of 100 to 200 mesh, in a dialysis tubing into the Fe gel system was also evaluated. The CER was prepared by washing, firstly with 500 ml of 5% HCl over 0.5 h, then with 500 ml of 12% NaCl for a further 0.5 h, and finally with deionized water until the presence of the chloride ion was not detectable with silver nitrate.

6.2.4.2 Electro-ultrafiltration

The operation of the EUF apparatus has been described in some detail by Nemeth (1976). Briefly, the PR and solution are placed in a central chamber containing a stirrer and cooling coil and this is placed between two platinum mesh electrodes with semi-permeable filters separating the solution from the electrodes. An electric potential is then applied between the electrodes and, in the electric field, the cations are attracted by the cathode and the anions by the anode and washed away after movement through the filter by a continuous stream of water. The ions can therefore be released continuously from the PR into the solution. The rate at which ions are extracted will depend on the rate of dissolution of the PR and the rate of transport of ions to the electrodes. The former is directly proportional to the voltage applied and in theory should also be directly related to the solubility of the PR. The rate of transport of ions is directly proportional to the field intensity and inversely proportional to the coefficient of friction of the ions.

In initial studies, the automatic control mode with seven fractions was used to evaluate the effect of varying solution:solid ratio on the dissolution of SPR. In this procedure the EUF apparatus was programmed to collect the filtrates at 5-min intervals for 35 min, giving seven fractions. The voltage applied was 50V initially, increased to 200V, after 5 min, and to 400V after 30 min. The volume of each anion filtrate was determined by weight and then a suitable aliquot was taken. Initially samples were also filtered through 0.45-μm Millipore filters to check on the efficiency of filtration of the EUF apparatus, but this was subsequently found to be unnecessary. Duplicate samples at each ratio were run. Deionized water was used in these initial studies because of poor replication of results with distilled water.

In subsequent studies, the EUF apparatus was set to operate at a constant voltage (400V) and the filtrate was manually collected at 5-min intervals for up to 50 min. Again the filtrate volume was determined by weight and a suitable aliquot taken for P analysis by the Watanabe and Olsen (1965) modification of the Murphy and Riley (1962) method. In addition to running a range of PR materials with deionized water, the effect of varying the pH by HCl and NaOH addition, and the conductivity by addition of NaCl and other salts, on the dissolution of the PR materials in the manual mode was also evaluated.

6.3 Results and Discussion

6.3.1 Agronomic evaluation of phosphate rock materials in the glasshouse

6.3.1.1 Response of perennial ryegrass

The total yield of ryegrass for the four harvests combined showed a significant ($P < 0.01$) response to applied P with all six soils (Table 6.3). The size of the response, however, varied with the source and rate of application of P, and across the six soils. Of the five PR materials, NCPR was the most effective when compared to superphosphate. Apart from the ryegrass yields with the Ramiha soil and with the Maharahara soil at 150 kgP ha^{-1}, NCPR was as effective as superphosphate (Table 6.3). In fact with the Wainui soil NCPR was more effective ($P < 0.01$) than superphosphate at 150 kgP ha^{-1}. With one exception (Ramiha soil), SPR was as effective as superphosphate at the low rate of application (75 kgP ha^{-1}), although at the high rate (150 kgP ha^{-1}) SPR was inferior ($P < 0.01$) to superphosphate with four soils (Ramiha, Konini, Maharahara, and Kumeroa) and to NCPR with two (Ramiha and Maharahara) of the six soils (Table 6.3).

In contrast to both NCPR and SPR, CRP was inferior ($P < 0.01$) to superphosphate at both rates of application on all soils except the Wainui. In fact even when compared at 75 kgP ha^{-1}, CRP was still less effective ($P < 0.01$) than either NCPR or SPR with four (Ramiha, Konini, Maharahara, and Kumeroa) of the six soils (Table 6.3). TPR was inferior ($P < 0.01$) to the other P sources, including Calciphos, which was less effective ($P < 0.01$) than superphosphate, NCPR, SPR, and CRP in increasing ryegrass yields at both rates of application with all six soils (Table 6.3).

Table 6.3 Total yield (g) in four harvests of perennial ryegrass on six soils as influenced by phosphate source and rate of application

Treatment	Application rate (kgP ha^{-1})	Soil type					
		Ramiha	Konini	Maharahara	Kumeroa	Wainui	Tokomaru
Control	0	2.24 L*	4.86 J	4.03 K	5.86 I	7.50 H	4.74 H
Superphosphate	75	7.15 E	8.66 DE	8.62 EF	8.82 D	9.68 D	7.64 CDE
	150	9.40 A	10.40 A	10.87 A	10.94 A	10.82 B	9.25 A
NCPR	75	6.92 F	8.54 DE	8.68 E	8.70 D	9.77 CD	7.70 CDE
	150	8.95 B	10.28 AB	10.58 B	10.80 AB	11.20 A	9.19 A
SPR	75	6.79 FG	8.48 E	8.37 F	8.64 D	9.61 D	7.54 DE
	150	8.72 C	10.17 B	10.24 C	10.67 B	11.01 AB	9.05 AB
CRP	75	6.46 H	7.95 F	7.97 G	8.31 E	9.63 D	7.28 E
	150	8.13 D	9.73 C	9.78 D	10.23 C	10.95 AB	8.64 B
Calciphos	75	4.96 I	7.17 G	6.72 H	7.16 F	9.00 E	6.64 F
	150	6.59 GH	8.75 D	8.45 EF	8.79 D	9.97 C	8.05 C
TPR	75	3.04 K	5.29 I	4.56 J	6.20 H	7.85 G	5.82 G
	150	3.61 J	5.80 H	5.06 I	6.59 G	8.42 F	6.56 F

* Capital letters denote Duncan's symbols for assessing significant ($P < 0.01$) differences for treatments within each soil.

To enable an evaluation of the P sources on a relative basis, response curves were drawn for all the P sources with each of the six soils, and the five PR materials were then compared at 90% of the yield maxima obtained from superphosphate. The relative yield values for NCPR (96-101), SPR (94-99), and CRP (90-99) were similar, whereas those for TPR (40-81) were inferior to all other P sources, including Calciphos (69-93).

As with total yield of ryegrass, total P uptake by ryegrass for the four harvests combined varied with the source and rate of application of P, and also varied between the soils (Table 6.4). In contrast to the yield data, NCPR was inferior ($P < 0.01$) to superphosphate at 150 kgP ha^{-1} across all six soils, as was SPR. Although no differences in total P uptake by ryegrass were found between CRP and SPR at 75 kgP ha^{-1}, CRP was still inferior ($P < 0.01$) to NCPR with four (Ramiha, Konini, Maharahara, and Tokomaru) of the six soils (Table 6.4). Again, TPR was markedly inferior ($P < 0.01$) to all other P sources; no differences were found between TPR at 75 kgP ha^{-1} and the controls on any of the six soils. In contrast to the conclusion drawn from yield data, Calciphos was as effective as CPR with four (Konini, Maharahara, Wainui, and Tokomaru) of the six soils using P uptake data as the criterion. With one exception, Calciphos was less effective ($P < 0.01$) than NCPR and SPR. This finding is in agreement with the results reported in previous Chapters (Chapters 3 and 5) and with the literature (Hagin et al., 1978; 1978b) where differences, particularly in the short term, between water-soluble and sparingly water-soluble P sources, are more pronounced when P uptake by ryegrass is used to assess agronomic effectiveness rather than yield data. However, unless differences in P uptake are expressed in increased yield, then conclusions drawn concerning the likely agronomic effectiveness of a PR source could be misleading if based solely on P uptake data.

Table 6.4 Total P uptake (mg) in four harvests by perennial ryegrass on six soils as influenced by phosphate source and rate of application

Treatment	Application rate (kgP ha^{-1})	Soil type					
		Ramiha	Konini	Maharahara	Kumeroa	Wainui	Tokomaru
Control	0	3.08 H*	6.95 G	5.46 G	12.34 E	16.34 H	6.85 I
Superphosphate	75	13.03 DE	17.96 C	18.85 DE	22.17 CD	30.30 CD	19.81 CD
	150	22.07 A	28.99 A	32.97 A	37.22 A	45.57 A	34.42 A
NCPR	75	13.54 D	18.04 C	19.93 CD	21.77 CD	28.50 D	17.98 DE
	150	19.57 B	24.88 B	27.31 B	31.04 B	35.51 BC	25.64 B
SPR	75	11.58 DE	16.03 CD	16.65 DE	21.12 CD	25.99 DEF	15.11 F
	150	17.41 C	22.76 B	22.87 C	29.85 B	35.96 B	22.51 C
CRP	75	11.17 E	14.62 DE	15.58 EF	18.79 D	25.94 DEF	13.10 FG
	150	13.32 D	17.57 C	18.46 DE	23.51 C	26.35 DEF	15.46 EF
Calciphos	75	8.38 F	13.16 E	12.64 F	15.44 E	22.09 EFG	11.08 GH
	150	11.22 E	17.29 C	15.41 EF	19.58 D	27.67 DE	14.21 F
TPR	75	4.61 GH	8.51 FG	7.33 G	12.97 E	18.16 GH	9.39 HI
	150	5.80 G	9.83 F	8.17 G	13.63 E	21.20 FGH	10.29 H

* Capital letters denote Duncan's symbols for assessing significant ($P < 0.01$) differences for treatments within each soil.

The differences found between P sources in total yield of ryegrass and P uptake by ryegrass after four harvests were found to exist from the first harvest. An example of these differences is shown by the relative cumulative yield differences from three of the six soils over the four harvests, presented graphically in Fig. 6.1. Each curve represents the average effect of the two rates within a fertilizer treatment. This method of comparison differs from the criterion used earlier to compare total yields. The increases in ryegrass yield from added P varied from less than 30% with the Wainui (Fig. 6.1a) to greater than 80% with the Ramiha (Fig. 6.1c) soil at the first harvest. For all these soils CRP ranked behind both NCPR and SPR, but again these differences were small. These three PR materials and Calciphos all increased in effectiveness with successive harvests, when compared to superphosphate.

The relative effectiveness of the PR materials did not appear to be affected by the P-sorption capacity of the six soils (Table 6.2), although the results for the high P-sorbing Ramiha soil (Table 6.3) suggest that the rate of dissolution may not have been sufficient to maintain maximum growth, even with NCPR. Also, the P status of the six soils only appeared to affect the size of the response to applied P. As in Chapters 3 and 4, soil pH in the range 5.0 to 6.2 had no obvious effect on the performance of the PR materials, although results from the Wainui soil suggest that the effectiveness of the PR materials increased, when compared to superphosphate, at this relatively low pH.

Although the grass component usually makes up the bulk of pasture production, the legume component controls the vigour of the sward (Chapter 4.4). With differences existing between plant species in their ability to utilize P from a PR (Deist et al., 1971) it may be dangerous to draw conclusions on the effectiveness of a PR based solely on one

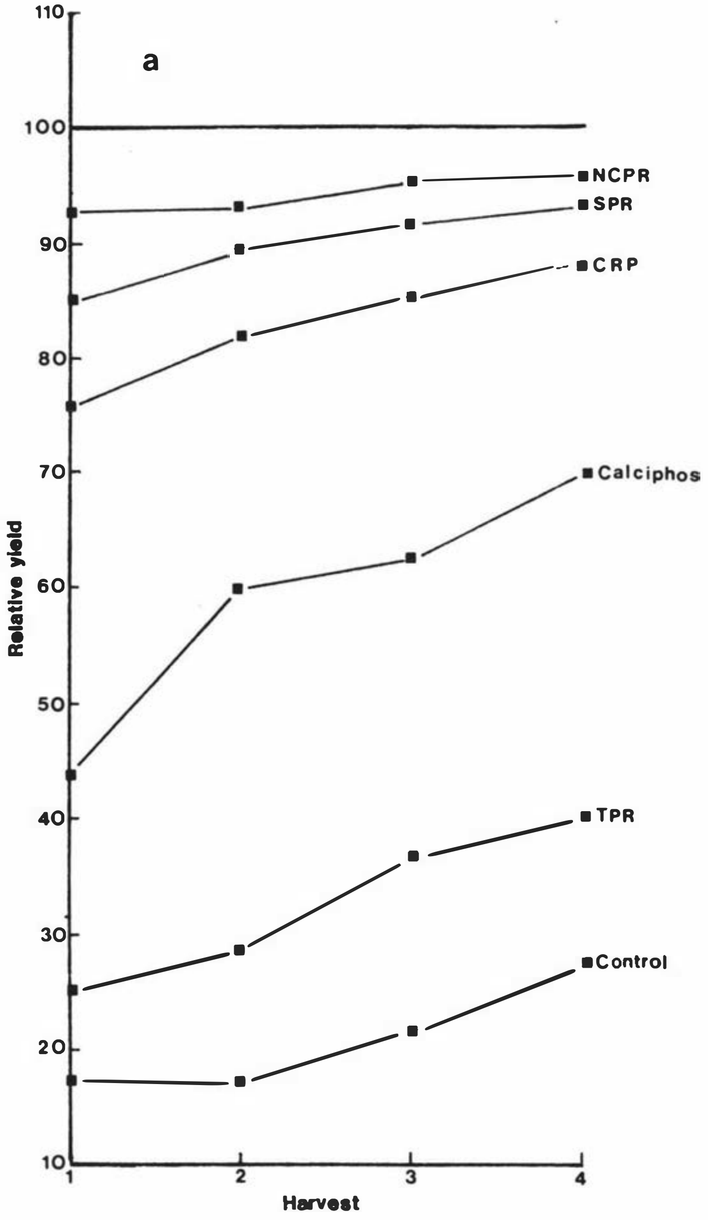


Figure 6.1 Relative cumulative ryegrass yield data for four harvests as influenced by phosphate source (superphosphate = 100). a = Ramiha, b = Konini, and c = Wainui.

Figure 6.1 contd.

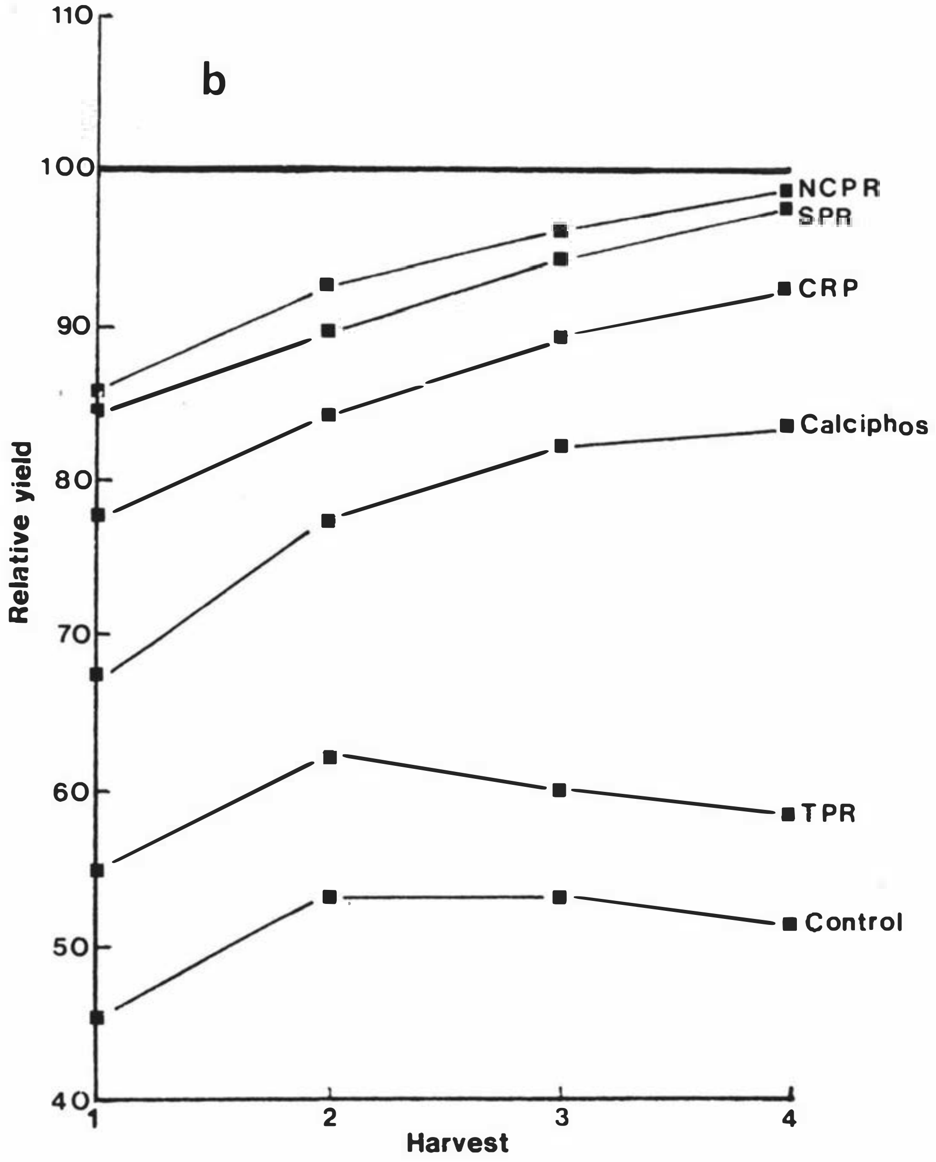
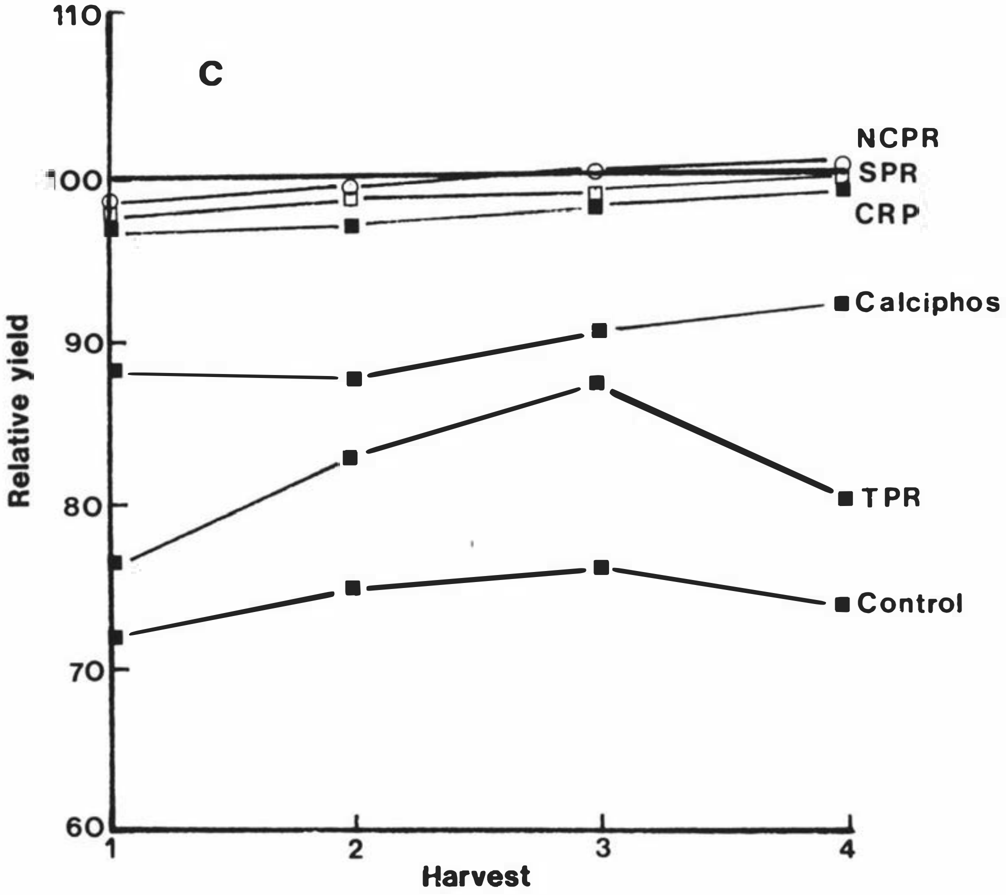


Figure 6.1 contd.



plant species.

6.3.1.2 Response of white clover

The yield of white clover for the four harvests combined, showed a significant ($P < 0.01$) response to applied P with all three soils (Table 6.5). As with the ryegrass yields, the size of the response varied markedly with the source and rate of application of P, and across the three soils. However, unlike the finding with total ryegrass yields, CRP was as effective as superphosphate with two of the three soils and as effective as SPR with all three soils (Table 6.5). In fact with the Ramiha soil, SPR gave greater ($P < 0.01$) white clover yields than superphosphate at both rates of application. Again, TPR was markedly inferior ($P < 0.01$) to both SPR and CRP, and also to superphosphate at both rates of application with all three soils.

On a relative basis, SPR, CRP, and TPR, when compared at 90% of the yield maximum of superphosphate (taken as 100), gave relative yield values of 99 to 104, 93 to 101 and 44 to 85, respectively, across the three soils. A comparison of the three PR materials with superphosphate, based on relative cumulative yield differences over the four harvests with the three soils, showed a similar ranking of the P sources (Fig. 6.2).

In contrast to the ryegrass data, no differences were found in total P uptake by white clover for the four harvests combined, between superphosphate and either SPR or CRP at each application rate (Table 6.6). This was the case with all three soils. TPR was markedly inferior ($P < 0.01$) to the other three P sources and in fact no differences were measured between TPR applied at 75 kgP ha^{-1} and the controls with any of the three soils. The increased effectiveness of SPR and CRP, when compared to superphosphate, illustrates the differences between white clover and ryegrass in their ability to utilize P from a PR, particularly

Table 6.5 Total yield (g) in four harvests of white clover on three soils as influenced by phosphate source and rate of application

Treatment	Application rate (kgP ha^{-1})	Soil type					
		Ramiha		Konini		Wainui	
Control	0	0.84	G*	5.67	G	7.36	E
Superphosphate	75	5.84	D	9.65	C	9.53	BC
	150	8.15	B	12.89	A	11.48	A
SPR	75	6.23	C	9.56	C	8.50	B
	150	8.63	A	12.81	A	9.16	C
CRP	75	5.94	CD	8.94	D	9.36	BC
	150	8.38	AB	12.26	B	11.15	A
TPR	75	2.47	F	7.07	F	9.67	B
	150	3.79	E	7.97	E	11.48	A

* Capital letters denote Duncan's symbols for assessing significant ($P < 0.01$) differences for treatments within each soil.

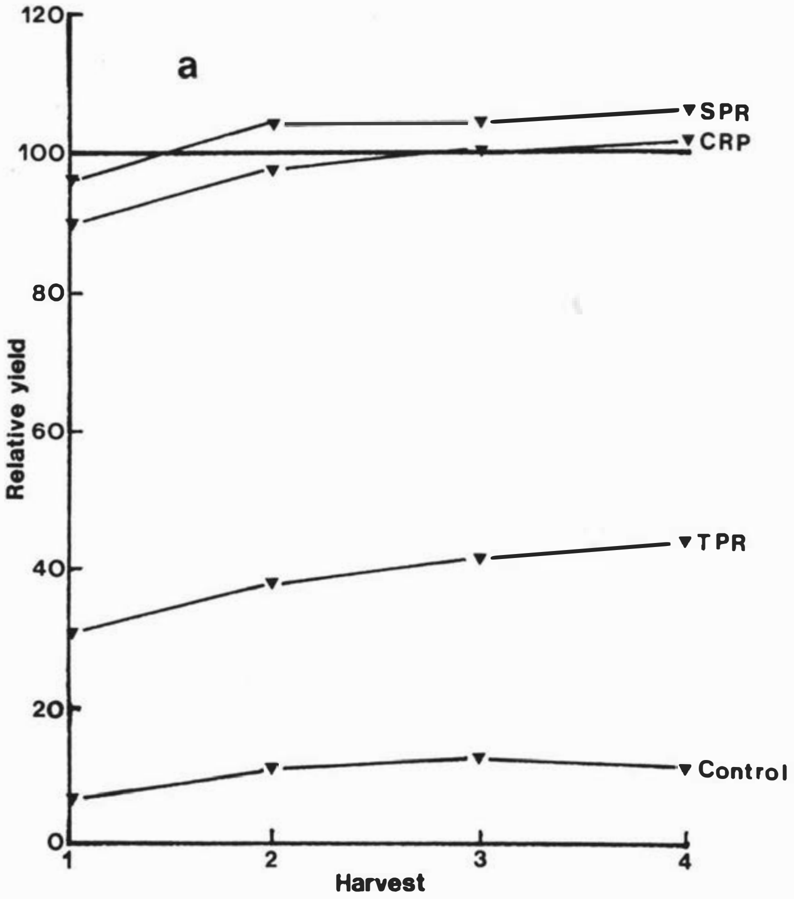


Figure 6.2 Relative cumulative white clover yield data for four harvests as influenced by phosphate source (superphosphate = 100). a = Ramiha, b = Konini, and c = Wainui.

Figure 6.2 contd.

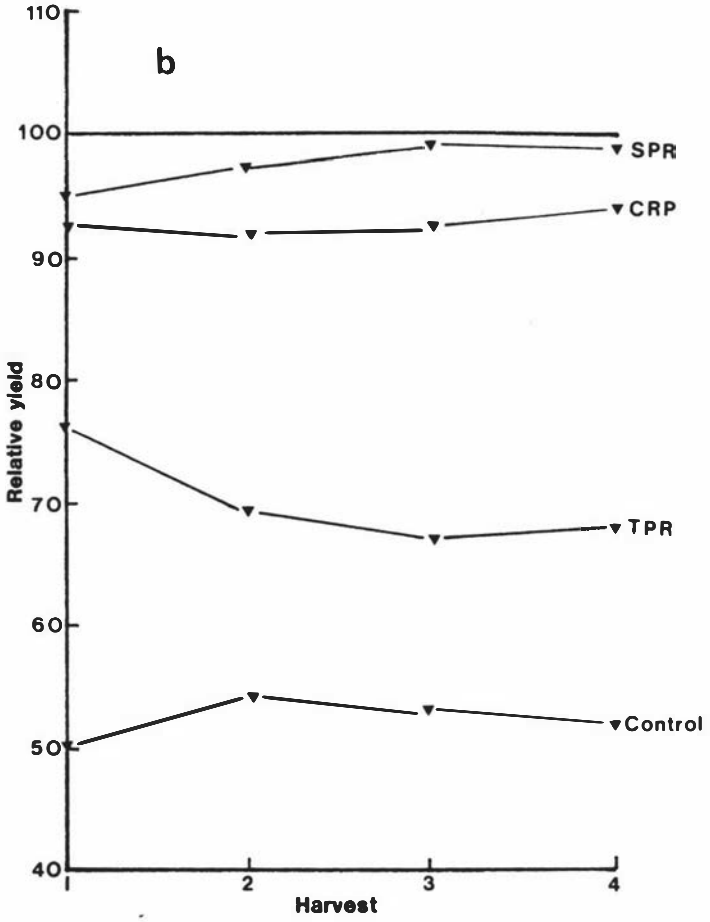


Figure 6.2 contd.

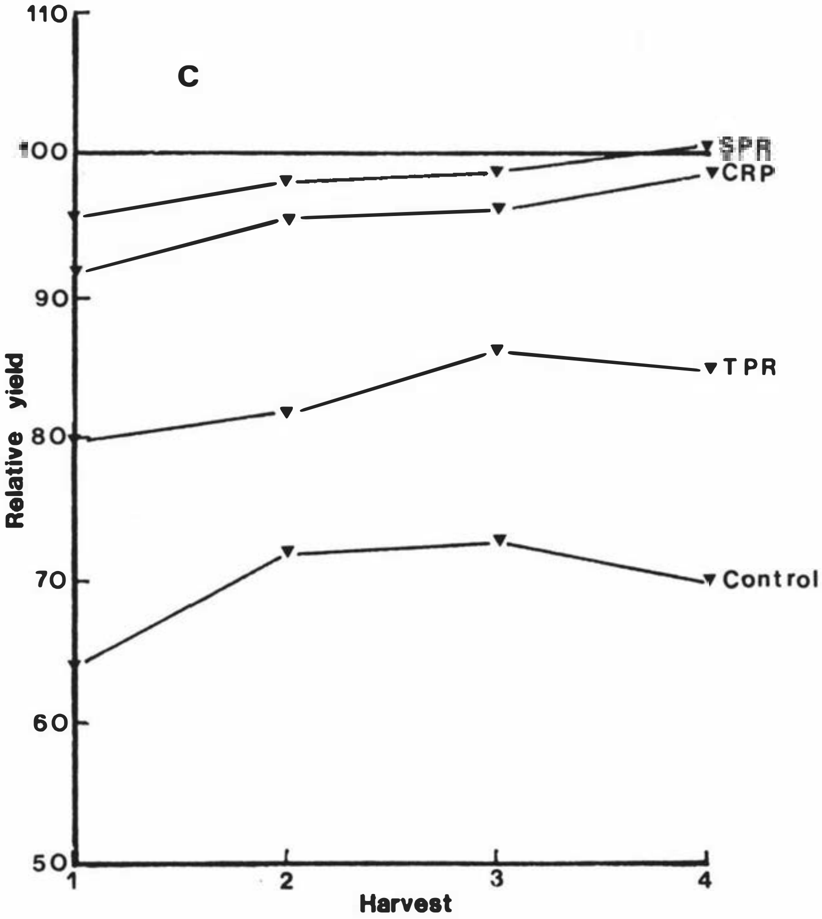


Table 6.6 Total phosphorus uptake (mg) in four harvests by white clover on three soils as influenced by phosphate source and rate of application

Treatment	Application rate (kgP ha^{-1})	Soil type					
		Ramiha		Konini		Wainui	
Control	0	1.29	D*	10.42	D	17.10	E
Superphosphate	75	11.73	B	21.08	B	23.69	CD
	150	17.63	A	31.37	A	32.88	A
SPR	75	13.50	B	20.37	BC	27.77	BC
	150	20.13	A	28.90	A	36.34	A
CRP	75	12.34	B	21.27	B	26.64	C
	150	18.90	A	26.30	A	32.42	AB
TPR	75	3.51	CD	14.45	D	21.29	DE
	150	5.59	C	15.34	CD	23.03	CD

* Capital letters denote Duncan's symbols for assessing significant ($P < 0.01$) differences for treatments within each soil.

when the comparison between the two species is based on P uptake data.

6.3.2 Comparison of chemical extraction procedures for predicting the agronomic effectiveness of phosphate rock materials

Data for the solubility of P sources in seven chemical extraction procedures (Table 6.7) show that whereas only small differences were found in the amount of total P extracted from superphosphate (76 to 99%), marked differences were found between the five PR materials (2 to 100%). The expression of soluble P as a percentage of total P, rather than as a percentage of the material, seems preferable where the P sources vary widely in P content (Table 6.1). In contrast to the conventional chemical extraction procedure, a cumulative extraction procedure, particularly 2% formic acid (sum of 2), both the 2% citric acid (sum of 3) procedures, and NAC (sum of 4) appear to rank the PR materials, with the exception of Calciphos, according to their agronomic effectiveness reported in the previous section (6.3.1).

The presence of $CaCO_3$ (27.6%) in CRP had a more pronounced effect on its solubility than that present in either NCPR (11.7%) or SPR (8.9%). In fact the solubility of CRP was similar to TPR in the first extraction with 2% citric acid, although these two PR materials differ markedly in their agronomic effectiveness (Section 6.3.1). An analysis of the CRP residue after one extraction with 2% citric acid showed that most of the $CaCO_3$ (80%) had been removed because of its greater solubility. Whereas, increasing the extraction time with 2% citric acid from 0.5 (The Fertilisers Regulations, 1969) to 1 h (AOAC, 1960) did not increase, to any significant degree, the amount of P extracted from the P sources, increasing the strength of citric acid, increased the amount of P extracted particularly with NCPR, SPR, CRP, and TPR (Table 6.7). The solubility data for the single superphosphate investigated (Table 6.7), suggest that

Table 6.7 The solubility of the phosphate sources (% of total P) as measured by the various chemical extraction procedures

Chemical extraction procedure		Phosphate source					
		Super*	NCPR	SPR	CRP	Calciphos	TPR
2% formic acid	1 †	82	88	71	47	18	23
	2	96	100	100	93	30	44
2% citric acid (1 h)	1	80	43	42	21	22	21
	2	91	83	79	59	26	40
	3	96	99	96	90	30	58
2% citric acid (0.5 h)	1	79	42	39	19	15	19
	2	91	78	73	58	21	37
	3	99	100	98	89	24	54
Neutral ammonium citrate	1	75	20	17	6	85	6
	2	81	40	35	27	91	14
	3	87	61	52	49	94	21
	4	90	78	67	67	95	28
Alkaline ammonium citrate	1	78	13	8	2	91	4
	2	78	26	17	12	92	10
	3	78	37	24	21	92	11
5% citric acid	1	76	70	64	44	21	33
15% citric acid	1	85	85	86	59	22	49

*Superphosphate

†Cumulative amount extracted in indicated extraction number.

there is more than one form of P present. The increasing solubility of Calciphos with the increasing alkalinity of the citrate solutions is consistent with the presence of Al-P in this material.

To assess the ability of the chemical extraction procedures to predict the likely agronomic effectiveness of the six P sources the extraction data were compared with the results from the previous study (6.3.1). To make this comparison, the "Relative Agronomic Effectiveness" (RAE) of the P sources was calculated (Engelstad et al., 1974; Reinhorn et al., 1978; Chien and Hammond, 1978a) at each of the two rates of application as follows:

$$\text{RAE} = \frac{\text{Yield or P uptake of PR - control}}{\text{Yield or P uptake of superphosphate - control}} \times 100$$

The relationship between the RAE and solubility of the P sources, expressed as a percentage of total P, was subsequently established using linear regression analysis.

6.3.2.1 Relationships for perennial ryegrass

The RAE of the PR materials, based on ryegrass yield, over the four individual and combined harvests with the six soils, varied widely with the source and rate of application of P, harvest, and soil (Fig. 6.3a).

Of the seven chemical extraction procedures at the first extraction, the amounts of P extracted by 2% formic acid and 5% citric acid were the most closely correlated with the agronomic effectiveness of the P sources (Table 6.8). The exclusion of Calciphos from the linear regression analysis improved the predictive ability of both NAC and AAC at the first extraction. Both, however, were less effective than the other five chemical extraction procedures (Table 6.8). The lower solubility of NCPR, SPR, CRP and TPR in AAC, even after three extractions (Table 6.7),

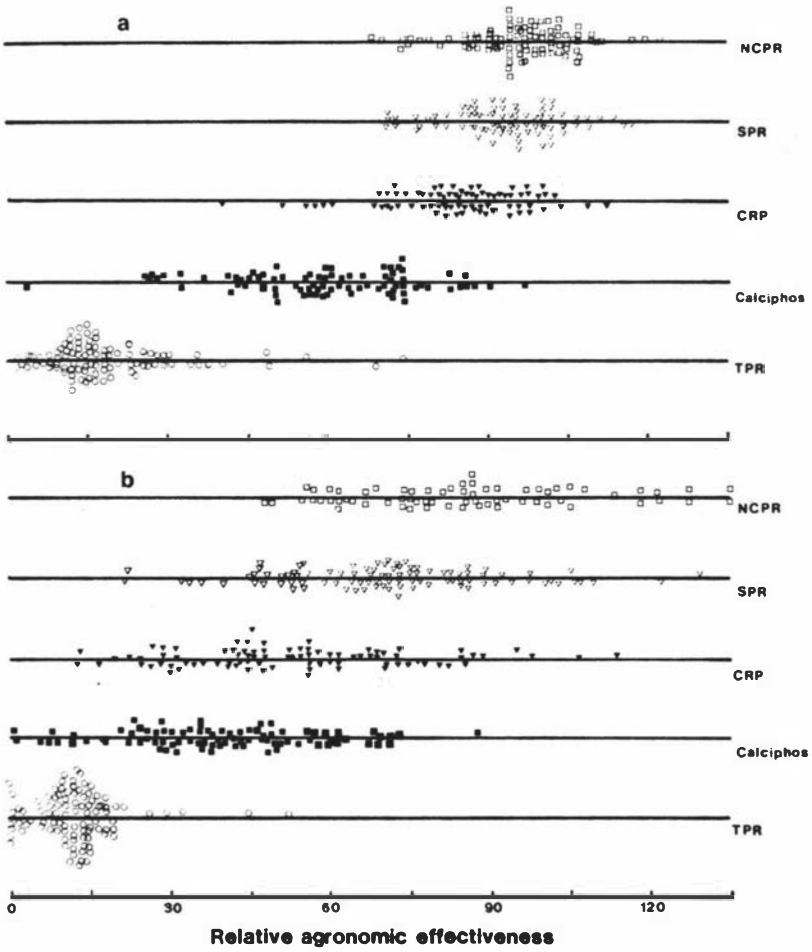


Figure 6.3 Relative agronomic effectiveness of the five phosphate rock materials using yield of ryegrass (a) and phosphorus uptake by ryegrass (b) over individual and combined harvests at both rates of application on six soils.

Table 6.8 Correlation coefficients between amounts of phosphorus extracted by the indicated extractant and yield of ryegrass at the first harvest on six soils

Chemical extraction procedure		Soil type					
		Ramiha	Konini	Maharahara	Kumeroa	Wainui	Tokomaru
2% Formic acid	1	0.922**	0.891*	0.941**	0.912*	0.783	0.952**
	2	0.924**	0.774	0.921**	0.954**	0.844*	0.874*
2% Citric acid (1 h)	1	0.745	0.892	0.763	0.652	0.544	0.862*
	2	0.913*	0.886*	0.934**	0.912*	0.751	0.954**
	3	0.854*	0.721	0.861*	0.907*	0.743	0.948*
2% Citric acid (0.5 h)	1	0.762	0.893*	0.782	0.671	0.542	0.871*
	2	0.921**	0.882*	0.937**	0.916*	0.753	0.948*
	3	0.864*	0.733	0.874*	0.918*	0.743	0.857*
Neutral ammonium citrate	1	0.092 (0.592)†	0.332 (0.791)	0.072 (0.634)	0.083 (0.472)	0.092 (0.404)	0.161 (0.741)
	2	0.203 (0.764)	0.424 (0.913*)	0.194 (0.795)	0.072 (0.663)	0.244 (0.602)	0.255 (0.873)
	3	0.384 (0.921*)	0.546 (0.973**)	0.368 (0.934*)	0.251 (0.844)	0.446 (0.812)	0.404 (0.951*)
	4	0.546 (0.982**)	0.631 (0.962**)	0.526 (0.995**)	0.454 (0.956)	0.643 (0.933**)	0.526 (0.976**)
Alkaline ammonium citrate	1	-0.021 (0.532)	0.273 (0.733)	0.082 (0.564)	0.138 (0.409)	0.041 (0.347)	0.109 (0.678)
	2	-0.062 (0.608)	0.305 (0.782)	0.076 (0.636)	0.102 (0.472)	0.083 (0.412)	0.131 (0.735)
	3	-0.683 (0.716)	0.359 (0.769)	0.104 (0.747)	0.067 (0.586)	0.172 (0.543)	0.198 (0.814)
5% Citric acid	1	0.906*	0.894*	0.923**	0.884*	0.724	0.952**
15% Citric acid	1	0.832*	0.766	0.841*	0.855*	0.643	0.874*

* Significant at 5% level.

** Significant at 1% level.

† Calciphos is excluded from calculation.

limits the usefulness of this extractant, a conclusion also reached by Hoffman and Breen (1964) in an earlier study. The high solubility of Calciphos in the alkaline extractants does not equate with its only moderate agronomic effectiveness, illustrating one of the limitations of chemical extraction procedures for assessing the likely agronomic effectiveness of P sources which vary widely in mineralogy.

Whereas a combination of the first and second extractions with 2% formic acid gave no real added benefit to the correlation with ryegrass yield at the first harvest, the predictive ability of both of the 2% citric acid procedures improved markedly when an additional extraction was used. The predictive ability of NAC also improved, particularly when Calciphos was excluded, when additional extractions were used (Table 6.8).

While the inclusion of Calciphos had only a minor effect on the predictive ability of 2% formic acid and 2% citric acid at the first harvest, in later harvests the inclusion of Calciphos markedly reduced the predictive ability of all extractants, particularly NAC and AAC. Correlation coefficients for the four individual harvests with two (Ramiha and Maharahara) of the soils (Table 6.9), with Calciphos excluded, showed that although combining the first and second extractions with 2% formic acid had no added benefit at the first harvest, in later harvests the combined extractions were a better indicator of likely agronomic effectiveness. The data presented in Table 6.9 are the average for the two rates. The predictive ability of both of the 2% citric acid procedures also improved when an additional extraction was used (sum of 3), particularly in later harvests. Essentially the same result was obtained for NAC (sum of 4). Similar conclusions were reached on the other four soils and when individual harvests were combined.

Table 6.9 Correlation coefficients between amounts of phosphorus extracted by the indicated extractant and yield of ryegrass at the first, second, third, and fourth harvests on the Ramiha silt loam and Maharahara sandy loam. Calciphos is excluded from calculations.

