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LIME-ALUMINIUM-PHOSPHATE INTERACTIONS
IN SELECTED ACID SOILS FROM FIJI

A thesis presented in partial fulfilment of
the requirements for the degree of
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ABSTRACT

Poor crop production in Fiji has long been associated with Al-toxicity and/or P deficiency problems. Although attempts have been made to alleviate these problems, the lack of suitable soil-testing procedures and a limited understanding of lime-Al-P interactions are restricting the better utilization of these soils.

Following a preliminary investigation, 4 contrasting Fijian soils (Batiri, Koronivia, Nadroloulou, and Seqaqa) were chosen for a lime-Al-P interaction study. The soils, which had pH and M KCl-extractable Al values ranging from 3.9 to 4.9 and 35.6 to 0.3 mmol kg⁻¹, respectively, were used to investigate the effect of liming on surface charge, P-sorption characteristics, the amounts of P extracted by a number of soil-testing procedures, and plant uptake of P.

A study was conducted to compare M KCl-extraction procedures for exchangeable Al and analytical techniques used in the determination of Al. For each soil, different extraction procedures and analytical techniques measured significantly ($P < 0.01$) different amounts of extractable Al. It was recommended that extractable Al in Fijian soils could be best determined by the oxine reagent following a 2 x 1-h shaking with M KCl.

The ion retention method, which is commonly used to measure charge, was examined critically with a view to standardising it for the range of soils used in the present study. The method involves an initial washing of soils with an electrolyte of high concentration to remove exchangeable ions, equilibration of the washed soils with an electrolyte of the desired concentration and subsequent extraction of the equilibrated soils. The concentrations of prewash electrolyte (0.5M CaCl₂, 0.1M CaCl₂, and 0.01M CaCl₂) used to remove exchangeable ions prior to equilibration with 0.01M CaCl₂ and the soil:solution ratio were found to have a marked effect on the magnitude of the surface negative charge of unlimed soils. However, these differences were largely related to the amount of Al removed during the prewash and the equilibration procedures. Thus when the Al released in the extracting solution (0.5M KNO₃) was included in the calculation of charge, the differences in the measured negative charge obtained either because of varying concentrations of prewash electrolyte or for the effect of soil:solution ratio were reduced.

Surface charge, determined in 0.01M CaCl₂, was always found to be higher than that determined in 0.03M NaCl and this difference was more pronounced in limed soils at high pH values. Subsequent studies revealed that this anomaly was largely due to the inability of Na to exchange with Ca at high pH values. The results of these studies, together with those involving the prewash electrolytes and the soil:solution ratio, suggested that a suitable method of measuring surface charge of limed soils would use 0.01M CaCl₂ as the equilibration electrolyte and include in the calculation of charge the amount of Al released in the extracting solution.

Incubation of soils with added lime caused a large increase in surface negative charge. However, the magnitude of increase in the negative charge varied considerably between soils. For example, the negative charge in the Seqaqa soil increased from 8 to over 38 cmol(p)kg⁻¹, compared to only a small increase of 2 to 10 cmol(p)kg⁻¹ in the Batiri soil over the same pH range.

In contrast to liming, P additions resulted in only a small increase in negative charge. Interestingly, all soils possessed positive charge up to 1 cmol(p)kg⁻¹, even at pH values as high as 7. Subsequent studies showed that this may have been due to substitution of Ti⁴⁺ and/or Mn⁴⁺ in the iron oxide lattice.

Extraction of lime- and P-treated soils with Olsen and Mehlich reagents showed that liming had a marked effect on the amount of P removed. Whereas Olsen P increased on either side of pH values 5.5 - 6.0, Mehlich P consistently decreased with increasing soil pH. For example, in the high P-sorbing Seqaqa soil, Mehlich P decreased from 0.2 mmol kg⁻¹ at pH 4.5 to < 0.01 mmol kg⁻¹ in soils with pH higher than 7.0. The decrease in Mehlich P was shown to be due to the neutralizing effect of lime on the extractant. An isotopic-exchange study revealed an increase in exchangeable P up to a pH approximating 7, above which there was a sharp decrease, possibly indicating the formation of insoluble Ca-P compounds.

Although liming had only a small effect on the sorption of added P, this was sufficient to have a significant effect on equilibrium solution P concentration. Generally, liming caused an increase in equilibrium solution P concentration up to pH values of 5.0 - 6.0, above which there was a marked decrease. The initial increase in equilibrium solution P concentration appeared to result from an interaction between added P,

surface negative charge and electrostatic potential in the plane of sorption. Subsequent sorption studies using Nadroloulou soil incubated with either KOH or $\text{Ca}(\text{OH})_2$ showed that the decrease in solution P at high pH values was probably due to the formation of insoluble Ca-P compounds.

The effects of lime and P addition on the growth of the tropical legume Leucaena leucocephala were studied in a controlled-climate laboratory. With all 4 soils, there was an initial increase in the dry matter yield of the plant tops with liming which was followed by a marked decrease. This trend was most pronounced in the Seqaqa soil where dry matter yield of tops increased by ~2000% at the pH at which maximum growth occurred. Similar but smaller increases were noted in the other soils.

The concentration of Al in plant tops increased on either side of the pH of maximum growth, but Al uptake by the whole plant (tops + roots) declined steadily with increasing pH. Poor growth at low pH values was attributed to Al-induced P deficiency within the plant and at high pH values largely to a soil P deficiency and to a smaller extent to the increased concentration of Al in the plant tops. P deficiency at high pH values was attributed to the formation of insoluble Ca-P compounds and this was supported by the data obtained from isotopic-exchange and P-sorption studies.

A further plant growth study was conducted on the limed soils, previously used for the growth of Leucaena leucocephala, Ryegrass (Lolium perenne L) plants were initially grown in sand and then transferred onto the soils. Plant growth was again retarded at low and high pH values but comparison with control plants grown in a similar manner but not transferred onto the soils demonstrated that the poor growth at both high and low pH was due in part to a toxicity effect rather than simple P deficiency. It is likely that Al was responsible.

Comparison of the data obtained by resin extraction and plant P uptake gave a close 1:1 relationship. In contrast, Olsen-, Colwell-, Bray (I)-, Bray (II)-, and Mehlich-extractable P were only weakly correlated with P uptake. The difficulty in relating plant P uptake data to extractable P levels was attributed to the problems associated with extracting P from limed soils.

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CHAPTER 1

CHAPTER 1

INTRODUCTION

1.1 Introduction

Low nutrient status (e.g., P deficiency) and high concentrations of certain elements (e.g., Al, Mn) are two of the most important factors limiting crop production on highly-weathered, acid soils. Such soils are widespread in Fiji and occupy large areas of land which could potentially be used for crop production if the nutrient status could be improved. It has been estimated (Twyford and Wright, 1965) that production on these soils could be doubled by proper management but how this could be accomplished was not stated.