Chemical extraction procedure		Soil type							
		Ramiha				Maharahara			
		Harvest				Harvest			
		1	2	3	4	1	2	3	4
2% Formic acid	1	0.934*	0.893*	0.904*	0.862	0.942*	0.891*	0.872	0.863
	2	0.965**	0.984**	0.981**	0.983**	0.944*	0.994**	0.993**	0.994**
2% Citric acid (1 h)	1	0.706	0.615	0.602	0.564	0.733	0.612	0.532	0.523
	2	0.957*	0.912*	0.913*	0.887*	0.962**	0.904*	0.873	0.878
	3	0.983**	0.991**	0.992**	0.994**	0.961**	0.993**	0.992**	0.994**
2% Citric acid (0.5 h)	1	0.704	0.623	0.609	0.562	0.723	0.614	0.523	0.516
	2	0.951*	0.912*	0.902*	0.876	0.964**	0.914*	0.862	0.863
	3	0.992**	0.991**	0.991**	0.992**	0.984**	0.993**	0.992**	0.995**
Neutral ammonium citrate	1	0.592	0.502	0.498	0.453	0.635	0.506	0.497	0.392
	2	0.763	0.693	0.687	0.644	0.794	0.695	0.603	0.594
	3	0.924*	0.874	0.863	0.835	0.936*	0.878	0.819	0.798
	4	0.982**	0.965*	0.964*	0.946*	0.991**	0.971**	0.938*	0.933*
5% Citric acid	1	0.912	0.856	0.842	0.814	0.924*	0.858	0.816	0.802

* Significant at 5% level.

** Significant at 1% level.

The 5 and 15% citric acid procedures were included in the present study as possible substitutes or alternatives to the sequential extraction procedure with 2% citric acid. Although these stronger chemical extractants were initially more effective (Table 6.8), the effect of $CaCO_3$ on 5% citric acid and the increased solubility of TPR in 15% citric acid (Table 6.7), limit the value of these two chemical extraction procedures (Table 6.9). Both of these extractants grossly underestimated the effectiveness of Calciphos, as was the case with 2% formic acid and 2% citric acid.

Both 2% citric acid and NAC at the second extraction gave a good correlation with the yield of ryegrass at the first harvest. Chien and Hammond (1978) found the second extraction with NAC to be a better indicator than the first, with Huila phosphate rock from Columbia because the more soluble $CaCO_3$ (Silverman et al., 1952) had been removed during the initial extraction with NAC. In later harvests in the present study, however, the second extraction with either 2% citric acid or NAC was poorly correlated with agronomic performance of the P sources. The necessity to exclude superphosphate from all comparisons and Calciphos from those with NAC further limits the value of these extraction procedures.

The variation in RAE values, when based on P uptake by ryegrass (Fig. 6.3b), was appreciably greater than that reported earlier using ryegrass yields (Fig. 6.3a). In contrast to the conclusions drawn for the predictive ability of both of the 2% citric acid procedures at the first extraction, using ryegrass yields as the criterion for assessing agronomic effectiveness, both procedures were far more effective at the first extraction for predicting P uptake by ryegrass. Although they still ranked behind 2% formic acid and 5% citric acid (Table 6.10), the lower RAE of the PR materials when based on P uptake by ryegrass, which is consistent with the findings of the previous study (6.3.1), may

Table 6.10 Correlation coefficients between amounts of phosphorus extracted by the indicated extractant and phosphorus uptake by the ryegrass at the first harvest on six soils

Chemical extraction procedure		Soil type					
		Ramiha	Konini	Maharahara	Kumeroa	Wainui	Tokomaru
2% Formic acid	1	0.944**	0.773	0.949**	0.913*	0.626	0.802**
	2	0.882*	0.795	0.824*	0.834*	0.493	0.603
2% Citric acid (1 h)	1	0.824*	0.713	0.846*	0.845*	0.706	0.982**
	2	0.932**	0.814*	0.917*	0.911*	0.593	0.821*
	3	0.826*	0.742	0.793	0.792	0.444	0.613
2% Citric acid (0.5 h)	1	0.834*	0.713	0.855*	0.862*	0.712	0.984**
	2	0.935**	0.814*	0.912*	0.924**	0.623	0.845*
	3	0.846*	0.765	0.803	0.813*	0.454	0.626
Neutral ammonium citrate	1	0.152 (0.682)+	0.242 (0.563)	0.164 (0.722)	0.188 (0.755)	0.469 (0.731)	0.402 (0.954*)
	2	0.256 (0.832)	0.223 (0.706)	0.256 (0.838)	0.279 (0.879)	0.538 (0.814)	0.446 (0.982**)
	3	0.404 (0.959*)	0.339 (0.798)	0.398 (0.937*)	0.412 (0.956*)	0.617 (0.864)	0.494 (0.943*)
	4	0.542 (0.984**)	0.468 (0.829)	0.515 (0.943*)	0.531 (0.964**)	0.665 (0.832)	0.508 (0.833)
Alkaline ammonium citrate	1	0.092 (0.622)	0.243 (0.528)	0.125 (0.669)	0.133 (0.712)	0.431 (0.716)	0.373 (0.938*)
	2	0.123 (0.694)	0.246 (0.552)	0.147 (0.734)	0.162 (0.778)	0.468 (0.769)	0.382 (0.964**)
	3	0.194 (0.796)	0.234 (0.623)	0.219 (0.826)	0.228 (0.859)	0.516 (0.824)	0.404 (0.992**)
5% Citric acid	1	0.924**	0.783	0.926**	0.918*	0.602	0.844*
15% Citric acid	1	0.844	0.746	0.824*	0.803	0.436	0.692

* Significant at 5% level.

** Significant at 1% level.

+ Calciphos is excluded from calculation.

explain this difference in the results.

Exclusion of Calciphos from the linear regression analysis again improved the predictive ability of NAC and AAC at the first extraction with all soils. Nevertheless NAC was less effective than 2% formic acid and 2% citric acid up to the third cumulative extraction (Table 6.10).

Again, in contrast to the conclusions drawn for the ability of the extractants to predict ryegrass yields in later harvests, there was no advantage in using a second sequential extraction with 2% formic acid or a third sequential extraction with 2% citric acid, to improve the ability of these two chemical extraction procedures to predict P uptake by ryegrass in later harvests with the Ramiha and Maharahara soils (Table 6.11). A similar conclusion was also reached with the other four soils and when individual harvests for each soil were combined. The inclusion of Calciphos again decreased the predictive ability of all extractants in later harvests, confirming the suggestion made earlier that these chemical extractants are limited to comparisons of P sources of similar mineralogy only.

6.3.2.2 Relationships for white clover

The RAE of the PR materials, based on white clover yield for the individual and combined harvests at both rates of application for the three soils, varied with the source and rate of addition of P, harvest, and, in addition, with soil (Fig. 6.4a). Correlation coefficients for the relationship between the amounts of P extracted from the P sources and white clover yield at first harvest for the soils (Table 6.12) showed that the predictive ability of the 2% formic acid procedure was superior to the other extractants, at the first extraction. Sequential extractions again improved the predictive ability of 2% citric acid, NAC, and AAC at first harvest (Table 6.12).

Table 6.11 Correlation coefficients between amounts of phosphorus extracted by the indicated extractant and phosphorus uptake by the ryegrass at the first, second, third, and fourth harvests on the Ramiha silt loam and Maharahara sandy loam. Calciphos is excluded from calculation.

		Soil type							
		Ramiha				Maharahara			
Chemical		Harvest				Harvest			
extraction procedure		1	2	3	4	1	2	3	4
2% Formic acid	1	0.952*	0.921*	0.932*	0.902*	0.942*	0.883*	0.954*	0.931*
	2	0.904*	0.815	0.943*	0.973**	0.814*	0.862*	0.902*	0.964*
2% Citric acid (1 h)	1	0.801	0.742	0.721	0.597	0.812	0.798	0.732*	0.633
	2	0.972**	0.914*	0.955**	0.902*	0.946*	0.901*	0.954*	0.934*
	3	0.943*	0.855*	0.946*	0.984**	0.855	0.847	0.929*	0.975**
2% Citric acid (0.5h)	1	0.752	0.743	0.726	0.599	0.816	0.736	0.733	0.634
	2	0.973**	0.912*	0.967**	0.892*	0.955*	0.930*	0.940*	0.922*
	3	0.954*	0.865	0.978**	0.968**	0.872	0.864	0.942*	0.981**
Neutral ammonium citrate	1	0.683	0.648	0.623	0.453	0.723	0.751	0.603	0.501
	2	0.834	0.786	0.782	0.645	0.844	0.872	0.754	0.682
	3	0.955*	0.892*	0.921*	0.816	0.930*	0.935*	0.882*	0.843
	4	0.987**	0.914*	0.984**	0.927*	0.941*	0.974**	0.921*	0.945*
5% Citric acid	1	0.948*	0.901*	0.912*	0.862	0.967**	0.881*	0.941*	0.894*

* Significant at 5% level.

** Significant at 1% level.

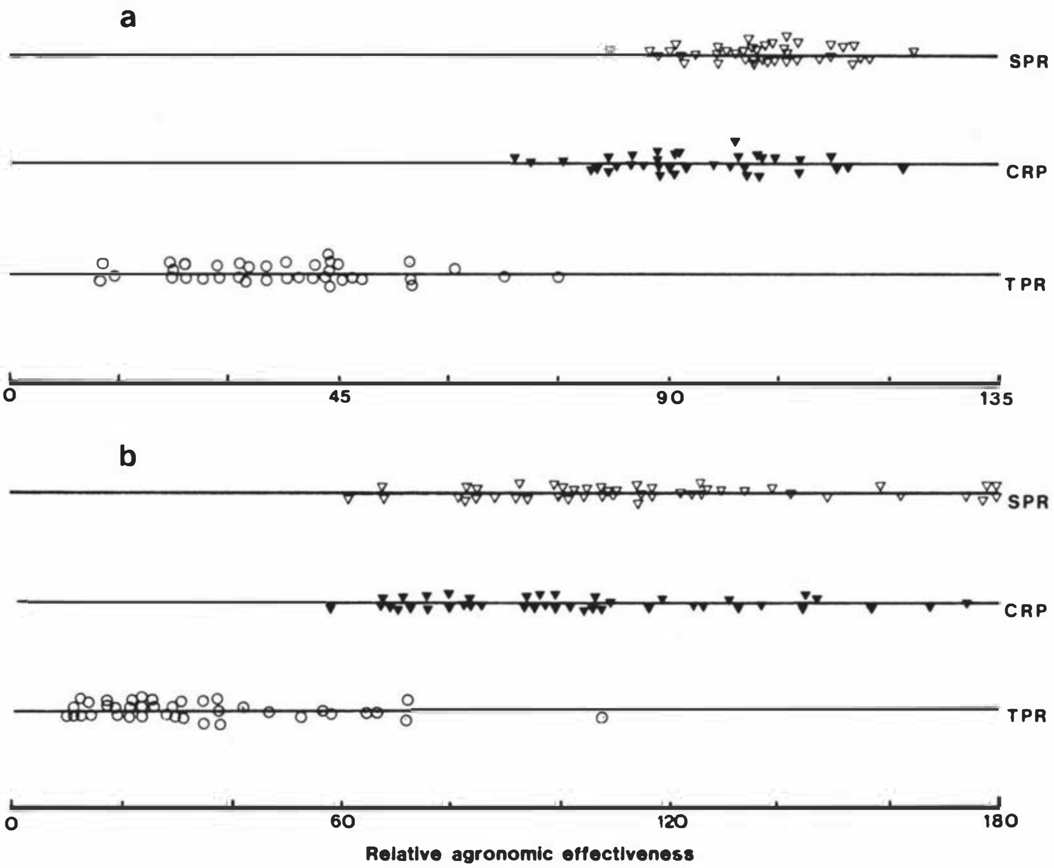


Figure 6.4 Relative agronomic effectiveness of the three phosphate rock materials using yield of white clover (a) and phosphorus uptake by white clover (b) over individual and combined harvests at both rates of application on three soils.

Table 6.12 Correlation coefficients between amounts of phosphorus extracted by the indicated extractant and yield of white clover and phosphorus uptake by white clover at the first harvest on three soils.

		Yield of white clover			P uptake by white clover		
Chemical extraction procedure		Ramiha	Konini	Wainui	Ramiha	Konini	Wainui
2% Formic acid	1	0.893	0.952*	0.972*	0.912	0.901	0.767
	2	0.982*	0.933	0.934	0.954*	0.874	0.894
2% Citric acid (1 h)	1	0.581	0.801	0.771	0.661	0.741	0.369
	2	0.875	0.945	0.976*	0.953*	0.892	0.738
	3	0.994**	0.954*	0.973*	0.962*	0.903	0.886
2% Citric acid (0.5 h)	1	0.572	0.752	0.773	0.614	0.744	0.353
	2	0.883	0.954*	0.974*	0.900	0.918	0.685
	3	0.994**	0.960*	0.974*	0.975*	0.907	0.878
Neutral ammonium citrate	1	0.525	0.693	0.706	0.596	0.706	0.324
	2	0.676	0.824	0.827	0.747	0.825	0.386
	3	0.847	0.932	0.928	0.889	0.924	0.587
	4	0.958*	0.987*	0.971*	0.958*	0.952*	0.699
Alkaline ammonium citrate	1	0.459	0.646	0.649	0.544	0.663	0.323
	2	0.512	0.685	0.683	0.586	0.696	0.311
	3	0.594	0.754	0.752	0.673	0.764	0.300
5% Citric acid	1	0.816	0.901	0.934	0.852	0.851	0.674
15% Citric acid	1	0.813	0.862	0.916	0.821	0.782	0.780

* Significant at 5% level.

** Significant at 1% level.

A comparison of the chemical extraction procedures in later harvests showed that 2% formic acid (sum of 2), 2% citric acid (sum of 3), and NAC (sum of 4) gave the best correlations with white clover yield. Although the reliability of this finding could be questioned, because of the limited number of data points obtained with clover and used for the linear regression analysis, it agrees with the conclusion reached earlier using ryegrass yield data.

As was the case for RAE values of the PR materials based on P uptake by ryegrass (Fig. 6.3b), the RAE of the PR materials based on P uptake by white clover (Fig. 6.4b) varied widely with the source and rate of application of P, harvest, and also across the three soils. The predictive ability of the extractants at the first harvest (Table 6.12) and in later harvests followed very similar trends to those already reported for ryegrass and white clover yield data, although the actual correlation coefficients were generally lower. This was particularly the case in later harvests, where the variability in RAE increased with all three soils. The good agreement between yield of white clover and P uptake by white clover contrasts with the results reported earlier with ryegrass (see Section 6.3.2.1).

6.3.3 Two new approaches for assessing the agronomic effectiveness of phosphate rock materials

6.3.3.1 Hydrous ferric oxide gel

An initial study evaluating the potential use of hydrous ferric oxide gel (Fe gel) for characterizing the release of P from PR materials used the method developed by McLaughlin and Syers (1978) to investigate the stability of ferric phosphates. The results obtained with six PR materials show that the extent of their dissolution over 17 days was low compared to that of superphosphate (Fig. 6.5), with the

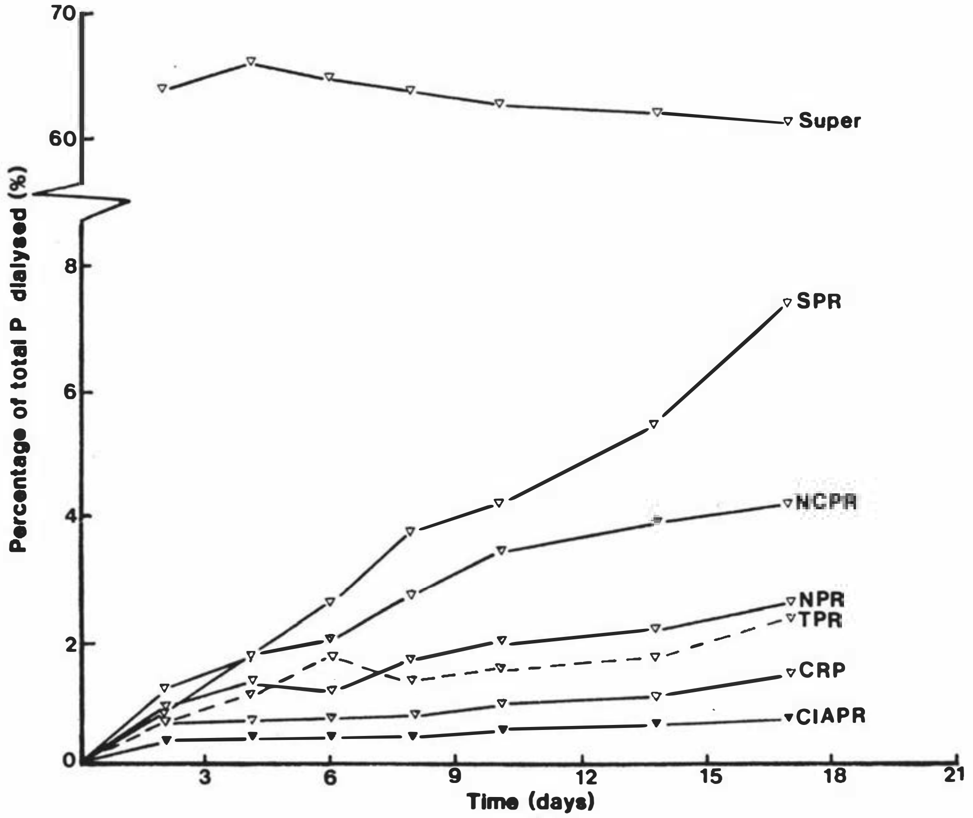


Figure 6.5 Release of phosphorus to hydrous ferric oxide gel (pH 6.0) as influenced by phosphate source during 17 days.

solubility of these PR materials deviating from the expected pattern. In fact the dissolution of CRP was less than that of both NPR and TPR after only three days. The lower solubility of NCPR and in particular that of CRP, when compared to SPR, appears to result from an increase in the pH of the Fe gel suspension due to the dissolution of $CaCO_3$ present in the first two PR materials (Table 6.13). Although NCPR contains a similar amount of $CaCO_3$ to SPR (Table 6.1), a difference was found between these two PR materials in the pH and the Ca concentration of the solution in the dialysis tubing after 14 days, suggesting that the solubility of the $CaCO_3$ in SPR and NCPR differs. The marked increase in both the pH and Ca concentration obtained with CRP, probably reflects the difference in the amount of $CaCO_3$ present, compared to that in SPR and to a lesser extent NCPR. The lower dissolution of CRP demonstrates the importance of these two factors in controlling the dissolution of a PR (Table 6.13). This is discussed in greater detail in a later Chapter (7.3.4).

In an attempt to overcome the effect of $CaCO_3$ on P release a series of studies was undertaken to evaluate the effect on the dissolution of a PR of varying the initial pH of the Fe gel suspension and of introducing a cation exchange resin (CER). By decreasing the initial pH of the Fe gel suspension the dissolution of SPR and TPR increased from 7 to 35% and from 2.4 to 13%, respectively, at 17 days (Fig. 6.6). Introduction of the CER in a separate dialysis tube into the Fe gel suspension to maintain a concentration gradient for Ca, further increased the dissolution of SPR (Fig. 6.7). In contrast, although not shown, the CER had no additional effect on the dissolution rate of the TPR at pH 4.0. Interestingly, the amount of Fe gel in suspension over the range 2.5 to 10 mg ml^{-1} had no effect on the rate of dissolution of the P sources, although the results for the dialysis of SPR against deionized water (Fig. 6.7) demonstrate the importance of having a sink for P.

Table 6.13 Effect of phosphate source on the pH of the hydrous ferric oxide gel suspension over 14 days of dialysis

	pH of Fe gel								
	0.8	2.8	4.8	5.8	6.8	11.8	14.0	14.0*	14.0†
Phosphate source				(Time in days)					
NPR	5.85	5.90	6.05	6.00	6.00	6.00	6.00	(6.15)	(1,250)
CIAPR	5.80	5.85	5.90	5.90	6.00	6.00	5.90		
TPR	5.95	5.95	6.05	6.00	6.00	6.00	6.00	(6.10)	(500)
CRP	6.00	6.15	6.30	6.30	6.35	6.40	6.45	(7.70)	(5,750)
SPR	5.85	5.95	6.00	6.00	6.00	6.00	6.00	(5.90)	(1,750)
NCPR	5.85	5.90	6.05	6.05	6.05	6.20	6.35	(6.5)	(3,750)
Superphosphate	6.30	6.40	6.45	6.35	6.35	6.35	6.35	(6.5)	(13,000)

* pH of solution in dialysis tube after filtration (<0.45 μm).

† Concentration of Ca (μg g^{-1} of PR) in filtrate from dialysis tubing.

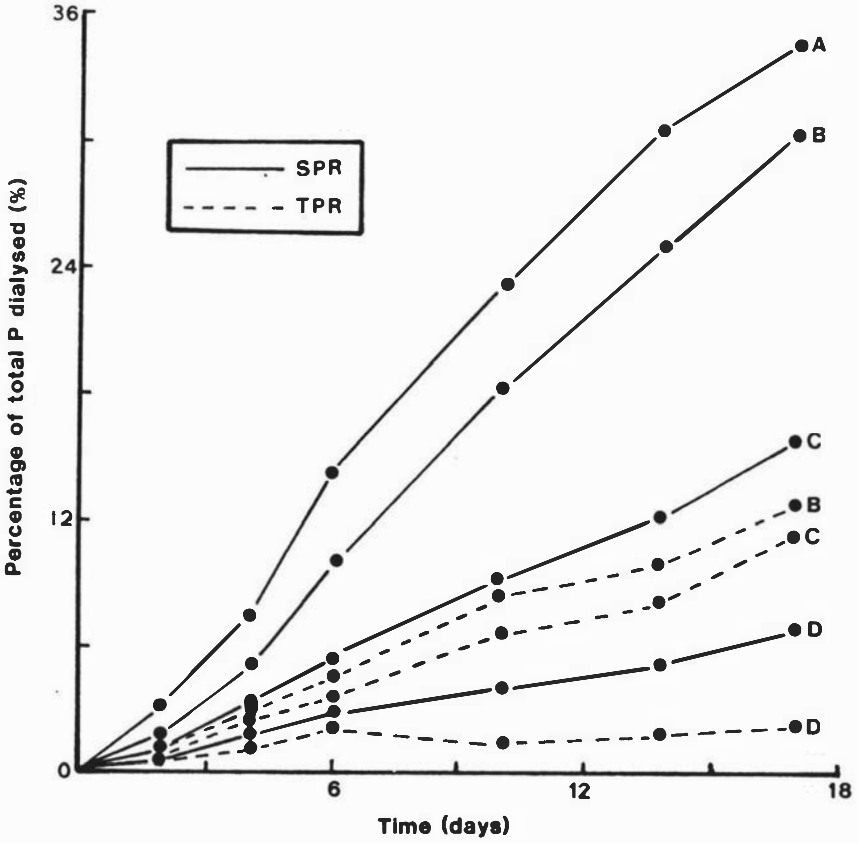


Figure 6.6 Effect of pH of hydrous ferric oxide gel on the dissolution of Sechura phosphate rock (SPR) and Tennessee phosphate rock (TPR) during 17 days of dialysis. A = pH 3, B = pH 4, C = pH 5, and D = pH 6.

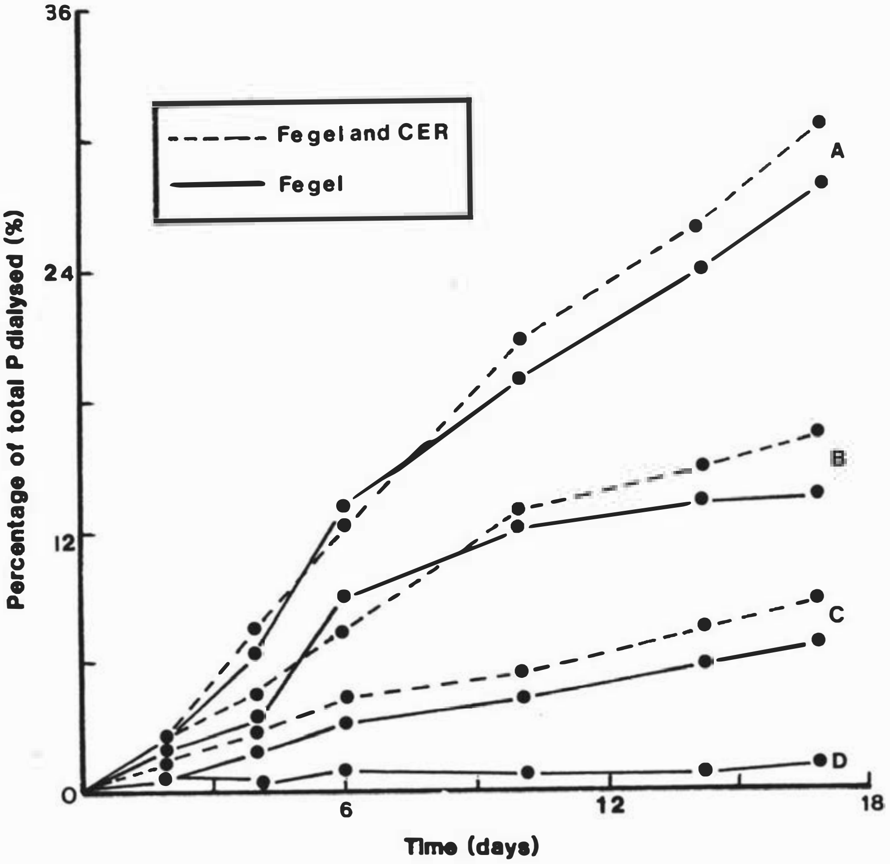


Figure 6.7 Effect of pH of hydrous ferric oxide gel (Fe gel) and the presence of a cation exchange resin (CER) on the dissolution of Sechura phosphate rock during 17 days of dialysis. A = pH 4, B = pH 5, C = pH 6, and D = deionized water.

Provided the pH and Ca concentration of the system are controlled then the Fe gel approach shows promise as a method for characterizing the initial release of P from a wide range of P sources, varying not only in solubility but also in mineralogy (Fig. 6.8). The abrasive nature of the internal surfaces of the polypropylene containers used in the present series of studies, which led to tearing and rupturing of the dialysis tubing during shaking, prevented the measurement of dissolution beyond 17 days. An extension of the dialysis period beyond 17 days would probably have improved predictive ability, by removing a greater proportion of total P and possibly increasing the relative differences between the P sources, particularly Calciphos and TPR from NCPR, SPR, and CRP.

In addition to providing information on the dissolution rate of P sources of varying composition, the Fe gel approach also furnishes information on the likely behaviour of these P sources in soil. This is because Fe gel can be used as a model for soil systems, with respect to P sorption (Ryden et al., 1977). The approach to an equilibrium solution P concentration is continuously disturbed by the Fe gel, which acts as a P sink in a similar manner to the components involved in P sorption in soil. The good agreement between the results of the present study for the dissolution rates of CRP, and in particular SPR and TPR, with those presented in a later Chapter (7.3.3.1) across a range of soils confirms that this approach provides a useful approximation of the soil system.

6.3.3.2 Electro-ultrafiltration

Both the solution (deionized water):solid ratio and voltage had a marked effect on the dissolution of the PR materials in both the automatic (Fig. 6.9) and manual modes of the EUF apparatus. Similarly,

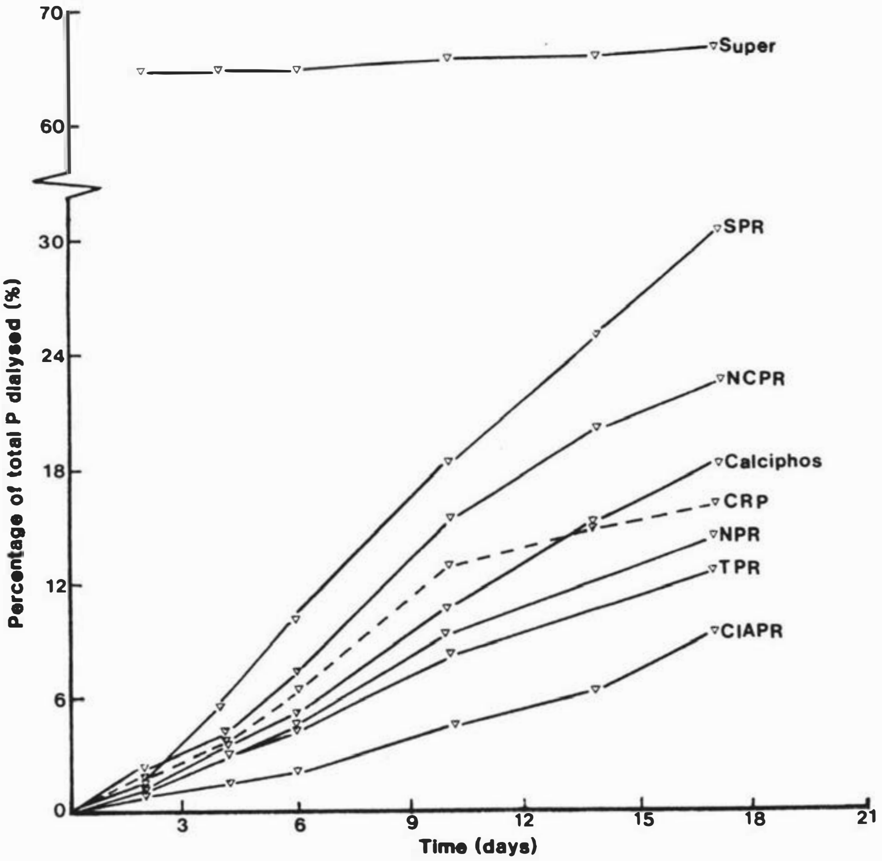


Figure 6.8 Release of phosphorus to hydrous ferric oxide gel (pH 4.0) containing a cation exchange resin, as influenced by phosphate source during 17 days.

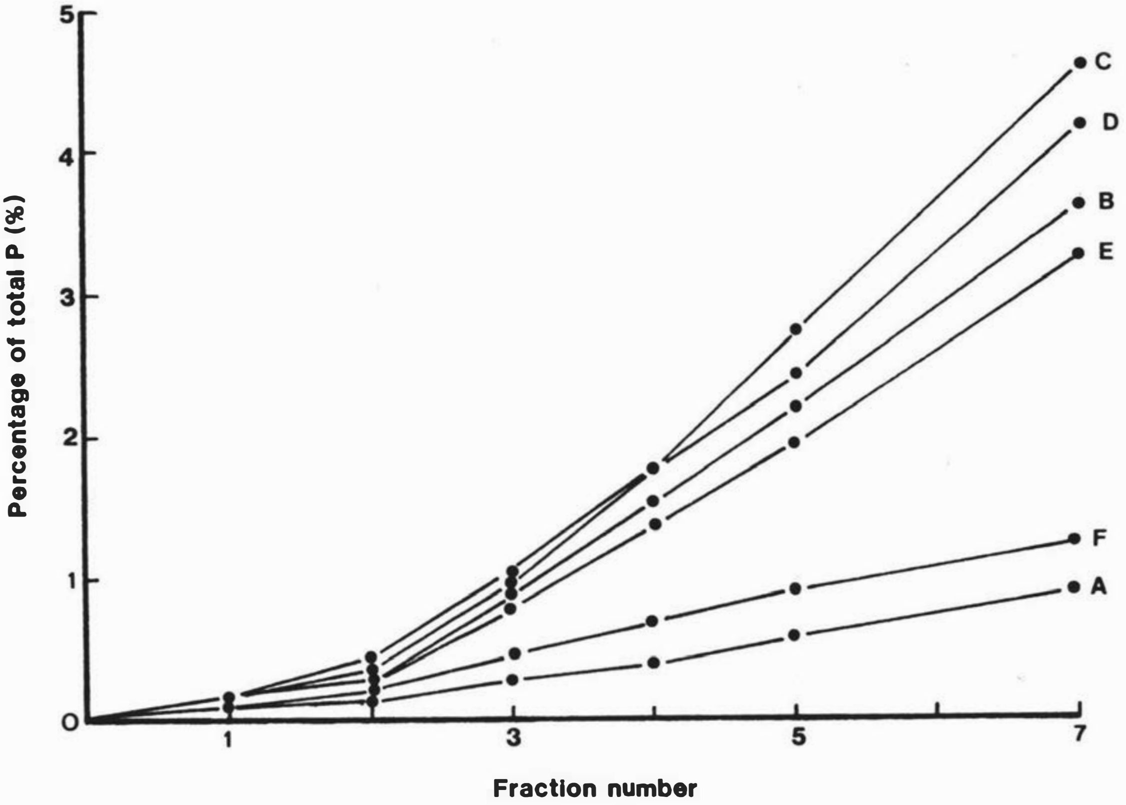


Figure 6.9 Release of phosphorus from Sechura phosphate rock during electro-ultrafiltration in the automatic mode as influenced by solution:solid ratio. A = 40:1, B = 100:1, C = 250:1, D = 500:1, E = 750:1, and F = 1000:1.

the conductivity of the solution in both the automatic and manual modes (Fig. 6.10) affected P release. Increasing the conductivity of the solution from 1.25 to 72 μS (0.036 mg NaCl ml^{-1}) resulted in an increase in the dissolution of SPR from less than 6 to over 50% of total P after ten, 5-min extractions at 400V, presumably by increasing the current carried in solution (Fig. 6.10). The poorer duplication obtained when distilled rather than deionized water was used in EUF studies is probably explained by the greater variability in the conductivity of distilled water (15.5 ± 5.0 μS)

In preliminary studies using deionized water only a small percentage of the total P of the PR material was extracted by EUF (Fig. 6.9). This would increase the likely effect of such factors as surface-held P, broken surfaces, fine particles present on surfaces, and accessory minerals on P release. Increasing the percentage of total P extracted during EUF (Fig. 6.10) by increasing the conductivity of the solution should minimize such effects.

In addition to the effects of solution:solid ratio, voltage, and conductivity on the dissolution rate of the PR materials, the solubility of the PR also had a marked effect on the release of P during EUF at 400V, using both deionized water (Fig. 6.11a) and a weak NaCl (0.030 mg NaCl ml^{-1}) solution (Fig. 6.10b). The EUF procedure does not allow the direct evaluation of either water-soluble (superphosphate) or sparingly water-soluble (dicalcium phosphate) P sources. When deionized water was used, the EUF procedure, separated out SPR, NCPR, and CRP from TPR, although the dissolution of SPR was far greater than that of CRP, and in particular NCPR (Fig. 6.11a). This apparent difference in dissolution between SPR and either NCPR or CRP may be due to differences in the physical characteristics of these PR materials. Unlike particles of NCPR and CRP which are irregular in shape, particles of SPR have an

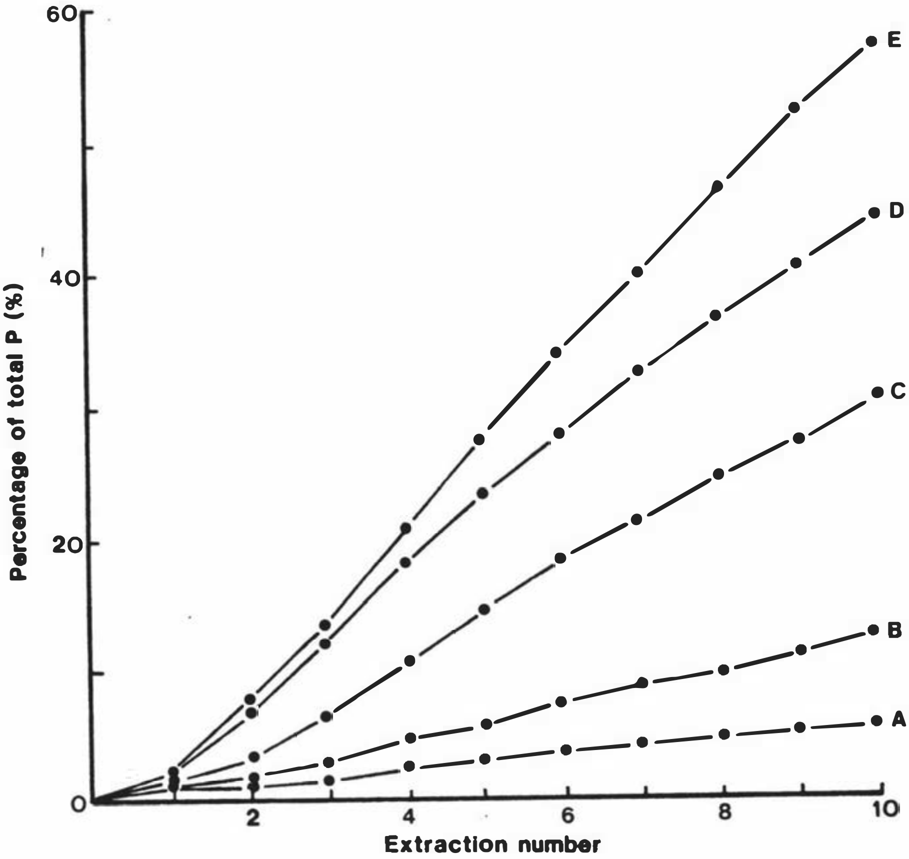


Figure 6.10 Cumulative amount of phosphorus released from Sechura phosphate rock during electro-ultrafiltration in the manual mode, with 10, 5-min extractions at 400V at a solution:solid ratio of 250:1, as influenced by solution conductivity. A = 1.25 μS, B = 12 μS, c = 31 μS, D = 55 μS, and E = 72 μS.

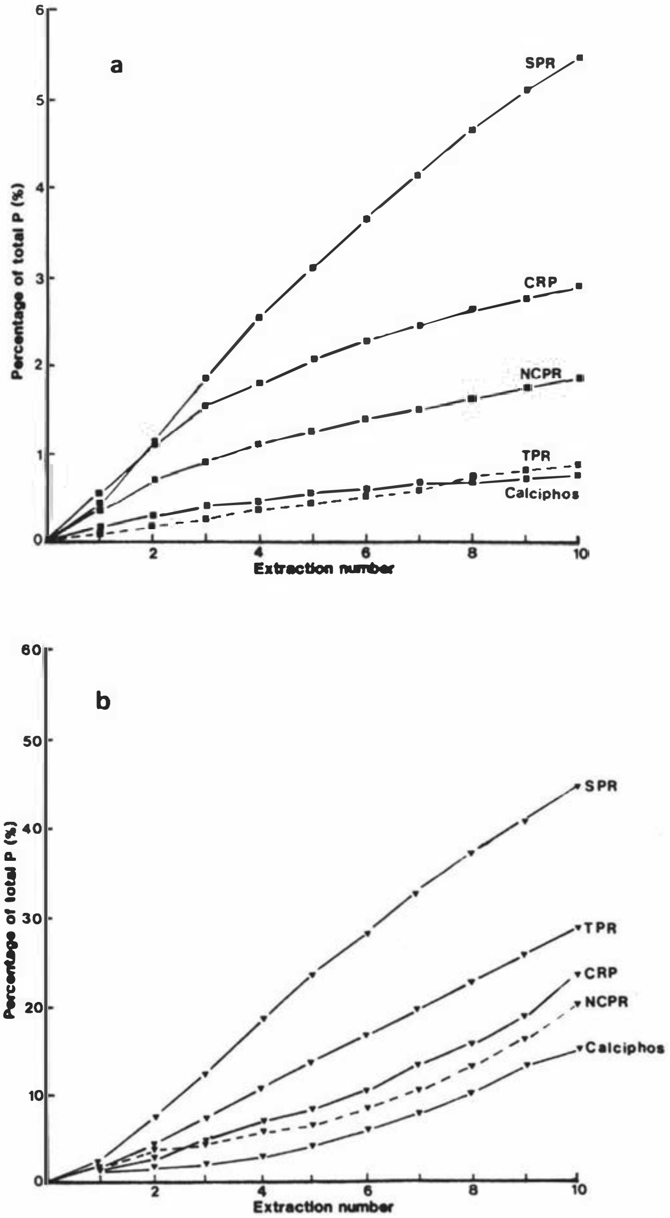


Figure 6.11 Cumulative amount of phosphorus released during electro-ultrafiltration in the manual mode, with 10, 5-min extractions at 400V at a solution, deionized water (a) and 0.03 mg NaCl ml^{-1} solution (b):solid ratio of 250:1, as influenced by the phosphate source.

orbicular shape, due to the mode of deposition (Cheney et al., 1979) and therefore behave in a similar manner to fine sand in shaking systems. Whereas SPR remained in solution during EUF, NCPR and CRP readily formed coatings over the semi-permeable membranes at the two electrodes. The small differences reported in the Fe gel studies (6.3.3.1) between the dissolution of SPR and NCPR, may also be explained by differences in physical properties important in shaker systems, in addition to any effect of $CaCO_3$ on dissolution.

Although addition of dilute NaCl solution (0.030 mg ml^{-1}) increased the dissolution of the five PR materials (Fig. 6.11b) evaluated in the previous studies (see 6.3.1), the EUF method failed to rank the PR materials in the order of agronomic effectiveness established by the glasshouse study (see 6.3.1). It was found in subsequent studies that the use of other salts, and both weak acids and alkalis, also gave conflicting results. Thus it appears that the problems associated with both physical differences between P sources unique to shaking systems and the varying effect of the conductivity of the solution during EUF limits this technique as an alternative approach for evaluating P release from low water solubility P sources.

6.4 General Discussion

The results obtained in the present glasshouse study with six soils not only extend the preliminary agronomic evaluation of CRP (Chapter 3) and permit CRP to be ranked as a reactive PR along with NCPR and SPR, but also provides the first comprehensive comparison of CRP with a range of P sources of varying agronomic effectiveness. The six P sources evaluated can be ranked in the following decreasing order of agronomic effectiveness, superphosphate $\geq$ NCPR $\geq$ SPR > CRP >> Calciphos >> TPR. The difference found between NCPR and superphosphate is consistent with that reported in the literature for these two P sources (Bengtson et al., 1974; Englestad et al., 1974; Chien and Hammond, 1978); as is the difference between SPR and superphosphate (Fassbender, 1965; Hammond, 1978), CRP and superphosphate (Chapters 3 and 5; Powell, 1979; Powell et al., 1980; Rajan, 1981a), Calciphos and superphosphate (Buchan et al., 1970; Stephens and Lipsett, 1975; Gilkes and Palmer, 1979), and TPR and superphosphate (Armiger and Fried, 1957; Hammond and Leon, 1977).

The differences found in the ability of the two indicator plant species to utilize P from a PR have also been reported by a number of workers with other plant species (Fried, 1953; Mclean and Hoelscher, 1954; Marais et al., 1970). The reasons for this difference, which is generally greater in dicotyledons than monocotyledons (Deist et al., 1971), and which was reflected more in P uptake than in yield data in the present study, are not well understood. The most likely mechanism operating is an increase in the rate at which Ca is removed from solution, either by simply an increased requirement for Ca by dicotyledons (Deist et al., 1971), or a greater cation-exchange capacity of the root surfaces of dicotyledons (Drake et al., 1951), or a combination of both. This would lead to an increase in the rate of dissolution of the PR in the soil and consequently its plant availability.

An evaluation of chemical extraction procedures for predicting the agronomic effectiveness of PR materials, and superphosphate at the first harvest showed that, except for 2% formic acid and 5% citric acid, the extractants were of only limited value if a single extraction was used. This is in line with the findings of Hoffman and Breen (1964), Cooke (1956), Amberger (1978), and Chien and Hammond (1978a), but conflicts with the results of Armiger and Fried (1957), Engelstad et al. (1974) and Bengtson et al. (1974), highlighting the variability in the literature of information on the predictive ability of these chemical extractants. This variability may be due to some extent to the effect of $CaCO_3$, which is associated with many PR materials (Lehr et al., 1967). Whereas the initial solubility of NCPR and SPR appeared to be affected to only a minor degree by the presence of $CaCO_3$ in the present study, the solubility of CRP was markedly reduced at the first extraction, particularly in 2% citric acid and NAC. Interestingly, in the studies of Armiger and Fried (1957), Engelstad et al (1974), and Bengtson et al. (1974), in which 2% citric acid and NAC, respectively, were found to be good indicators of agronomic effectiveness at the first harvest, none of the PR materials evaluated contained appreciable amounts of $CaCO_3$.

In later harvests the predictive ability of all the chemical extraction procedures using a single extraction declined further, a finding supported by the work of Bengtson et al. (1974) and Engelstad et al. (1974), who found that the relationship between the relative agronomic effectiveness of PR materials and their solubility in NAC decreased at the second harvest. An increase in the effectiveness of less-reactive PR materials (Engelstad et al., 1974; Chien and Hammond, 1978a), and also the increasing influence of the soil on the applied PR (Bengtson et al., 1974; Hagin et al., 1978b) are the most likely reasons for the decreasing predictive ability of the extractants after the initial harvest. The importance of these two factors is likely to increase as the rate of application of P decreases. Whereas, in the present study no marked differences were found in the correlation coefficients at the two application rates used, several workers have noted a marked interaction at lower application rates (Chien, 1977; Hammond and Leon, 1977).

Of the sequential extraction procedures investigated in this study, 2% formic acid (sum of 2), both of the 2% citric acid (sum of 3) procedures which behaved very similarly, and NAC (sum of 4) were best correlated with agronomic performance. This supports and extends the findings of Hoffman and Breen (1964). In addition to improving the predictive ability of both of the 2% citric acid and, in particular NAC, the sequential approach also improved the predictive ability of these extractants in later harvests, with the application rates used in the present study. This requires clarification at lower application rates. A procedure employing two, three, or even four sequential extractions, however, is time consuming and therefore less suitable for routine analysis. Of the single chemical extraction procedures evaluated, 2% formic acid appears to offer the most promise for assessing the likely agronomic effectiveness of PR materials.

If a PR has appreciable amounts of $CaCO_3$, such as CRP, however, then a single extraction appears to be of limited value. Increasing the strength of the citric acid to say 15%, in an attempt to decrease the effect of $CaCO_3$ and thus eliminate the necessity for a sequential extraction, results in an increase in the solubility of the less reactive PR. Use of a wider solution:solid ratio (350:1) with either 2% formic acid or 2% citric acid (Ankorion, 1978) or pH = 3 ammonium citrate (Chien and Hammond, 1978a) appears to only overcome the problems associated with the presence in a PR of a small amount of free $CaCO_3$. A sequential extraction procedure therefore appears to offer the only technique for assessing the likely agronomic effectiveness of PR materials containing appreciable amounts of $CaCO_3$.

All of the extraction procedures tested failed to adequately assess the agronomic effectiveness of Calciphos. Hoffman and Breen (1964) reached a similar conclusion, finding that the solubility of two PR materials (Connetable Islands and Senegal), containing mainly aluminium phosphates which increased with the increasing alkalinity of the citrate solutions, depended more on the extracting solution than on the likely agronomic effectiveness of the PR materials. A number of workers (Doak et al., 1965; Roberts and White, 1974) have found NAC to be a useful indicator of the likely agronomic effectiveness of Calciphos. In general, however, it has been found to grossly overestimate the relative agronomic effectiveness of Calciphos compared to superphosphate (Buchan et al., 1970; Palmer et al., 1979). Palmer (1980) did find that NAC was a useful extractant when comparisons were restricted within the group of calcined products, and this fact probably explains some of the conflicting reports as to the value of NAC in the literature. The sequential extraction procedure also failed to improve the predictive ability of the conventional extractions when Calciphos was included in the comparison.

Only 79% of the total P in the superphosphate used in the present study was soluble in 2% citric acid (The Fertilisers Regulations, 1969). Because of the increasing proportion of Christmas Island A grade PR in blends with Nauru PR in the manufacture of superphosphate in New Zealand (Quin, 1981), citric-soluble P levels are lower than are desired, due to the precipitation of Fe-P and Al-P. Higher amounts of unreacted, rather inert PR are also likely to be present in the superphosphate due to under-acidulation and preferential dissolution of the Fe and Al minerals by sulfuric acid during manufacture (Gilkes and Lin Nunez, 1980). This leads to a further decline in citric-soluble P values. The presence of these insoluble phosphate, although in fairly small quantities in the superphosphate used in the present study, is reflected in their varying solubilities in the extractants after the first extraction. Gilkes and Lin Nunez (1980) found that these poorly-soluble Fe-P and Al-P compounds, and unreacted PR materials (Nauru and Christmas Island A grade) often found in superphosphate are less effective than monocalcium-phosphate monohydrate (MCPM) as a source of P for wheat. In a recent glasshouse study conducted at Massey University (Currie, pers. comm.) the plant availability of the citric acid-insoluble P component of a range of commercially-available superphosphates was found to vary widely, when compared to MCPM, but in some cases was no greater than that of the unreacted rock from which the superphosphate was made.

Present fertilizer regulations (The Fertilisers Regulations, 1969) require information on the amount of total and 2% citric acid-soluble P in superphosphate for registration. Both the 2% citric acid methods evaluated in the present study were found to be poor indicators of likely agronomic effectiveness. Until recently, however, the choice of extractant to evaluate the chemical quality of superphosphate has been of little importance as the proportion of citric acid-soluble P in superphosphate has generally exceeded 90% of total P, of which over 85% is soluble in water (During, 1972). Clearly, with a decline in the citric-soluble and, in particular, the water-soluble P fraction in the superphosphate products available in New Zealand, the official method employed for assessing the chemical quality, and indirectly agronomic effectiveness, becomes of increased importance. Based on the results of the present study, a re-evaluation of this question is warranted.

Whereas the Fe gel approach showed promise as a technique for assessing the agronomic effectivness of PR materials, the EUF showed several limitations. Nemeth (1980) has suggested that the EUF technique could be used for nutrient fractionation of both plant materials and fertilizers, in addition to soils. To date the use of the EUF technique for investigating the behaviour of PR materials has been restricted to a study by Obigbesan and Mengel (1981) with incubated soils. The problems associated with physical differences between the PR materials and the varying effect of solution conductivity on the rate of dissolution of a PR appear to prevent a direct assessment of PR materials by EUF.

The ability of the Fe gel approach to index Calciphos in line with its moderate agronomic effectiveness, was a feature of this study and underlines the potential of approaches which attempt to characterize the pattern of P release. McLaughlin and Syers (1978) also found that the Fe gel approach differentiated more effectively the differences in the stability of ferric phosphates, one of the major reaction products believed to form following the dissolution of superphosphate on contact with moist acid soil, (Lindsay et al., 1959) than did a single water extraction. An extension of the dialysis period beyond 17 days may have improved the predictive ability of this approach.

CHAPTER 7

CHAPTER 7

REACTIONS OF PHOSPHATE ROCK MATERIALS IN SOILS

7.1 Introduction

In contrast to the initial decline in water-extractable P in soil to which a PR is added (Chien, 1979; Mokwunye and Chien, 1980a; Chien et al., 1980a, b), both Bray- and bicarbonate-extractable P have been shown to initially increase (Chien, 1978; Shinde et al., 1978). The significance of these changes to short-term plant-available P in soil has not been established. Several workers (Chien, 1979; Hammond, 1978; Chien et al., 1980a), have used water-extraction to evaluate the changes in P in the soil to which a PR was added. Results from the field trials (Chapter 4), suggest that the modified single-water extraction procedure of Ryden and Syers (1977), which has been shown to correlate well with plant uptake of P after the addition of superphosphate (Gillingham, 1978; Rennes, 1978; Luscombe et al., 1979), was a poor indicator of the plant-available P in the soil to which CRP was added, at least in the short term. Because of the marked effect of solution:soil ratio (Hope, 1977) and shaking time (Chien, 1979) on the amounts of P extracted from soils by dilute salt solutions and water, these results may not be directly comparable.

As with water extraction, the bicarbonate method of Olsen et al. (1954) also appears to underestimate the short-term, plant-available P in the soil derived from a PR (Chapter 4). In contrast, the Bray extraction appears to provide a good estimate of plant-available P in the soil to which a PR has been added (Chapter 4). However, the variability in the field results due to factors other than applied P and the use of an indirect measure of plant-available P in the soil, makes these conclusions rather tentative. Therefore, before the agronomic significance of the reactions of a PR in soils can be assessed with any confidence, the relationship existing between the amounts of extractable P and plant-available P in soil containing a PR requires clarification.

Methods used for measuring the dissolution of a PR in soil, as distinct from the methods used to estimate the subsequent plant-available P fraction, have invariably been based on the fractionation procedure of Chang and Jackson (1957) or one of its various modifications (Robertson et al., 1966; Amberger et al., 1971; Cescas and Tyner, 1976). Increases in the Fe-P and Al-P fractions are considered to give an estimate of the total P in the PR which has dissolved, whereas the increase in the Ca-P fraction is considered to indicate the amount of unreacted PR. Apart from the study of Chu et al. (1962), where the Fe-P and Al-P fractions were combined, giving a direct estimate of the amount of PR dissolved, no other workers appear to have attempted to use their results in this manner. The extent to which the Chang and Jackson (1957) fractionation procedure differentiates between the Fe-P and Al-P fractions in soils is debatable, as Bromfield (1967) and Williams et al., (1971) have found that NH_4F is not specific for Al-P, but it can also remove considerable Fe-P during the extraction. A single NaOH extraction, which has been shown (Syers et al., 1972) to remove both these fractions, may therefore provide a useful method for measuring the dissolution of a PR in a soil. Because apatite does not dissolve to any significant extent in dilute NaOH (Chang and Jackson, 1957), the use of this reagent is preferable to methods which attempt to measure the unreacted PR fraction remaining in the soil, which would require a fractionation procedure.

In addition to PR-related factors such as solubility and particle size, the rate of dissolution of a PR in soil will be dependent on a source of hydrogen ions and on the concentration of the reaction products (Ca^{2+} and $H_2PO_4^-$) in the solution immediately surrounding the PR. As a result soil pH, which to some degree provides a rough estimate of exchangeable Ca, and the P-sorption capacity of the soil, which controls to a large extent the P concentration in solution, are likely to be the overriding soil factors controlling the rate of dissolution of a PR. Of these two, soil pH has been studied the most extensively (Joos and Black, 1950; van der Paauw, 1965; Ensminger et al., 1967), as has the effect of liming (Jones, 1948; Ellis et al., 1955). Most of the data have been obtained from agronomic rather than incubation studies. Both soil pH, per se , and exchangeable Ca have been shown to be important (Graham, 1955; Peaslee et al., 1962) in influencing the dissolution of a PR. However, except for the study of Khasawneh and Doll (1978) their relative importance has received little attention. In addition to finding that the dissolution of a PR increased as the P-sorption capacity of the soil increased, both Chu et al. (1962) and Chien et al. (1980b) also found that the effect of soil pH on the dissolution of a PR could be modified by the P-sorption capacity of the soil. In fact Chu et al. (1962) showed that the importance of soil pH in the dissolution of a PR decreased as the P-sorption capacity of a soil increased. The relationship which exists between P-sorption capacity and soil pH per se, and exchangeable Ca as it affects both the dissolution of a PR and the subsequent plant-available P fraction requires further investigation.

It has recently been suggested by Khasawneh and Doll (1978) that increasing the P concentration sustained in the soil solution should lead to a decrease in the dissolution of a PR, in a similar manner to the decrease in dissolution measured by Khasawneh and Doll (1978) with increasing Ca concentrations in the soil. To date no published data are available on this soil factor, although results obtained with the Tokomaru silt loam used in both the glasshouse (Chapter 3) and field (Chapter 4) suggest that soil P status is of little importance in this regard.

In this Chapter, the reactions of PR materials in soil are investigated, particularly in relation to the soil factors which influence dissolution. In addition, an initial attempt is made to develop a simple model to describe and predict the initial dissolution of PR materials in soils.

7.2 Materials and Methods

7.2.1 Phosphate sources and soils

Three PR materials (SPR, CRP, and TPR) and superphosphate were used in this series of studies. Results for particle size, total P, $CaCO_3$, and solubility in water (The Fertilisers Regulations, 1969) and in 2% Citric acid (The Fertilisers Regulations, 1969) are given in Table 7.1. In each case, <180-μm PR material was used in the studies reported in this Chapter.

A total of six soils, five surface and one subsurface soil, with contrasting pH values, P-sorption capacities, P status, organic matter contents, and Ca status were chosen for this series of studies. Results for soil pH in water, organic carbon (Chapter 4.2.1), exchangeable Ca (Chapter 5.2.1), P sorption capacity (Chapter 3.2.2), and P removed by single-water (Chapter 4.2.1), by bicarbonate (Chapter 3.2.2), by Bray (Chapter 4.2.6.1) and by 0.5M NaOH (Chapter 4.2.6.1) extraction for the six soils are presented in Table 7.2.

Table 7.1 Some physical and chemical characteristics of superphosphate, Tennessee phosphate rock (TPR), Sechura phosphate rock (SPR), and Chatham Rise phosphorite (CRP)

Phosphate source	Particle size fraction (μm)	Total P (%)	Total $CaCO_3$ (%)	P extracted by	
				Water	2% Citric acid
				(% of total P)	
Superphosphate	< 250	10.0	0	45.00	79.5
TPR	< 180	15.7	1.7	< 0.01	21.3
SPR	< 180	13.7	8.9	< 0.01	42.4
CRP	< 180	9.2	25.2	< 0.01	20.7

Table 7.2 Some chemical characteristics of the six soils

New Zealand Soil Group	Soil type	Organic carbon (%)	pH_{H_2O}	Exchangeable Ca (meq %)	P-sorption capacity (%)	Extractable P in soil ($\mu g\ g^{-1}$)			
						Water	Bicarbonate	Bray	NaOH
Yellow-grey earth	Tokomaru silt loam	2.39	5.6	6.6	22	2.8	6.2	5.5	72
Yellow-grey/ yellow-brown earth intergrade	Wainui silt loam	4.71	5.0	4.4	35	2.2	6.3	6.8	74
Yellow-brown earth/ yellow-brown loam intergrade	Konini silt loam	6.04	5.7	6.5	50	1.8	5.8	4.1	82
Yellow-brown pumice	Taupo sandy silt loam	8.48	5.3	8.2	73	3.2	28.8	15.8	339
Yellow-brown loam	Ramiha silt loam	9.70	5.3	2.9	86	0.9	4.5	2.8	218
Control Yello-brown loam	Egmont brown loam (subsoil)	2.69	6.5	6.6	91	0.6	5.6	3.1	795

7.2.2 Preliminary incubation studies on the effect of phosphate rock materials on extractable phosphorus in soil

Changes with time in water-extractable P in soil to which a PR was added was evaluated using the Wainui, Konini, and Ramiha soils (Table 7.2).

The TPR and SPR materials were thoroughly and separately mixed with sieved (< 2 mm), air-dried soil and placed into plastic pots, 10 cm in diameter and 6 cm deep. Each pot held 150g of soil. The P sources were added to give 500 μgP g^{-1} of soil, which is equivalent to the addition of 0.478 and 0.549 g of TPR and SPR, respectively to 150g of soil. The treatments were duplicated and each pot was moistened to field capacity (0.42, 0.46, and 0.58 g of water g^{-1} of soil for the Wainui, Konini, and Ramiha soils, respectively) and incubated at 15°C. Duplicate samples were incubated for up to 90 days after addition of P and analysed for changes in water-extractable P in the soil.

The effect of varying the rate of P additions to the soil on the changes in water- and bicarbonate-extractable P in the soil with time following addition of SPR, CRP and superphosphate was evaluated with the Wainui and Ramiha soils. These were added to give 250, 500, and 1000 μgP g^{-1} of soil, which is equivalent to the addition of 0.275, 0.549, and 1.098 g of SPR, respectively, 0.409, 0.819, and 1.637 g of CRP, respectively, and 0.375, 0.750, and 1.500 g of superphosphate, respectively, to 150 g of soil. The fertilizers were added to the soil as described previously. Duplicate soil samples were taken 1, 3, 9, 16, 37, 78, 112, 174, 203, and 298 days after addition of P and analysed for changes in water- and bicarbonate-extractable P.

7.2.3 An evaluation of laboratory estimates of plant-available phosphorus in soil

A further experiment was conducted to evaluate the effectiveness of the water-, bicarbonate- and Bray-extraction methods in providing estimates of plant-available P in the soil following the addition of SPR, CRP, and superphosphate to the Wainui, Konini, and Ramiha soils. The SPR, CRP, and superphosphate were added as described previously at a rate to give 500 μgP g^{-1} of soil. Duplicate samples were taken 1, 9, 16, 37, 78, 112, 203, and 298 days after P addition and analysed for changes in water-, bicarbonate-, and Bray-extractable P in the soil.

To measure the actual changes in plant-available P in these three soils with time following fertilizer P addition, the technique of Stanford and De Ment (1957) was used on triplicate soil samples taken on the above sampling dates from all treatments. This technique facilitates very rapid uptake of P by plants established at varying time intervals following the addition of P to soils. Small plastic pots (10 cm in diameter and 6 cm deep with their bases removed) were placed within similar intact pots and the resulting pair filled with 250 g of washed river sand. Fifteen seeds of perennial ryegrass (*Lolium perenne*) were placed in each pot which was watered regularly with a complete, but minus P nutrient solution (Middleton and Toxopeus, 1973). Following a 60-day growth period, 10 g (air-dried equivalent) of incubated pot soil was spread evenly on the bottom of a second pot. The inner pot of sand and grass was lifted from its enclosing pot and the exposed root mat placed in contact with the soil layer in the new pot. Watering with a minus P nutrient solution was continued and a herbage cut was taken after 25 days. Soils and P sources were pre-incubated so that the range of sampling dates required fell on the same day. This was done to eliminate variations in growth of ryegrass with season. Herbage was oven dried (60°C for 24 h), weighed, ground, and analysed for P following Kjeldhal digestion. The relationship between plant-available P (plant uptake) and extractable-soil P (water-, bicarbonate- and Bray-extractable P) were subsequently established using linear regression analysis.

7.2.4 Effect of soils of contrasting phosphorus characteristics on the reactions of phosphate rock and superphosphate in soils

To evaluate the effect of P-sorption capacity on the reactions of a PR and superphosphate in soil a further incubation study was conducted using a wider range of soils, including the Tokomaru, Wainui, Konini, Taupo, Ramiha, and Egmont soils (Table 7.2). As the major changes in extractable P in the soil to which either a PR or superphosphate was added, occurred within the first 90 days (Fig. 7.2, 7.3, 7.4) this and subsequent studies were limited to this time period. The SPR, CRP, TPR and superphosphate were added to give 500 μgP g^{-1} of soil. The fertilizers were added to the soil which was moistened to field capacity (0.40, 0.42, 0.46, 0.55, 0.58, and 0.57 g of water g^{-1} of soil for the Tokomaru, Wainui, Konini, Taupo, Ramiha, and Egmont soils, respectively), and incubated at 15°C. Duplicate samples were taken at increasing time intervals for up to 90 days and analysed for changes in water-, bicarbonate- and Bray-extractable P in the soil.

To compare the fraction of P extracted by the three extraction methods from soils of contrasting P-sorption capacities a ^{32}P isotope study was included with the incubation study. Carrier-free ^{32}P (5 μCi) was added to the air-dried Wainui, Konini, Ramiha, and Egmont soils in sufficient water to attain field capacity, thoroughly mixed, and incubated at 15°C for 14 days. Gillingham (1978) has shown that the equilibrium between ^{32}P and ^{31}P can be reached in 24 h in soils of relatively low P status, while on soil of relatively high P status this can take up to 12 days. After 14 days of incubation the four soils were extracted using the three extraction methods. To compare the ^{32}P activity in the extracts a 1-ml aliquot was added to 10 ml of tritontoluene scintillation coctail (Patterson and Green, 1965) in a counting vial. Isotopic acitivity was determined using a Beckman <5-350 liquid scintillation counter (discriminator channel opening at range 30-1000 and Gain setting on 490). The concentration of ^{31}P in the same extracts was determined by the usual method.

In addition to following the changes in the potentially plant-available P fraction, an attempt was made to measure the fraction of total P added as a PR which had dissolved. Because apatite is essentially insoluble in NaOH (Chang and Jackson, 1957) and because this reagent is an effective extractant of sorbed inorganic P from a soil (Williams et al., 1967) increases in NaOH-extractable P in a soil to which a PR is added should provide a good estimate of the amount of P dissolved and retained by the soil. Implicit in this, however, is the essentially zero solubility of PR in NaOH. To check on this, air-dried soil to which 500 μgP as SPR g^{-1} of soil had been added and thoroughly mixed, was immediately extracted with 0.5M NaOH. Increases in 0.5M NaOH-extractable P ranged from 2 to 5% of total P added as SPR in three (Wainui, Konini, and Ramiha) contrasting soils. Extraction of SPR, CRP, or TPR with NaOH removed only small amounts of P (3 to 8%). Because up to 3% of the total P in a PR can be present as "surface P", which is isotopically exchangeable (Cano Ruiz and Talibudeen, 1957), these results confirm that a PR is essentially insoluble in NaOH.

Before extracting a soil with NaOH, a preliminary extraction with 0.1M NaCl was given to remove any free or exchangeable Ca which could precipitate as $Ca(OH)_2$ in the NaOH extract and sorb inorganic P. Therefore in this and subsequent studies the extent of dissolution of a PR in a soil was evaluated by extraction with 0.5M NaOH, at a solution: soil ratio of 100:1 for 16 h, following a pre-wash with NaCl.

A separate incubation study was conducted on one soil to evaluate the effect of P status on the reactions of a PR and superphosphate. The Wainui soil was pre-incubated at field capacity (0.42g of water g^{-1} of soil) at $15^{o}C$ with increasing amounts of P added as KH_2PO_4 for 42 days. Again SPR, TPR, and superphosphate were added (500 μgP g^{-1} of soil), as previously described, the soil moistened to field capacity, (0.42 g of water g^{-1} of soil) and incubated at $15^{o}C$ for 90 days. Duplicate samples were taken at increasing time intervals up to 90 days and analysed for water-, bicarbonate-, Bray-, and NaOH-extractable P.

7.2.5 Evaluation of the effect of soil pH and exchangeable calcium on the reactions of a phosphate rock and superphosphate in soils

Liming of a soil not only increases pH, but also the Ca concentration. The purpose of this incubation study was to investigate the relative influence of these two factors on the reactions of a PR in a soil. As in the previous study, this investigation was restricted to one soil, rather than using a range of soils of varying pH, to eliminate the effect of other soil properties. To obtain a range of soil pH values, the Wainui silt loam was pre-incubated with finely-ground $Ca(OH)_2$ for six weeks. The actual amounts of $Ca(OH)_2$ required to give a pH range from 5.0 to 6.8 were investigated in a preliminary study. To obtain a range of Ca concentrations, without increasing soil pH, Ca as $CaCl_2$ was added at equivalent concentrations of Ca as those added in the $Ca(OH)_2$ treatment. These samples were also pre-incubated with soil for six weeks. As in the previous study, SPR, TPR, and superphosphate were added to give 500 μgP g^{-1} of soil. In addition to measuring changes in bicarbonate-, Bray-, and NaOH-extractable P over 90 days, soil pH changes were also monitored.

7.3 Results and Discussion

7.3.1 Changes in extractable phosphorus in soil to which a phosphate rock and superphosphate were added

7.3.1.1 Effect of phosphate rock solubility on water-extractable phosphorus in soil

The differences in water-extractable P in soil following the addition of TPR and SPR to three contrasting soils (Fig. 7.1) are consistent with the differences found in the solubility of these two PR materials (Chapter 6). For TPR, increases (> 0.5 μgP g^{-1} of soil) in water-extractable P in the soil were only obtained during the first 10 days of the incubation period with each of the three soils. Rennes (1978) also only found small increases in water-extractable P in the soil when Christmas Island A grade PR (unreactive) was added to soil. In contrast to the small differences obtained with TPR, both the initial values and those at 90 days were appreciably higher when SPR was added to the three soils (Fig. 7.1). Except for an initial increase with the Wainui soil, a similar pattern of decline was measured with all three soils, although the initial values for the slope of the decline curve and the values at 90 days differed between the soils. A comparison of the water-extractable P in the soil at 90 days on the Wainui (Fig. 7.1a) and Ramiha (Fig. 7.1c) soils highlights this difference.

Rennes (1978) attributed the small initial increases in water-extractable P in the soil from the addition of Christmas Island A grade PR to the presence of "surface" P, which is isotopically exchangeable and therefore partially water-extractable (Ryden and Syers, 1977). Several workers (Olsen, 1952; Cano Ruiz and Talibudeen, 1957) have found that rapidly-exchangeable "surface" P, expressed as a percentage of total P, varies widely between PR materials. Cano Ruiz and Talibudeen (1957) found that up

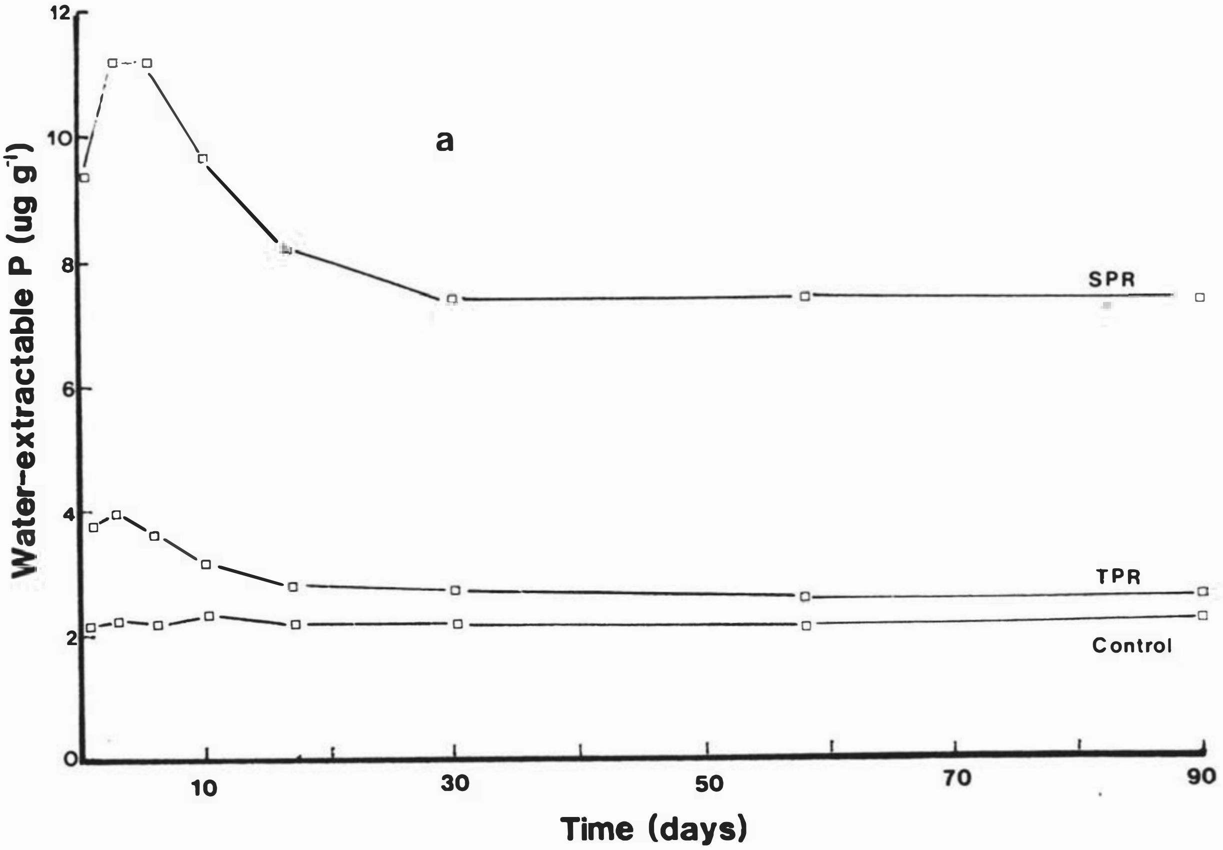
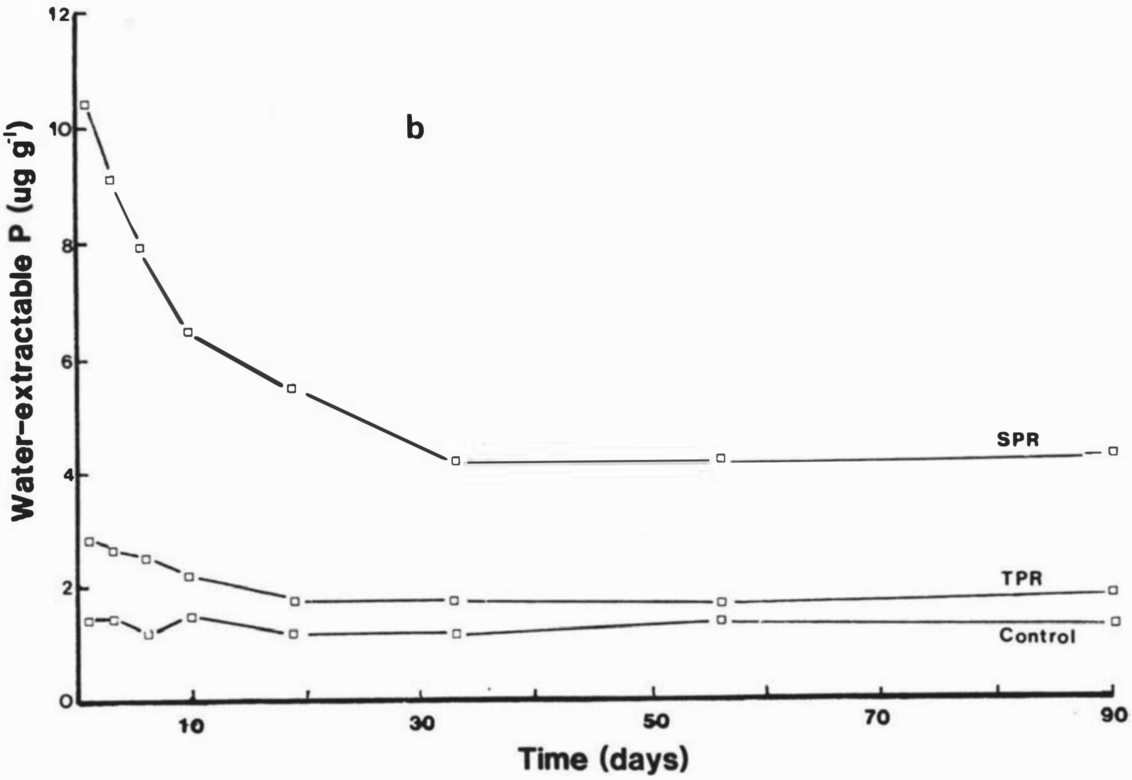
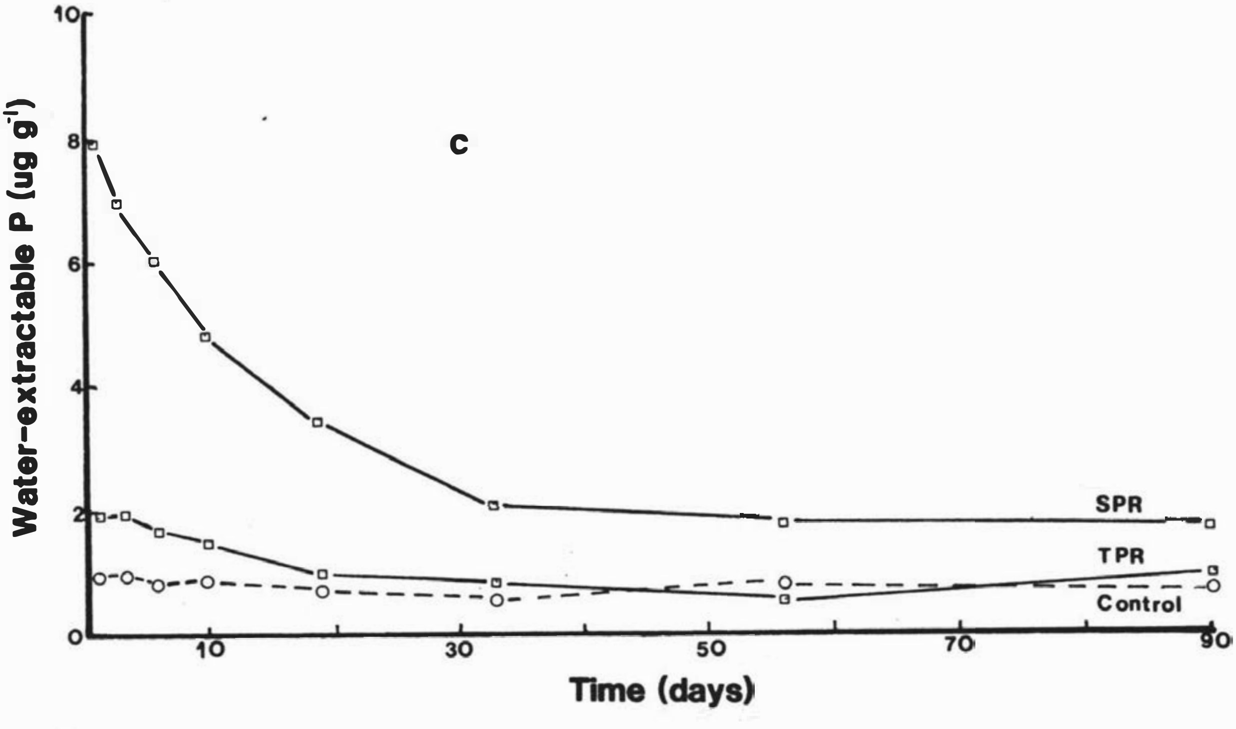


Figure 7.1 Change in water-extractable phosphorus in the soil over 90 days following Sechura phosphate rock (SPR) or Tennessee phosphate rock (TPR) addition at 500 μgP g^{-1} of soil to three contrasting soils. a = Wainui, b = Konini, and c = Ramiha.

Figure 7.1 contd.





to 3% of total P was exchangeable over 10 days from a wide range of PR materials. In addition to the presence of "surface" P, the dissolution of fine particles present on the surface could also lead to an initial increase in water-extractable P in the soil (Rennes, 1978), although the work of Caro and Hill (1956) suggests that a decrease in particle size below 150 μm has no effect on the solubility of a PR. The fact that no real difference (< 0.5 μgP g^{-1} of soil) was found between TPR and control soils after 10 days, whereas the addition of SPR markedly increased water-extractable P in the soil, also suggests that the initial increases from TPR probably resulted more from the extraction of "surface" P, than from the dissolution of P from the PR.

Although the results from the field (Chapter 4) suggest that the single-water extraction underestimates, at least in the short term, the amount of plant-available P derived from a PR in soil, this procedure appears to be useful in pointing up differences in the stability of PR materials in soils and thus may be useful in evaluating differences in the behaviour of a PR and superphosphate in soil.

7.3.1.2 Effect of rate of application of superphosphate and a phosphate rock on water- and bicarbonate-extractable phosphorus in soil

Values for both water- and bicarbonate-extractable P in soil to which superphosphate was added showed a similar pattern of decline at all three rates of addition of P for both the Wainui (Fig. 7.2a) and Ramiha (Fig. 7.2b) soils. The three values obtained for either water- or bicarbonate-extractable P in the soil at each sampling date were proportional to the three initial rates of addition of P as superphosphate. Rennes (1978) also found that for any soil, the value of water-extractable P in the soil was directly proportional to the rate of addition of P as superphosphate. However, there were differences between the two soils

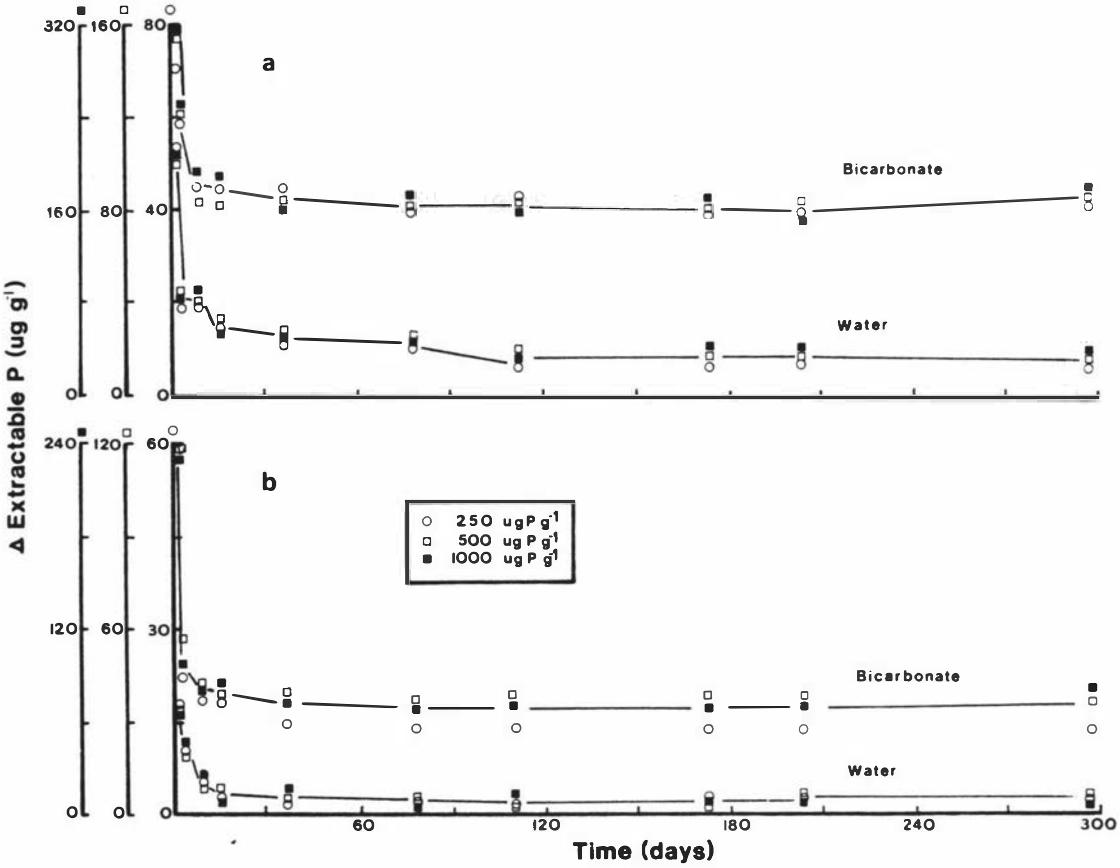


Figure 7.2 Change (Δ) in water- and bicarbonate-extractable phosphorus in soil over 300 days following superphosphate addition at three rates to two soils. a = Wainui and b = Ramiha.

in both the initial rates of decline in P and in the final amounts of P at 298 days. Water- and bicarbonate-extractable P in the soil in the first 9 days were far higher for the Wainui (Fig. 7.2a) than for the Ramiha (Fig. 7.2b) soil, as were the values at 60 days. Again this is in line with the findings of Rennes (1978), but differs from the result obtained by Ryden et al., (1976) who suggested that the relative water extractability of P in soil following P addition was essentially common to different soils.

Addition of both CRP and SPR significantly increased water-extractable P in the soil with both the Wainui (Fig. 7.3a) and Ramiha (7.3.b) soils at all three rates of P addition. Except for an initial increase in water-extractable P over the first 3 days with the Wainui soil (Fig. 7.3a), water-extractable P declined in both soils at all rates of addition of P as either CRP or SPR for the remainder of the incubation period. Initially, the decline in water-extractable P in the soil to which these two PR materials were added was far more pronounced with SPR than with CRP.

The differences in free calcite (Table 7.1) between these two materials may explain, in part, these initial differences. After 200 days, however, differences between the two PR materials were small (Fig. 7.3). In contrast to superphosphate, water-extractable P in the soil from either SPR or CRP was not proportional to the three initial rates of addition of P, but the relative amounts decreased as the rate of addition increased.