Phosphate deficiency results from an inadequate supply of available P at the soil-root interface (Barber, 1962). This is compounded in acid soils by a high P-sorption capacity which further limits the diffusion of P in the plant root zone. Soluble P compounds which are added to correct P deficiency react with soil minerals by precipitation (Kittrick and Jackson, 1956; Lindsay et al., 1962) and/or sorption reactions (Bache, 1964; Hsu, 1968; Syers et al., 1971; Ryden and Syers, 1977; Ryden et al., 1977a,b), and the plant availability of the added P declines rapidly. Also, high levels of exchangeable and soluble Al, Mn, and Fe further limit plant P uptake by restricting root growth and through chemical interactions with soluble P. Recent studies (Bolland et al., 1976; Gillman, 1984) showed that a considerable proportion of negative sites in strongly-acid soils are occupied by Al^{3+} . Aluminium toxicity is often manifested as P deficiency (Foy and Brown, 1964; Lowe and Bortner, 1973).

Phosphate deficiency and Al toxicity problems in acid soils have often been overcome by liming. Liming acid soils can reduce P sorption and Al toxicity by decreasing the concentration of soluble Al which could otherwise interact with fertilizer P; it also increases the net cation-exchange capacity of these soils (Wann and Uehara, 1978). However, considerable controversy exists in the literature as to the effect of liming on P sorption. It has been reported that liming

highly-weathered, acid soils can cause an increase (Griffin, 1971; Ryan and Smillie, 1975), decrease (Griffin, 1971) or not affect (Martini et al., 1974) the amount of P that can be extracted from acid soils. Furthermore, Sumner (1979) quoting the work of Amarasiri and Olsen (1973) and Janghorbani et al. (1975) suggested that a similar controversy exists in the literature on the effect of liming on plant growth. Part of the problem appears to result from the difficulty of separating direct and indirect effects of liming using either only plant data or only laboratory-based data. It is important to have an understanding of the chemical processes governing the interaction of Al and P when acid soils are limed if increased agricultural production is to be obtained.

This thesis describes studies designed to develop a better understanding of the importance of various mechanisms controlling plant-available P levels in selected, highly-weathered, acid soils from Fiji.

The study was divided into two sections. Section 1 was designed to (i) investigate the effect of liming on the chemistry of selected acid soils and (ii) examine how changes in pH, as influenced by liming, affect the P-sorption capacity and the extractability of added P from these soils. Section 2 deals with glasshouse studies in which the interaction between lime, Al, and P was examined in relation to plant growth, and the extent to which this interaction affects the availability of P as assessed by plant uptake and a range of soil-testing procedures.

CHAPTER 2

CHAPTER 2

REVIEW OF LITERATURE

2.1 Introduction

The interaction between P and soil components and the influence that this has on the concentration of P in the soil solution has been studied extensively. Several reviews relating to this subject have been published. The more recent reviews include those by Parfitt (1978), Hingston (1981), and White (1981). These reviews have dealt with the interaction between P and soil components (e.g., gibbsite, goethite, calcite, clay minerals, short-range order material, etc.) in considerable detail.

Because this thesis is concerned with lime-Al-P interactions, this literature review will emphasise: (i) the mechanisms of P retention, (ii) the chemistry of Al^{3+} , and (iii) lime-Al-P interactions.

The term retention is used to indicate both precipitation and sorption processes.

2.2 Mechanism of Phosphate Retention

Retention of P by soils is characterised by an initial rapid reaction between the substrate and solution P, followed by a slower reaction which continues for a long time without reaching any true equilibrium (Barrow & Shaw, 1975). The mechanisms involved in the retention of P have been under investigation for many years. Two different hypotheses have been proposed, namely precipitation and sorption. It is now generally believed that P can be retained by either of these processes.

Chemical precipitation and sorption processes are similar in many respects, the major difference being that sorption is a 2-dimensional process whereas precipitation is 3 dimensional (Corey, 1981). Sorption generally occurs on surfaces of minerals that are themselves precipitates. If an adsorbing species is identical to one of the component mineral ions, sorption will contribute to crystal growth, making the sorption reaction an

integral part of the precipitation process (Bache, 1964). Thus, sorption and chemical precipitation theories were generally considered together by many investigators in the 1960's (e.g., Hsu and Rennie, 1962a).

The chemical precipitation theory involves the removal of 2 or more components from a solution by their mutual combination to form a new solid-phase compound (Bache, 1964). This process can also involve the dissolution of cations from the solid phase (Cole and Jackson, 1950; Kittrick and Jackson, 1956) and the subsequent stoichiometric precipitation of these cations with P ions present in the soil solution.

Chemical precipitation processes are governed by the solubility product principle, which for a solid electrolyte M_aX_b , in equilibrium with its saturated solution at constant temperature and pressure is:



$$K_{sp} = [M^{b+}]^a [X^{a-}]^b \quad 3.2$$

The most common cations responsible for the precipitation of P are Fe^{3+} and Al^{3+} in acid solutions and Ca^{2+} and Mg^{2+} in neutral and alkaline solutions. All of these cations can form a range of compounds with P which differ in their solubilities and are sensitive to the pH of the system. The precipitation of P compounds is not possible until the ionic product of the ions exceeds the solubility product and therefore in soils it occurs only under conditions of high P concentration. The formation of Al-P compounds by precipitation has been reported by Kittrick and Jackson (1956), Hsu and Rennie (1962b) and more recently by Van Riemsdijk et al. (1975). Van Riemsdijk et al. (1975) reported the synthesis of a new P mineral when P ions were reacted with X-ray amorphous Al hydroxide. The formation of Ca-P through precipitation processes has been reported by many investigators (e.g. Cole et al., 1953; Kamprath, 1971; Holford and Mattingly, 1975; Sanchez and Uehara, 1980).

The retention of P through sorption processes involves the concentration of P ions from solution at the surfaces of a solid phase in forms that are exchangeable or replaceable (Kittrick and Jackson, 1956). Sorption theory is much older than the chemical precipitation theory. However, the difficulty in explaining the observed decrease in exchangeability or availability of P with time using simple sorption models and direct observations of the role of P in crystal formation (Parfitt, 1978), led to

the development of the chemical precipitation theory. Several workers have attempted to explain the observed decrease in exchangeability with time by postulating diffusion of P into soil particles (Cooke, 1966; Evans and Syers, 1971; Tambe and Savant, 1978). More recently, Barrow (1983b) proposed a model for describing the sorption and desorption of P by soils and this model is believed to explain the decrease in exchangeability with time. The model includes 3 components:

- (i) the reaction between divalent P ions and soil constituents,
- (ii) the assumption that there is a range of values of surface properties, and
- (iii) the assumption that the initial sorption induces a diffusion gradient towards the interior of the particle which begins a solid-state diffusion process. The important difference between this model and other models involving diffusion (Cooke, 1966; Evans and Syers, 1971; Tambe and Savant, 1978) is that it attempts to take the change in surface charge into account (Bolan, 1983).

Sorption processes can be separated broadly into 2 groups, depending on the affinity of the adsorbent for the adsorbates. When anions are bound by electrostatic forces, simply to balance the positive charge on oxide surfaces, the process is classed as 'non-specific sorption' and the magnitude of non-specific sorption equals the positive charge on the surface. Non-specifically sorbed ions include Cl^- , NO_3^- , ClO_4^- , etc., and are easily replaced by ions from neutral, monovalent salts, such as NaCl. In the second type of sorption, anions are bound tightly to the adsorbent surface. This process, termed specific sorption usually leads to a net change in the surface charge (Hingston et al., 1967). Specific sorption may occur whether the surface is positive, neutral, or negative (Bowden et al., 1980b). Ions which can be specifically sorbed include PO_4^{3-} , AsO_3^{3-} , and MoO_4^{2-} .

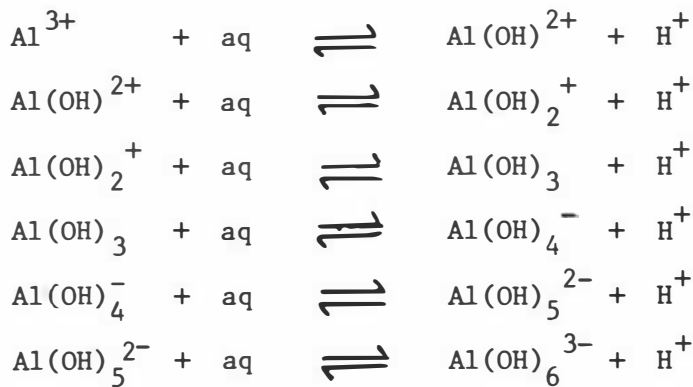
2.3 Effect of Liming on Aluminium and Phosphate Chemistry of Acid Soils

This section is subdivided into 3 parts:

- (i) the solution chemistry of pure Al systems and its implication to soils
- (ii) the origin of exchangeable Al and its interaction with added P, and
- (iii) the interaction between Al and P when soil is limed.

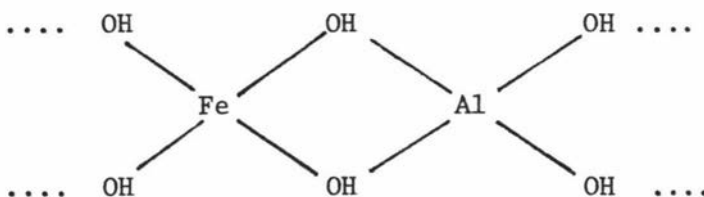
2.3.1 Solution chemistry of pure Aluminium systems and its implication to soils

The solution chemistry of Al has been studied by numerous workers (Magistad, 1925; Smith, 1971; Nair and Prenzel, 1978) who have reported that Al is soluble at both low and high pH. Magistad (1925) reported that at pH 4 and below, Al is present as alumino hydronium ions; $\text{Al}(\text{H}_2\text{O})_6^{3+}$. As the solution pH increases (Fig. 2.1), the alumino hydronium ions continually dissociate H^+ ions, leaving OH^- ions in place of the OH_2 groups. According to McLean (1976), such a dissociation step can be represented as follows:



As the pH of the solution increases, monomeric Al^{3+} ions hydrolyse to form a series of soluble Al-hydroxy compounds up to a pH of about 5; between pH 5.0 and pH 7.5, insoluble Al hydroxide is formed, above which, soluble aluminate complexes (e.g., $\text{Al}(\text{OH})_4^-$) are formed.

Recent studies by Rengasamy and Oades (1978; 1979) indicate that hydroxy Al polymers can form with increasing pH and these can vary in size and chemical properties depending on the OH/Al ratio. Two groups of polymers can be formed; when the OH/Al ratio is < 2.0 , most of the polymers formed have a molecular weight $< 50,000$, but when the OH/Al is > 2.0 , the molecular weight is $> 100,000$. The smaller polymers are highly charged and apparently possess a chain-like structure. In the presence of Fe^{3+} , copolycondensations can also form by bridging of Al^{3+} and Fe^{3+} through hydroxyls as follows:



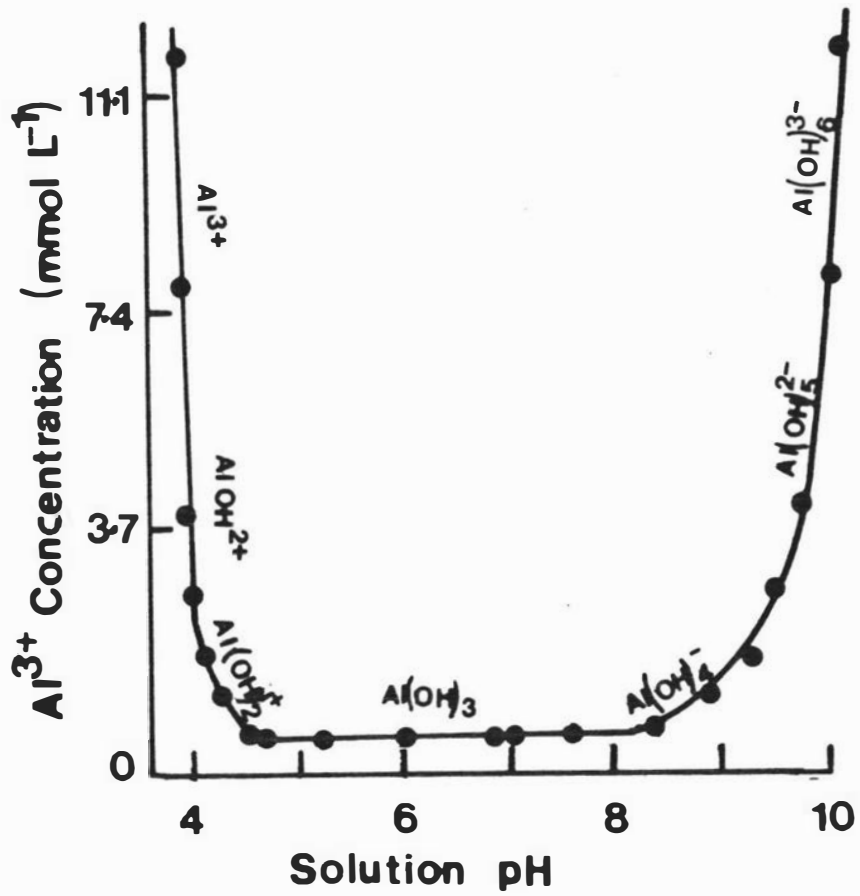


Fig. 2.1 Solubility of aluminium in water solution as affected by pH of solution (McLean, 1976).

Aluminium can also co-polymerize at $\text{pH} < 5$ with Si (Farmer et al., 1979) to form a colloiddally stable, poorly-organized compound. Such a compound was named proto-imogolite as its structure and composition is close to that of imogolite.

The course of the hydrolytic reactions discussed above and the nature of the products formed depends on the rate of addition of base, temperature, and the concentration of Al (Smith, 1971; Farmer et al., 1979). Thus, most of the work which has been conducted using pure systems has involved Al concentrations exceeding 1.0 mol L^{-1} , whereas in soil systems and soil extracts the concentration is usually less than 0.001 mol L^{-1} . Based on these comparisons it would seem that polymerisation occurs less readily in dilute solutions. According to Bache and Sharp (1976a) it would not be easy to partition Al into monomeric and polymeric species because of the extreme reactivity of the former species.