The relative water-extractability of P in the soil to which either SPR or CRP was added decreased with increasing rates of P addition to both soils at 298 days, when compared to equivalent additions of superphosphate. For instance,on a percentage basis, the relative water-extractability of SPR and CRP decreased to 298 days when compared to

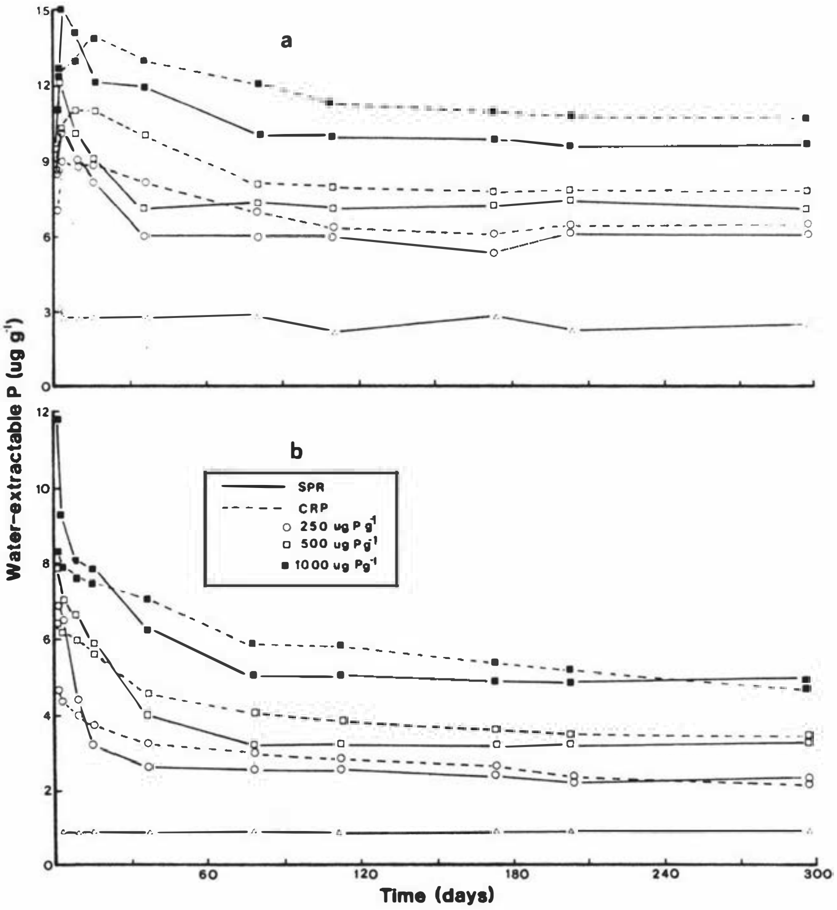


Figure 7.3 Change in water-extractable phosphorus in soil over 300 days following Sechura phosphate rock (SPR) and Chatham Rise phosphorite (CRP) addition at three rates to two soils. a = Wainui and b = Ramiha.

superphosphate added to the Wainui soil (Fig. 7.3a), from 52 to 20%, as the rate of application of superphosphate increased from 250 to 1000 μgP g^{-1} of soil. Differences were also found between soils. With the Ramiha (Fig. 7.3b) the relative water-extractability of P from either SPR or CRP was higher, although still decreasing from 59 to 43% as the rate of application of superphosphate increased from 250 to 1000 μgP g^{-1} of soil. This suggests that the water-extractability of P from a PR added to soil, when compared to superphosphate, increases with increasing P-sorption capacity of the soil.

In marked contrast to the decline in water-extractable P in the soil following the addition of either superphosphate (Fig. 7.2) or the three PR materials (Fig. 7.1, 7.3), and to the decline in bicarbonate-extractable P following the addition of superphosphate (Fig. 7.2), bicarbonate-extractable P in the soil to which CRP and SPR were added increased initially with the three rates of application of P and with both soils, before reaching an essentially constant value (Fig. 7.4). The exception was an initial increase in water-extractable P following the addition of TPR, SPR, and CRP to the Wainui soil (Fig. 7.1a, 7.3a). Again, marked differences were found between the Wainui (Fig. 7.4a) and Ramiha (Fig. 7.4b) soils in both the initial increases in bicarbonate-extractable P in the soil and the values at 298 days. The differences in the initial solubility of CRP and SPR, probably resulting from the difference in the calcite content of the two materials (Table 7.1), were more pronounced with bicarbonate- (Fig. 7.4) than with water- (Fig. 7.3) extractable P in the soil, particularly at the highest rate of addition of P. Increases in bicarbonate-extractable P in the soil to which the PR materials were added were not proportional to the rate of addition of P with either of the soils. The relative extractabilities of both PR materials, when compared to superphosphate, decreased markedly with

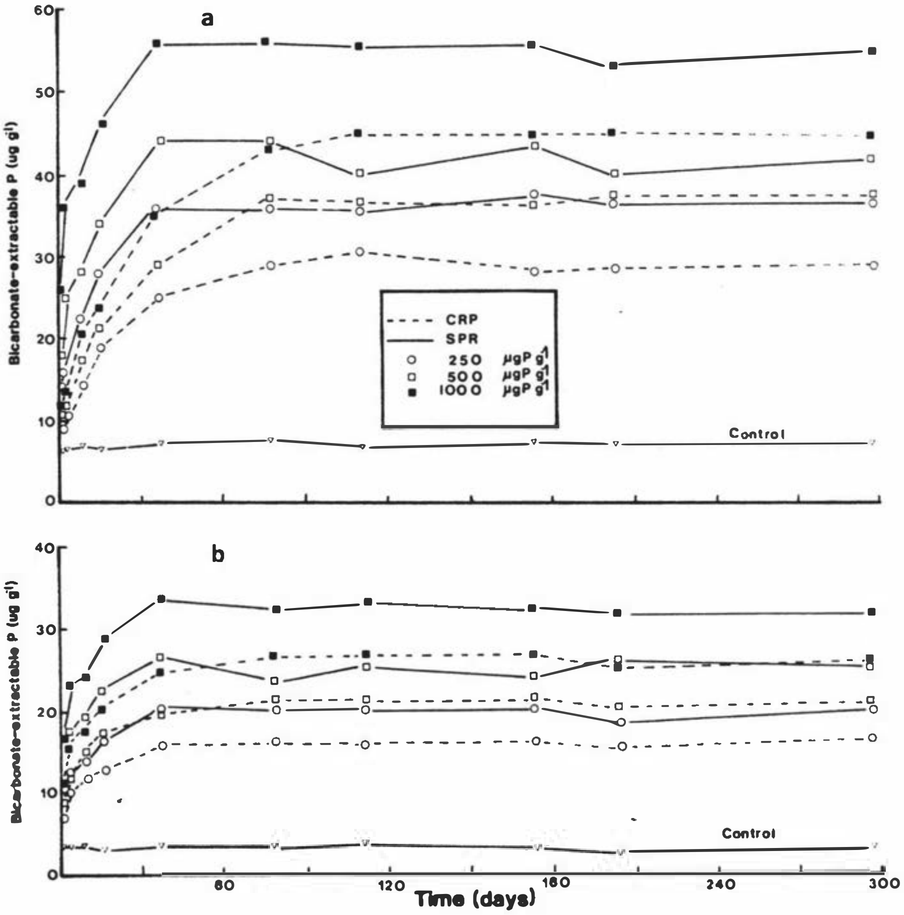


Figure 7.4 Change in bicarbonate-extractable phosphorus in soil over 300 days following Sechura phosphate rock (SPR) and Chatham Rise phosphorite (CRP) addition at three rates to two soils. a = Wainui and b = Ramiha.

increasing rate of application to both soils.

In the field trial results reported for CRP (Chapter 4) the highest rate of application of P was 70 kgP ha^{-1} (764 kgCRP ha^{-1}), which is equivalent to an addition of 350 μgP g^{-1} of soil, assuming interaction with the upper 2 cm of soil. The increases measured in water- and bicarbonate-extractable P in the soil at both the Ballantrae (Wainui silt loam) and Pahiatua (Ramiha silt loam) sites in the first year were between the values obtained for these two soils at the 250 and 500 μgP g^{-1} of soil addition rates in the present incubation study. In the presence of growing plants in the field, both the water- and bicarbonate-extractable P curves for CRP approached the superphosphate curves after approximately one year. In contrast, in the incubation study a marked difference was found in the apparent equilibrium value (at 298 days), particularly at the highest rate of addition of P (1000 μg g^{-1} of soil). Therefore, although incubation studies provide a useful indication of the initial plant-availability of a P source in soils, and the differences obtained between SPR and CRP illustrate this point, no prediction can be made regarding the longer-term plant-availability of P souces.

The results from the field (Chapter 4) indicate that the effectiveness of the three extractions (water, bicarbonate, and Bray) evaluated as estimates of plant-available P in soil, was dependent on the P source, particularly in the first year. Whereas the decrease in water-extractable P in the soil to which superphosphate was added is consistent with the decrease in plant-available P in the soil with this P source from the time of application (Chapter 4), this is not the case for a PR because the decreases in water-extractable P in the soil do not appear to be consistent with the initial changes in plant-available P when a PR is added to soil. In contrast, the Bray and to a lesser extent the bicarbonate reagents appeared to provide better estimates of the initial changes in plant-available P in the soil to which a PR was added and then relate these to the three estimates of plant-available P in the soil.

7.3.2 Relationship between extractable phosphorus in soil and uptake of phosphorus by plants

The decline in water- and bicarbonate-extractable P in soil following the addition of superphosphate was similar to the decrease in the recovery of P by ryegrass plants from each of the three soils (Fig. 7.5). Although the amounts of water-extractable P in the soil were less than those recovered by the plant from all three soils, the water-extractable P curve approximated more closely the decrease in plant-available P in the soil than did the curve for bicarbonate-extractable P. Bray-extractable P grossly overestimated plant-available P when superphosphate was the P source, particularly with the Wainui (Fig. 7.5a) and Konini (Fig. 7.5b) soils. There was a closer correlation between water-extractable P in the soil and plant uptake of P (Fig. 7.6a) than between bicarbonate-extractable P and plant uptake of P (Fig. 7.6b) for the three individual soils and when the data were combined. Although the regression line obtained for bicarbonate-extractable P (Fig. 7.6b) passed closer to the origin than the regression line obtained for water-extractable P (Fig. 7.6a) the slope of the regression line obtained, increasingly overestimated plant-available P with increasing bicarbonate values when superphosphate was added. Lower correlation coefficients were obtained for Bray-extractable P with each of the three soils (Fig. 7.6c).

The total amount of P added to each of the soils as superphosphate was 500 μgP g^{-1} of soil. From Fig. 7.5 it is clear that the total amount of P recovered by the plant, even immediately after the addition of superphosphate, was no greater than 105, 75, and 33 μgP g^{-1} of soil from the Wainui, Konini and Ramiha soils, respectively. These amounts represent approximately 18, 15, and 7% of the total P added as superphosphate to the

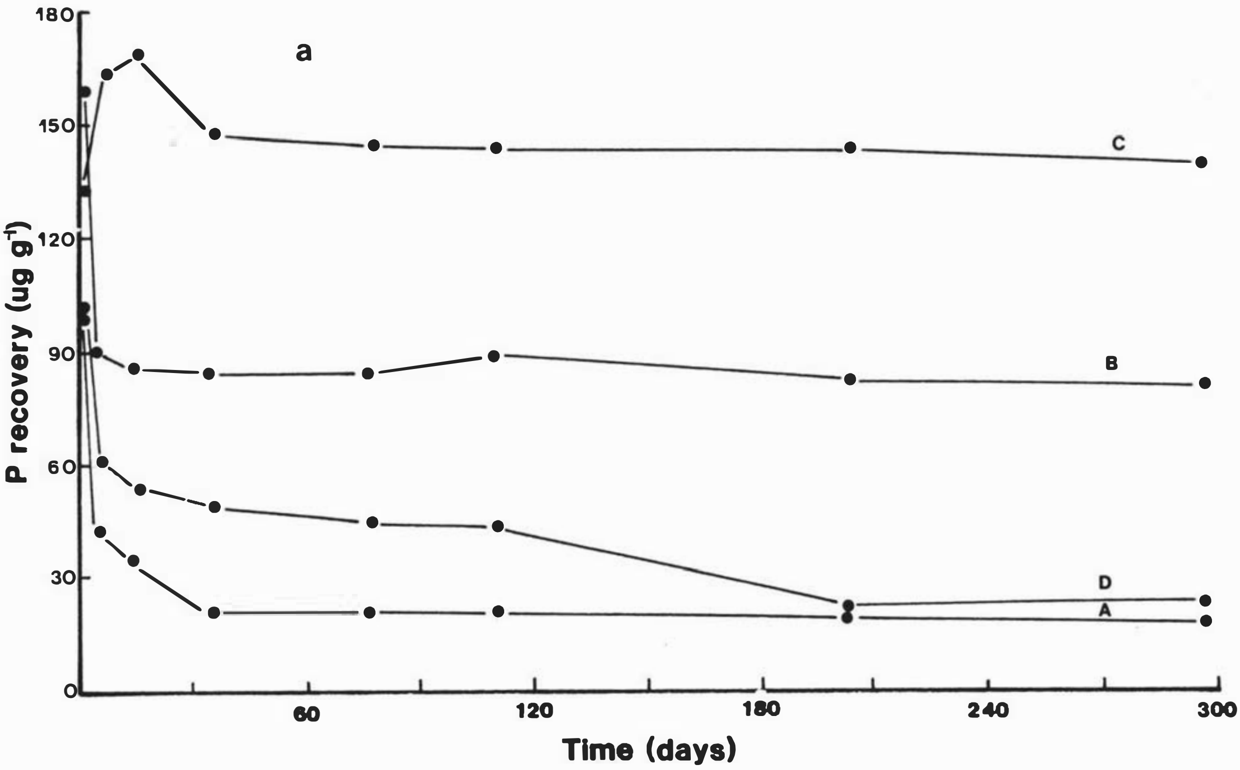
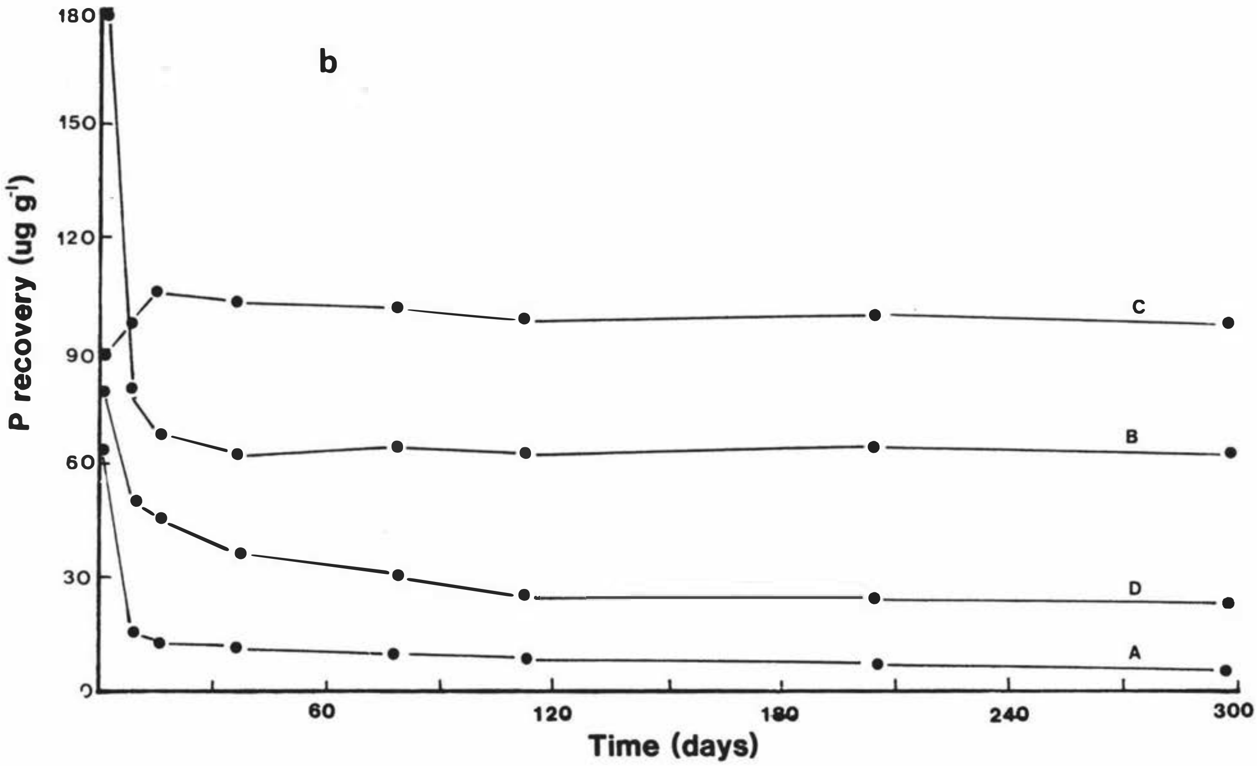
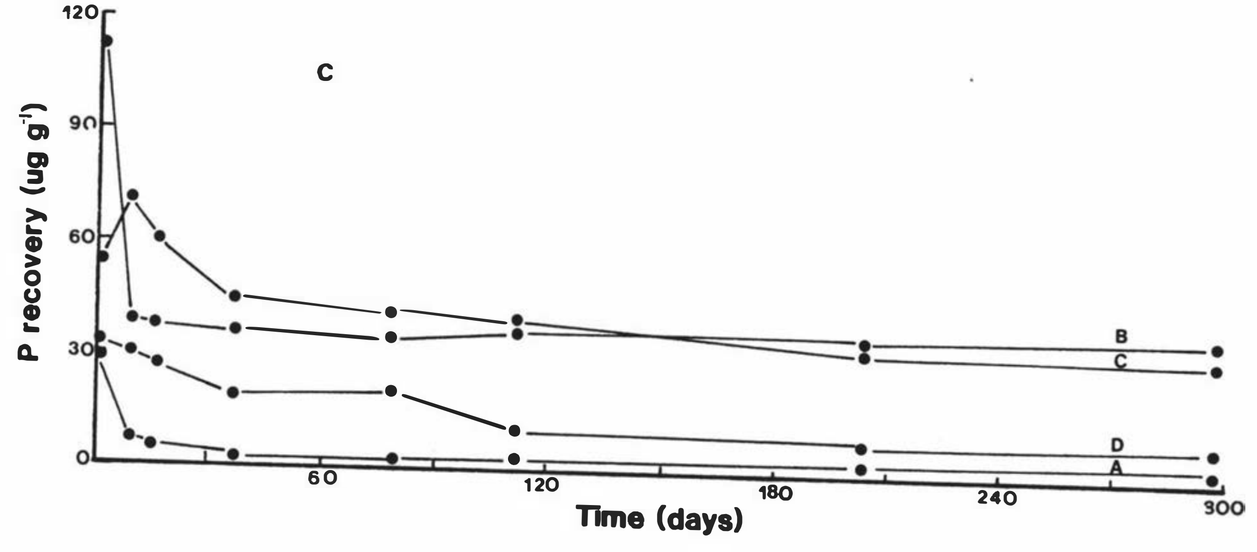


Figure 7.5 Recovery of phosphorus from three soils of contrasting phosphate-sorption capacity over 300 days following superphosphate addition at 500 μgP g^{-1} of soil. A = water-extractable phosphorus, B = bicarbonate-extractable phosphorus, C = Bray-extractable phosphorus and D = uptake of phosphorus by ryegrass. a = Wainui, b = Konini and c = Ramiha.

Figure 7.5 contd.





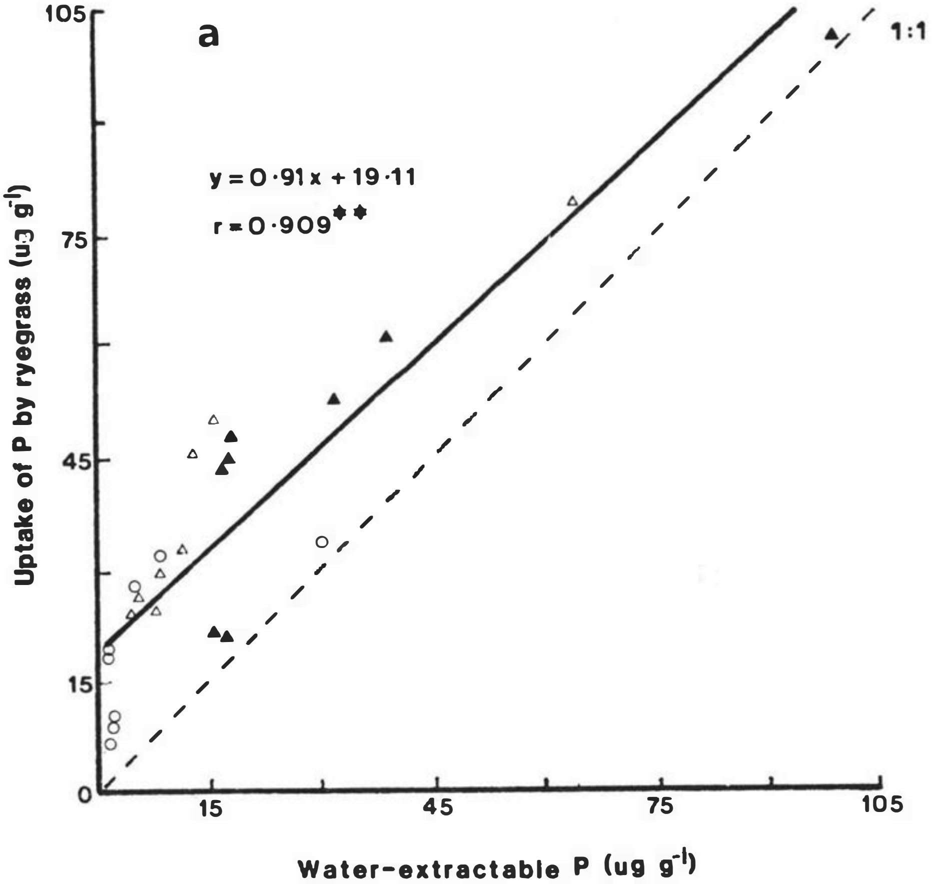
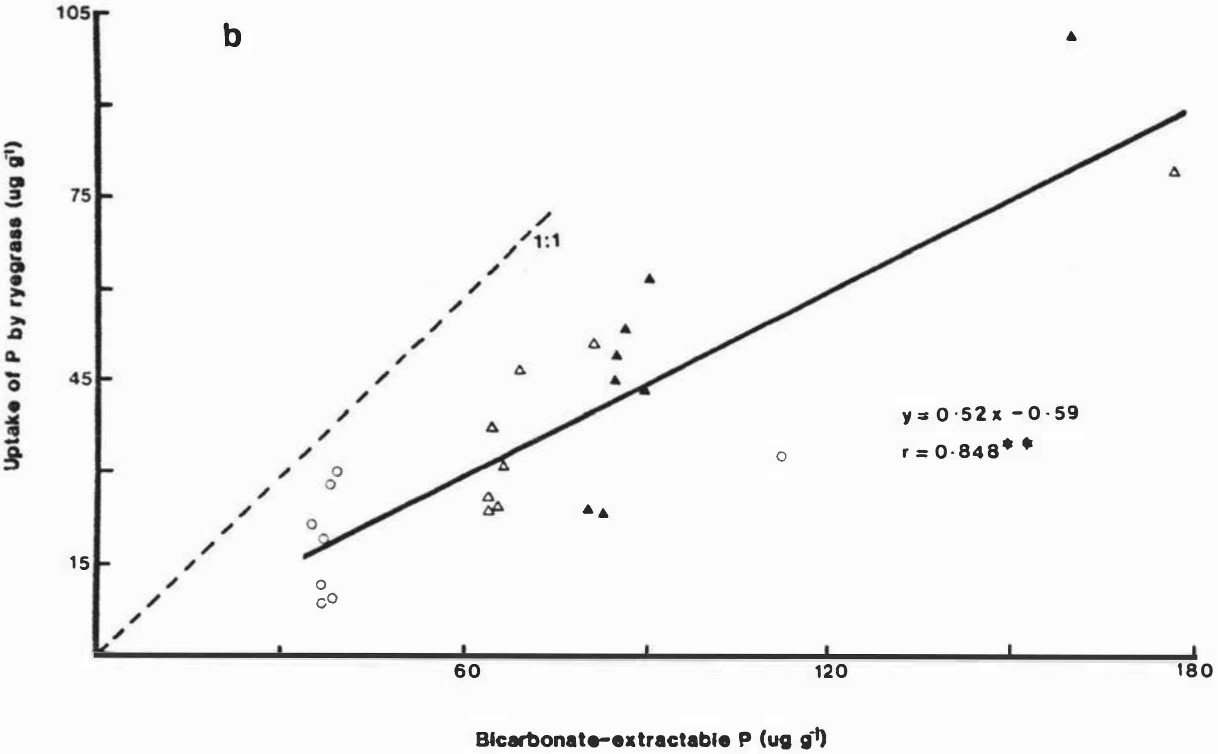
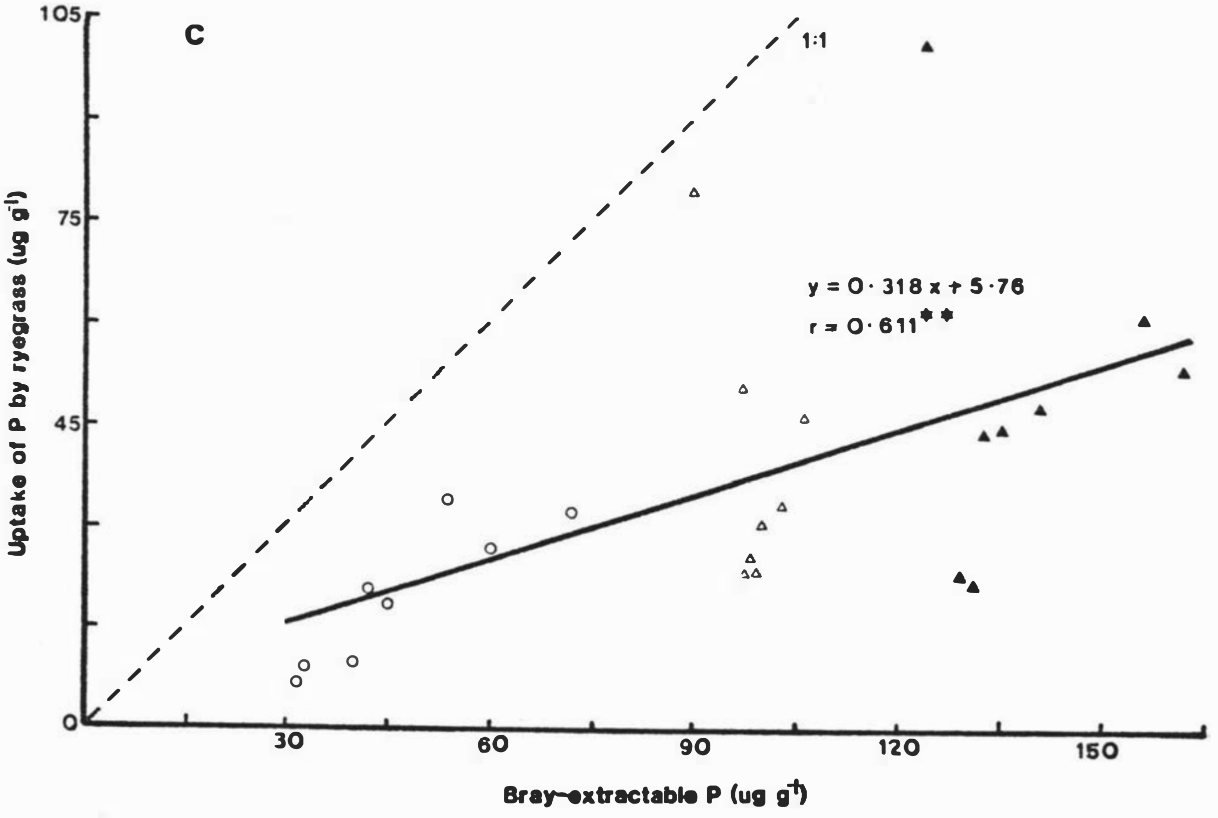


Figure 7.6 Relationship between uptake of phosphorus by ryegrass and amounts of (a) water-, (b) bicarbonate- and (c) Bray-extractable phosphorus in three contrasting soils at various times following superphosphate addition at 500 µgP g^{-1} of soil.

Figure 7.6 contd.





Wainui, Konini, and Ramiha soils, respectively. These low recoveries probably reflect, in part, the short (20 days) soil-plant contact time in the present study, although Rennes (1978) also recovered less than 20% of total P added as superphosphate even after a soil-plant contact time of up to 50 days. Similar P recovery values are, however, not uncommon in conventional glasshouse (Chapter 6) and field (Chapter 4) trials in the short term. In the study by Rennes (1978), which compared the availability of P in the water-soluble and water-insoluble P fractions of superphosphate, the water-insoluble P fraction did not start to become water-extractable until 100 days after addition. This suggests that the water-insoluble fraction in superphosphate is unavailable to the plant in the short-term. Even with the low P-sorbing Wainui soil, the recovery of P by ryegrass was less than 40% of the water-soluble P fraction of the superphosphate used. Neither the Bray nor the bicarbonate extractants recovered more than 75% of this water-soluble P fraction, demonstrating the rapid decline in the initial plant-available P in superphosphate on contact with soil.

In marked contrast to the initial decrease in the plant-available P in superphosphate from the time of application, the recovery of P by ryegrass following the addition of either SPR (Fig. 7.7) or CRP (Fig.7.8) increased initially with all three soils. Maximum recovery of P following the addition of either SPR or CRP was less than 9, 6, and 5% of the total P added to the Wainui, Konini, and Ramiha soils, respectively. The recovery for the Wainui and Konini soils was approximately half that obtained with superphosphate for these two soils, although on the third soil, the Ramiha, the recovery was similar (5% for the PR materials and 7% for superphosphate). The initial recoveries were also very low at the four field trial sites (Chapter 4). The increases in both bicarbonate- and Bray-extractable P in the soil following addition of the two PR

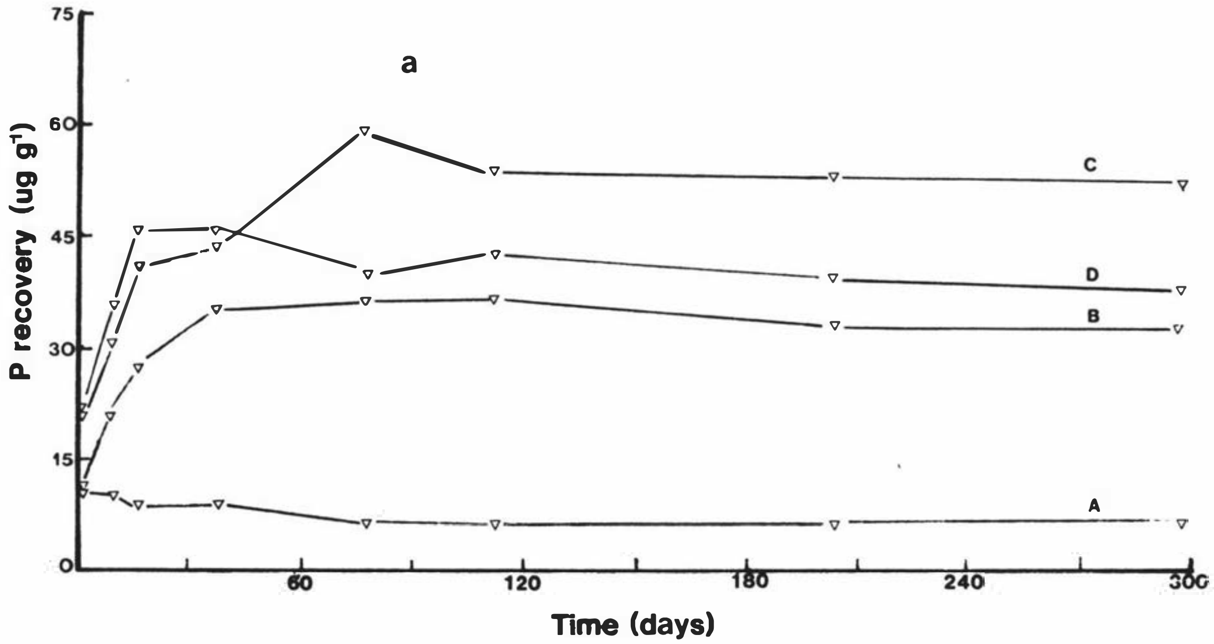
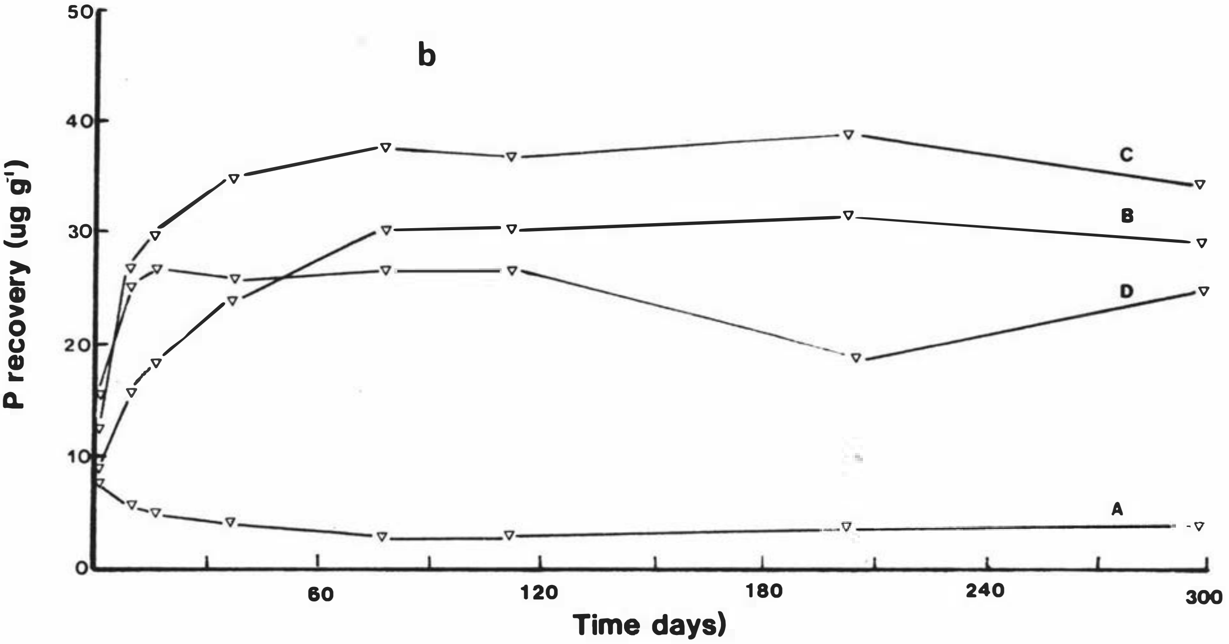
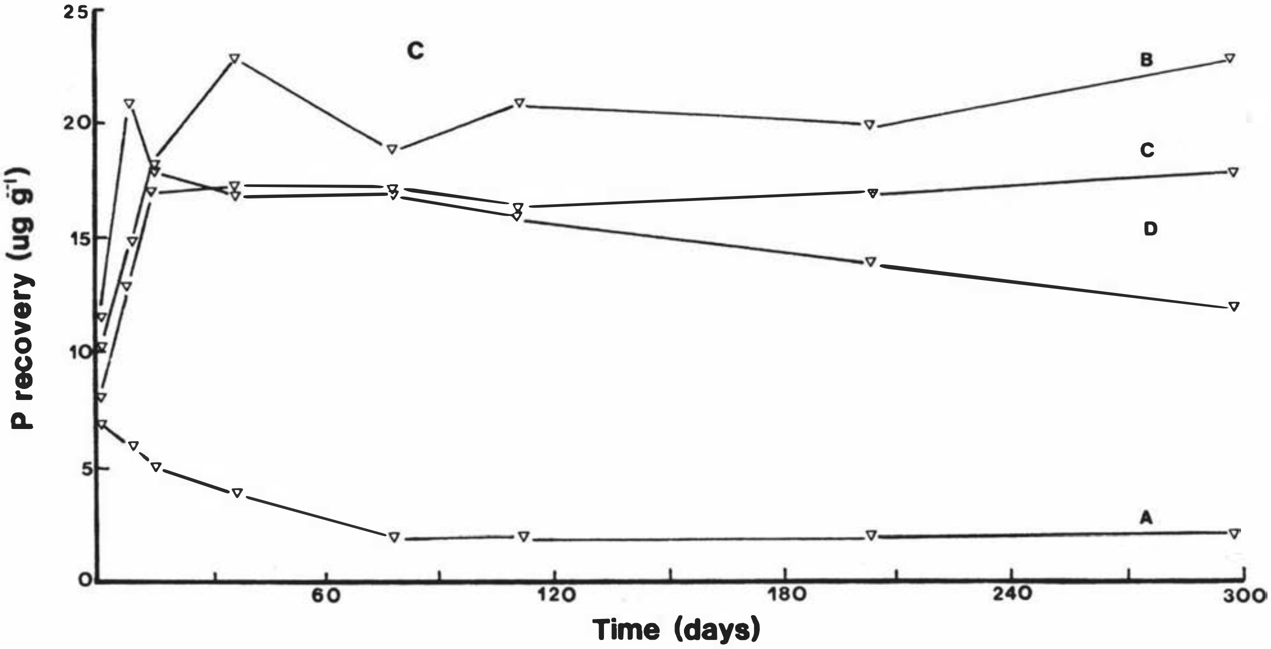


Figure 7.7 Recovery of phosphorus from three soils of contrasting phosphate-sorption capacity over 300 days following Sechura phosphate rock (SPR) addition at 500 μgP g^{-1} of soil. A = water-extractable phosphorus, B = bicarbonate-extractable phosphorus, C = Bray-extractable phosphorus and D = uptake of phosphorus by ryegrass. a = Wainui, b = Konini and c = Ramiha.

Figure 7.7 contd.





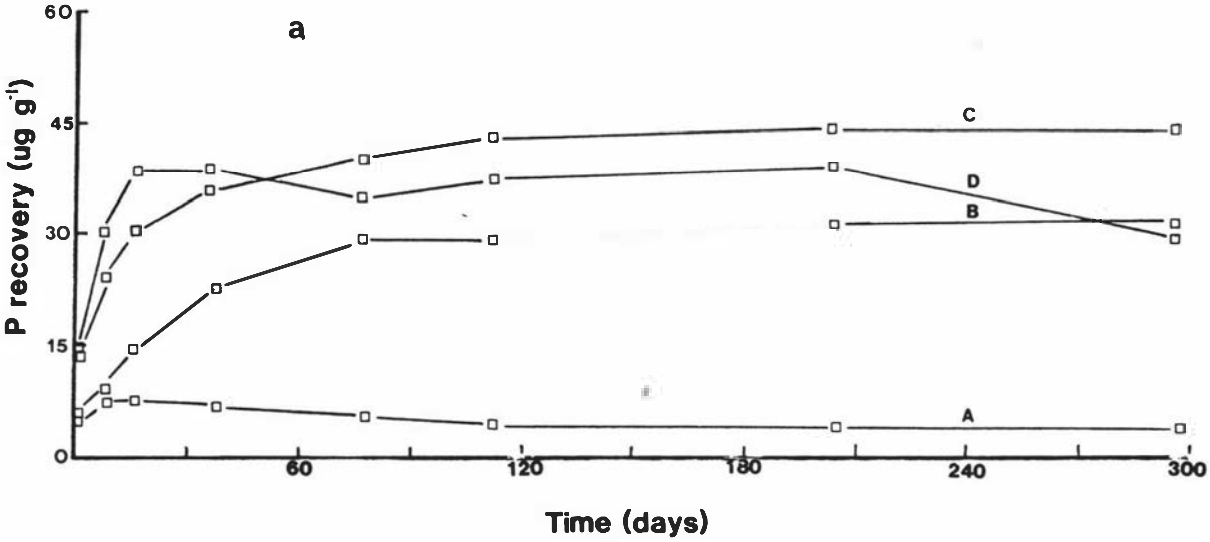
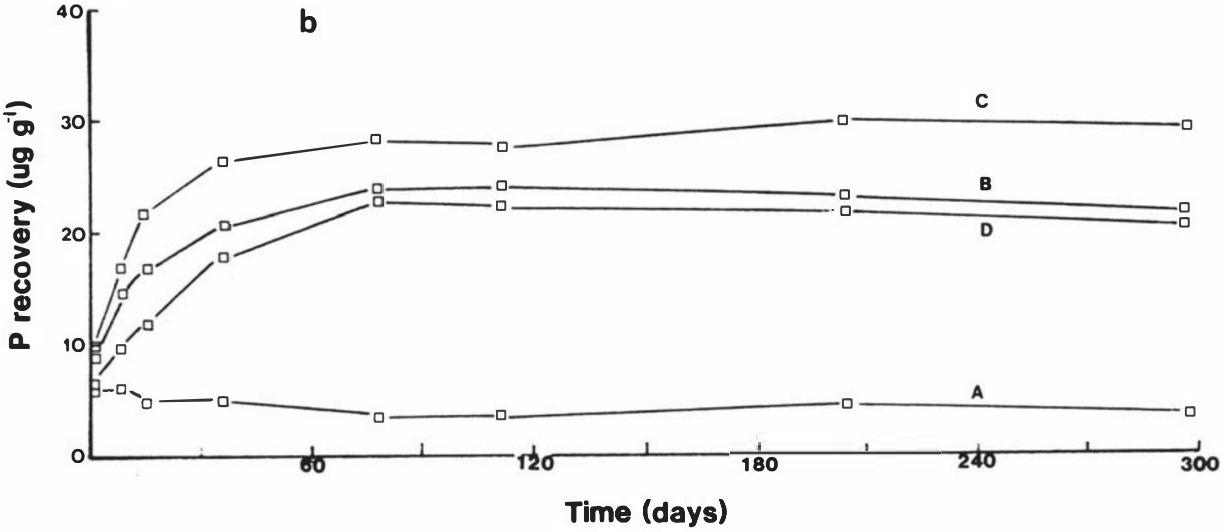
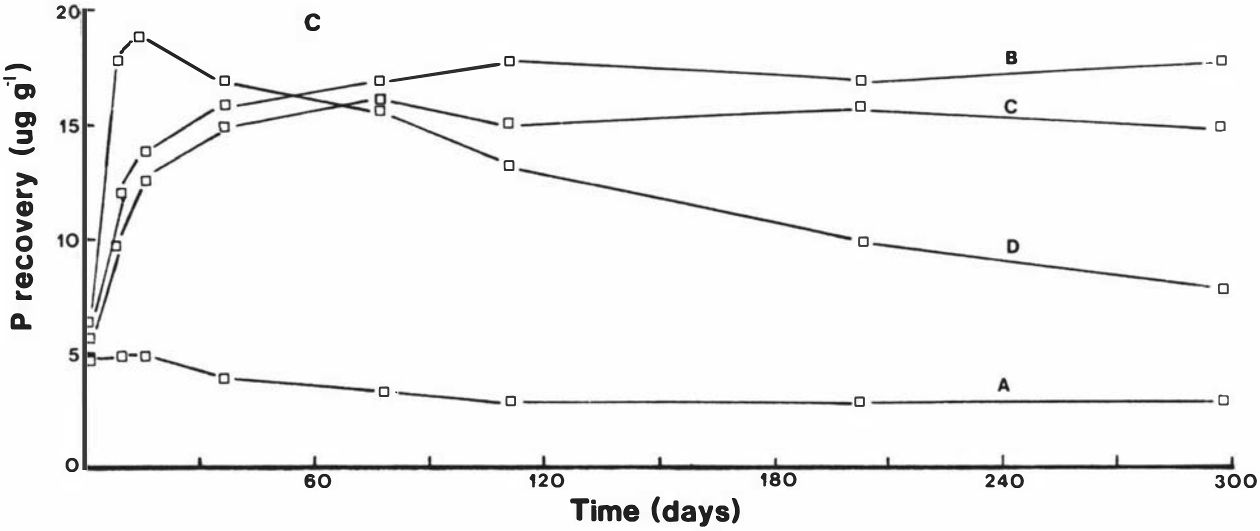


Figure 7.8 Recovery of phosphorus from three soils of contrasting phosphate-sorption capacity over 300 days following Chatham Rise phosphorite (CRP) addition at 500 μgP g^{-1} of soil. A = water-extractable phosphorus, B = bicarbonate-extractable phosphorus, C = Bray-extractable phosphorus and D = uptake of phosphorus by ryegrass. a = Wainui, b = Konini, and c = Ramiha.