The implication from the studies conducted in pure systems is that, in soils, Al can be present in a variety of forms which can range from simple monomeric species to polymeric species of varying molecular weight, either in combination with Fe or Si or both, depending on the pH of the soil. Such polymeric hydroxy species may also form when soils rich in exchangeable Al and Fe are limed (Amarasiri and Olsen, 1973).

2.3.2 Origin of exchangeable aluminium and its interaction with added phosphate

In soils, Al is generally released from octahedral co-ordination in minerals by weathering processes (McLean, 1976), the rate and extent of the process being dependent on H^+ ion concentration. As the pH of the solution decreases to 4 or below, Al^{3+} ions dissolve from the edges of mineral structures (Jackson, 1963). Upon release, these ions combine with water to form $\text{Al}(\text{H}_2\text{O})_6^{3+}$ in solution and with an increase in soil pH, there is a subsequent dissociation of the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ into various species, as discussed in Section 2.3.1. A large proportion of the released Al ions in acid soils is sorbed on permanent cation-exchange sites (Brown and Newmann, 1973; McLean, 1976; Gillman, 1984) from which they can be removed by unbuffered, neutral salt solutions (McLean, 1965). Aluminium removed by this method has been considered exchangeable (McLean, 1965). However, recent studies of the displacement of Al by neutral salt solutions have shown that Al continues to be released from acid soils with successive salt

extractions and in amounts that vary considerably with the time of extraction (Amedee and Peech, 1976; Bache and Sharp, 1976a; Lee et al., 1985). Such a continued release of Al is thought to be caused by a gradual release of non-exchangeable forms of Al from polymeric hydroxy-Al species, which may be strongly sorbed on clay surfaces (Bache and Sharp, 1976a) or present in interlayer positions in vermiculite (Lee et al., 1985). Slow release of Al can also result from dissociation of Al-organic complexes (Bloom et al., 1979). In view of the possible release of non-exchangeable Al in the salt extracts of soils, many investigators (Amedee and Peech, 1976; Bache and Sharp, 1976a,b; Grove et al., 1982; Lee et al., 1985) have suggested that it would be difficult to define a precise fraction of exchangeable Al in soils.

A number of workers have shown that the P-sorption capacity of soils could be related to exchangeable Al content. For example, Syers et al. (1971) reported that for a range of Brazilian soils, P-sorption capacity was related to exchangeable Al content. This supports the work of Beckwith (1965) who showed that after leaching the exchangeable Al from the subsoil of an acid, dark clay from Queensland, there was a large decrease in P-sorption capacity. In a series of papers, Muljadi et al. (1966a,b,c) showed that if clay minerals have exchangeable Al^{3+} or hydroxy-Al polymers as part of their exchangeable cations, P can be retained by these forms of Al. Although P-sorption capacity has been related to the exchangeable Al content of soils, the results of such studies may not be entirely reflective of the interaction between exchangeable Al and added P. This is because studies which involved removal of exchangeable Al, for example by leaching (Beckwith, 1965), could result in a considerable increase in the pH of the system (Bache and Sharp, 1976a) and therefore the decrease in P-sorption capacity of the leached soils could be a pH effect rather than due to removal of exchangeable Al, per se.

Cation-exchange resins saturated with Al^{3+} have been used to infer the mechanism of the interaction between exchangeable Al and P. Using an Al-saturated resin, Wild (1953) showed that "fixation" of P became larger as the pH was increased and the Al hydrolysed more completely. However, he emphasised that the "fixation" of P depended on several factors, in particular, on the type of reagent (NaOH, $Ca(OH)_2$) used to increase the pH and also on whether P was added together with the base or before increasing the resin pH. Thus, in the case of monovalent electrolytes, such as NaOH, sorption of P was found to decrease consistently above pH 5.0. Hsu and

Rennie (1962b) reacted P with a cation-exchange resin saturated with Al^{3+} and presented evidence that precipitation was taking place even though P retention conformed to Langmuir and Freundlich sorption isotherms.

Although in the above discussions evidence is presented to show the interaction between exchangeable Al and solution P in both soil systems and with Al-saturated resins, it has been suggested that in many acid soils X-ray amorphous Al hydroxide or Al-hydroxy polymers attached to clay or organic matter are responsible for most of the P sorption of the soils (Amarasiri and Olsen, 1973; Sims and Ellis, 1983). Using a cation exchange resin, Robarge and Corey (1979) showed that the Al-hydroxy species formed during neutralization of Al^{3+} provided the primary P-sorbing surface. As percentage neutralization of exchangeable Al increased, at constant total P concentrations, P in solution was found to initially decrease, pass through a minimum, and then increase. They suggested that Al-hydroxy species formed during neutralization of Al^{3+} could be sorbed on clay surfaces. This study has important implications to the interaction of Al and P during the liming of soils.

2.3.3 Lime-aluminium-phosphate interactions in acid soils

Aluminium toxicity and acidity problems in soils are usually ameliorated by liming. Liming of acid soils increases the pH, thereby binding active Al^{3+} ions in the form of Al-hydroxy compounds. As discussed in Section 2.3.2., an increase in soil pH results in the formation of a range of Al-hydroxy compounds, the solubilities of which are dependent on pH. In soils, of pH >4.5 , Al-hydroxy polymers are dominant, the monomeric $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_2^+$ tending to polymerise to species such as $\text{Al}_6(\text{OH})_{15}^{3+}$ (Hsu and Rich, 1960). However, on clay surfaces there can be further polymerization until "gibbsite islands" are formed (Rich, 1968). Formation of such "gibbsite islands" would be expected to occur at pH >5.0 , and more commonly in interlayered minerals, such as vermiculite.

There are two interacting factors which influence the effect of pH on the sorption of P by a substrate (Bowden et al., 1980b; Haynes, 1982). Firstly, as the pH increases, the surface becomes increasingly negative, thereby resulting in a greater electrostatic repulsion and a decrease in electrostatic potential. Secondly, the pK_1 and pK_2 of the H_3PO_4 occur at pH 2 and 7. Thus, as the pH increases from 2 to 7, the concentration of HPO_4^{2-} increases 10-fold for each unit increase in pH. This increase

in the concentration of the divalent ion partially offsets the decrease in electrostatic potential. Thus, for pure systems, including goethite (Bowden et al., 1980a,b; Fig. 2.2a) and X-ray amorphous hydroxy-Al polymers (Kwong et al., 1978; Fig. 2.2b), P sorption would be expected to decrease relatively slowly due to an increase in surface negative charge until the pK_2 of H_3PO_4 is reached at 7. Above pH 7 the increase in concentration of divalent ion slows to zero, whereas the decrease in surface potential continues, hence sorption decreases more rapidly.

Although P sorption has been found to consistently decrease with increasing pH of pure systems, the effect of liming soils on P-sorption characteristics, as well as on the amount of extractable P, is less consistent. For example, Murrmann and Peech (1969) reported that as the pH of acid soils was increased, the concentration of P in solution initially decreased, passed through a minimum and then increased (Fig. 2.3). These workers related the solubility minimum of P to the solubility minimum of Al-hydroxy species. They suggested that when limed soils were incubated, P was occluded during the formation of Al-hydroxy polymers in the pH range <5.5 - 6.5. As the pH increased above 6.5 to 7, the Al-hydroxy species became increasingly soluble as the negatively charged aluminate formed, and previously sorbed P was released. However, numerous workers (Amarasiri and Olsen, 1973; Soltanpouret al., 1974; Haynes and Ludecke, 1981) have shown that, irrespective of whether P was added simultaneously or after lime application, similar results were obtained. This suggests that an occlusion mechanism probably does not operate.

Recent studies by Sorn-srivichai et al. (1984) suggest that some of the inconsistencies reported on the amount of P extracted from limed soils may be explained by careful consideration of the experimental parameters involved and also the soil-testing procedure used. Their studies showed that the observed decrease in Olsen P with liming was possibly due to an artefact in the Olsen procedure.

A survey of literature shows that whenever liming caused an increase in sorption of P, highly-weathered acid soils were used (Lucas and Blue, 1972; Amarasiri and Olsen, 1973; Mokwunye, 1975) for study. Because these soils contained high amounts of exchangeable Al, Amarasiri and Olsen (1973) and Mokwunye (1975) suggested that increased sorption when the soils were limed was caused by the formation of active, X-ray amorphous Al-hydroxy polymers. This hypothesis seems to be consistent with the results

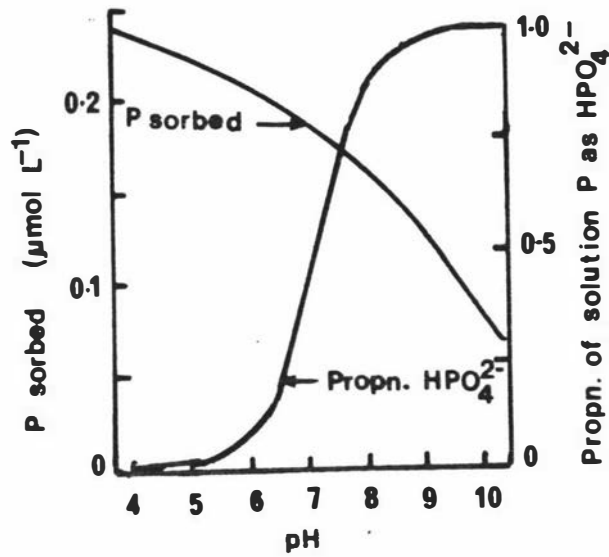


Fig. 2.2a Influence of pH on the phosphate sorbed by goethite at a solution concentration of 0.2 mmol L^{-1} together with the proportion of phosphate present as the divalent ion (Bowden et al., 1980b).

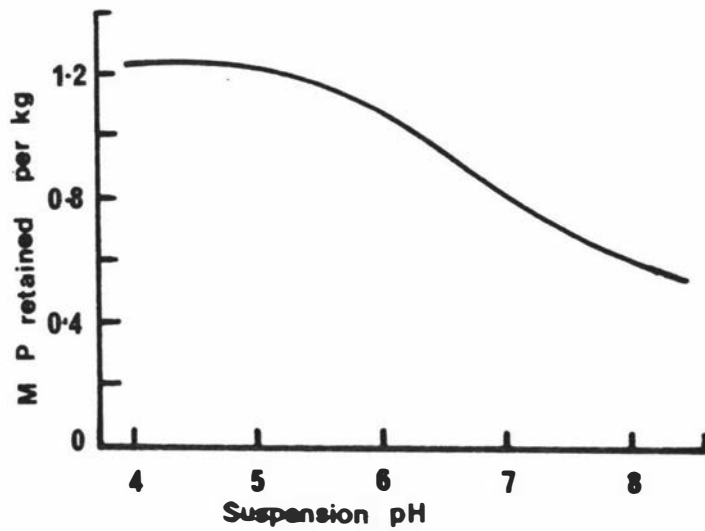


Fig. 2.2b Retention of phosphate by hydrolytic reaction products of aluminium formed in systems at the initial aluminium concentration of 1.10 mmol L^{-1} and OH/Al molar ratio of 3.0 as a function of time (Kwong et al. (1978)).

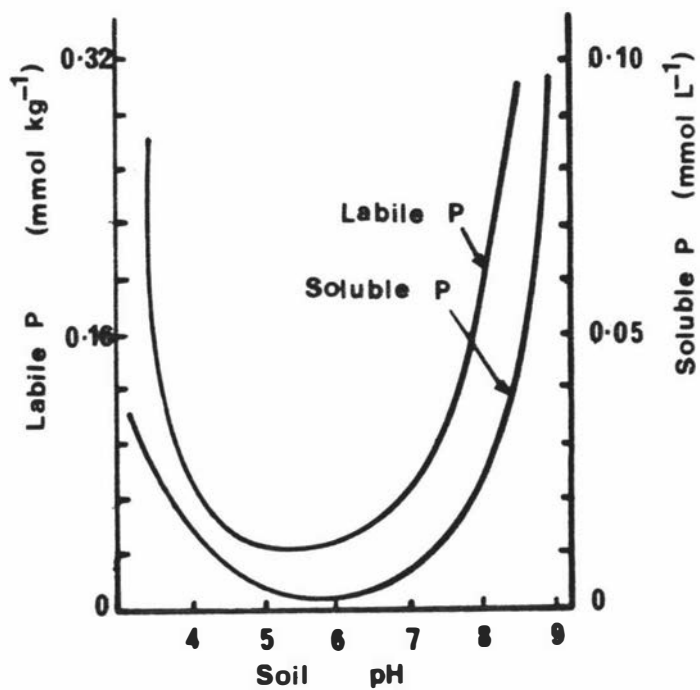


Fig. 2.3 Effect of pH on the amount of phosphate in soil solution and on the amount of labile phosphate present in an Illinois soil studied by Murrmann and Peech (1969), (Reproduced from Haynes, 1982).

of the study by Robarge and Corey (1979) in which Al-hydroxy polymers were shown to sorb P more actively than Al^{3+} . Sims and Ellis (1983) suggested that active Al-hydroxy polymers formed during liming of soils could coat the surfaces of minerals thereby affecting surface charge characteristics. Such a change in surface charge would be expected to influence the P-sorption characteristics of the soils.