Figure 7.8 contd.





materials followed a similar pattern (Fig. 7.7, 7.8). Water-extractable P in the soil, however, declined (Fig. 7.7, 7.8). Surprisingly, only small differences were found in the initial plant-available P in the soil between SPR and CRP and, as a result, the data for both PR materials were combined for the linear regression analysis. In the glasshouse (Chapter 6), initial differences were found in the agronomic effectiveness of the two PR materials.

The fact that the regression line obtained with both bicarbonate- (Fig. 7.9b) and Bray- (Fig. 7.9c) extractable P in the soil passed close to the origin and had slopes approaching one, indicates that both of these extractants may provide useful estimates of plant-available P in soil to which a PR was added. More of the variation was accounted for by the Bray extractant (Fig. 7.9c, $r = 0.865^{**}$) than by bicarbonate (Fig. 7.9b, $r = 0.677^{**}$) with both PR materials and with all three soils, although the predictive ability of both extractants with the Ramiha soil was limited. Again these results are in good agreement with those from the field (Chapter 4), where water extraction was also found to give a poor estimate of plant-available P in the soil to which a PR was added (Fig. 7.9a, $r = 0.279^{*}$).

For the remaining studies in this Chapter, the water- and bicarbonate-extraction methods are used for estimating the changes in plant-available P in the soil to which superphosphate has been added and the bicarbonate and Bray extractants are used for estimating the changes in plant-available P in the soil to which a PR has been added.

7.3.3 Reactions of superphosphate and a phosphate rock in soils of contrasting phosphorus characteristics

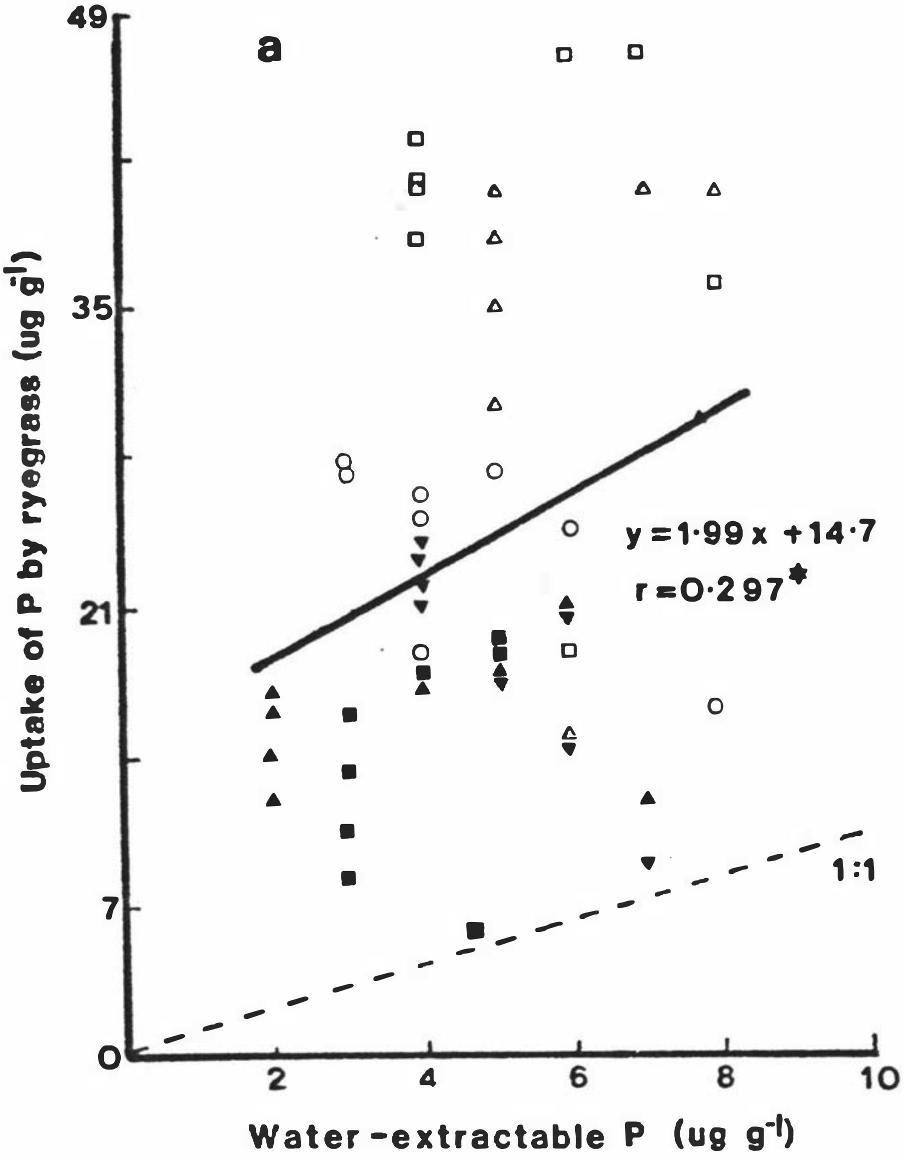
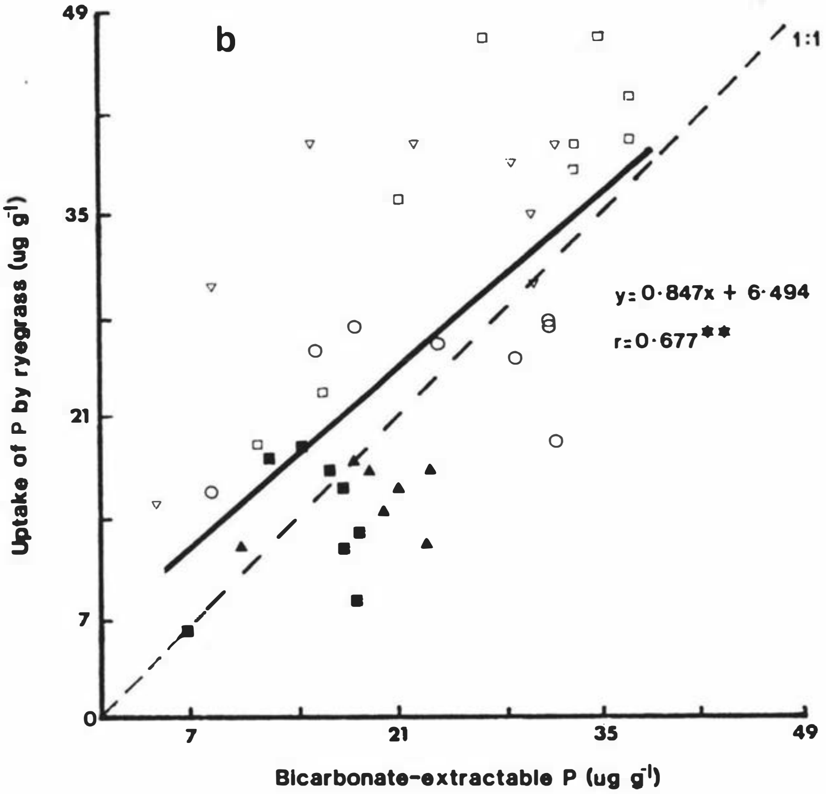
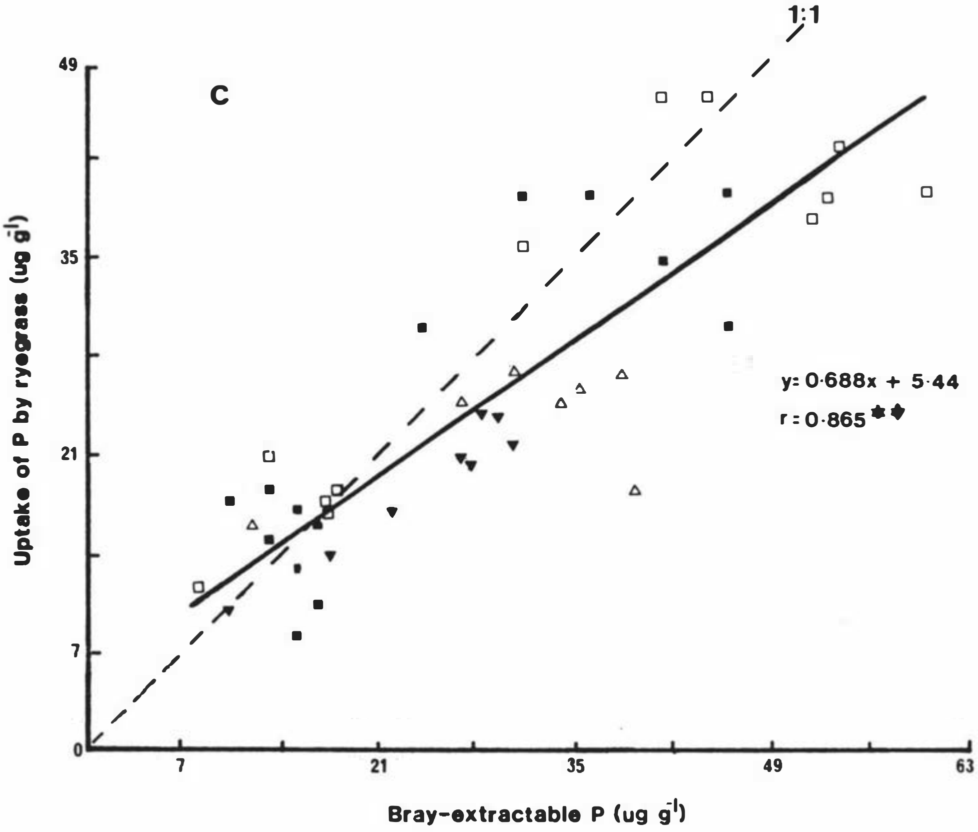


Figure 7.9 Relationship between uptake of phosphorus by ryegrass and amounts of (a) water-, (b) bicarbonate- and (c) Bray-extractable phosphorus in three contrasting soils at various times following either Sechura phosphate rock or Chatham Rise phosphorite addition at 500 µgP g^{-1} of soil.

Figure 7.9 contd.





7.3.3.1 Effect of phosphate sorption capacity on the reactions of superphosphate and a phosphate rock in soils

Following the addition of superphosphate, the initial rate of decline of water-extractable P increased and the final amounts persisting at 90 days decreased as the P-sorption capacity of the six soils studied increased (Fig. 7.10a). The increase (Δ) in water-extractable P in the low P-sorbing Tokomaru soil, to which 500 μgP g^{-1} of soil as superphosphate was added, was 26 μgP g^{-1} of soil at 90 days, whereas on the high P-sorbing Egmont soil the increase was less than 2 μgP g^{-1} of soil. The P status and pH of the six soils (Table 7.2) appear to have had little effect on the pattern of decline of water-extractable P in the soils. Differences were also obtained between the six soils in the initial rate of decline and in the final amounts of bicarbonate-extractable P at 90 days (Fig. 7.10b). The amounts of bicarbonate-extractable P in the soil at 90 days were three to five times greater than those of water-extractable P. These P data are further evidence to support the view that although the pattern of decline is similar for each soil (Chapter 7.3.1.2 and 7.3.2), the relative extractability of P, following P addition, decreases as the P-sorption capacity of the soil increases (Rennes, 1978).

Marked differences were found in bicarbonate-extractable P in the soil following the addition of SPR to the six contrasting soils in terms of the initial increases obtained and the values persisting at 90 days (Fig. 7.11a). With the exception of the changes in bicarbonate-extractable P for the Tokomaru soil following addition of SPR, the initial increases in bicarbonate extractable P for the remaining five soils decreased as the P-sorption capacity of the soils increased, as did the final values persisting at 90 days. The difference found in bicarbonate-extractable P

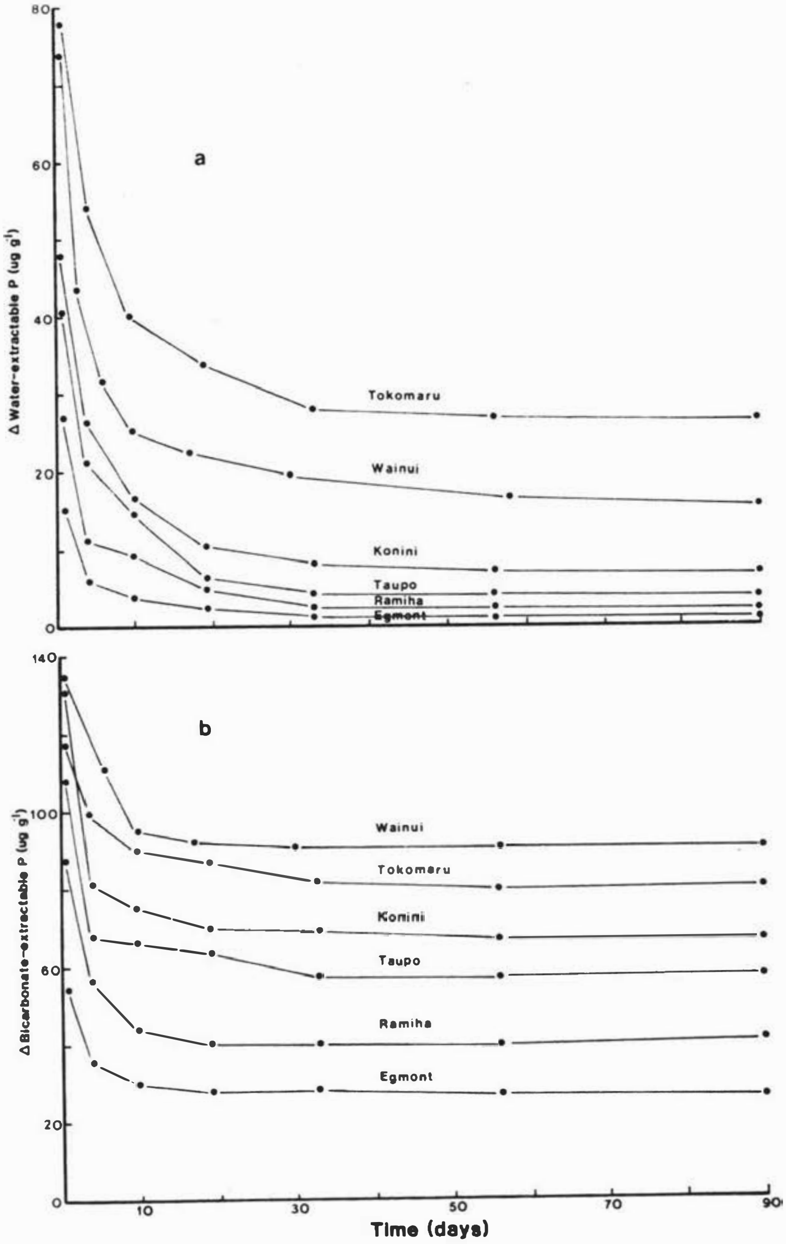


Figure 7.10 Change (Δ) in (a) water- and (b) bicarbonate-extractable phosphorus in soil over 90 days following superphosphate addition at 500 μgP g^{-1} of soil to six soils of contrasting phosphate-sorption capacity.

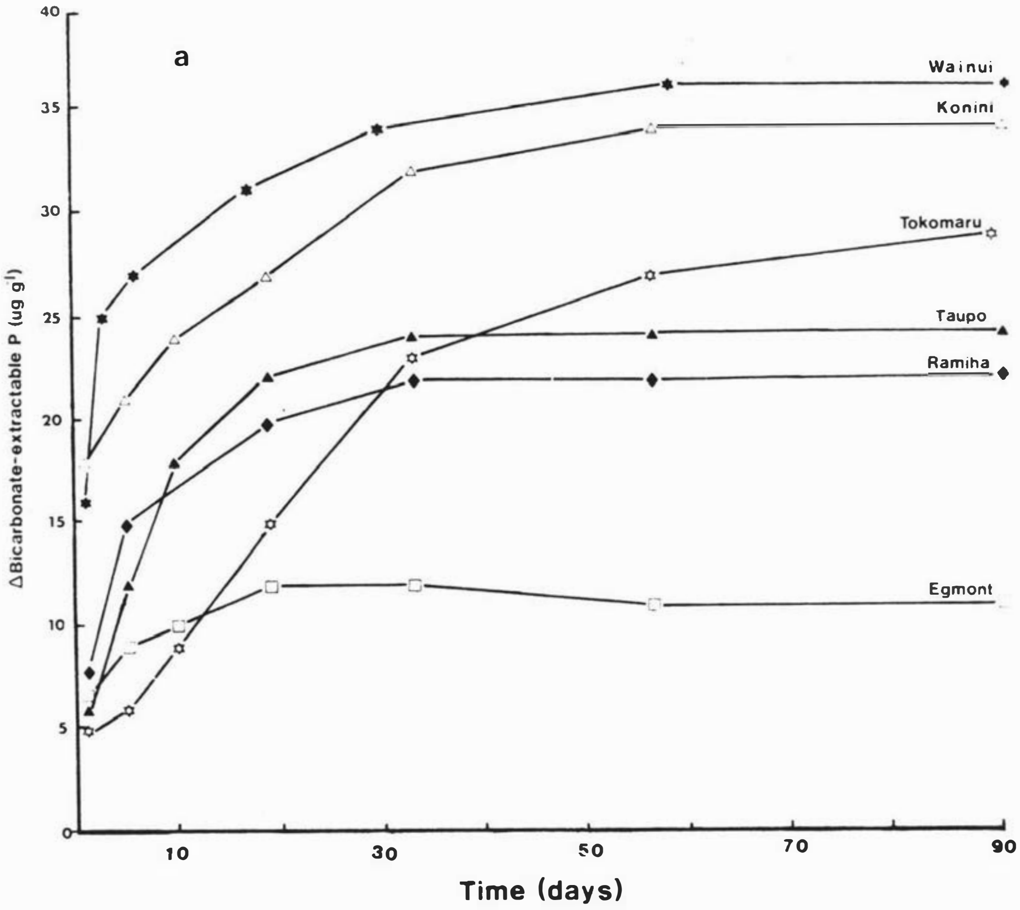
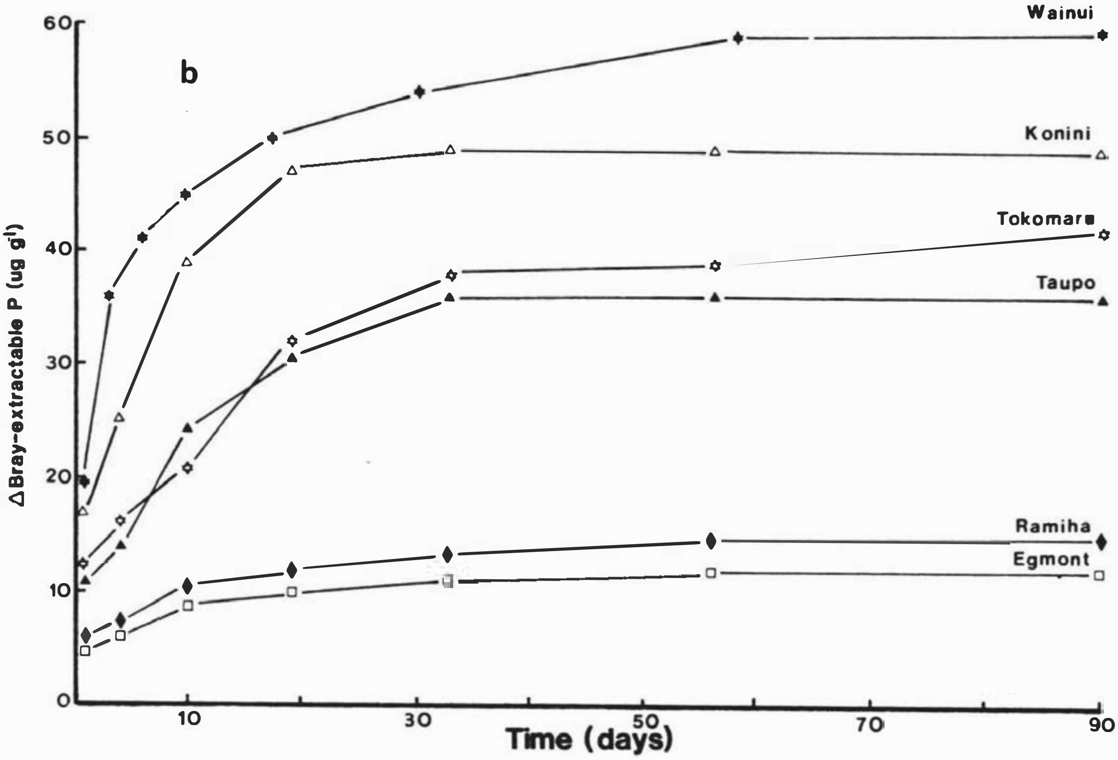


Figure 7.11 Change (Δ) in (a) bicarbonate- and (b) Bray-extractable phosphorus in soil over 90 days following Sechura phosphate rock addition at 500 μgP g^{-1} of soil to six soils of contrasting phosphate-sorption capacity.

Figure 7.11 contd.



between the Tokomaru and Konini soils (Fig. 7.11a) suggests that the importance of soil pH in influencing the increase in extractable P in soil, to which a PR was added, decreases as the P-sorption capacity of the soil increases. The marked decrease from the Ramiha to the Egmont soil in both the initial increases in bicarbonate-extractable P and in the values at 90 days (Fig. 7.11a), may result from a difference in the pH of the two soils, in addition to a difference in P-sorption capacity. In addition to reducing the dissolution of SPR, the high pH of the Egmont soil may have reduced the effectiveness of the bicarbonate extractant, which has been shown to decrease with increasing soil pH (Chapter 4.3.3.4; see 7.3.4; Lambert and Grant, 1980).

The relative bicarbonate extractability of P in the soil to which SPR was added, when compared to superphosphate at 90 days, did not increase with an increase in P-sorption capacity. This contrasts with earlier findings for water extractable P in the soil to which a PR was added, which increased, as the P-sorption capacity of the soil increased (Chapter 7.3.1.2). On a percentage basis, bicarbonate-extractable P in the soil to which SPR was added was 36, 40, 51, 43, 55, and 42% for the Tokomaru, Wainui, Konini, Taupo, Ramiha, and Egmont soils, respectively, of that obtained with superphosphate on these six soils. This is in agreement with the findings in the glasshouse (Chapter 6), where SPR performed as effectively as superphosphate across a similar range of soils.

With the exception of the changes for the Tokomaru soil following the addition of SPR, both the initial increases and values for Bray-extractable P in the soil at 90 days also decreased as the P-sorption capacity of the soils increased (Fig. 7.11b). With the exception of the Ramiha and Egmont soils, the initial increases in Bray-extractable P and final values at 90 days (Fig. 7.11b) were greater than those for bicarbonate-extractable P (Fig. 7.11a). The increases ranged from 44 to 69% at 90 days. Isotopic exchange studies indicated that, on soils of low to medium P-sorption capacity, the bicarbonate and Bray extractants removed a similar fraction of P from the soil. In fact the total counts and specific activity of ^{32}P in both the bicarbonate and Bray extracts were found to be similar for both the Wainui and Konini soils (Table 7.3). Whereas, the bicarbonate extractant is alkaline (pH 8.5) and removes P by desorption, the Bray reagent is acid (pH 2.0) and releases P to solution by dissolution of sorbing components and desorption. The increases in Bray-extractable P (Fig. 7.11b), compared with bicarbonate-extractable P (Fig. 7.11a), for the Tokomaru, Wainui, Konini, and Taupo soils following addition of SPR may therefore result from the dissolution of some unreacted PR.

For both the Egmont and Ramiha soils, ^{32}P-equilibrium studies indicated that the total counts and specific activity of ^{32}P in the bicarbonate extracts were approximately 9 and 3 times greater, respectively, than those in the Bray extracts (Table 7.3). This suggests that the net removal of sorbed P by the Bray reagent, when compared to the bicarbonate reagent, is reduced on soils of high P-sorption capacity. In addition, the lower specific activity of ^{32}P also suggests that the P removed by the Bray reagent was not all sorbed, but occurred in a non-exchangeable form. This result suggests that the increases in Bray-extractable P following the addition of a PR to soils of high P-sorption capacity are due to the dissolution of unreacted PR rather than to P held on sorption sites which is the fraction largely removed by the bicarbonate extractant. Comparison of these two extractants in Chapter 7.3.2 suggested that neither was a satisfactory indicator of plant-available P on the high P-sorbing Ramiha soil. This suggests that an accurate measurement of plant-available P when a PR is added to soil should include both the P derived from the PR and present on sorption sites which can be desorbed fairly readily and

Table 7.3 Total counts and specific activity of ^{32}P in bicarbonate and Bray extracts of four soils of contrasting phosphate-sorption capacity

	Total counts in		Specific activity of ^{32}P in	
Soil type	Bicarbonate extract	Bray extract	Bicarbonate extract	Bray extract
	(cpm)		($\text{cpm}\,\mu g^{-1}\,P$)	
Wainui	212,840	253,050	15,400	16,740
Konini	173,740	141,730	23,800	22,200
Ramiha	123,900	11,710	18,440	6,970
Egmont	91,620	12,800	22,910	8,050

the P remaining as unreacted PR which is likely to dissolve within a reasonable period of time. The good correlations for the Wainui and Konini soils between Bray-extractable P and plant uptake of P (Chapter 7.3.2) may reflect this.

Data for changes in 0.5M NaOH-extractable P in the six soils to which SPR was added (Fig. 7.12) showed an increase in the dissolution of SPR with both time and with increases in soil P-sorption capacity. This result contrasts sharply with the changes in bicarbonate- and Bray-extractable P in the soil (Fig. 7.11) and highlights the importance of drawing a distinction between the dissolution of a PR and its subsequent plant availability. The amounts of 0.5M NaOH-extractable P in these six soils, presented in Table 7.2, varied from 72 to 795 μgP g^{-1} of soil. During the incubation study only small changes were found in the amount of organic P in the NaOH extracts of soil, suggesting that microbial immobilization of added P was not significant. The slightly lower pH of the Wainui soil appears to have caused an increase in the extent of PR dissolution, giving a similar result to that obtained for the Konini soil (Fig. 7.12), which has a higher P-sorption capacity (Table 7.2). The difference in the dissolution of SPR with the Tokomaru and Konini soils, again suggests that the effect of soil pH can be modified by a soil P-sorption capacity.

A close correlation was obtained (Fig. 7.13, $r = 0.935^{**}$) between the dissolution of SPR, measured by NaOH extraction, and the P-sorption capacity of the six soils used in the incubation study. In contrast the same correlation for superphosphate was poor ($r = 0.359$), as might be expected. Only the 2% citric acid-soluble P fraction (79.5% of total P) of the P added as superphosphate was extracted from soil by 0.5M NaOH, ranging from 62 to 78% of total P on the six soils (Table 7.4). The dissolution of SPR showed little relationship to its citric-soluble P

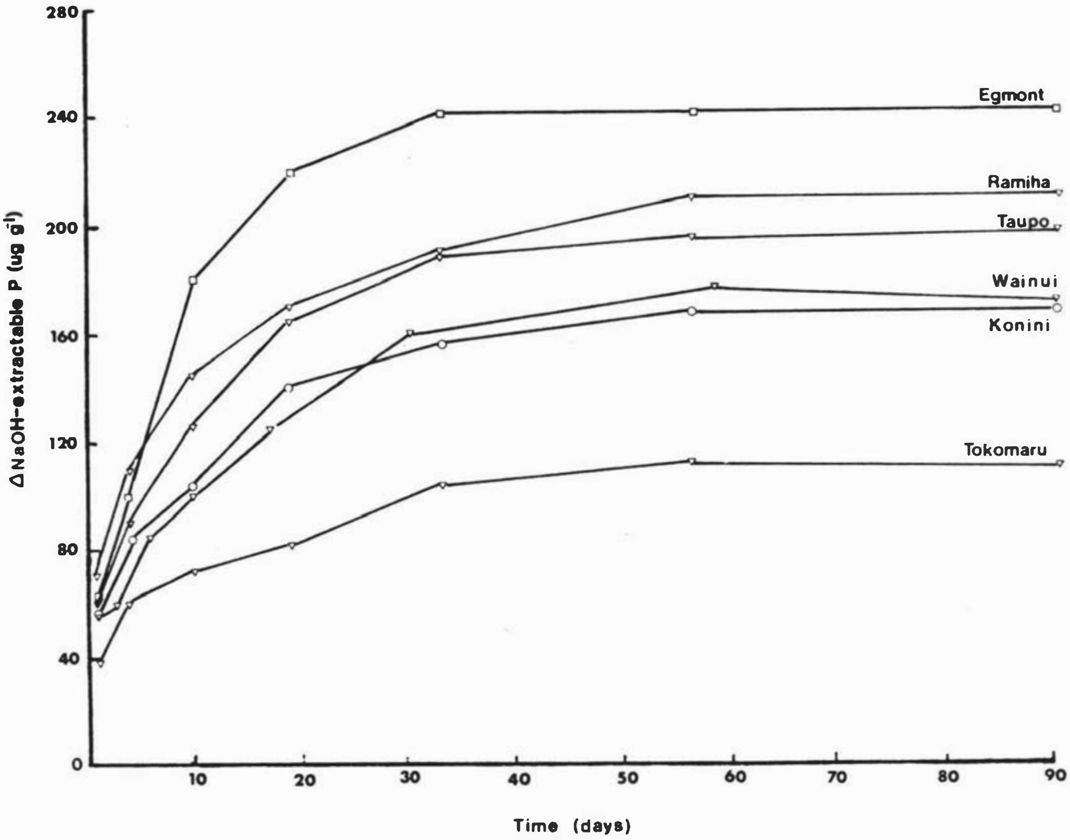


Figure 7.12 Change (Δ) in NaOH-extractable phosphorus over 90 days following Sechura phosphate rock addition at 500 μgP g^{-1} of soil to six soils of contrasting phosphate-sorption capacity.

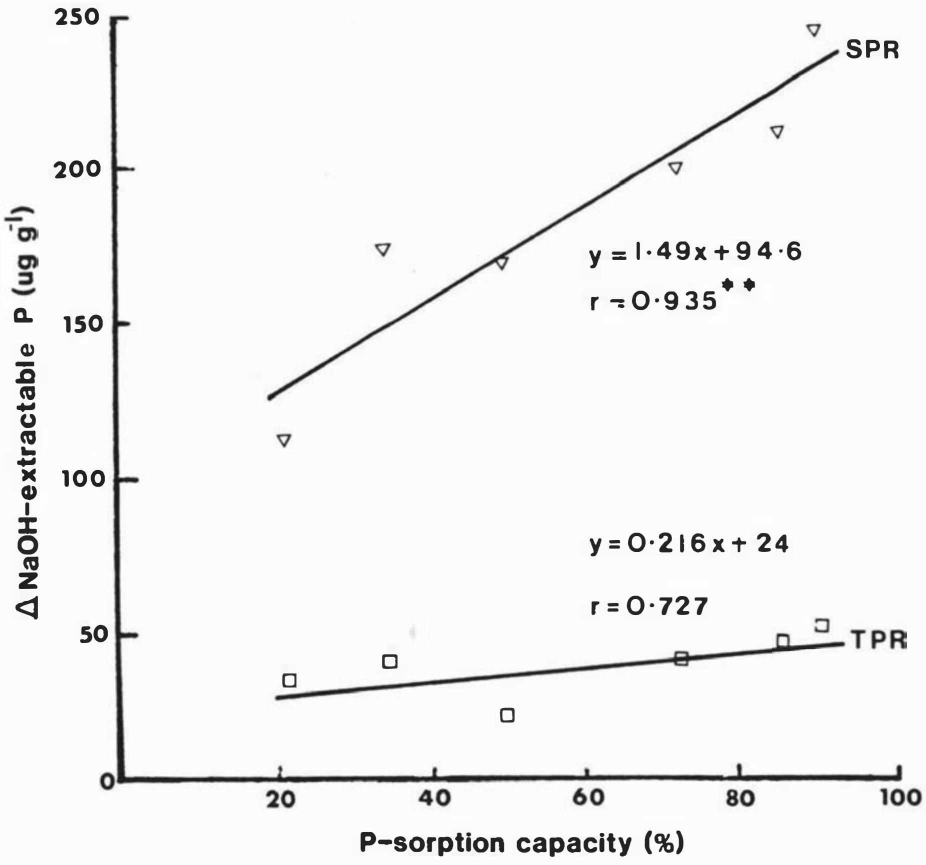


Figure 7.13 Relationship between dissolution of Sechura phosphate rock (SPR) or Tennessee phosphate rock (TPR) in soils, measured by increases (Δ) in NaOH-extractable phosphorus, and phosphate-sorption capacity of the soils.

Table 7.4 Dissolution of Tennessee phosphate rock (TPR), Sechura phosphate rock (SPR), and superphosphate, measured by NaOH extraction at 90 days, expressed as increases (Δ) in 0.5M NaOH-extractable phosphorus in soil and as a percentage of the total phosphorus added (500 μgP g^{-1} of soil)

Soil type	Increases (Δ) in NaOH-extractable P in soil from: TPR	SPR ($\mu g\ g^{-1}$)	Superphosphate	Fraction of P source dissolved from: TPR	SPR (% of total P added)	Superphosphate
Tokomaru	32	110	312	7.4	22.0	62.4
Wainui	37	172	392	7.4	34.4	78.4
Konini	20	168	312	4.0	33.6	62.4
Taupo	37	198	323	7.4	39.6	64.6
Ramiha	42	210	370	8.4	42.0	74.0
Egmont	49	242	379	9.8	48.4	75.8

fraction (42% of total P) ranging from 22% on the low P-sorbing Wainui soil, to 48% of total P on the high P-sorbing Egmont soil (Table 7.4). The lower solubility of the TPR is again evident (Fig. 7.13), although on the high P-sorbing Egmont soil approximately 10% of total P had dissolved at 90 days (Table 7.4).

The differences obtained between SPR and CRP, in terms of both water- and bicarbonate-extractable P in the soil (Chapter 7.3.1.2), were far smaller than those for 0.5M NaOH-extractable P at 90 days (Fig. 7.14). On all three soils (Fig. 7.14) both the initial dissolution and values at 90 days were greater with SPR. These differences may help to explain the difference found in the agronomic effectiveness of the two PR sources in the field (Chapter 4; Gregg et al., 1981). The greater agronomic effectiveness of SPR, when compared to CRP in the field in the first year (Gregg et al., 1981) is consistent with the greater dissolution obtained in incubation studies. The greater residual effect shown by CRP in the field (Chapter 4) and in the study of Gregg et al (1981), is probably explained by the slower rate of dissolution of CRP, resulting from the presence of $CaCO_3$ in intimate contact with the phosphorite.

Soil P extracted by the bicarbonate and Bray reagents grossly underestimates the dissolution of a PR in soil. For example, values for bicarbonate-extractable P for the Wainui and Egmont soils, following the addition of SPR (Fig. 7.11a), were only 22% and 4%, respectively, of 0.5M NaOH-extractable P (Fig. 7.12). It is also apparent that with increasing P sorption this difference increases.