Studies by Haynes and Ludecke (1981) indicate that the observed increase in sorption with liming was largely an artefact in the method employed during the incubation of the soil. They showed that if limed soils were dried prior to incubation with P, liming decreased subsequent P sorption at any given equilibrium solution P concentration. If the soil was incubated with lime and the moist soil equilibrated with P, without intervening drying, the liming increased the P-sorption capacity of the soil. Based on these results it would appear that drying, occurring under field conditions, can be important in relation to the effect of liming on P availability in acid soils. By determining oxalate-extractable Al, these workers suggested that the intervening drying process increased the ordering of X-ray amorphous Al-polyhydroxy species, thereby decreasing net surface area and reactivity. However, there is evidence in the literature in favour of the stability of Al-hydroxy species on clays (Brown and Newman, 1973) and therefore the drying process would have to be extremely severe and prolonged for the activities of surfaces to decrease to the point where their capacity to sorb P is less than that of the soils before liming (White, 1983). Indeed, Westfall et al. (1973) showed that only severe wetting and drying cycles had any significant effect on the amount of extractable Al in soils. Furthermore, Amarasiri and Olsen (1973) and Friesen et al. (1980a) dried and rewetted their soils several times following liming, yet obtained a decrease in extractable P.

Working with a range of limed soils, Barrow (1984) concluded that many of the inconsistencies reported in lime-P interaction studies may be explained by consideration of 4 factors namely, the pH range over which sorption is measured, the background electrolyte, the amount of desorbable P in the soil, and the relationship between the pH and the potential on the soil surface. The soils used by Barrow (1984) were incubated with lime at $60^{\circ}C$ to accelerate the reaction between lime and soil components. Such a high temperature may have had a significant effect on other physical and chemical characteristics of the soils such that there was some influence on the results of the sorption study.

Although liming of acid soils has been shown to have a variable effect on P-sorption capacity and the extractability of P, it has generally been reported to increase plant growth up to pH 6 (Kamprath, 1971). This positive growth response to lime has commonly been attributed to amelioration of Al-toxicity and/or increased P availability (Sanchez and Uehara, 1980). Large applications of lime which increase the pH values above 6 have been observed to cause a depression in plant growth (e.g., Kamprath, 1971). From the review of Kamprath (1971), 3 possible reasons can be listed for this decline in plant growth at high pH values. These are: (i) the tendency of liming to promote formation of smaller aggregates and thus reduce the rate of infiltration, making the soils more susceptible to erosion in the field, (ii) micronutrient deficiencies (e.g., B, Mn, Zn), and (iii) P deficiency in some soils could be induced by formation of insoluble calcium phosphate (Ca-P) compounds.

However, Sumner (1979) recently related yield depressions at high pH values to P deficiency and the initial exchangeable Al content of soils. He suggested that the level of exchangeable Al at a given pH reflected the reactivity of the aluminous surfaces which, in turn, governed the solubility of P. From his studies and those reported earlier he showed that when soils with exchangeable Al ranging from 1.4 to 10 mmol kg⁻¹ were limed, there was a depression in plant growth at high pH values. This contrasted with soils which contained 1 to 1.4 mmol Al kg⁻¹; these soils showed a consistent increase in plant growth even when limed to high pH values. In subsequent studies, Farina et al. (1980a,b) related the depression in the growth of corn at high pH values to the presence of a high concentration of Al in the corn leaf.

It is evident from this brief review that there is some confusion in the area of lime-P interactions in soils. The effects of liming on the amounts of soil extractable P are not consistent, neither are the explanations suggested by the investigators to explain such effects. Moreover, there is still a dilemma as to the actual effect of liming on the P-sorption characteristics of highly-weathered, acid soils.

Although Sumner (1979) provided evidence for the importance of exchangeable Al levels with regard to solubility of P during liming, the work of Soltanpouret al. (1974) and Haynes and Ludecke (1981) shows that the method adopted during liming and P incubation of the soils is also an important criterion determining the amounts of solution P.

2.4 Effects of Excess Soil Aluminium and Low Phosphate on Plant Growth

When released by weathering processes, Al undergoes hydrolysis with a resultant increase in soil acidity through the release of protons (Jackson, 1967). In addition to being a source of soil acidity, Al is a toxic element, particularly to leguminous plants grown in acid soils.

Toxic quantities of Al limit root growth and thereby reduce the uptake of water and nutrients, thus decreasing plant growth (Foy et al., 1978). Levels of Al toxic to growth vary with plant species (Foy and Brown, 1964). It has also been demonstrated, that in terms of molar activities, the amount of Al toxic to plant growth is reasonably similar for different soils (Adams and Lund, 1966). The toxic effects of excess Al on the growth of plants have been discussed by Foy (1971), Foy et al. (1978), and Helyar, (1978).

2.4.1 Uptake of aluminium by plants

Huett and Menary (1979) reported that the uptake of Al by plants was kinetically controlled and dependent on plant species. They showed that uptake occurred in two steps; (i) a rapid initial phase which was more pronounced and more extensive for cabbage and lettuce than for Kikuyu grass, and (ii) a second phase which represented a linear (steady state) uptake for cabbage and a slightly curvilinear uptake for lettuce.

According to Jackson (1967), Al taken up by roots is largely precipitated in the root-free space, especially in the epidermis. Clarkson (1967) has shown that much of this Al is exchangeable. The latter investigator presented data to show that in the initial stages of uptake, most of the Al becomes bound to the sorption sites in the cell wall.

Rasmussen (1968) used electron microprobe techniques to determine the mode of entry of Al and its distribution and localization in corn plants. He found that Al precipitated on the surface of the epidermal cells of the root with no penetration into the cortex so long as the root surface remained intact. The penetration of a lateral root through the endodermis cortex and epidermis provided a channel of entry for Al into the cortex and conductive tissues of both the lateral and the main root.

2.4.2 Toxicity symptoms

The symptoms of Al toxicity are not easily identifiable. Munns (1965a,b)

identified the effects of excess Al on lucerne and clover growth. He showed that, in both species, a concentration of 200 μM Al reduced root and shoot weights in about equal proportions. The observed symptoms were inhibition of root elongation and lateral formation, roots becoming brown and thickened, leaves of plants with higher Al becoming bluish green, and the stems and petioles becoming red, as in P deficiency. Often foliar symptoms resemble those of P deficiency and include overall stunted growth; small dark green leaves; late maturity; purpling of stems, leaves and leaf veins; and late yellowing and death of leaf tips. In some plants, Al toxicity appears as an induced-Ca deficiency or a reduced Ca transport problem, as indicated by curling or rolling of young leaves, and collapse of growing points or petioles (Foy et al., 1978).

2.5 Conclusions

Several conclusions may be drawn from this brief literature review. Chemical precipitation and sorption mechanisms have been proposed to explain the retention of P by soil components. However, the chemical precipitation theory probably becomes important only when very large concentrations of either P or Al are present in the soil solution of acid soils or of P and Ca in weakly acid soils or soils of neutral pH.

Liming has a significant effect on the charge characteristics of soils, thereby affecting the interaction between added P and soil components.

Although liming is commonly practised to ameliorate acidity and/or Al toxicity problems, it has been observed to have a variable effect on not only the amount of P extracted by soil-testing procedures, but also on the P-sorption characteristics of soils.

Whenever liming was found to cause a depression in plant growth at high pH values, it was always associated with soils in which exchangeable Al was higher than 1.4 mmol kg^{-1} soil.