An increase in the amount of organic matter (Table 7.2) was associated with the increase in the P-sorption capacity of the six soils, with the exception of the Egmont soil which is a sub-surface sample. In fact, a close correlation was obtained (Fig. 7.15, $r = 0.994^{**}$) between the organic carbon content and P sorption capacity of five soils. Data for the

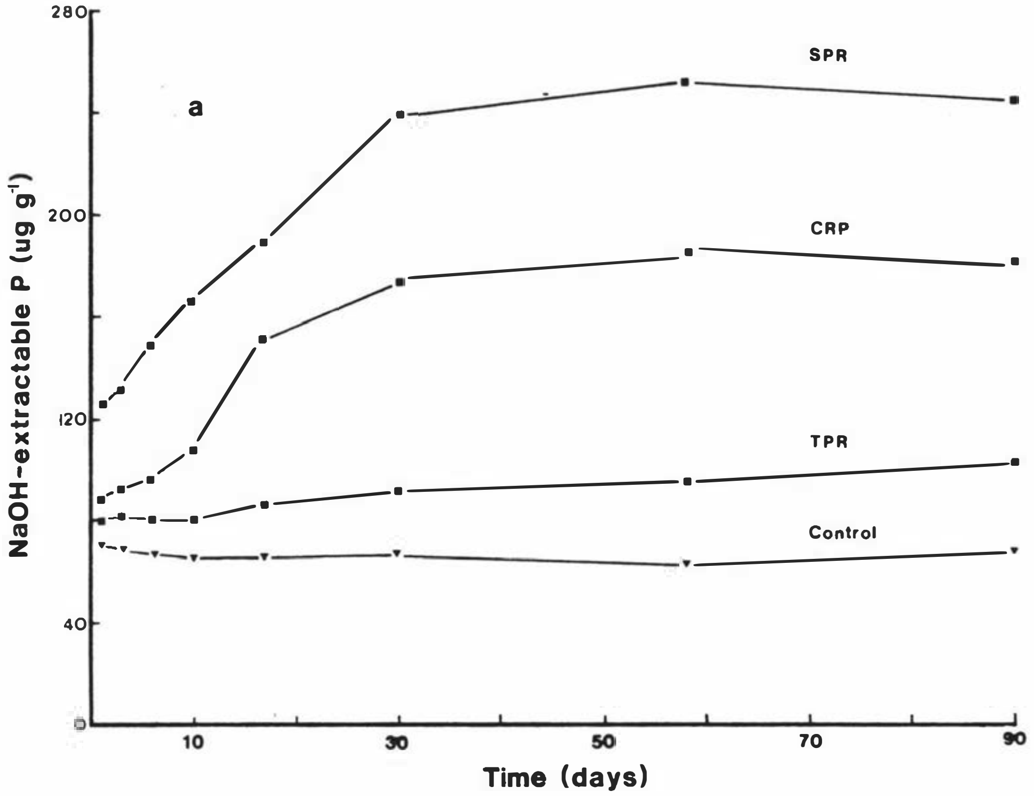
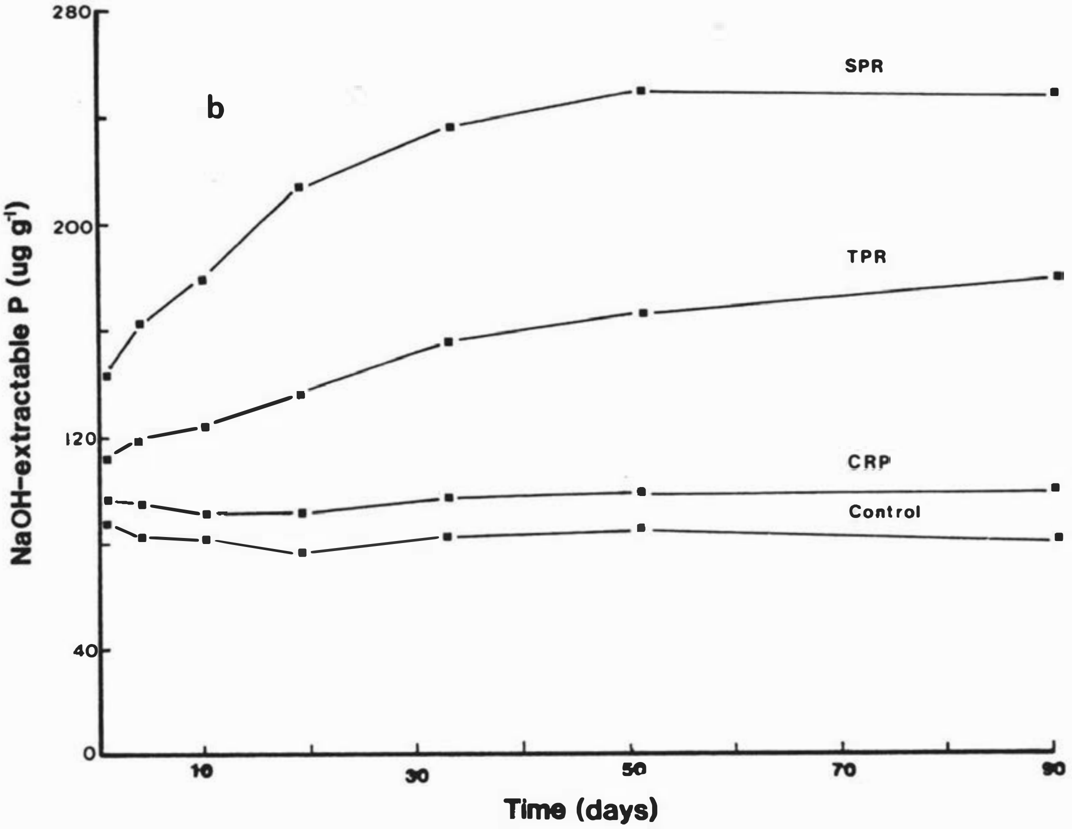
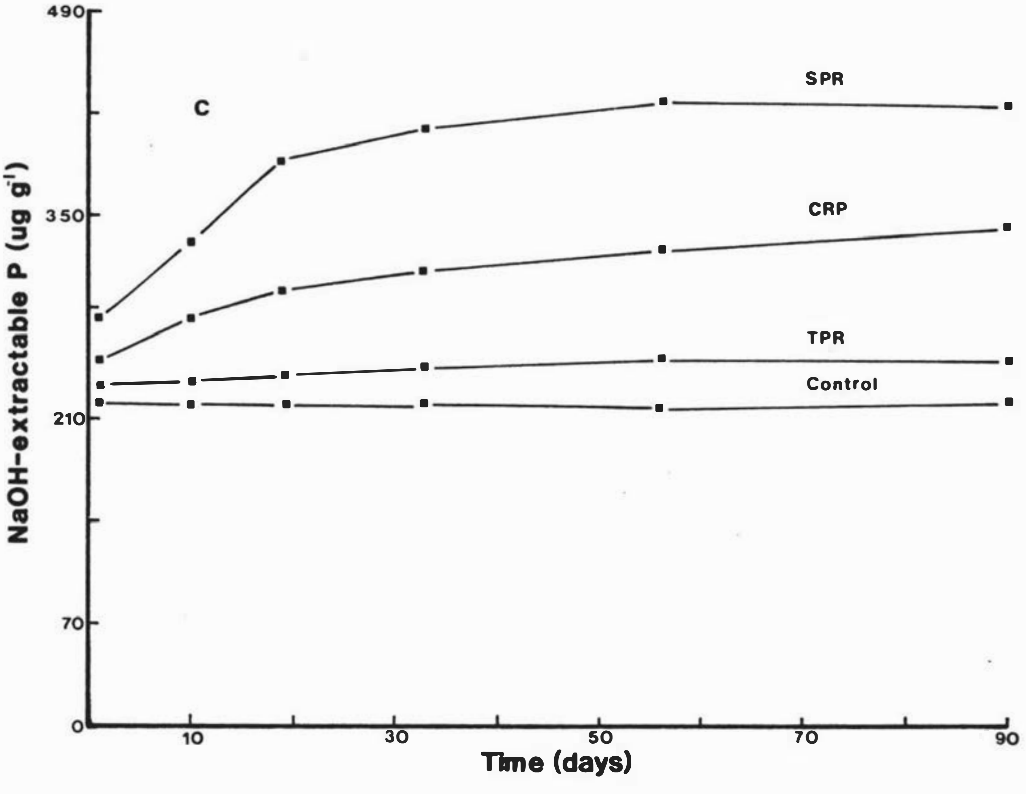


Figure 7.14 Changes in NaOH-extractable phosphorus in soil over 90 days following Tennessee phosphate rock (TPR), Chatham Rise phosphorite (CRP), or Sechura phosphate rock (SPR) addition at 500 μgP g^{-1} of soil to three soils of contrasting phosphate-sorption capacity. a = Wainui, b = Konini, and c = Ramiha.

Figure 7.14 contd.





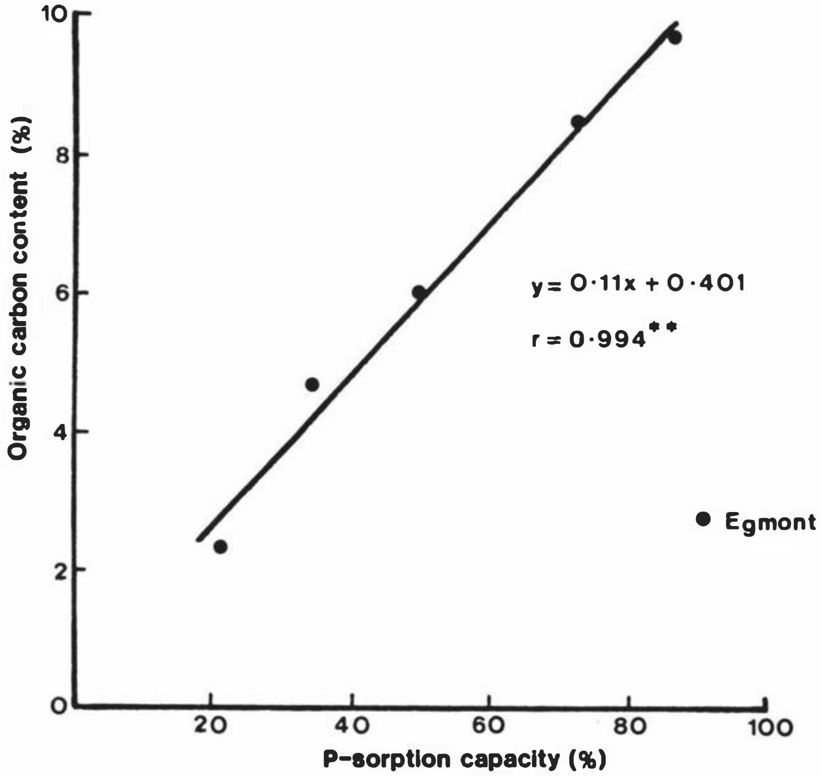


Figure 7.15 Relationship between organic carbon content and phosphate-sorption capacity of six soils. Data for Egmont soil not included in linear regression analysis.

Egmont soil was excluded from this linear regression analysis. Evaluation of this for the far wider range of soils used in the study of Martin (1964), also produces a similar relationship ($y = 0.098x + 2.260$; $r = 0.849$**). Any effect of organic matter on the dissolution of SPR, through the chelation of Ca or through the supply of hydrogen ions (Khasawneh and Doll, 1978) was apparently overridden by the increasing P-sorption capacity of the soils, based on the results from the Ramiha and Egmont soils (Table 7.2; Fig. 7.12).

The effect of soil pH on the dissolution and subsequent plant availability of P in a PR will be considered in more detail in Chapter 7.3.4. It appears from the results of this study that the effect of soil pH is more pronounced on soils of low P-sorption capacity, namely the Tokomaru and Wainui. The limited range in neutral, M ammonium acetate-extractable Ca in these six soils prevents an evaluation of the effect of exchangeable Ca in the soil on the reactions of PR materials in soils. This soil property will also be dealt with in more detail in Chapter 7.3.4, because of the close association with soil pH.

In addition to the effect of P-sorption capacity, pH, and exchangeable calcium, the P status of a soil has also recently been implicated (Khasawneh and Doll, 1978) as a factor which influences the dissolution and subsequent plant availability of P from a PR in soil. With the exception of the Taupo soil, the differences in P status, measured for instance by the bicarbonate extractant, of the remaining five soils were small. Comparison of 0.5M NaOH-extractable P and bicarbonate-extractable P in the Tokomaru and Egmont soils indicates that addition of P is likely to have a more pronounced effect on the P status, measured by the bicarbonate extractant, of the Tokomaru than the Egmont soil. As a result, the effect of soil P status on the reactions of a PR are more likely to be relevant to a soil of low sorption capacity.

7.3.3.2 Influence of soil phosphate status on the reactions of superphosphate and a phosphate rock in a soil

Bicarbonate-extractable P levels in the Wainui soil following the addition of 0, 40, 90, and 180 μgP g^{-1} of soil as KH_2PO_4 ranged from 6 to 58 μgP g^{-1} of soil after 42 days of incubation at field capacity at 15°C. The rate of initial decline in water-extractable P and the values at 94 days in the soil to which superphosphate was added were independent of the initial P status of the Wainui soil (Fig. 7.16). This confirms and extends the findings of Ryden et al., (1976).

The initial increases and values at 94 days for both bicarbonate- (Fig. 7.17) and Bray- (Fig. 7.18a) extractable P in the soil to which SPR was added were also largely independent of the P status of the Wainui soil. The increases (Δ) in bicarbonate-extractable P in the Wainui soil of increasing P status to which SPR was added, were 37, 34, 35, and 28 μgP g^{-1} of soil, at 90 days (Fig. 7.17). The values of Bray-extractable P were far greater, being 58, 66, 62, and 53 μgP g^{-1} of soil at P0, P1, P2, and P3, respectively (Fig. 7.18a). Only at the highest addition of P was there a meaningful decrease in the increase in both bicarbonate- and Bray-extractable P. The increases in Bray-extractable P in the soil to which TPR was added, although only 16% of those increases obtained for SPR, were also largely unaffected by P status of the Wainui soil (Fig. 7.18b).

The addition of 45, 90, and 180 μgP (as KH_2PO_4) g^{-1} of soil increased the amount of 0.5M NaOH-extractable P in the Wainui soil by 39, 85, and 165 μgP g^{-1} of soil, respectively (Table 7.5). As was the case with both bicarbonate- and Bray-extractable P in the soil to which SPR was added, values for NaOH-extractable P were also largely unaffected by initial P status of the Wainui soil (Fig. 7.19). Expressed as a percentage

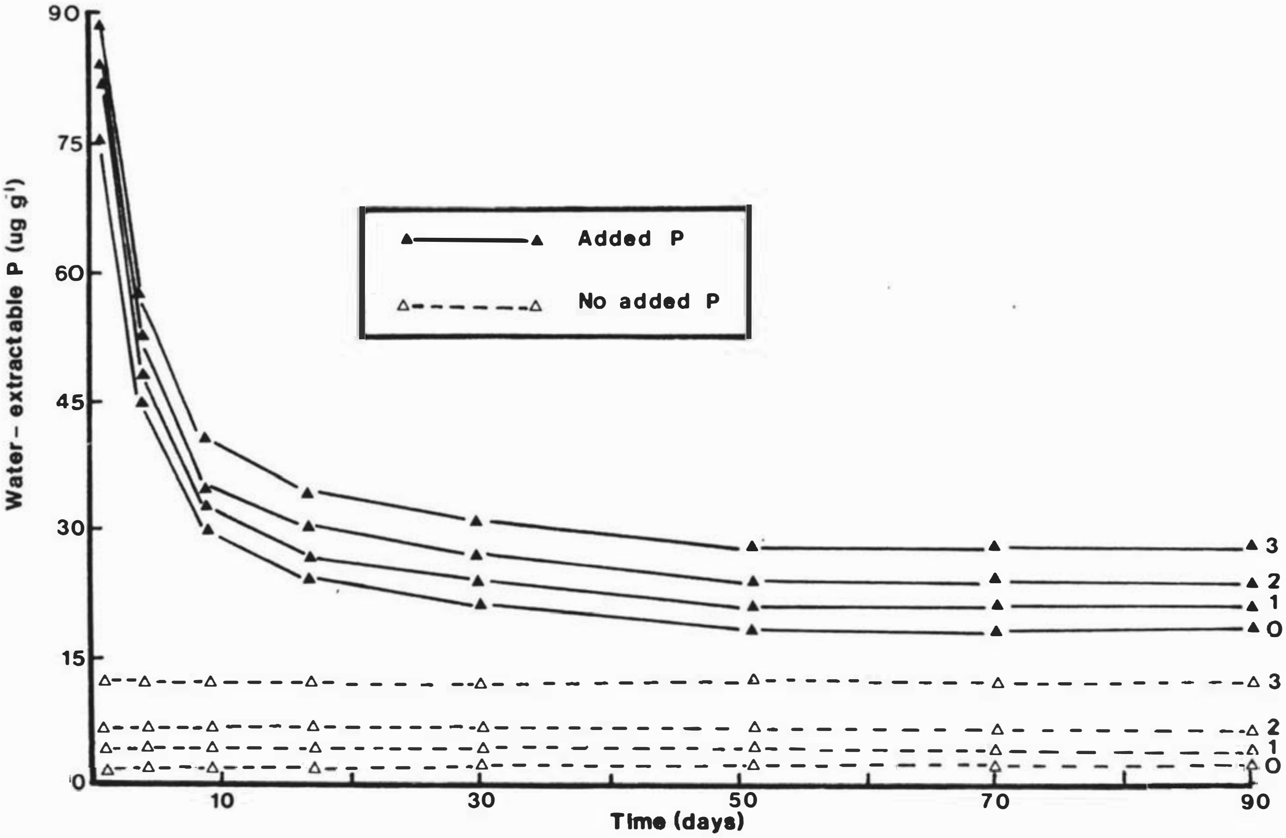


Figure 7.16 Change in water-extractable phosphorus in the soil over 90 days following superphosphate addition at 500 μgP g^{-1} of soil to the Wainui soil with increasing initial phosphate status (P0, P1, P2, and P3).

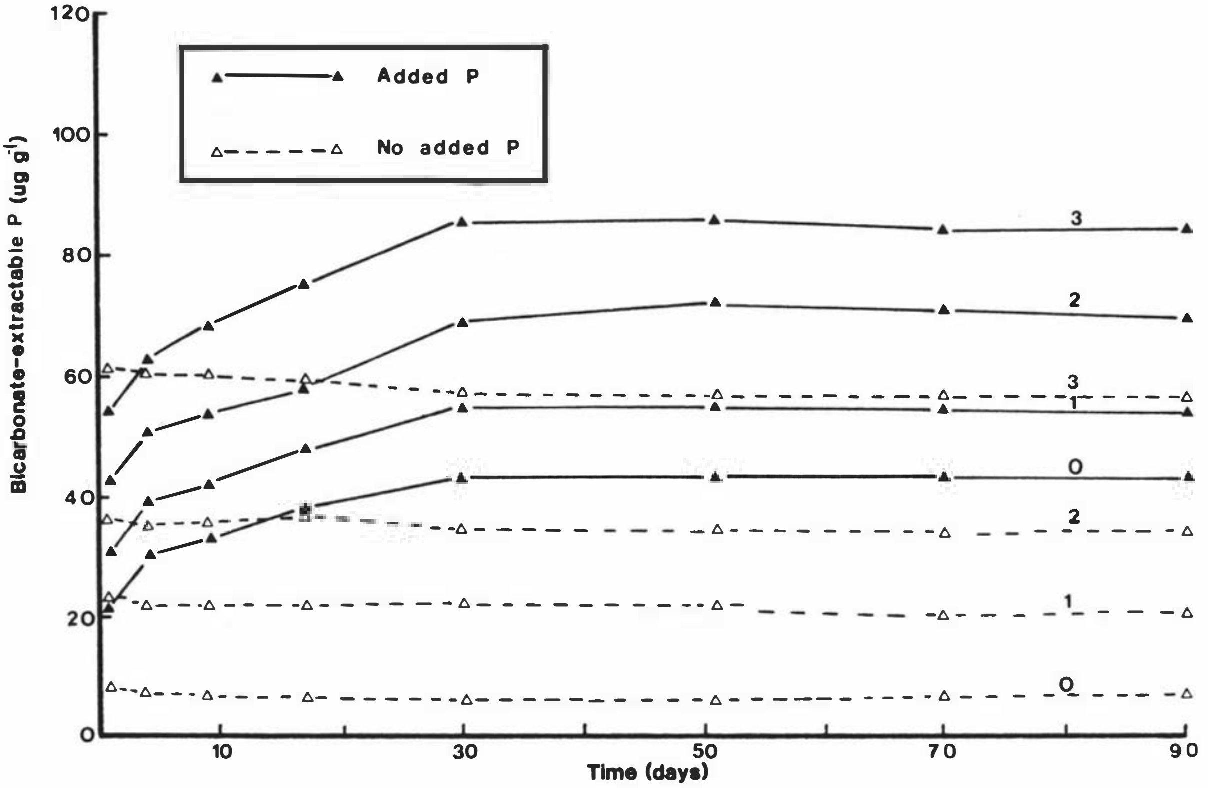


Figure 7.17 Change in bicarbonate-extractable phosphorus in soil over 90 days following Sechura phosphate rock addition at 500 μgP g^{-1} of soil to the Wainui soil with increasing initial phosphate status (P0, P1, P2, and P3).

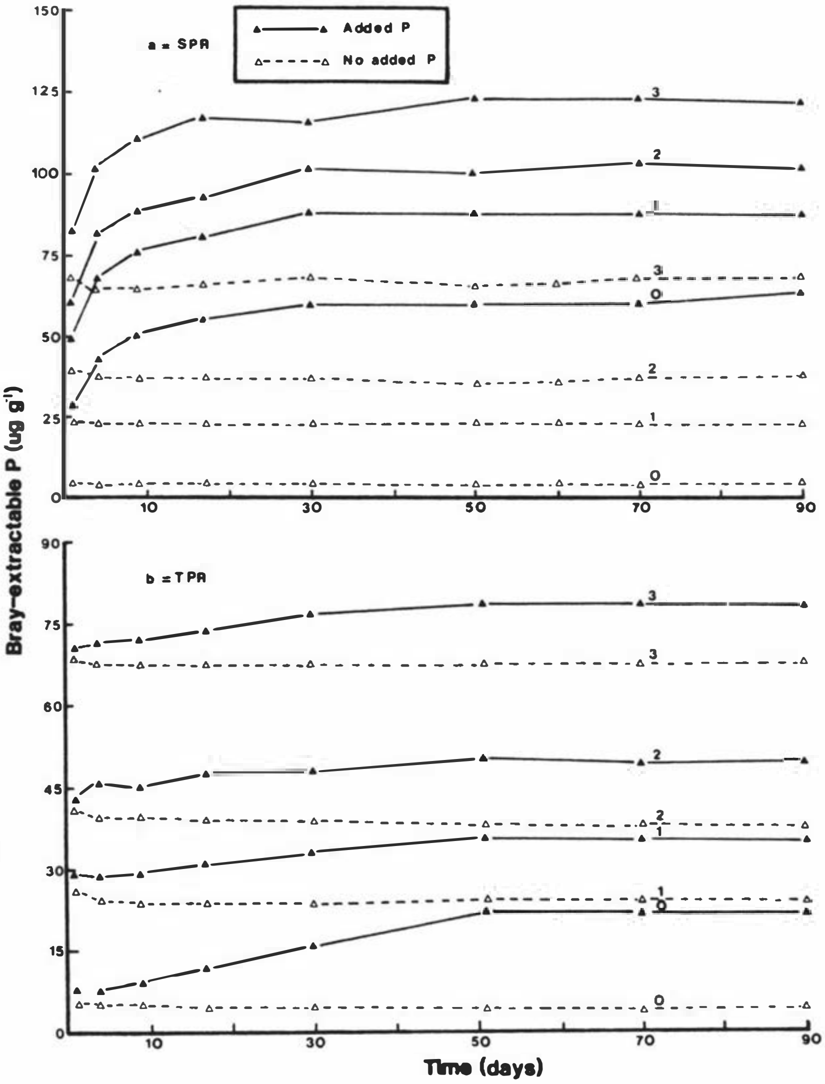


Figure 7.18 Changes in Bray-extractable phosphorus in soil over 90 days following (a) Sechura phosphate rock (SPR) and (b) Tennessee phosphate rock (TPR) addition at 500 μgP g^{-1} of soil to the Wainui soil with increasing initial phosphate status (P0, P1, P2, and P3).

Table 7.5 Effect of adding increasing amounts of KH_2PO_4 on the phosphate status of Wainui silt loam at 42 days

P added (µg g^{-1})	pH_{H_2O}	P-sorption capacity (%)	Extractable P in soil			
			Water	Bicarbonate	Bray	NaOH
				(µg g^{-1})		
P0 0	4.9	34	2.2	6.0	3.8	93
P1 45	4.9	29	4.1	19.2	24.0	132
P2 90	4.8	30	6.4	33.6	37.2	178
P3 180	4.9	30	12.1	57.6	67.5	258

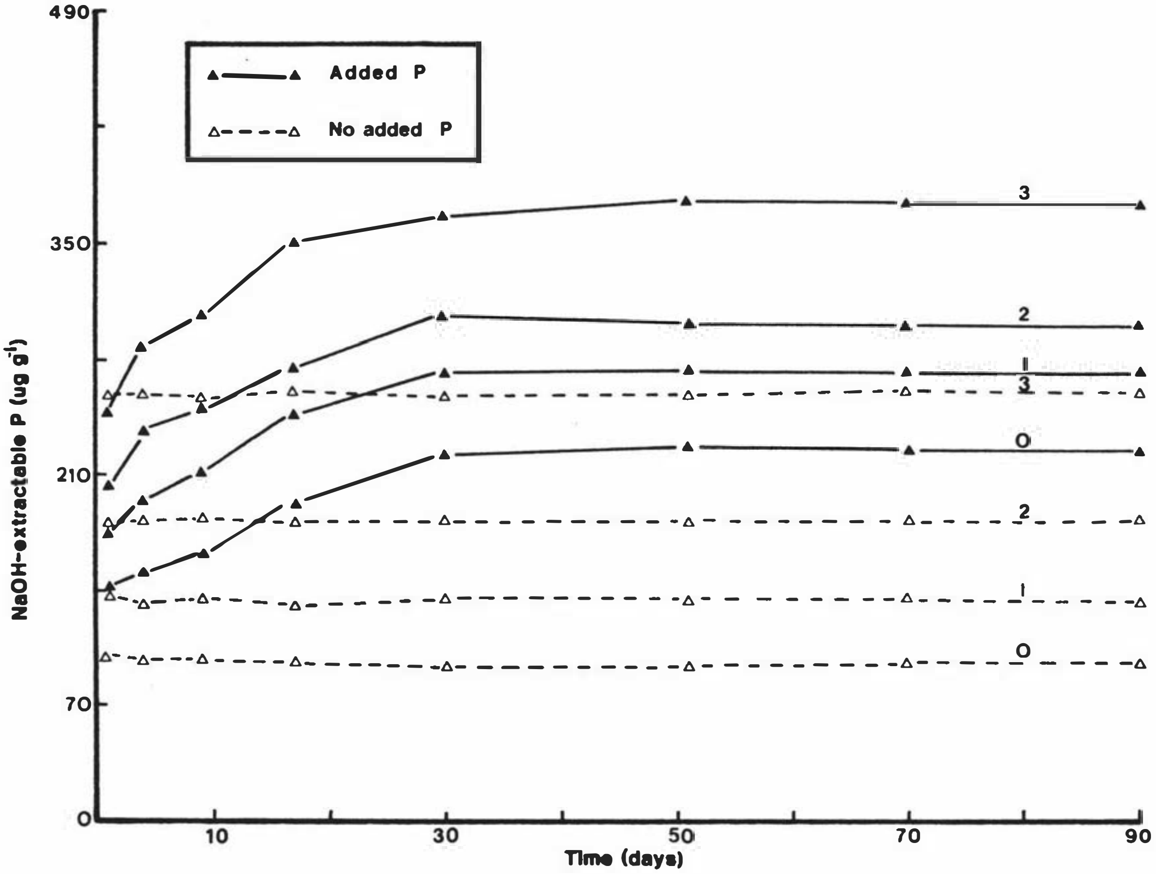


Figure 7.19 Changes in NaOH-extractable phosphorus in soil over 90 days following Sechura phosphate rock addition at 500 μgP g^{-1} of soil to the Wainui soil with increasing initial phosphate status (P0, P1, P2, and P3).

of total P added as SPR, dissolution varied from 22 to 28%.

These results provide further evidence which suggests that the use of reactive PR materials does not have to be restricted to soils of relatively low P status, as previously suggested (Khasawneh and Doll, 1978). They may be used across a wide range of soil P status, provided other soil factors which also affect the dissolution and subsequent plant availability of a PR, namely P-sorption capacity and soil pH, are favourable.

7.3.4 Effect of soil pH and exchangeable calcium on the reactions of superphosphate and a phosphate rock in soil

Results from the previous study (see 7.3.3.1) suggest that the effect of soil pH on the dissolution and subsequent plant availability of P from a PR in soil is more important with soils of low P-sorption capacity. Consequently, to evaluate the relative significance of pH and exchangeable Ca on the reactions of a PR in soils, the low P-sorbing Wainui silt loam was again used. This is a yellow-grey earth/yellow-brown earth intergrade soil which constitutes one of the major soils groups in the hill country of the North Island of New Zealand and gives responses to lime (Lambert and Grant, 1980).

Addition of $Ca(OH)_2$ to the Wainui soil and incubation (15^{o}C) at field capacity for 42 days gave a range of soil pH values varying from 5.2 to 6.9 (Table 7.6). This is not an uncommon pH range for agricultural soils within New Zealand (During, 1972), although the highest value would fall outside the normal range encountered. Although the water extractability of Ca following the addition of $Ca(OH)_2$ was lower than with equivalent additions of Ca as $CaCl_2$ reflecting the increasing negative charge of the soil with increasing pH, the neutral, M ammonium acetate reagent removed equivalent amounts of Ca (Table 7.6).

Table 7.6 Effect of adding increasing amounts of $Ca(OH)_2$ or $CaCl_2$ on pH and exchangeable Ca of Wainui silt loam at 42 days

Calcium addition			Exchangeable Ca	pH_{H_2O}	P-sorption capacity	Extractable P in soil			
System	Form	Amount $(mg\ g^{-1})$	(meq %)		(%)	Water	Bicarbonate $(\mu g\ g^{-1})$	Bray	NaOH
0	0	0	4.44	5.20	34	1.5	6.4	8.1	72
Ca 1	$CaCl_2$	1.35	6.93	5.20	36	1.5	6.4	8.1	71
Ca 2	$CaCl_2$	2.03	10.95	5.10	35	1.5	6.3	8.0	70
Ca 3	$CaCl_2$	2.70	15.30	5.10	35	1.5	6.1	8.0	70
pH 1	$Ca(OH)_2$	1.35	8.76	5.80	33	1.5	5.3	7.5	70
pH 2	$Ca(OH)_2$	2.03	11.26	6.40	32	1.4	5.0	7.5	70
pH 3	$Ca(OH)_2$	2.70	13.63	6.90	30	1.4	4.9	7.0	69

In contrast to the minor effect which increasing Ca additions (as $CaCl_2$) had on bicarbonate-extractable P in the Wainui soil to which superphosphate was added, increasing soil pH in conjunction with increasing Ca (as $CaCl_2$) resulted in a marked decrease, up to 40% at the highest soil pH (Fig. 7.20). This decrease, as discussed previously (Chapter 4.3) is an artifact of the bicarbonate-extraction procedure, rather than representing a decrease in actual plant-available P in the soil. Recently, Syers et al. (1981) have suggested that this decrease in bicarbonate-extractable P with increasing soil pH may result from the co-precipitation of P with Ca during extraction with bicarbonate. The decrease at 90 days in NaOH-extractable P from superphosphate as the pH of the Wainui soil increased (Table 7.7), suggests that sorption reactions become less important with a soil of low P-sorption capacity as soil pH increases. This would also lead to a decrease in bicarbonate-extractable P in the soil, as this extractant largely removes P by desorption.

In addition to any effect of soil pH on the effectiveness of the bicarbonate extractant as an estimate of plant-available P, the decrease in bicarbonate-extractable P with increasing pH of the Wainui soil to which SPR was added (Fig. 7.21a), probably represents an actual decrease in plant-available P. Bicarbonate-extractable P from SPR at 90 days decreased by 20, 30, and 34 $\mu gP\ g^{-1}$ of soil as soil pH increased from 5.15 to 5.80, 6.40, and 6.85, respectively (Fig. 7.21a). The decrease in bicarbonate-extractable P in the soil to which SPR was added following the addition of increasing amounts of Ca, without an increase in pH, expressed as a percentage of the decrease resulting from increasing both soil pH and exchangeable Ca, ranged from 77 to 88% (Fig. 7.21a). Changes in Bray-extractable P for the Wainui soil to which SPR was added showed a similar pattern (Fig. 7.21b). Again, the effect of $CaCl_2$, which

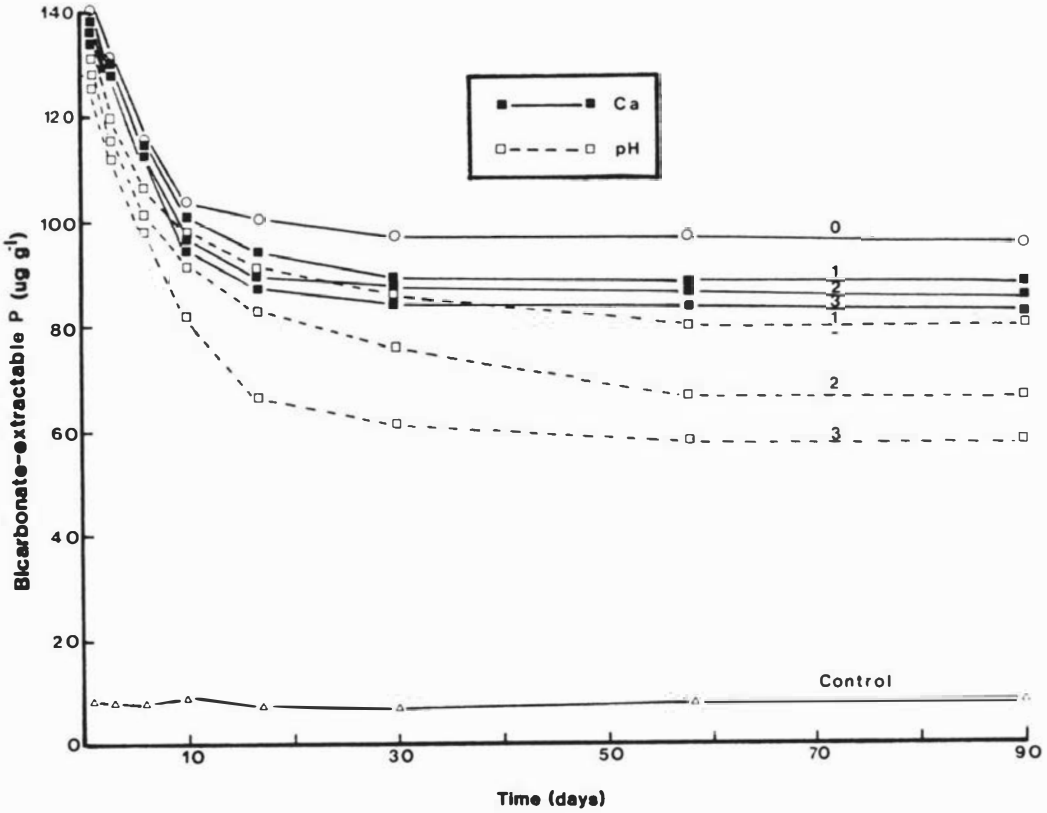


Figure 7.20 Change in bicarbonate-extractable phosphorus in soil over 90 days following superphosphate addition at 500 μgP g^{-1} of soil to the Wainui soil without (o) and with increasing pH and exchangeable Ca (pH 1, pH 2, and pH 3) or increasing exchangeable Ca (Ca 1, Ca 2, and Ca 3). Control is for no Sechura phosphate rock addition.

Table 7.7 Dissolution of Tennessee phosphate rock (TPR), Sechura phosphate rock (SPR), and superphosphate, measured by NaOH extraction at 90 days, as influenced by pH and exchangeable Ca of Wainui silt loam, and expressed as increases (Δ) in 0.5M NaOH-extractable phosphorus in soil and as a percentage of the total phosphorus added (500 μgP g^{-1} of soil)

	Increases (Δ) in NaOH-extractable P in soil from			Fraction of P source dissolved from		
System	TPR	SPR (μg g^{-1})	Superphosphate	TPR	SPR (% of total P added)	Superphosphate
0*	37	168	392	7.4	33.6	78.4
Ca 1	30	92	385	6.0	18.4	77.0
Ca 2	20	57	363	4.0	11.2	72.6
Ca 3	15	43	352	3.0	8.6	70.0
pH 1	21	71	375	4.2	14.2	75.0
pH 2	16	20	363	3.2	4.0	72.6
pH 3	8	10	328	1.6	2.0	65.6

*See Table 7.6.

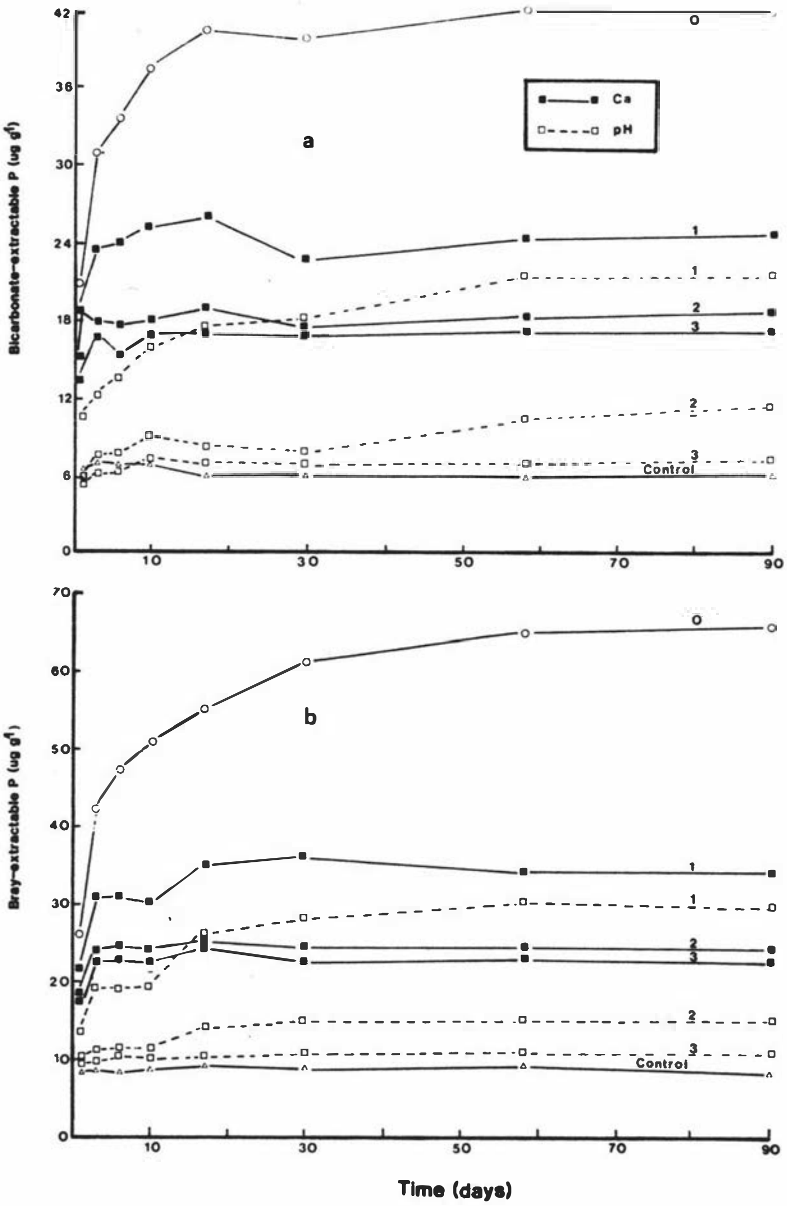


Figure 7.21 Change in (a) bicarbonate- and (b) Bray-extractable phosphorus in soil over 90 days following Sechura phosphate rock addition at 500 µg P g^{-1} of soil to the Wainui soil without (o) and with increasing pH and exchangeable Ca (pH 1, pH 2, and pH 3) or increasing exchangeable Ca (Ca 1, Ca 2, and Ca 3). Control is for no Sechura phosphate rock addition.

had no marked effect on soil pH (Table 7.6), accounted for 80 to 89% of the effect that $Ca(OH)_2$ had on Bray-extractable P in the soil to which SPR was added. As with the bicarbonate reagent, the effectiveness of the Bray reagent in extracting P was probably reduced at the higher soil pH values due to both the neutralizing effect of any free Ca and the complexing of F by $CaCO_3$ (Smillie and Syers, 1972). Thus it may be dangerous to draw conclusions as to the relative effect of increasing pH and exchangeable Ca, using these two reagents.

However, the decreases in the dissolution of SPR, measured by NaOH extraction following the addition of increasing amounts of $Ca(OH)_2$ or $CaCl_2$ (Table 7.7), showed the same trend (Fig. 7.22), confirming the suggestion that exchangeable Ca has a more pronounced effect on the dissolution and subsequent plant availability of a PR than soil pH, *per se*, particularly over the pH range commonly encountered. The results from the Egmont soil (Chapter 7.3.3.1) also support this conclusion.

Care must be taken, however, in interpreting the effect of soil pH and exchangeable Ca on the dissolution and subsequent plant availability of a PR based on the results of this study. This arises because of the interaction between these two soil properties and P-sorption capacity, particularly for soils of lower (< 30%) P-sorption capacity.

7.3.5 Initial development of a simple model to describe the dissolution of phosphate rock materials in soils

An initial attempt at modelling the dissolution of a PR material in soils used the data obtained for the dissolution of SPR, measured by NaOH extraction, in soils of contrasting P-sorption capacity (see 7.3.3.1), P status (see 7.3.3.2), and pH and exchangeable Ca status (see 7.3.4). The dissolution of SPR in the soils increased with time, reaching an equilibrium at 90 days, and this could be described by a modified Mitscherlich equation of the form:

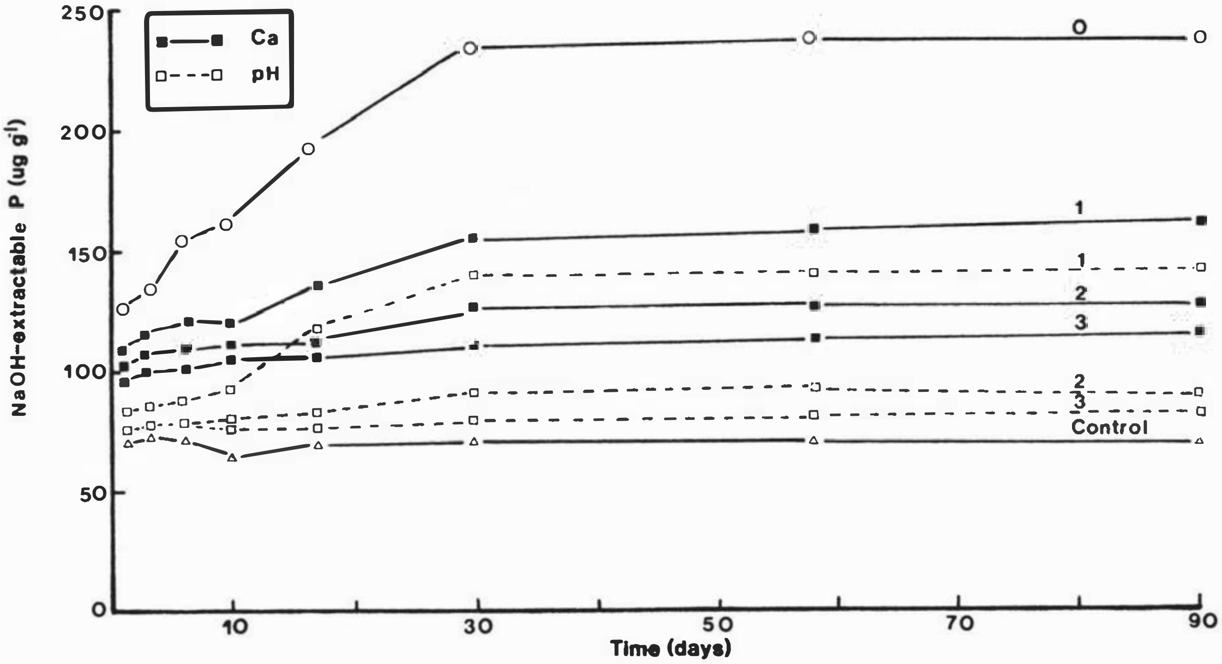


Figure 7.22 Change in NaOH-extractable phosphorus in soil over 90 days following Sechura phosphate rock addition at 500 μgP g^{-1} of soil to the Wainui soil without (o) and with increasing pH and exchangeable Ca (pH 1, pH 2, and pH 3) or increasing exchangeable Ca (Ca 1, Ca 2, and Ca 3). Control is for no Sechura phosphate rock addition.

$$Y = A\,(1 - e^{-cx})$$

in which Y is the amount of SPR dissolved, as measured by NaOH extraction at time (x); A is the asymptote; and c is the curvature coefficient. In this form, the exponential equation is constrained to pass through the origin.