CHAPTER 3

CHAPTER 3

GENERAL MATERIALS AND METHODS

3.1 Soils

The Fiji archipelago rises from a shallow platform at the Northern end of a suboceanic ridge extending south to New Zealand. It has experienced a large number of volcanic eruptions (Twyford and Wright, 1965) and most of the soils are developed on parent materials which are mainly andesitic in nature.

Six sampling sites (Fig. 3.1), representative of important crop production areas in the two major islands, were selected for preliminary investigation. These soils (Table 3.1) represent the Seqaqa soil series (Seqaqa Research Station), Batiri soil series (Seqaqa Research Station), Koronivia soil series (Koronivia Research Station), Sote soil series (Nadruloulou Research Station), Lega Lega soil series (Lega Lega Research Station), and Drasa soil series (Lololo Pine Station). Detailed descriptions of these soils have been presented by Twyford and Wright (1965) and Leslie (1984).

3.2 Analytical Procedures

Soil samples (0-300 mm) representative of the soils selected for study were, in the first instance, subjected to chemical and physical examination by standard procedures.

Mechanical analyses to determine the amounts of sand, silt, and clay were performed by the sedimentation method (Jackson, 1956) after peroxide treatment of the soil. Soil pH values were measured in water and M KCl solution using a glass electrode and a 1:2.5 soil:solution ratio after equilibration for 16 h. After the initial characterisation of the soils, all subsequent pH measurements in this study were determined in M KCl unless stated otherwise. Phosphate retention was determined using the method of Saunders (1965).

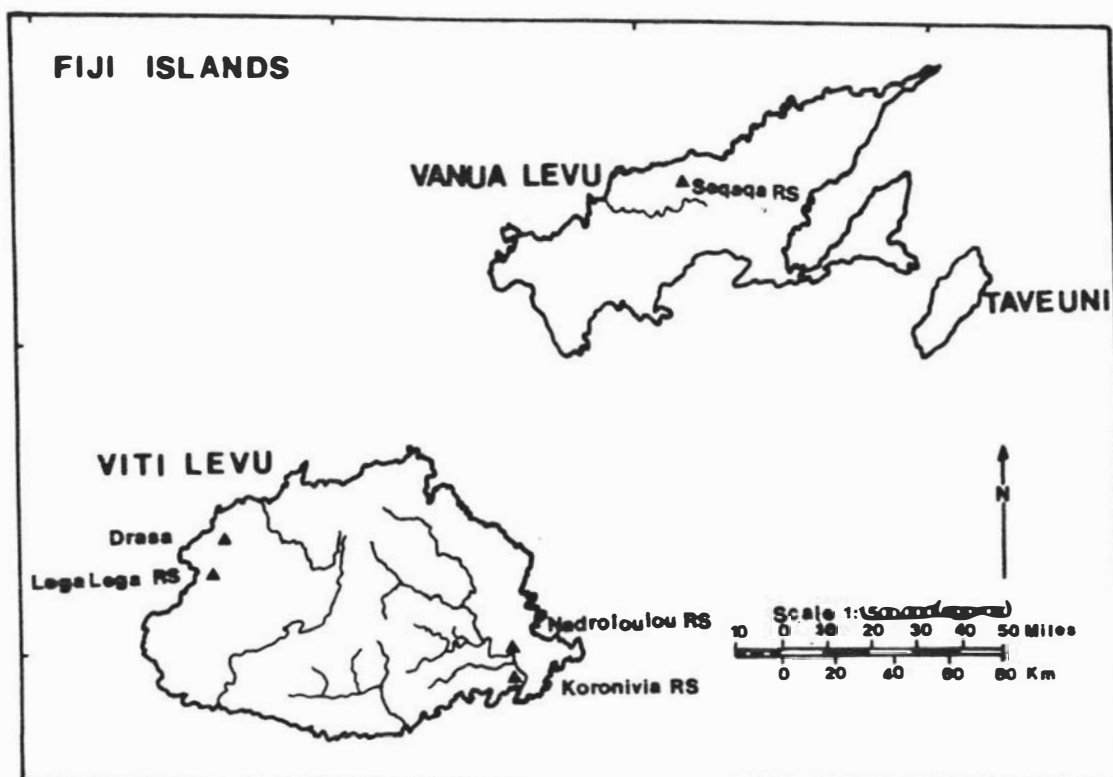


Fig. 3.1 Map of the Fiji Islands showing the location of soils used for the present study.

Table 3.1 USDA and Twyford and Wright (1965) classification
of soils used for preliminary analyses.

Soil series	Soil sample	Classification	
		U.S. Soil Taxonomy	Twyford and Wright (1965)
Koronivia	Koronivia	Humoxic Tropohumult	Red yellow podzolic
Sote	Nadroloulou	Typic Humitropept	Humic latosol
Batiri	Batiri	Oxic Paleustult	Ferruginous latosol
Seqaqa	Seqaqa	Typic Haplustox	Humic latosol
Drasa	Drasa	Ustic Dystropept	Ferruginous latosol
Lega Lega	Lega Lega	Aquic Paleustult	Ferruginous latosol

Exchangeable cations were determined after extraction with neutral M ammonium acetate; calcium (Ca) and magnesium (Mg) in the extract were measured using atomic absorption spectrophotometry (AAS), and sodium (Na) and potassium (K) by atomic emission spectrophotometry (AES). Exchangeable Al and H were extracted from the soils with M KCl and determined by the aluminon (Hsu, 1963) and titration (Yuan, 1959) methods, respectively. Total P was measured colorimetrically after dry combustion of soil and extraction with 0.1M H₂SO₄ (Syers et al., 1968). The organic carbon content of the soils was determined using the dichromate method (Black, 1965). The results of these analyses are presented in Table 3.2.

Mineralogical analysis of the clay fraction (<2 μm) was performed by X-ray diffraction. Quantitative estimates of gibbsite and kaolinite were obtained by differential thermal analysis. These results are presented in Table 3.3.

3.3 Selective Chemical Dissolution Techniques

According to Mitchell et al (1964), poorly-ordered inorganic gel material is the most reactive component of the soil system. A number of chemical extraction procedures are available for determining this material. In the present investigation oxalate (Blakemore et al., 1981) and citrate-dithionite-bicarbonate (Jackson, 1956) extractions were used to estimate this component of the soil. The results of these investigations are presented in Table 3.3.

3.3.1 Determination of oxalate-extractable Iron and Aluminium

Soil samples (<2 mm, 100-250 mg) were shaken with 40 mL ammonium oxalate (0.30 M, pH 3.0) in darkness (because ammonium oxalate removes crystalline iron oxides under the influence of light, Schwertmann (1964)) end-over-end at 20 ± 2°C twice for 2 h, centrifuged, and Al and Fe determined using AAS with a nitrous oxide-acetylene and air-acetylene flame respectively.