Fitted curves for the dissolution of SPR, measured by NaOH extraction, in four of the soils used in this study are presented in Fig. 7.23 and the calculated A and c values obtained from the exponential equation describing the dissolution of SPR in all thirteen soils are listed in Table 7.8. Except for the Wainui soil at the two $CaCl_2$ additions, this simple exponential equation appears to describe very well the dissolution of SPR, as judged from r^2 values of greater than 0.917 (Table 7.8). Dissolution of SPR in the Wainui soil at the highest $CaCl_2$ and $Ca(OH)_2$ additions (Chapter 7.3.4) could not be described by this model. A straight line better described the experimental data for these two systems. Because of this and because of the fact that the pH and exchangeable Ca concentrations in these two systems are extreme, they were not included in the initial attempt at modelling the dissolution of SPR in soil.

Whereas A was found to vary markedly across the thirteen soils (Table 7.8), with values ranging from 240 in the Egmont to less than 30 on the Wainui soil at pH 2, c was found to be largely independent of soil type (Table 7.8). In fact c showed only small changes, with most values falling between 0.089 and 0.190 (Table 7.8). By setting the c value constant and by taking the average c value for the thirteen soils (0.137), the shape (Fig. 7.24) and fit (Table 7.9) of the modified Mitscherlich curve describing the dissolution of SPR in soil and calculated A values (Table 7.9) were only affected to a minor degree. Although only half of the data points are on the rapidly-changing portion of the curve,

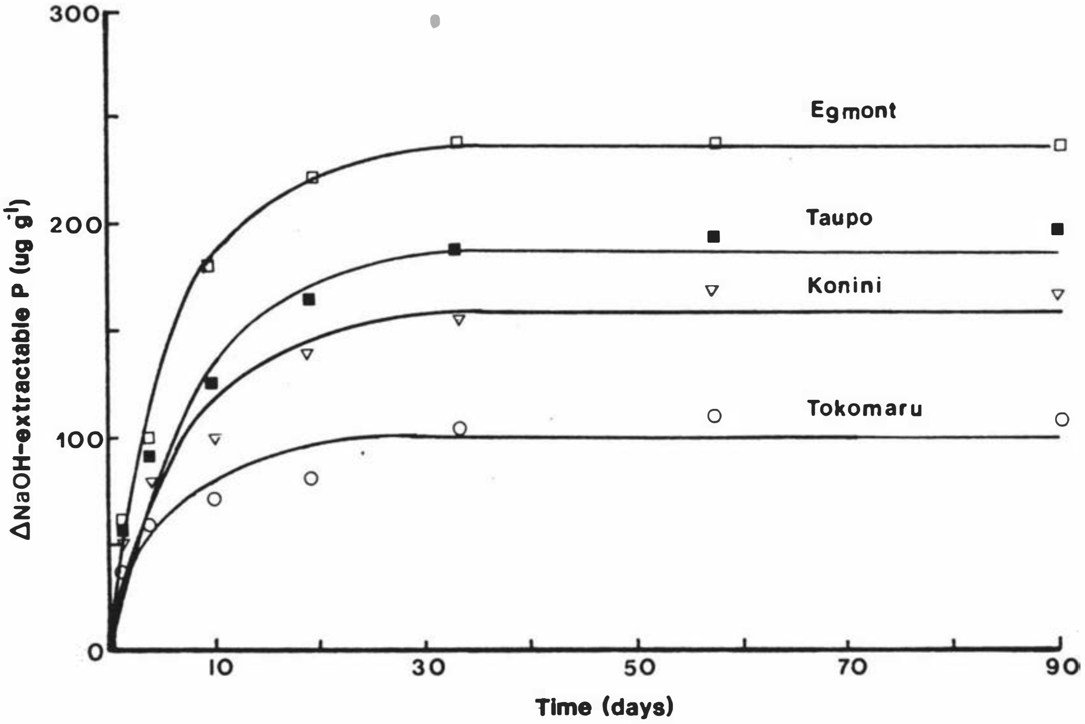


Figure 7.23 Fitted curves, calculated from the modified Mitscherlich equation, for describing the dissolution of Sechura phosphate rock in four soils, expressed as Δ NaOH-extractable phosphorus values.

Table 7.8 Values for asymptote (A) and curvature coefficient (c) calculated from the modified Mitscherlich equation describing the dissolution of Sechura phosphate rock in soils and an estimate (r^2) of the fit of the exponential curve to the experimental data

Soil type		A	c	r^2
Egmont		240	0.144	0.993
Ramiha		195	0.190	0.948
Taupo		190	0.135	0.976
Konini		161	0.134	0.960
Wainui		169	0.106	0.969
Tokomaru		102	0.182	0.917
Wainui	pH 1*	93	0.058	0.972
	pH 2*	23	0.089	0.941
	Ca 1*	84	0.157	0.885
	Ca 2*	53	0.278	0.821
	P 1†	140	0.110	0.966
	P 2†	121	0.113	0.970
	P 3†	113	0.080	0.994

*See Table 7.6.

†See Table 7.5.

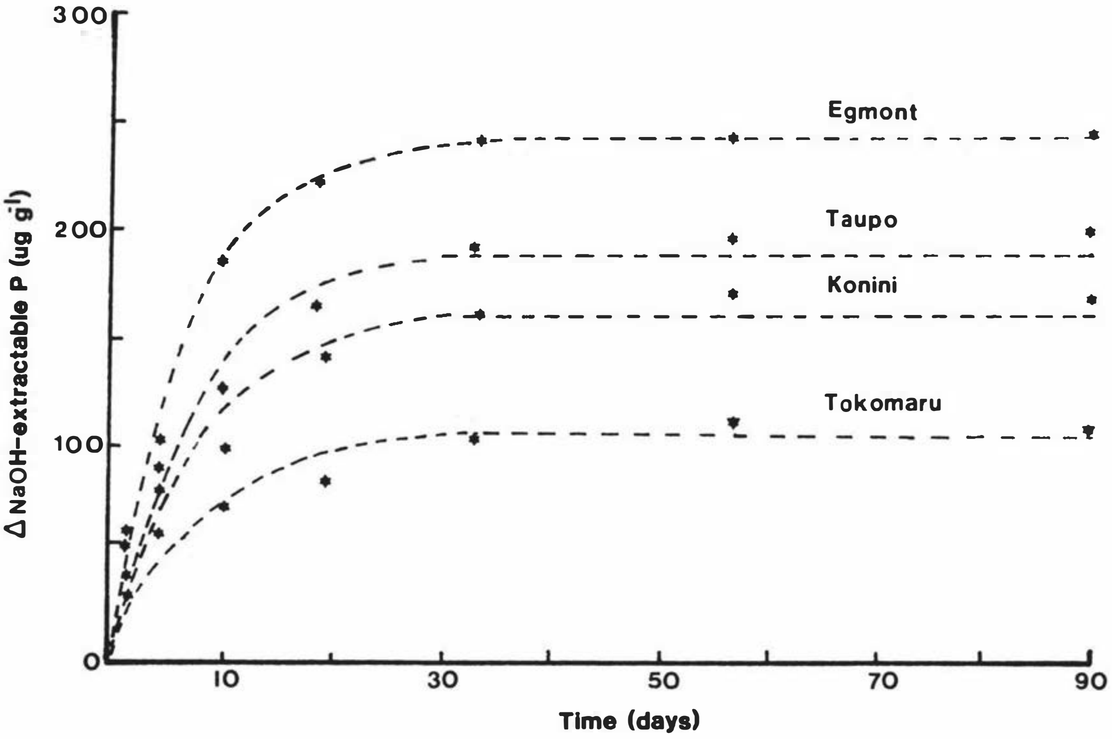


Figure 7.24 Curves calculated from the modified Mitscherlich equation with a constant curvature coefficient ($c = 0.137$) for describing the dissolution of Sechura phosphate rock in four soils, expressed as Δ NaOH-extractable phosphorus values. Actual data points indicated by *.

Table 7.9 Values for asymptote (A) calculated from the modified Mitscherlich equation with a constant curvature coefficient (c = 0.137) describing the dissolution of Sechura phosphate rock in soils and an estimate (r^2) of the fit of the exponential curve to the experimental data

Soil type		A	r^2
Egmont		242	0.995
Ramiha		203	0.974
Taupo		190	0.975
Konini		160	0.958
Wainui		161	0.940
Tokomaru		106	0.945
Wainui	pH 1*	59	0.880
	pH 2*	21	0.901
	Ca 1*	86	0.909
	Ca 2*	58	0.934
	P 1†	138	0.946
	P 2†	118	0.959
	P 3†	104	0.977

* See Table 7.6.

† See Table 7.5.

increasing the number of points on this part of the curve would probably not have changed the shape of the curve to any marked degree, because of the constraint to pass through the origin and because of the well-defined asymptote (Fig. 7.23). In fact the fit of the exponential equation was relatively insensitive to a range of c values (0.09 to 0.200), the range within which most of the c values fell (Table 7.8).

Because c appears to be essentially constant for SPR in soils, it should be possible, by establishing the relationship between A and soil properties over a range of soils, to predict the initial dissolution of a PR in other soils. The value of c will need to be calculated for individual PR materials, however, because of differences in the rate and extent of dissolution of PR materials in soils (see 7.3.3.1; Shinde et al., 1978).

As a first step to establishing the relationship between A and soil properties in the thirteen soils used in this initial study, correlation coefficients between A and soil properties were determined to identify the soil properties most closely related to the dissolution of SPR in soil. From the linear regression analysis, two soil properties, namely, P-sorption capacity and exchangeable Ca, were found to be the most closely associated with A (Table 7.10). This agrees with the results obtained with the six soils presented earlier (see 7.3.3.1) and with the results in 7.3.4 where increases in exchangeable Ca explained most of the decrease in the dissolution of SPR in the Wainui soil as the pH increased from 5.0 to 6.4. Because the dissolution of SPR appears to be dependent on more than one soil property, the initial evaluation was extended to a multiple regression analysis. Stepwise multiple regression showed that P-sorption capacity accounted for 59% of the variance in the dissolution of SPR between the thirteen soils, with the addition of exchangeable Ca improving this to 80%. Inclusion of values

Table 7.10 Correlation coefficients (r^2) between the asymptote (A) and several properties of the thirteen soils

Soil property	r^2
P-sorption capacity	0.790
Exchangeable Ca	0.570
Organic carbon	0.314
Soil pH	0.001
Bicarbonate-extractable P	0.001
Bray-extractable P	0.137
Water-extractable P	0.113

for organic C content, pH, and Bray-extractable P only increased the variance accounted to 80.2%. The multiple regression for SPR:

$$A = 111.42 + 1.98 \text{ P-sorption capacity} - 11.08 \text{ exchangeable Ca}$$

indicates that dissolution increases with an increase in the P-sorption capacity and a decrease in exchangeable Ca in a soil. Consequently, from a knowledge of a P-sorption capacity and exchangeable Ca it should be possible to predict the dissolution of SPR in soil.

Although all the available data for the dissolution of SPR in soils were used in the development of the initial model, by re-running the stepwise multiple-regression analysis, omitting one of the thirteen soils on each run, an initial evaluation of this simple model can be attempted. The thirteen recalculated multiple regressions were then used to predict, separately, the dissolution of SPR in the soil omitted from the recalculated multiple regression, from a knowledge of the P-sorption capacity and exchangeable Ca of that soil. By repeating this for all thirteen soils it was possible to undertake an initial evaluation of this model. A comparison of A values obtained from the thirteen recalculated multiple regressions (predict A) and the A calculated from the modified Mitscherlich equation with a constant c (actual A, Table 7.9) shows, that with the exception of the Ramiha soil, this simple model gave a reasonable prediction of the dissolution of SPR in the incubated soils (Fig. 7.25). A more detailed breakdown of the P-sorption capacity of a soil, as in the study by Chien et al. (1980b) into active Al, reactive Al, and free Fe_2O_3 components, and the inclusion of more soils, particularly of moderate and high P-sorption capacity, in the initial construction of the model would probably improve this model further.

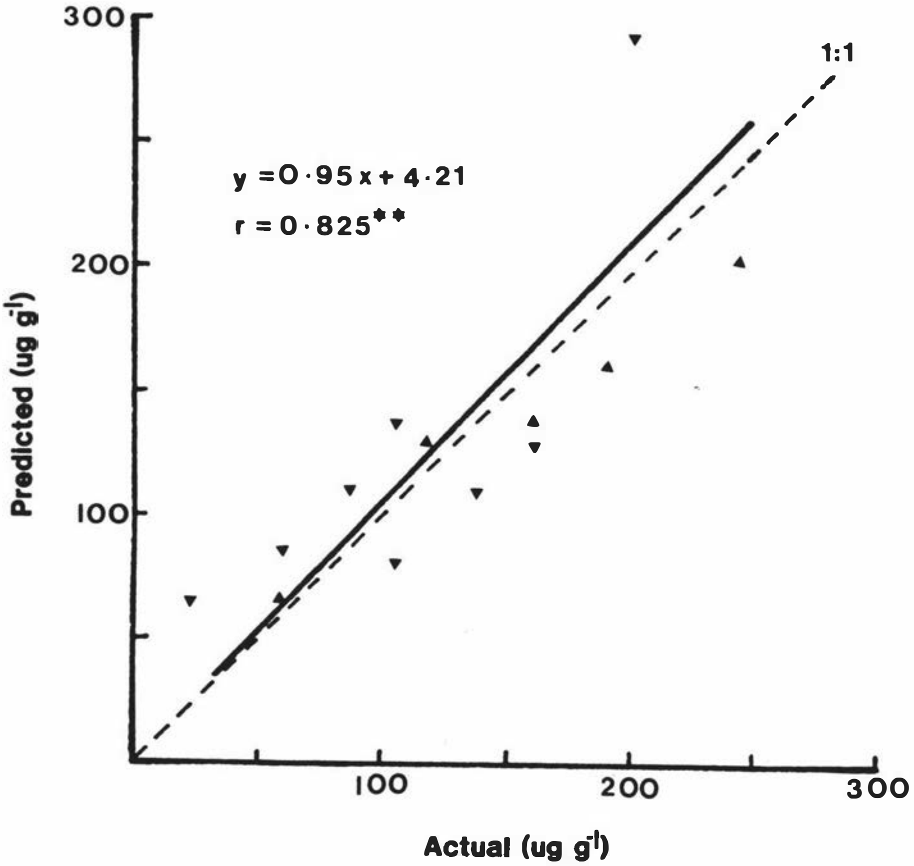


Figure 7.25 Relationship between asymptote (A) values obtained from a recalculated multiple regression equation (Predicted A) and A values calculated from the modified Mitscherlich equation using a constant curvature coefficient (Actual A) for the dissolution of Sechura phosphate rock in the thirteen soils.

7.4 General Discussion

Although the decline measured in water-extractable P in the soil to which a PR was added, is consistent with the findings of several workers (Hammond, 1978; Chien, 1979; Chien et al., 1980a; Mokowunye and Chien, 1980), the water-extraction procedure greatly underestimated the amount of short-term, plant-available P in the soil to which SPR or CRP was added, determined using ryegrass in the glasshouse. This confirms an earlier suggestion (Chapter 4.3.3.4). In contrast, the water-extraction procedure was a good predicter of plant-available P in the soil to which superphosphate was added, a conclusion also reached by other workers (Luscombe, 1976; Rennes, 1978). This difference can be explained by the initial reactions of these two P sources on contact with soil. With superphosphate, the usually high water solubility may lead to a localised saturation of sorption sites, where part of the P is held by a more-physical type of sorption mechanism and, thus has a high water extractability (Ryden and Syers, 1977). The decline in water-extractable P, which is rapid initially and then more gradual, probably results from the movement or redistribution of P to sites where P is chemisorbed (Ryden et al., 1977). Further evidence for this suggestion comes from the small increases noted in 0.5M NaOH-extractable P in the soil following the addition of superphosphate after the initial 3 days of the incubation period.

In contrast, the dissolution of P from a PR in soil is largely a function of its solubility and because this is initially slow, it is highly unlikely that there is any localized saturation of sorption sites. Instead, there is probably a continuous movement of P from the sites where P is held by a more-physical sorption mechanism to the sites where the P is chemisorbed. The gradual increase in 0.5M NaOH-extractable P in the soil, with both increasing P-sorption capacity of the soils and time following the addition of a PR, supports this viewpoint. Consequently, although water extraction and possibly dilute salt solution may be useful for measuring relative differences between PR materials (Chien et al., 1980a), they are of little value in predicting the amount of short-term, plant-available P in soil to which a PR is added.

Both the Bray procedure of Bray and Kurtz (1945) and the bicarbonate procedure of Olsen et al. (1954) were useful indicators of plant-available P when SPR and CRP were added to three contrasting soils. Of the two, the Bray procedure accounted for more of the variability, which agrees with the conclusions from the field (Chapter 4) and with those of a number of workers (Barnes and Kamprath, 1975; Shinde et al., 1978). Several workers have found both procedures to be useful (Salmon and Smith, 1956; Grigg and Crouchley, 1980), whereas others have found bicarbonate to be a good indicator (Mattingly, 1968; Sarangamath et al., 1975). The good agreement found between field and greenhouse data indicates that the Stanford and De Ment (1957) method used in the present study, although of short duration, followed closely the initial changes in plant-available P in the soil. Because of the exhaustive nature of this technique, the dependence placed on added P in the soil, makes this a useful and rapid method of evaluating not only the influence of soil properties on the short-term effectiveness of a P source, but also the effectiveness of extraction methods in measuring changes in plant-available P in the soil.

Isotopic exchange studies indicated that on low to moderate P-sorbing soils, the Bray and bicarbonate extractants removed similar pools of P, although the mechanisms by which the P is removed probably differ markedly. In contrast, on the high P-sorbing Ramiha soil, these extractants appear to remove different pools of P. The actual amounts of P removed by the two extractants decreased markedly with increasing

P-sorption capacity of the soil. Whereas the bicarbonate reagent removes P by desorption, the Bray reagent removes P by dissolution of sorption components, in addition to extracting some sorbed P by desorption. In addition, the Bray procedure removes some P from any unreacted PR in the soil. Until the recent work of Chien (1978), however, most researchers considered that the increases in Bray-extractable P in the soil, to which a PR was added, were attributed to PR which had dissolved in the soil rather than to unreacted PR (Smith and Grava, 1958; Barnes and Kamprath, 1975; Hammond et al., 1976). The differences obtained for Bray- and bicarbonate-extractable P with the four low to moderate P-sorbing soils (Fig. 7.11) probably result from unreacted PR. As a result, the better predictive ability of the Bray extractant on these soils may result from the fact that it measures some unreacted PR which is likely to dissolve, in addition to sorbed P. Both of these forms of P are potentially plant-available, confirming and extending the conclusion reached by Chien (1978).

The Bray extractant overestimated the amount of plant-available P in the soil to which superphosphate was added, a conclusion also reached by Barnes and Kamprath (1975) and Reinhorn and Hagin (1978). These workers in fact obtained two distinct curves when they plotted Bray-extractable P in the soil derived from superphosphate and from a PR against yield data. Rearranging the P uptake data obtained in the present study also produces two distinct curves with the uptake of P obtained for a given amount of Bray-extractable P in the soil to which a PR was added being greater than the uptake of P obtained for an equivalent amount of Bray-extractable P in soil to which superphosphate was added. These two distinct curves again reflect not only the differing behaviour of the two P sources on contact with soil, but also the mechanisms by which the Bray extractant removes P. The partial dissolution of sorbing components by the Bray reagent, in soil to which superphosphate was added, would release P not only from sites where the P is more-physically sorbed and potentially plant-available (Ryden and Syers, 1977), but also from those sites where the P is chemisorbed and of varying and sometimes low plant availability.

Interpretation of the likely agronomic effectiveness of a PR, compared to that of superphosphate, if based solely on chemical extraction data with soils, can be misleading. For instance, the single water-extraction data obtained in the present study suggest that the effectiveness of both SPR and CRP increases, relative to superphosphate, as the P-sorption capacity of the soil increased. Chien et al. (1980b) also suggested that the agronomic effectiveness of NCPR increased as the P-sorption capacity of a soil increased, based on water-extractable P data; a viewpoint supported by the data of Wong Yun Cheong (1966) and Mclean and Logan (1970), but conflicting with the results of van der Paauw (1965) and Juo and Kang (1978). Changes in bicarbonate-extractable P, which was found to give a better estimate of plant-available P in the soil than water-extractable P for both P sources, also conflict with this suggestion. The results from the glasshouse (Chapter 3 and 6) and from the field (Chapter 4) also suggest that there is little or no difference in the relative agronomic effectiveness of a PR applied to soils of varying P-sorption capacity, even though dissolution is greater in soils of high P-sorption capacity. In fact there was a suggestion from the glasshouse studies (Chapter 3 and 6) that the reactive PR materials were less effective on the high P-sorbing Ramiha soil, although there was an interaction with rate of P addition. This may be one of the reasons for the conflicting data reported in the literature.

Some of the most interesting results in the present study were obtained with the 0.5M NaOH extractant. As an alkaline extractant, it does not dissolve or extract a significant amount of P from unreacted PR and thus when used with soils, it provides a direct measure of the extent of dissolution of a PR in a soil. Unlike the bicarbonate and Bray reagents, it is largely unaffected by pH. In marked contrast to the decrease measured in water-, bicarbonate-, and Bray-extractable P in the soil to which SPR was added, the amount of 0.5M NaOH-extractable P increased with increasing P-sorption capacity of the soil. For instance, on the high P-sorbing Egmont soil, 48% of the P added as SPR was recovered by NaOH extraction at 90 days, whereas the Bray extractant recovered only 3% of added P. Because an increase in dissolution does not necessarily result in an increase in the amount of plant-available P in the soil, a distinction should be made not only between the dissolution of a PR and the subsequent plant-available fraction, but also between those factors which promote the dissolution of a PR and those factors which control the plant-available P pool in the soil.

A high correlation ($r^2 = 0.935^{**}$), was obtained for the relationship between the dissolution of SPR, measured by NaOH extraction, and the P-sorption capacity of the six soils used. Chu et al. (1962) also showed a good correlation between the dissolution of a PR (unspecified), measured by the increase in the combined Al-P and Fe-P fractions in soil obtained by the Chang and Jackson (1957) fractionation method, and free iron oxide content (i.e., related to P sorption capacity, Saunders, 1965). More recently, Chien et al. (1980b) found that the dissolution of NCPR increased with an increase in active Al in the soil, which correlated significantly with P-sorption capacity, although the dissolution of NCPR was not measured directly in that study. Using increases in exchangebale Ca in soil, as an indirect estimate of PR dissolution, Smyth and Sanchez (1982) also found that the dissolution of a PR increased as the P-sorption capacity of a soil increased.

In the present study, the extent of dissolution of SPR varies from 22% of added P on the low P-sorbing Tokomaru soil to 48% on the high P-sorbing Egmont soil at 90 days. Combining the Fe-P and Al-P fractions from the Chang and Jackson (1957) fractionation method used by a number of workers gives a similar range of values for the extent of dissolution of certain PR materials. For example, Juo and Kang (1978) found that the dissolution of NCPR varied from approximately 22 to 54% of added P across three soils. Sarangamath et al. (1977) found a similar range (32 to 53%) with GPR across three soils of similar pH (5.5 to 6.4), although on a fourth soil with a pH of 8.4, dissolution was less than 3%. Shinde et al. (1978) reported that the dissolution of both NCPR and GPR varied from 41 to 71% and 30 to 57%, respectively, on two soils (pH 5.4 to 5.9) and from 15 to 13%, respectively, on a third soil (pH 6.4).

After 90 days of incubation, only 18 and 27% of the total P added as CRP had dissolved in the Wainui and Ramiha soils, respectively. Even in the field (Chapter 4) in the presence of growing plants, only 62% of the total P added as CRP was recovered by extraction with NaOH and by the sward at Ballantrae (Wainui silt loam) during 3 years. At Pahiatua (Ramiha silt loam), 48% of total P added as CRP was recovered by NaOH and the sward during 3 years. In contrast, in the incubation study at 90 days, 78 and 74% of the total P added as superphosphate had dissolved in the Wainui and Ramiha soils, respectively. In the field (Chapter 4) after 3 years, however, only 44 and 50% of total P added as superphosphate was recovered by NaOH and by the sward at Ballantrae and Pahiatua, respectively. This apparent decrease in the recovery of P added as superphosphate, may result from the slow diffusion of inorganic P from surface sorption sites into short-range order hydrous ferric oxides, found in soil (Ryden et al., 1977).

Although in the field, the presence of growing plants increased the extent of dissolution of CRP in soil, a significant fraction of the PR appears to remain undissolved, even after 3 years. This suggests that the dissolution of a PR in soil, after the initial reaction, was reduced. The development of surface coatings of short-range order material, such as hydrous oxides of Fe and Al, on a PR could restrict the release of P from the PR to the soil solution, because of the high affinity of hydrous metal oxides for P (Bache, 1964; Ryden et al., 1977). The increasing stability of colloidal ferric phosphates with time in the study of McLaughlin and Syers (1978) was attributed to the presence of short-range order hydrous ferric oxide as a surface coating. These workers suggested that, in the long term, these short-range order materials control the release of P from the colloidal ferric phosphate to the soil solution. A similar mechanism may control the long-term release of P from a PR added to soil.

Both Sarangamath et al. (1977) and Juo and Kang (1978) noted a difference in the dissolution of the PR materials in their respective studies. A comparison of the dissolution of the seven PR materials in the study by Shinde et al. (1978) with bound-carbonate contents, which has been shown by Caro and Hill (1956) and Lehr and McClellan (1972) to correlate well with agronomic effectiveness for PR materials, produced a good relationship. The differences measured in the present study for the dissolution of SPR, CRP, and TPR using NaOH extraction (Fig. 7.14) are consistent with the differences found between the agronomic effectiveness of the three PR materials in the glasshouse (Chapter 6) and may explain, in part, the initial and residual differences found between SPR and CRP in the field in the study of Gregg et al. (1981) and discussed previously (Chapter 4.4).

Results for the extent of dissolution of SPR, CRP, and TPR added to the Wainui soil (Fig. 7.14a), measured by NaOH extraction, are also very similar to those found previously (Chapter 6.3.3) using Fe gel. In addition to overcoming the problems associated with differences between PR materials in shaking systems and the problems associated with pH control, due to the presence of free calcite, when the Fe gel system is used, measurement of the dissolution of PR materials in soils by NaOH extraction enables a direct evaluation of the effect of soil properties on the dissolution of a PR. Consequently, this method provides a simple and useful measure of the dissolution of a PR in soil.

The results obtained with the Egmont (pH 6.5), Ramiha (pH 5.2), Tokomaru (pH 5.6), and Konini (pH 5.6) soils in the present study suggest that soil pH is not the over-riding factor controlling the dissolution of a PR in soil. Support for this suggestion comes from the marked difference found in the extent of dissolution of SPR on the limed Wainui (pH 6.4) and Egmont (pH 6.5) soils, where the dissolution of SPR was 3 and 48%, respectively. Thus, the importance of soil pH in controlling the dissolution of a PR in soil is initially dependent on the P-sorption capacity of the soil. This is consistent with the findings of Chu et al. (1962) and Chien et al. (1980b) who found that the correlation between soil pH and the extent of dissolution of a PR was lower than that with active Al, even though the study was restricted to 16 acid soils. The differences reported in the studies by Juo and Kang (1978), Shinde et al. (1978), and Chien et al., (1980a) for soils of similar pH may partly be explained, by differences in the P-sorption capacity of soils. However, it would be dangerous to dismiss the importance of soil pH as a factor in PR dissolution as there is good evidence in the literature to show that as soil pH increases the agronomic effectiveness of a PR material decreases in some soils (van der Paauw, 1965;

Ensminger et al., 1967).

Associated with an increase in soil pH with liming is an increase in exchangeable Ca, both of which have been shown to affect plant-available P in soil following the addition of a PR (Graham, 1955; Peaslee et al., 1962; Khasawneh and Doll, 1978) although their relative importance has not been fully investigated. Of the decreases in the extent of dissolution of SPR, in the Wainui soil on liming in the present study, measured by NaOH extraction, 75 to 79% of the decrease could be accounted for by the addition of Ca. Although a question arises as to the validity of the Bray- and bicarbonate-extractable P data, due to the influence of soil pH on the effectiveness of these two extractants as estimates of plant-available P in the soil, both decreased with increasing soil pH. The results from this study, along with the results obtained with the Egmont soil (pH 6.5), suggest that soil pH, *per se*, is not of great importance in influencing PR dissolution over the range of values generally encountered with agricultural soils, particularly with soils where P-sorption capacity exceeds 30%. In fact with an increase in P-sorption capacity, Ca probably also becomes of less importance in PR dissolution because, associated with an increase in the sorption of P, is an increase in the negativity of the surface (Ryden and Syers, 1976). This would lead to an increase in the sorption of Ca. Ryden and Syers (1976) showed that the removal of Ca from solution increased with an increase in the sorption of P. The danger of extrapolating the results from the Wainui soil to soils of lower P-sorption capacity is highlighted by the data of Khasawneh and Doll (1978), where the effects of soil pH and exchangeable Ca on the effectiveness of NCPR in increasing the yield of corn were roughly equal.

Recently Khasawneh and Doll (1978) suggested that, from a practical viewpoint, PR materials have little or no value on moderately-fertile soils which have a relatively high soil solution concentration of P. They argued that as effective P fertilizers, PR materials are limited to soils that are severely to moderately deficient in P. Addition of SPR to the low P-sorbing Wainui soil of widely varying P status resulted in remarkably little decrease in either the extent of dissolution of SPR, or in the subsequent plant-availability of P, estimated by either the Bray or bicarbonate extractants, although at the highest P status, there was some indication of a downward trend. This contrasted with the effect that added Ca had on the extent of dissolution of SPR and may reflect, in part, the fact that the concentration of Ca in the soil solution is generally several orders of magnitude greater than that of P. Results from both the glasshouse (Chapter 3) and field (Chapter 4) with the Tokomaru soil also indicate that PR materials are agronomically effective on soils of moderate to high P status. With an increase in the P-sorption capacity of a soil the effect of added P on the extent of dissolution of a PR would decline, provided other soil factors were favourable for dissolution.

A modified Mitscherlich equation formed the basis for the simple model developed to describe and predict the dissolution of PR in soil. Because c was found to be essentially constant for a given PR it was possible to predict the dissolution of a PR in other soils. This was done by establishing the relationship between A, which was found to vary markedly across the soils, and soil properties over a range of soils. Although only an initial evaluation of this simple model was possible, the promising results obtained in this initial study have initiated a more comprehensive evaluation of this approach.

To date, attempts at modelling the dissolution of PR materials in soil have been restricted to two studies (Chien et al., 1980a; Chien et al., 1980b). In both these studies a modified Elovich equation:

$$Ct = Co - (\frac{1}{\beta})\ln(\alpha\beta) - (\frac{1}{\beta}) \ln t,$$

was used to describe the dissolution of PR in soil. In the equation, C_t is the P concentration in a water extract at time t, Co is the maximum P concentration in the water extract when t → o, and α and β are constants. Although the NaOH extraction procedure, used in the present study, provides a more direct method for measuring the dissolution of PR in soils than the water-extraction method used by Chien et al. (1980b), the good agreement between the two studies, indicates that both models are useful for describing the dissolution of PR materials in soils. The results obtained in the present study with the modified water extraction procedure of Ryden and Syers (1977), however, suggest that the modified Elovich equation may not adequately describe the dissolution of a PR in soil, at least initially. With the low P-sorbing Wainui soil, water-extractable P was found to initially increase in the soil to which either SPR or CRP was added. Because Co is assumed to be the maximum P concentration in the water-extract when t → o and is calculated by taking a sufficiently small value of t ($^1/60$ h) to approximate time zero, the model developed by Chien et al. (1980b) to describe the dissolution of a PR in soil may be restricted to soils of moderate- and high-P sorption capacity where this assumption holds. The inclusion of only four soils of moderate to high P-sorption capacity in the present study, prevents a more comprehensive evaluation of the model developed by Chien et al. (1980a).

Although the dissolution of a PR is a prerequisite for plant uptake of P, an increase in the rate and extent of dissolution does not necessarily imply an increase in the plant availability of P, as other factors may intervene. Consequently, the simple model developed to describe and predict the dissolution of a PR in soils in the present study can not be used in isolation to predict the plant uptake of P from soils to which PR materials have been added.

SUMMARY AND CONCLUSIONS

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

1. A brief review of the literature indicates that the origin, source, and chemical composition of apatites in PR materials vary widely. An apparent failure to recognise that differences exist in the agronomic effectiveness of PR materials because of differences in apatite composition explains to a large extent the variable agronomic results obtained with PR materials as direct-application P fertilizers throughout the world.

2. In an initial evaluation in the glasshouse with four soils, CRP was found to be an effective source of P for ryegrass when compared to superphosphate over six harvests. The form and method of application of CRP were found to have a marked effect on its agronomic effectiveness. The effectiveness of CRP, when compared to superphosphate, decreased in the order of powdered and incorporated > powdered and surface applied > pelletised and surface applied > pelletised and incorporated.

3. Results from the first comprehensive, long-term field evaluation of CRP at four contrasting sites over 3 years with permanent pasture confirms and extends the findings of the preliminary glasshouse study with CRP in the powdered form. Apart from some initial differences, CRP was as effective as superphosphate at all four sites, and at two of the hill-country sites (Ballantrae and Wanganui), it showed a marked residual effect in the third year. In fact a single initial application of 70 kgP ha^{-1} of CRP was agronomically as effective in the third year as three annual applications of 35 kgP ha^{-1} as superphosphate at these two sites.

4. The origin of the marked residual effect shown by CRP at Ballantrae and Wanganui in the third year appears to result from the effect of $CaCO_3$ on the rate of release of P from the phosphorite. The presence of $CaCO_3$ in close proximity to the phosphorite probably decreases the rate of dissolution of the phosphorite by increasing the pH and Ca concentration in the solution film immediately surrounding the phosphate particle.

5. In marked contrast to the residual effect shown by CRP at Ballantrae and Wanganui, no measurable differences were found in the residual effect of CRP and superphosphate in the 2.5 years of study at Pahiatua. This suggests that at the application rates used in this study, and with the criterion used to separate initial and residual effects, the residual effect of CRP is dependent on soil type. This may reflect the dominating effect that P-sorption reactions have on the behaviour of added P on the high P sorbing Ramiha silt loam at Pahiatua.

6. Marked differences were found in the response to CRP by the grass and clover components of swards at all four sites. Whereas grass production remained relatively constant, clover production varied markedly with the form and amount of added P. This difference appears to reflect a varying sensitivity of these two plant species to available P levels in the soil. The ability of a single initial application of CRP to maintain a similar level of clover production as annual applications of superphosphate over 3 years, at both Ballantrae and Wanganui, has implications to future topdressing practises.

7. The finding that pelletised CRP was as effective as powdered CRP and superphosphate at the three hill-country sites, except for some

initial differences at Ballantrae, contrasts with the results of the preliminary glasshouse study and with the bulk of the literature, the results in which are also derived largely from glasshouse studies. This discrepancy probably results in part from the fact that in glasshouse studies a number of factors which can operate in the field and which may contribute to an increased effectiveness of a PR material, are usually excluded (e.g., earthworms).

8. Results of a glasshouse study using perennial ryegrass over seven harvests showed that earthworms increased the agronomic effectiveness of CRP by 15 to 30%. In contrast, the effect of earthworms on the agronomic effectiveness of superphosphate was restricted to initial harvests. Studies of the mechanism of incorporation of a surface-applied PR into soil by earthworms and of the ingestion of PR particles by earthworms indicate that both the burrowing and casting activity of earthworms indirectly increase the availability to ryegrass of P in the PR by improving the physical distribution and degree of contact of the PR with the soil.

9. Good agreement was found between the agronomic effectiveness of a pelletised PR in the field and in the glasshouse, when earthworms were included as a treatment in the glasshouse. In the absence of earthworms in the glasshouse comparable results were only obtained with those of the field when the PR was powdered and incorporated into the upper 2 cm of soil. Care must be taken in extrapolating the results obtained for pelletised PR materials in the glasshouse, in the absence of biological mixing, to the field situation.

10. In addition to permitting the ranking of CRP as a reactive PR along with NCPR and SPR, the results obtained from a glasshouse study, comparing the agronomic effectiveness of six P souces, across

six soils, provide the first comprehensive comparison of CRP with a range of P sources of varying agronomic effectiveness.

11. Of the conventional, single chemical-extraction procedures evaluated for assessing and predicting the agronomic effectiveness of PR materials, 2% formic acid appears to offer the most promise. For PR materials containing appreciable amounts of $CaCO_3$, however, sequential extraction appears to be necessary for assessing likely agronomic effectiveness. Of two new approaches (release of P to Fe gel and electro-ultrafiltration) evaluated, release of P to Fe gel appears to offer some potential as a method for assessing the agronomic effectiveness of PR materials of varying mineralogy; a limitation shown by all the conventional chemical extraction procedures.

12. Both the Bray and bicarbonate procedures were found to be useful indicators of short-term, plant-available P when SPR and CRP were added to three contrasting soils. Of the two, the Bray procedure accounted for more of the variability, possibly reflecting the difference in the mechanisms by which these two extractants remove P from soil. The single water-extraction procedure grossly underestimated the amount of short-term, plant-available P in the soil to which a PR was added. In contrast, this extractant provided a good estimate of the short-term, plant-available P in the soil to which superphosphate was added. This difference appears to reflect a varying initial behaviour of these two P sources on contact with soil.

13. A procedure involving a single extraction with 0.5M NaOH was developed for measuring the extent of dissolution of a PR in soil.

Because apatite minerals are largely insoluble in dilute NaOH and because this reagent extracts sorbed inorganic P, increases in 0.5M NaOH-extractable P in a soil to which a PR is added, provides a good estimate of the amount of P dissolved and retained by the soil on sorption sites.

14. In marked contrast to the decrease measured in water-, bicarbonate-, and Bray-extractable P in the soil to which SPR was added, the amount of 0.5M NaOH-extractable P increased with increasing P-sorption capacity of the soil. A high correlation (r = 0.935**) was obtained for the relationship between the dissolution of SPR, measured by NaOH extraction, and the P-sorption capacity of the six soils used. The extent of dissolution of SPR varied from 22% of added P on the low P-sorbing Tokomaru soil to 48% on the high P-sorbing Egmont soil during 90 days.

15. An attempt was made to determine the relative significance of soil chemical parameters in the dissolution of SPR in soil. Whereas increasing the P status of the Wainui soil, by the addition of KH_2PO_4, had no measurable effect on the dissolution of SPR, increasing addition of $Ca(OH)_2$ markedly decreased the dissolution of SPR in the Wainui soil. Of the decrease measured in the extent of dissolution of SPR on liming the Wainui soil, 75 to 79% of the decrease could be accounted for by the effect of Ca, which also increases on liming. Results with the Egmont soil suggest that the effect of soil pH on the extent of dissolution of a PR, can be modified by P-sorption capacity. Major emphasis has been given in the past to the importance of soil pH in influencing the dissolution of PR materials in soil. The present results suggest that pH is only one soil factor which is important in this respect.

16. A modified Mitscherlich equation formed the basis of a simple model which was developed to describe and predict the dissolution of a PR in soil. The model was developed using a range of contrasting soils and then used successfully to predict the dissolution of a PR in a series of other soils. This model appears to have good practical application and should prove to be useful in further studies of the reactions of PR materials in soils.

17. Although there appears to be considerable interest from a major New Zealand company in recovering CRP from the ocean floor, the material is not commercially available at present. The results obtained in the present study indicate that CRP has very good potential as a direct application P fertilizer for pasture and, of particular relevance to hill-country farming, it shows a good residual effect. A possible disadvantage is the relatively low P content (approximately 9%).

BIBLIOGRAPHY

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Alston, A.M., and K.W. Chin. 1974. Response of subterranean clover to rock phosphates as affected by particle size and depth of mixing in the soil. Aust. J. Exp. Agric. An. Husb. 14: 358 - 361.

Amberger, A. 1978. Experiences with soft rock phosphates for direct fertilizer application. Seminar on Phosphate Rock for Direct Application, pp. 349 - 366, Hafia, Israel.

Amberger, A., G. Summer, and R. Gutser. 1971. Dynamics of P in soft rock phosphates. Landw. Forsch. 24: 260 - 271.

Ames, L.L. Jr. 1959. The genesis of carbonate-apatites. Econ. Geol. 54: 829 - 841.

Ames, W.J., and K. Kitsuta. 1932. Availability of rock phosphate as indicated by phosphorus assimilation of plants. J. Am. Soc. Agron. 24: 103 - 122.

Andrews, K.C., A.G. Charleston, D.M. Douglas, G.R. Edwards, L. Evans, G. McSweeny, R.B. Muller, O.T. Roberts, and M.S. White. 1978. Pot experiments with phosphates: Apatites. pp. 30 - 31. Ann. Report. N.Z. Fert. Manuf. Res. Ass.

Ankorion, Y. 1978. Views on marketing of phosphate rock for direct application. Seminar on Phosphate Rock for Direct Application, pp. 426 - 447, Hafia, Israel.

Ansorge, H. 1966. Investigations on the phosphorus uptake by lupins and oats from Kola apatites and "Hyperphos". Albercht. Thaes. Arch. 10: 153 - 166. (Soils Ferts. 29(2730)).

Archer, F.C. 1978. Comparison of different forms of phosphate fertilizers. Part II: Grassland. J. Soil Sci. 29: 277 - 285.

Armiger, W.H., and M. Fried. 1957. The plant availability of various sources of phosphate rock. Soil Sci. Soc. Am. Proc. 21: 183 - 188.

Arnold, E.H. 1952. Phosphates and pasture production. N.Z. J. Agric. 85: 443.

Arrhenius, G. 1963. Pelagic Sediments. In. The Sea. Ideas and Observations on Progress on the Study of the Sea. M.H. Hill (ed.), Vol. 3, pp. 655 - 727, Wiley-Interscience Publishers Inc., New York.

Association of Official Analytical Chemists. 1960. Official Methods of Analysis, 9th ed., Sec. 2.031b.

Association of Official Analytical Chemists. 1970. Official Methods of Analysis, 12th ed., Sec. 2.042.

Bache, B.W. 1964. Aluminium and iron phosphate studies relating to soils. II. Reactions between phosphate and hydrous oxides. J. Soil Sci. 15: 110 - 116.

Ball, R., J.A.H. Inglis, and J.H. Mauger. 1976. Tactical application of fertilizer nitrogen to offset a seasonal feed shortage on a heavily stocked sheep farm in southern Hawkes Bay. Proc. N.Z. Grassland Ass. Conf. 37: 166 - 181.

Barley, K.P. 1961. Abundance of earthworms in agricultural land and their possible significance in agriculture. Adv. Agron. 30: 159 - 205.

Barley, K.P., and A.C. Jennings. 1959. Earthworms and soil fertility. III. The influence of earthworms on the availability of nitrogen. Aust. J. Agric. Res. 10: 364 - 370.

Barley, K.P., and C.R. Kleinig. 1964. The occupation of newly irrigated lands by earthworms. Aust. J. Sci. 26: 290 - 291.

Barnes, J.S., and E.J. Kamprath. 1975. Availability of North Carolina rock phosphate applied to soils. N.C. Agric. Exp. Sta. Tech. Bull. No. 229.

Barrow, N.J. 1975. The response to phosphate of two annual pasture species. I. Effect of the soil's ability to adsorb phosphate on comparative phosphate requirement. Aust. J. Agr. Res. 26: 137 - 143.

Bartholomew, R.P., and K.D. Jacob. 1933. Availability of iron, aluminium, and other phosphates. J. Ass. Official Agric. Chem. 16: 598 - 611.

Beevers, C.A., and D.B. McIntyre. 1946. The atomic structure of fluorapatite and its relation to tooth and bone material. Mineral. Mag. 27: 254 - 257.

Bengtson, G.W., E.C. Sample, and S.E. Allen. 1974. Response of slash pine seedlings to P sources of varying citrate-solubility. Plant and Soil. 40: 83 - 96.

Bennett, O.L., L.E. Ensminger, and R.W. Pearson. 1957. The availability of phosphorus in various sources of rock phosphate as shown by greenhouse studies. Soil Sci. Soc. Am. Proc. 21: 521 - 524.

Booth, A.K. 1956. Topdressing in Waimarino Country. N.Z. J. Agric. 90: 497 - 499.

Boswell, C.C. 1977. Effects of cutting regime on pasture production. N.Z. J. Exp. Agric. 5: 403 - 408.

Boxma, R. 1977. Evaluation of phosphate in fertilizers by means of the alkaline ammonium citrate extraction according to Petermann. Neth. J. Agric. Sci. 25: 42 - 50.

Bray, R.H., and L.T. Kurtz. 1945. Determination of total, organic and available forms of phosphorus in soils. Soil Sci. 59: 39 - 45.

Bremner, J.M. 1965. Total Nitrogen. In. Methods of Soil Analysis. C.A. Black et al. (eds) Agron. 9: 1149 - 1176, Am. Soc. Agron., Madison, Wisc.

Bremner, J.M., and D.S. Jenkinson. 1960. Determination of organic carbon in soil. I. Oxidation by dichromate of organic matter in soil and plant materials. J. Soil Sci. 11: 394 - 402.

Bromfield, S.M. 1967. Phopshate sorbing sites in acid soils. I. An examination of the use of ammonium fluoride as a selective extractant for aluminium-bound phosphate in soils. Aust. J. Soil Res. 5: 93 - 102.

Brougham, R.W., D.A. Grant, and V.C. Goodall. 1973. The occurrence of brown-top in the Manawatu. Proc. N.Z. Grassland Ass. Conf. 35: 86 - 94.

Brown, W.E., and J.R. Lehr. 1959. Application of phase rule to the chemical behaviour of monocalcium phosphate in soils. Soil Sci. Soc. Am. Proc. 23: 7 - 12.

Buchan, J.A.J., F.B. Muller, J. Rogers, R.M. Seager, and T.A. Yong. 1970. Agronomic use of calcined Christmas Island iron/aluminium phosphates. II. Pot trials. N.Z. J. Agric. Res. 13: 465 - 480.

X Buckenham, M.H., J. Rogers, and J.E. Rouse. 1971. Assessment of Chatham Rise phosphorites. Proc. Australasian Inst. Mining Metall. Ann. Conf. 8: 1 - 13.

Cano Ruiz, J., and O. Talibudeen. 1957. Surface properties of phosphate materials by isotopic exchange. I. Rock phosphate. J. Sci. Food Agric. 8: 305 - 308.

Caro, J.H., and W.L. Hill. 1956. Characteristics and fertilizer value of phosphate rock from different fields. J. Agric. Food Chem. 4: 684 - 687.

Cayeux, Lucien. 1941. Les phosphates de chaux sédimentaires de France et d'Outre-Mer. L'Afrique Septentrionale. 2: 351 - 659. (Cited by McKelvey et al. 1953).

Cescas, M.P., and E.H. Tyner. 1976. Rate of rock phosphate disappearance for the Morrow plots. Ann. Agron. 27: 891 - 924.

Chang, S.C., and M.L. Jackson. 1957. Fractionation of soil phosphorus. Soil Sci. 84: 133 - 144.

Cheney, T.M., G.H. McClellan, and E.S. Montgomery. 1979. Sechura phosphate deposits, their stratigraphy, origin, and composition. Econ. Geol. 74: 232 - 259.

Chien, S.H. 1977. Dissolution of phosphate rocks in a flooded acid soil. Soil Sci. Soc. Am. J. 41: 1106 - 1109.

Chien, S.H. 1978. Interpretation of Bray I extractable phosphorus from acid soil treated with phosphate rocks. Soil Sci. 126: 34 - 39.

Chien, S.H. 1979. Dissolution of phosphate rock in acid soils as influenced by nitrogen and potassium fertilizers. Soil Sci. 127: 371 - 376.

Chien, S.H. and L.L. Hammond. 1978a. A comparison of various laboratory methods for predicting the agronomic potential of phosphate rocks for direct application. Soil Sci. Soc. Am. J. 42: 935 - 939.

Chien, S.H., and L.L. Hammond. 1978b. A simple chemical method for evaluating the agronomic potential of granulated phosphate rock. Soil Sci. Soc. Am. J. 42: 615 - 617.

Chien, S.H., and G.H. McClellan. 1977. Variation of the Apatite Composition in Phosphate Rock and its Relationship to Rock's Chemical Reactivity and Agronomic Effectiveness. Paper, presented at Conf. on Classification and Management of Tropical Soils, 25 pp., Kuala Lumpur, Malaysia.

Chien, S.H., W.R. Clayton, and G.H. McClellan. 1980a. Kinetics of dissolution of phosphate rocks in soils. Soil Sci. Soc. Am. J. 44: 260 - 264.

Chien, S.H., L.A. Leon, and H.R. Tejeda. 1980b. Dissolution of North Carolina phosphate rock in acid Colombian soils as related to soil properties. Soil Sci. Soc. Am. J. 44: 1267 - 1271.

Chu, C.R., W.W. Moschler, and G.W. Thomas. 1962. Rock phosphate transformations in acid soils. Soil Sci. Soc. Am. Proc. 26: 476 - 478.

Cooke, G.W. 1956. The value of rock phosphates for direct application. Emp. J. Exp. Agr. 24: 295 - 306.

Cottier, K. 1952. Trials with Nauru rock phosphate as pasture topdressing. N.Z. J. Agric. 84: 183 - 189.

Crossley, D.A., D.E. Reichle, and C.A. Edwards. 1971. Intake and turnover of radioactive calcium by earthworms (Lumbricidae). Pedobiol. 11: 71 - 76.

Cullen, D.J. 1979. Mining minerals from the sea floor: Chatham Rise phosphorite. N.Z. Agric. Sci. 13: 85 - 91.

Cullen, D.J. and R.J. Singleton. 1977. The distribution of submarine phosphorite deposits on central Chatham Rise, east of New Zealand. I. Surface distribution from under water photographs, 24 pp. N.Z. Oceanagr. Inst. Oceanogs. Field Report, 10.

Cullen, N.A. 1958. A comparison of phosphatic fertilisers. N.Z. J. Agr. Res. 1: 418 - 431.

Darwin, C. 1881. The Formation of Vegetable Mould through the Action of Worms, with Observations on their Habits, Murray, London, 326 pp.

Dash, M.C., and U.C. Patra. 1979. Worm cast production and nitrogen contribution to soil by a tropical earthworm population from a grassland site in Orissa, India. Révue d'ecol. Biol. due Sol. 16: 79 - 83.

Davis, K.A. 1947. The phosphate deposits of the eastern province, Uganda. Econ. Geol. 42: 137 - 146.

Deer, W.A., R.A. Howie, and J. Zussman. 1966. In An Introduction to Rock Forming Minerals. Longmans, London, pp. 504 - 510.

Degens, E.T. 1965. Geochemistry of Sediments. Prentice-Hall, Inc. Englewood Cliffs, New Jersey, 342 pp.

Deist, J., P.G. Marais, R.B.A. Harry, and C.F.G. Heyns. 1971. Relative availability of rock phosphate to different plant species. Agrochemophysica 3: 35 - 40.

de Keyser, F., and I.R. Mcleod. 1968. Geological environment of Australian deposits of phosphate and gypsum. Proc. Sem. Sources of Mineral Raw Materials Fert. Indus. Asia and Far East. pp. 109 - 119. United Nations Resources Development Series. No.32.

Doak, B.W., P.J. Gallaher, L. Evans, and F.B. Muller. 1965. Low temperature calcination of "C" grade phosphate from Christmas Island. N.Z. J. Agric. Res. 8: 15 - 29.

Drake, M., J. Vengris and W.G. Colby. 1951. Cation exchange capacity of plant roots. Soil Sci. 72: 139 - 147.

Duncan, A.A. 1953. Phosphatic fertilisers. Wanganui and Raetihi trials. N.Z. J. Agric. 87: 367.

During, C. 1953. Phosphatic fertilisers: Nauru rock phosphate. N.Z. J. Agric. 87: 367.

During, C. 1967. Fertilizers and Soils in New Zealand Farming. Government Printer, Wellington, 322 pp.

During, C. 1972. Fertilizers and Soils in New Zealand Farming. Government Printer, Wellington, 312 pp.

Edwards, C.A., and G.W. Heath. 1963. The role of soil animals in breakdown of leaf material. In Soil Organisms. J. Doeksen and J. van der Drift (eds.) pp. 76 - 80, North-Holland, Amsterdam.

Edwards, C.A., and J.R. Lofty. 1972. Biology of Earthworms. Chapman and Hall, London, 283 pp.

Edwards, C.A., and J.R. Lofty. 1977. Biology of Earthworms. Chapman and Hall, London, 2nd Ed., 333 pp.

Edwards, C.A., and J.R. Lofty. 1978. The influence of arthropods and earthworms upon root growth of direct drilled cereals. J. Appl. Ecol. 15: 789 - 795.

Edwards, C.A., and J.R. Lofty. 1980. Effects of earthworm inoculation upon the root growth of direct drilled cereals. J. Appl. Ecol. 17: 533 - 543.

Elliot, J.C. 1969. Recent progress in the chemistry, crystal chemistry, and structure of the apatites. Calc. Tiss. Res. 3: 293 - 307.

Elliot, I.L., and P.B. Lynch. 1958. Techniques of measuring pasture production in fertiliser trials. N.Z. J. Agric. Res. 1: 498 - 521.

Ellis, R.M., R.A. Ouader, and E. Truog. 1955. Rock phosphate availability as influenced by soil pH. Soil Sci. Soc. Am. Proc. 19: 484 - 487.

Englestad, O.P., J.G. Getsinger, and P.J. Stangel. 1972. Tailoring of fertilizers for rice. Bulletin Y-52, 56 pp., National Fertilizer Development Centre, T.V.A., Muscle Shoals, Alabama.

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

Ensminger, L.E., R.W. Pearson, and W.H. Armiger. 1967. Effectiveness of rock phosphate as a source of phosphorus for plants. U.S. Dept. Agric. ARS, pp. 41 - 125, Washington, D.C.

Fassbender, H.W. 1965. Die Düngewirkung des Peruroh-phosphates im Vergleich mit anderen Phosphatdungemitteln. Agrochimica. 10: 18 - 53.

Fenster, W.E., and L.A. Leon. 1978. Utilization of phosphate rock in tropical soils of Latin America. (A research proposal). Seminar Phosphate Rock for Direct Application. pp. 174 - 210, Hafia, Israel.

Fivey, M.P. 1937. The apatite deposits of the Khibinian tundras. Trans. Sci. Inst. Fertilizers Insectofungicides U.S.S.R. 142: 8 - 21.

Fried, M. 1953. The feeding power of plants for phosphates. Soil Sci. Soc. Am. Proc. 17: 357 - 359.

Gilkes, R.J., and B. Palmer. 1979. Calcined Christmas Island C-grade rock phosphate fertilizers: Mineralogy properties, reversion and assessment by chemical extraction. Aust. J. Soil Res. 17: 467 - 481.

Gilkes, R.J., and R. Lin-Nunez. 1980. Poorly soluble phosphates in Australian superphosphate: their nature and availability to plants. Aust. J. Soil Res. 31: 85 - 95.

Gillingham, A.G. 1978. Phosphorus Cycling in Grazed, Steep Hill Country. Ph.D. Thesis, Massey University, 293 pp.

Gillingham, A.G., and C. During. 1973. Pasture production and transfer of fertility within a long-established hill pasture. N.Z. J. Exp. Agric. 1: 227 - 232.

Glasby, G.P., and C.P. Summerhayes. 1975. Sequential deposition of authigenic marine minerals around New Zealand: palaeoenvironment significance. N.Z. J. Geol. Geophy. 18: 477 - 490.

Graff, O. 1970. Phosphorus content of earthworm casts. Landbauforschung Völkenrode. 20: 33 - 36.

Graham, E.R. 1955. Availability of natural phosphorus according to energy changes. Soil Sci. Soc. Am. Proc. 19: 26 - 29.

Grant, D.A., and M.G. Lambert. 1979. Nitrogen fixation in pasture V. Unimproved North Island Hill country, "Ballantrae". N.Z. J. Exp. Agric. 7: 19 - 22.

Gregg, P.E.H. 1974. Efficient fertilizer use. Sheepfarming Ann. 15 - 20.

Gregg, P.E.H., J.K. Syers, and A.D. Mackay. 1981. Agronomic effectiveness of reactive phosphate rocks in hill country pastures. Proc. Tech. Workshop on Potential of Phosphate Rock as a Direct Application Fertilizer in New Zealand, pp. 4 - 10, Massey University, Palmerston North, Occasional Report No. 3.

Grigg, J.L. 1968. Prediction of plant response to fertilizers by means of soil tests. II. Correlations between soil phosphate tests and phosphate responses of ryegrass grown in pot experiments on recent, gley recent and gley soils. N.Z. J. Agric. Res. 11: 345 - 358.

Grigg, J.L. and G. Crouchley. 1980. Relative efficiency of phosphatic fertilizers in pasture topdressing II. On a Kokotau silt loam. N.Z. J. Agric. Res. 23: 49 - 65.

Hagin, J., T. Reinhorn, and S. Axelrod. 1978a. Comparison of finely ground phosphate rocks as P sources to plants. Seminar on Phosphate Rock for Direct Application, pp. 246 - 264, Hafia, Israel.

Hagin, J., T. Reinhorn, and S. Axelrod. 1978b. Effect of grinding on Arad phosphate rock availability. Seminar on Phosphate Rock for Direct Application, pp. 395 - 401, Hafia, Israel.

Hammond, L.L. 1978. Agronomic measurements of phosphate rock effectiveness. Seminar on Phosphate Rock for Direct Application, pp. 147 - 173, Hafia, Israel.

Hammond, L.L., and L.A. Leon. 1977. Annual Report. Centro Internacional de Agricultura Tropical, Cali, Colombia.

Hammond, L.L., R.H. Howeler, and E.C. Doll. 1976. Effectiveness of phosphate rocks in Colombia soils as measured by crop response and soil phosphorus levels. Agron. Abstr. p 146.

Hausenbuiller, R.L., and W.M. Weaver. 1960. A comparison between greenhouse and field procedures in phosphate fertilizer testing. Soil Sci. 90: 298 - 301.

Hill, W.L., J.H. Caro, and G.A. Wieczorek. 1954. Phosphate evaluation. Surface area of natural and processed phosphates. J. Agric. Food Chem. 2: 1273 - 1277.

Hoffman, E., and D. Mager. 1953. Solubility of phosphoric acid and phosphate rocks. Z. Pflanzen. Duengung u. Bodenkunde. 62: 262 - 264.

Hoffman, W.M. and H.J. Breen. 1964. Phosphate rock solubilization by repeated extractions with citrate solutions. J. Agric. Food Chem. 12: 344 - 346.

Hope, G.D. 1977. Interactions of Molybdate and Phosphate with Soils. Ph.D. Thesis, Massey University, 258 pp.

Hopkins, J.M. 1953. Phosphatic fertilizers: Horowhenua trials. N.Z. J. Agric. 87: 367.

Hopp, H., and C.S. Slater. 1949. The effect of earthworms on the productivity of agricultural soil. J. Agric. Res. 78: 325 - 339.

Howeler, R.M., and C.M. Woodruff. 1968. Dissolution and availability to plants of rock phosphates of igneous and sedimentary origins. Soil Sci. Soc. Am. Proc. 32: 79 - 82.

Hunt, O.J., and R.E. Wagner. 1963. Effects of management practises on yield and composition of three grass-legume mixtures. Agron. J. 55: 13 - 16.

Hutchinson, G.E. 1950. The biogeochemistry of vertebrate excretion. Am. Mus. Nat. Hist. Bull. 96, 554 pp.

Jackman, R.H., and M.C.H. Mouat. 1972a. Competition between grass and clover for phosphate. I. Effect of browntop (Agrostis tenuis Sibth) on white clover (Trifolium repens L.) growth and nitrogen fixation. N.Z. J. Agric. Res. 15: 653 - 666.

Jackman, R.H., and M.C.H. Mouat. 1972b. Competition between grass and clover for phosphate. II. Effect of root activity, efficiency of response to phosphate, and soil moisture. N.Z. J. Agric. Res. 15: 653 - 666.

Jacob, K.O., and W.H. Ross. 1932. Commercial Fertilizer Yearbook, 46: 19 - 26.

Jones, U.S. 1948. Availability of phosphorus in rock phosphate as influenced by potassium and nitrogen salts, lime, and organic matter. Am. Soc. Agron. 40: 765 - 770.

Joos, L.L., and C.A. Black. 1950. Availability of phosphate rock as affected by particle size and contact with bentonite and soil of different pH values. Soil Sci. Soc. Am. Proc. 15: 69 - 75.

Juo, A.S.R., and B.T. Kang. 1978. Availability and transformation of rock phosphates in three forests soils from southern Nigeria. Commun. Soil Sci. Plant Analysis 9: 493 - 505.

Karlovsky, J. 1958. Pasture responses to phosphatic fertilizers. N.Z. J. Agric. Res. 1: 51 - 60.

Karlovsky, J. 1961. Superphosphate superior to rock phosphate for pasture topdressing. N.Z. J. Agric. 103: 81 - 82.

Karlovsky, J. 1966. Assessing fertilizer maintenance requirements. Proc. Ruakura Farmers Conf. 115 - 126.

Karlovsky, J. 1975. Phosphorus utilization from solid and liquid fertilizers. N.Z. Fert. J. 45: 3 - 5.

Kay, M.I., R.A. Young, and A.S. Posner. 1964. Crystal structure of hydroxyapatite. Nature 204: 1050 - 1052.

Kazakov, A.V. 1937. The phosphorite facies and the genesis of phosphorites. In Geological Investigations of Agricultural Ores, U.S.S.R. Sci. Inst. Fertilizers and Insectofungicides Trans. 139: 3 - 73.

Khasawneh, F.E., and E.C. Doll. 1978. The use of phosphate rock for direct application to soils. Adv. Agron. 30: 159 - 206.

Knight, P.J., and G.M. Will. 1971. Pot trial evaluation and comparison of six potential sources of phosphate for forestry. N.Z. J. Forest Sci. 1: 22 - 36.

Kramer, M., and I. Lamberger. 1965. Hungarian data on the efficienty of rock phosphates. Magy. Tud. Akad. Agrar tud. Osztal. Kozl. 24: 411 - 416. (Soils Ferts. 29(1293)).

Lambert, M.G., and D.A. Grant. 1980. Fertilizer and lime effects on some sourthern North Island hill pastures. N.Z. J. Exp. Agric. 8: 223 - 229.

Landergren, S. 1962. In. Geochemistry. A. Muir (ed.), pp. 468 - 475, Clarendon, Oxford.

Ledgard, S.F., T.E. Ludecke, A.S. Black, and R.D. Mclenaghen. 1981. Responses by white clover to two application methods of superphosphate, Calciphos, and a blend on two soils of contrasting phosphate-fixing capacity. N.Z. J. Exp. Agr. 9: 161 - 167.

Le Geros, R.Z., O.R. Trantz, J.P. Le Geros, and E. Klein. 1967. Apatite crystallites: Effects of carbonate on morphology. Science 155: 1409 - 1411.

Lehr, J.R., and G.H. McClellan. 1972. A revised laboratory reactivity scale for evaluating phosphate rocks for direct application. Bull. Y-43, 36 pp., Tennessee Valley Authority. Muscle Shoals, Alabama.

Lehr, J.R., G.H. McClellan, J.P. Smith, and A.W. Fraizer. 1967. Characterisation of apatites in commercial phosphate rocks. Proc. Int. Colloq. Solid Inorg. Phosphates 12: 29 - 44.

Lindsay, W.L., J.R. Lehr, and H.F. Stephenson. 1959. Nature of the reaction of monocalcium phosphate monohydrate in soils: III. Studies with the metastable triple-point solution. Soil Sci. Soc. Am. Proc. 23: 243 - 245.

Luscombe, P.C. 1976. Evaluation of the Potential of Water Extraction of Soil Phosphate for Use in a Soil Test Procedure. B.Agr. Sc. (Hons.) Thesis, Massey University, 82 pp.

Luscombe, P.C. 1980. Nitrogen fertilizer responses on hill country pastures. Proc. N.Z. Grassland Ass. Conf. 41: 155 - 162.

Luscombe, P.C., J.K. Syers, and P.E.H. Gregg. 1979. Water extraction as a soil testing procedure for phosphate. Commun. Soil Sci. Plant Analysis 10: 1361 - 1369.

Lynch, P.B. 1951. Alternative fertilisers to superphosphate. N.Z. J. Agric. 83: 420 - 428.

Mackay, A.D., P.E.H. Gregg, and J.K. Syers. 1980. A comparison of dicalcium phosphate and single superphosphate as phosphate sources for pasture. N.Z. J. Exp. Agric. 8: 7 - 11.

Mansell, G.P., J.K. Syers, and P.E.H. Gregg. 1981. Plant availability of phosphorus in dead herbage ingested by surface-casting earthworms. Soil Biol. Biochem. 13: 163 - 167.

Marais, P.G., J. Deist, R.B.A. Harry, and C.F.G. Heyns. 1970. Ability of different plant species to absorb phosphates. Agrochemophysica. 2: 7 - 12.

Mattingly, G.E.G. 1968. Evlaution of phosphate fertilizers. II. Residual value of nitrophosphates, Gafsa rock phosphate, basic slag and potassium metaphosphate for potatoes, barley and swedes grown in rotation, with special reference to changes in soil phosphorus status. J. Agric. Sci. (Camb.) 70: 139 - 156.

Mauger, J.H. 1977. Selective topdressing in hill country. N.Z. J. Agric. 134: 40 - 42.

McClellan, G.H., and J.R. Lehr. 1969. Crystal chemical investigation of natural apatites. Am. Min. 54: 1374 - 1391.

McConnell, D. 1938. A structural investigation of the isomorphism of the apatite group. Am. Min. 23: 1 - 19.

McConnell, D. 1962. Dating of fossil bones by the fluorine method. Science. 136: 241 - 244.

McKelvey, V.E., J.B. Cathcart, Z.S. Attschuler, R. Swanson, and K.L. Buck. 1953. Domestic phosphate deposits. In. Soil and Fertiliser Phosphorus in Crop Nutrition, pp. 347 - 376, Agronomy Monograph IV, Academic Press, New York.

McKelvey, V.E. 1973. Abundance and distribution of phosphorus in the lithosphere. In Environmental Phosphorus Handbook. E.J. Griffith, A. Beeton, J.M. Spencer, and D.T. Mitchell (eds.), pp. 13 - 31, John Wiley and Sons, New York.

Mclaughlin, J.R., and J.K. Syers. 1978. Stability of ferric phosphates. J. Soil Sci. 29: 499 - 504.

Mclaughlin, J.R., J.C. Ryden and J.K. Syers. 1977. Development and evaluation of a kinetic model to describe phosphate sorption by hydrous ferric oxide gel. Geoderma. 18: 295 - 307.

Mclean, E.O., and J.E. Hoelscher. 1954. Factors affecting yields and uptake of phosphorus by different crops. I. Previous applications to the soil of rock phosphate and superphosphate. Soil Sci. 78: 453 - 462.

Mclean, E.O., and T.J. Logan. 1970. Sources of phosphorus for plants grown in soils of differing phosphorus fixation tendencies. Soil Sci. Soc. Am. Proc. 34: 907 - 911.

Middleton, K.R., and M.R.J. Toxopeus. 1973. Diagnosis and measurement of multiple soil deficiencies by a subtractive technique. Plant and Soil 38: 219 - 226.

Mokwunye, A.U. 1979. Evaluation of three phosphate sources applied to maize at Samaru. Trop. Agric. 56: 65 - 68.

Mokwunye, A.U., and S.H. Chien. 1980. Reaction of partially acidulated phosphate rock with soils from the tropics. Soil Sci. Soc. Am. J. 44: 477 - 482.

Monroe, W.H. 1941. Notes on deposits of Selma and Ripley age in Alabama. Alabank Geol. Survey Bull. 48, 150 pp.

Muller, F.B. 1970. Agronomic use of calcined Christmas Island iron/aluminium phosphates. I. Field trials. N.Z. J. Agric. Res. 13: 452 - 464.

Murphy, J., and J.P. Riley. 1962. A modified single solution method for the determination of phosphates in natural waters. Anal. Chim, Acta 27: 31 - 36.

Nemeth, K. 1972. The determination of desorption and solubility rates of nutrients in the soil by means of electro-ultrafiltration (EUF). Proc. 9th Colloq. Int. Potash Inst. 171 - 180.

Nemeth, K. 1976. Die effektive und potentielle Nährstoffver fügbarkeit im Boden und ihre Bestimmung mit Elektro-Ultrafiltration (EUF). Habilitation Sschrift, Justus. Liebig Universität, Giessen.

Nemeth, K. 1980. The availability of nutrients in the soil as determined by electro-ultrafiltration (EUF). Adv. Agron. 31: 155 - 188.

Newesley, H. 1963. Die Realstruktur der Oktocalcium-phosphat. Monatsh Chem. 95: 94 - 101.

New Zealand Fertiliser Statistics. 1981. Econ. Div. Min. Agr. Fish. Seventh publication, 32 pp.

Nielson, R.L. 1953. Earthworms. N.Z. J. Agric. 86: 74.

Norris, R.M. 1964. Sediments of Chatham Rise. Mem. N.Z. Oceanogr. Inst. 26, 36 pp.

Obigbesan, G.O., and K. Mongel. 1981. Use of electro-ultrafiltration (EUF) method for investigating the behaviour of phosphate fertilizers in tropical soils. Fert. Res. 2: 169 - 176.

O'Connor, P.W., and J.K. Syers. 1975. Comparison of methods for the determination of total phosphorus in waters containing particulate material. J. Environ. Qual. 4: 347 - 350.

Olsen, S.R. 1952. Measurement of surface phosphate on hydroxylapatite and phosphate rock with radio phosphorus. J. Phys. Chem. 56: 630 - 632.

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L.A. Dean. 1954. Estimation of available P in soils by extraction with sodium bicarbonate. USDA Cir. 939, 19 pp.

Ozanne, P.G., J. Keay, and E.F. Biddiscombe. 1969. The comparative applied phosphate requirements of eight annual pasture species. Aust. J. Agric. Res. 20: 809 - 818.

Paauw, van der F. 1965. Factors controlling the efficiency of rock phosphates for potatoes and rye on humic sandy soils. Plant and Soil 22: 81 - 98.

Palache, C., H. Berman, and C. Frondel. 1951. *Dana's System of Mineralogy*. 7th ed., Vol. 2. 1224 pp. Wiley, New York.

Palmer, B. 1980. A chemical, mineralogical and biological evaluation of calcined Christmas Island C grade rock phosphate. Ph.D. Thesis, University of Western Australia, 322 pp.

Palmer, B., M.D.A. Bolland, and R.J. Gilkes. 1979. A re-evaluation of the effectiveness of fertilizer produced by calcination of Christmas Island C-grade rock phosphate. Aust. J. Exp. Agric. Anim. Husb. 19: 605 - 610.

Parle, J.N. 1963. A microbiological study of earthworm casts. J. Gen. Micro. 31: 13 - 22.

Pasho, D.W. 1976. Distribution and Morphology of Chatham Rise phosphorite N.Z. Ocean. Inst. Mem. 77, 28 pp.

Patterson, M.S., and R.C. Green. 1965. Measurement of low energy beta emitters in aqueous solution by liquid scintillation counting of emulsions. Anal. Chem. 37: 854 - 857.

Peaslee, D.E., C.A. Anderson, G.R. Burns, and C.A. Black. 1962. Estimation of relative value of phosphate rock and superphosphate to plants on different soils. Soil Sci. Soc. Am. Proc. 26: 566 - 570.

Pimentel, W.A.C., N.C. Schmidt, and A.Z. Do. 1962. Availability of Brazilian natural phosphates as affected by soil pH. Bragantia 21: 271 - 284.

Powell, C. Ll. 1979. Effect of mycorrhizal fungi on recovery of phosphate fertilizer from soil by ryegrass plants. New Phytol. 83: 1 - 14.

Powell, C. Ll., D.M. Metcalfe, J.G. Buwalda, and J.E. Waller. 1980. Phosphate response curves of mycorrhizal and non-mycorrhizal plants. II. Responses to rock phosphates. N.Z. J. Agric. Res. 23: 477 - 482.

Quin, B.F. 1981. Performance of reactive phosphate rocks on irrigated and non-irrigated pasture. Proc. Tech. Workshop on Potential of Phosphate Rock as a Direct Application Fertilizer in New Zealand. pp. 12 - 30, Massey University, Palmerston North. Occasional Report No.3.

Rajan, S.S.S. 1981a. Use of low grade phosphate rocks as biosuper fertilizer. Fert. Res. 2: 199 - 210.

Rajan, S.S.S. 1981b. "Biosuper" and phosphate rock as phosphate fertilizers. Recent studies at Ruakura. Proc. Techn. Workshop. Potential of Phosphate Rock as a Direct Application Fertilizer in New Zealand, pp. 32 - 39, Massey University, Palmerston North, Occasional Report. No.3.

Reinhorn, T., and J. Hagin. 1978. Evaluation of the Bray P1 method for measuring phosphate rock availability in soils. Seminar on Phosphate Rock for Direct Application, pp. 402 - 412, Hafia, Israel.

Reinhorn, T., J. Hagin, and S. Axelrod. 1978. Relation of phosphate rock availability to some soil properties and cultivation time. Seminar on Phosphate Rock for Direct Application, pp. 234 - 247, Hafia, Israel.

Rennes, A.M.D. 1978. Field and Laboratory Studies of the Movement and Reactions of Phosphorus in Soils. Ph.D. Thesis, Massey University, 248 pp.

Roberts, G. 1930. Effect of associated soil treatments on the availability of applied phosphorus to field crops on different soil types. J. Am. Soc. Agron. 22: 489 - 497.

Roberts, O.T., and White, M.S. 1974. Some factors affecting agronomic response to apatites and to calcined Christmas Island iron/aluminium phosphates. N.Z. J. Agric. Res. 17: 479 - 484.

Robertson, W.K., L.G. Thompson, Jr., and C.E. Hutton. 1966. Availability and fractionation of residual phosphorus in soils high in aluminium and iron. Soil Sci. Soc. Am. Proc. 30: 446 - 450.

Russell, E.J. 1910. The effect of earthworms on soil productiveness. J. Agric. Sci. 2: 245 - 257.

Ryden, J.C., and J.K. Syers. 1977. Origin of the labile phosphate pool in soils. Soil Sci. 123: 353 - 361.

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

Ryden, J.C., J.K. Syers and P.E.H. Gregg. 1976. A new understanding of the nature and persistence of labile phosphate in soils: Implications to soil testing. Reviews in Rural Sci. 3: 55 - 67.

Salomon, M., and J.B. Smith. 1956. Residual soil phosphorus from various fertilizer phosphates extracted by different solvents. Soil Sci. Soc. Am. Proc. 20: 33 - 36.

Sarangamath, P.A., B.N. Shinde, and S. Patnaik. s 1975. Efficiency of water-soluble, citric acid-soluble and insoluble phosphate fertilizers for rice in different soils. Indian J. Agric. Sci. 45: 106 - 111.

Sarangamath, P.A., B.N. Shinde, and S. Patnaik. 1977. Effect of application of water- and citrate-soluble and insoluble phosphates on the trasnformation of inorganic P fractions and its relation with available P in different soils. Indian J. Agric. Sci. 47: 309 - 313.

Satchell, J.E. 1955. Some aspects of earthworm ecology. In Soil Zoology. D.K. McE. Devan (ed.), pp. 180 - 199, Butterworth, London.

Satchell, J.E. 1958. Earthworm biology and soil fertility. Soils and Fert. 21: 209 - 219.

Satchell, J.E. 1967. Lumbricidae. In Soil Biology. A Burges and F. Raws (eds.), pp. 259 - 322, Academic Press, London.

Saunders, W.M.H. 1965. Phosphate retention by New Zealand soils and its relationship to free sesquioxides, organic matter and other soil properties. N.Z. J. Agric. Res. 8: 30 - 57.

Scott, R.S. 1957. Phosphate trials at Invermay. N.Z. J. Agric. 95: 263.

Scott, R.S., and N.A. Cullen. 1965. Some residual effects of phosphatic fertilisers. N.Z. J. Agric. Res. 8: 652 - 666.

Shand, S.J. 1932. The granite-syenite-limestone complex of Palabora, E. Transval. Trans. Geol. Soc. S. Africa 34: 81 - 105.

Sharpley, A.N., and J.K. Syers. 1976. Potential role of earthworm casts for the phosphorus enrichment of runoff waters. Soil Biol. Biochem. 8: 341 - 346.

Sharpley, A.N., and J.K. Syers. 1977. Seasonal variation in casting activity and in the amounts and release to solution of phosphorus forms in earthworm casts. Soil Biol. Biochem. 9: 227 - 231.

Shinde, B.N., P.A. Sarangamath, and S. Patnaik. 1978. Phosphorus transformations from rock phosphates in acid soils and measures for increasing their efficiency for growing rice (Oryza sativa L.) Plant and Soil 49: 449 - 459.

Silverman, S.R., R.K. Fuyat, and J.D. Weiser. 1952. Quantitative determination of calcite associated with carbonate-bearing apatites. Am. Min. 37: 211 - 222.

Simpson, D.R. 1964. The nature of alkali carbonate apatites. Am. Min. 49: 363 - 376.

Smillie, G.W., and J.K. Syers. 1972. Calcium fluoride formation during extraction of calcareous soils with fluoride: II. Implications to the Bray P-1 Test. Soil Sci. Soc. Am. Proc. 36: 25 - 30.

Smith, R.W., and G.I. Whitlatch. 1940. The phosphate resources of Tennessee. Tenn. Dept. Conserv. Div. Geol. Bull. 48. pp. 444.

Smith, F.W., and J. Grava. 1958. Availability of phosphorus contained in phosphatic shale compared to that contained in monocalcium phosphate and raw rock phosphate. Soil Sci. 86: 313 - 318.

Smith, J.P., and J.R. Lehr. 1966. An X-ray investigation of carbonate apatite. J. Agric. Food Chem. 14: 343 - 349.

Smith, R.G. 1979. A Comparison of Two Phosphorus Soil Tests as Inputs to a Pasture Growth Model. M.Agric.Sci. Thesis, Massey University, 179 pp.

Smyth, T.J., and P.A. Sanchez. 1982. Phosphate rock dissolution and availability in Cerrado soils as affected by phosphorus sorption capacity. Soil Sci. Soc. Am. J. 46: 339 - 345.

Springett, J.A. 1981. A new method for extracting earthworms from soil cores with a comparison of four commonly used methods for estimating earthworm numbers. Pedobiol. 21: 213 - 218.

Stanford, G., and J.D. De Ment. 1957. A method for measuring short-term nutrient absorption by plants. I. Phosphorus. Soil Sci. Soc. Am. Proc. 21: 612 - 617.

Stephens, A., and J. Lipsett. 1975. Effect of pelletising on availability of phosphate in calcined C-grade rock phosphate from Christmas Island. Aust. CSIRO Div. Plant Ind. Field 5th Rec. 14: 9 - 15.

Stockdill, S.M.J. 1959. Earthworms improve pasture growth. N.Z. J. Agric. 98: 227 - 233.

Stockdill, S.M.J. 1966. The effect of earthworms on pastures. Proc. N.Z. Ecol. Soc. 13: 68 - 74.

Suckling, F.E.T. 1959. Pasture management trials, on unploughable hill country at Te Awa. 2. Results for 1951 - 1957. N.Z. J. Agric. Res. 2: 488 - 542.

Suckling, F.E.T. 1975. Pasture management trials on unploughable hill country at Te Awa. N.Z. J. Exp. Agric. 3: 351 - 436.

Syers, J.K. 1974. Effect of phosphatic fertilizers on agriculture and the environment. N.Z. Agric. Sci. 8: 149 - 164.

Syers, J.K., A.N. Sharpley, and D.R. Keeney. 1979. Cycling of nitrogen by surface-casting earthworms in a pasture ecosystem. Soil Biol. Biochem. 11: 181 - 185.

Syers, J.K., G.W. Smillie, and J.D.H. Williams. 1972. Calcium fluoride formation during extraction of calcareous soils with fluoride. I. Implications to inorganic P fractionation schemes. Soil Sci. Soc. Am. Proc. 36: 20 - 25.

Syers, J.K., M.E. Sumner, and A.N. Sharpley. 1981. Chemistry of lime-phosphorus interactions in four acid soils. In. Proc. "Soils with Variable Charge" Conf., pp. 98 - 99, Massey University, Palmerston North.

Terman, G.L., U.J. Kilmer, and S.E. Allen. 1969. Reactivity of phosphate rocks with acids in relation to effectiveness for crops. Phos. Agric. 54: 1 - 9.

Terman, G.L., S.E. Allen, O.P. Engelstad. 1970. Response of paddy rice to rate and sources of applied phosphorus. Agron. J. 62: 390 - 394.

The Fertilisers Regulations. 1969. Document 1969/88. Government Printer, Wellington, 34 pp.

Twine, J.R., and C.H. Williams. 1971. The determination of phosphorus in Kjeldahl digests of plant material by automatic analysis. Commun. Soil Sci. Plant Analysis. 2: 485 - 489.

Vimmerstedt, J.P., and J.H. Finney. 1973. Impact of earthworm introduction on litter burial and nutrient distribution on Ohio strip-mine spoil banks. Soil Sci. Soc. Am. Proc. 37: 388 - 391.

Vol'fkovich, S. 1945. Novyye resursy tu kovoi promshlennosti. (Fosfority Kara-Tau) Planovoye Khozyaistuo, Moscow. 5: 48 - 60. (Cited by McKelvey et al. 1953).

Walker, T.W., B.K. Thapa, A.F.R. Adams. 1959. Studies on soil organic matter. 3. Accumulation of carbon, nitrogen, sulfur, organic and total phosphorus in improved grassland soils. Soil Sci. 87: 135 - 140.

Warin, O.N. 1968. Deposits of phosphate rocks in Oceania. In Proc. Sem. Sources Mineral Raw Materials Fert. Ind. Asia and the Far East. U.N. Mineral Res. Devel. Ser. No.32: 124 - 132.

Watanabe, F.S., and S.R. Olsen. 1965. Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. Soil Sci. Soc. Am. Proc. 29: 677 - 678.

Waters, R.A.S. 1951. Earthworms and the fertility of pasture. Proc. N.Z. Grassland. Ass. 13: 168 - 175.

White, M.L. 1976. Compounds formed in the manufacture of superphosphates from the phosphates of Christmas and Nauru Islands and Queensland. N.Z. J. Sci. 19: 421 - 431.

Williams, J.D.H., J.K. Syers, and T.W. Walker. 1967. Fractionation of soil inorganic phosphate by a modification of Chang and Jackson's procedure. Soil Sci. Soc. Am. Proc. 31: 736 - 739.

Wolten, K.M. 1963. An investigation into the simulation of nutrient returns by the grazing animal in grassland experimentation. J. Br. Grassland Soc. 18: 213 - 219.

Wong You Cheong, Y. 1966. The availability of rock phosphate and the effect of fineness of grinding. Mauritius Sug. Ind. Res. Inst. Ann. Rep. 12: 69 - 75.

Wright, D.N. 1975. Calcined Christmas Island C grade rock phosphate as a fertilizer. Aust. J. Exp. Agric. Anim. Husb. 15: 419 - 423.