3.3.2 Determination of citrate-dithionite-bicarbonate-extractable Iron and Aluminium

40 mL trisodium citrate (0.30M) and 5 mL sodium bicarbonate (1M) were added to soil samples (100 mg) and the suspensions heated to 80°C on a water bath. Sodium dithionite (0.5 g) was added and the suspension dispersed

Table 3.2 Some chemical parameters used to characterise the soils.

Soil	pH		Extractable cations						Organic matter (1.72 x %C)	P retention
	H ₂ O	M KCl	M NH ₄ OAc				M KCl			
			Ca	Mg	K	Na	Al	H		
	mmol kg ⁻¹								%	
Koronivia	4.6	4.2	5.5	1.6	1.0	1.2	8.7	3.2	3.3	62
Nadroloulou	4.8	3.9	11.8	13.4	1.9	1.9	35.6	13.2	5.6	68
Batiri	4.8	4.9	4.8	1.3	0.4	0.6	0.3	0.0	4.2	88
Seqaqa	4.5	4.5	2.4	1.0	1.9	1.4	9.3	3.0	16.6	95
Drasa	5.0	4.0	3.1	6.2	0.8	1.2	25.0	7.2	1.9	68
Lega Lega	4.4	4.3	2.0	0.5	0.5	0.5	10.6	3.0	1.4	13

Table 3.3 Selective dissolution analyses and mineralogical composition of the soils used.

Soil	Oxalate-extractable		Dithionite-extractable		Particle size			Clay mineralogy*		
	Al	Fe	Al	Fe	Sand	Silt	Clay	Gibb.	Kaol.	Verm.**
	mmol kg ⁻¹				%			%		
Koronivia	49.5	68.1	193	472	40.9	43.3	15.8	0.8	56.6	tr.
Nadroloulou	111.9	62.9	288	951	24.1	31.6	44.3	0.5	52.7	+
Batiri	50.0	10.7	820	2399	19.8	37.9	42.3	25.0	21.1	n.d
Seqaqa	643.4	94.4	1029	1486	8.3	49.4	42.3	4.2	32.9	n.d
Drasa	82.6	9.7	211	946	13.8	40.2	46.0	<0.1	86.0	n.d
Lega Lega	22.9	21.4	167	324	86.0	5.0	9.0	not determined		

* All mineralogical analyses were performed on the clay fraction (< 2 μm).

n.d, tr., and + indicate not detected, trace, and subordinate amounts of mineral, respectively.

** gibb. = gibbsite; kaol. = kaolinite; verm. = vermiculite.

ultrasonically, the heat produced being sufficient to maintain the temperature at 80°C (Mitchell et al., 1971). Both Fe and Al were determined using AAS as described in section 3.3.1.

3.4 Preliminary Lime Incubation Study

Based on these chemical and mineralogical characteristics (Tables 3.2 and 3.3), the Koronivia, Nadroloulou, Batiri, and Seqqa soils were chosen for detailed laboratory and glasshouse studies. These soils varied widely in cation-exchange capacity, oxalate- and dithionite-extractable Al and Fe, and M KCl-extractable Al content. Because the objectives of this thesis were to investigate the chemical interaction between Al and P, a preliminary lime study was necessary to investigate the interaction between these two elements in the soil. The results of these investigations were used later in the planning of a glasshouse trial to assess the interaction between Al and P and the growth of plants.

3.4.1 Preparation of soil samples

Lime as $\text{Ca}(\text{OH})_2$ was added at either 9 or 10 rates to each soil (Table 3.4). The lime was thoroughly mixed through the soil which was then moistened to approximately field capacity and incubated in polythene bags, with provision for aeration, at a temperature of $20 \pm 2^\circ\text{C}$. Distilled water was added, as required, to compensate for evaporative loss. After a period of 6 weeks the soils were air dried, passed through a 2-mm sieve and subsamples were taken for incubation with P. Phosphate was added as a solution of KH_2PO_4 at 2 rates (8.1 and 16.1 mmol kg^{-1} soil) and the soils were brought to approximate field capacity and incubated as described above for a further 2 weeks. After incubation, the soils were air dried at a temperature of $20 \pm 2^\circ\text{C}$, passed through a 2-mm sieve, and stored in sealed polythene bags for further analysis.

3.5 Extraction of Aluminium from Soils using M KCl:

A Comparison of Methods

3.5.1 Introduction

During the early stages of the overall study it was decided to extract exchangeable Al from soils using 2 sequential 1-h extractions with M KCl and

Table 3.4 Amounts of Ca(OH)_2 added to the soils during the preliminary incubation studies.

Soil	Level of Ca(OH)_2 added									
	L0	L1	L2	L3	L4	L5	L6	L7	L8	L9
	mmol kg^{-1}									
Koronivia	0	4.86	21.6	27.0	32.4	46.0	54.1	64.9	81.1	135.1
Nadroloulou	0	40.6	46.0	77.3	81.1	99.7	127.6	148.5	159.5	189.0
Batiri	0	5.4	21.6	27.0	32.4	54.1	59.5	94.6	135.1	--
Seqaqa	0	33.8	36.5	67.6	73.0	135.1	162.2	175.7	229.7	--

then to determine this Al by a modified aluminon method (Hsu, 1963). As the work progressed, however, it became apparent that the nature of the Al extracted and determined by this procedure would greatly influence the interpretation of the results obtained.

Thus it was decided to conduct a comparison of methods for both extracting and analysing for Al so that the procedures used in this thesis could more easily be compared with other published work and also to ensure that the results obtained were not the result of weakness in the analytical procedure.

Estimates of exchangeable Al are usually made by extracting soils with M KCl solution (Coleman et al., 1959). However, in recent years, increased interest in relating M KCl-exchangeable Al to the lime requirement of soils has resulted in a considerable diversity in the range of extraction procedures used. For example, in the last five years, exchangeable Al has generally been extracted either by shaking soils with M KCl solution for a few seconds (Pratt and Bair, 1961), by overnight standing of soils in M KCl solution (Yuan, 1959), or by leaching soils with M KCl solution for 2 h (Black, 1965). It is unlikely that all of these methods would give a similar estimate of exchangeable Al. Such a diversity in the extraction procedures could also be one reason why there has been increasing difficulty in quantitatively relating exchangeable Al to plant growth studies.

Although some M KCl-exchangeable Al extraction procedures have been compared in a number of studies (McLean et al., 1958, 1959; Pratt and Bair, 1961; Bache and Sharp, 1976a), it is surprising that there is no published report in which the leaching, shaking, and standing methods have been compared in the same study. Such a comparison is important, particularly in ensuring the selection of a method which gives the best estimate of exchangeable Al.

Considerable diversity also exists in the analytical techniques which have been used to determine Al in the M KCl extracts of soils. Some of the commonly-used methods include AAS, titration, and colorimetric procedures involving aluminon or oxine. However, all of these analytical techniques differ in their sensitivity to Al (Hesse, 1971) and also suffer from varying degrees of interference from the presence of other elements, such as Ca, and Fe (Hesse, 1971).

In this study selected unlimed and corresponding limed soils were extracted with M KCl using five different procedures and Al in the extracts

was determined by colorimetric procedures involving the aluminon and oxine reagents, and by titrimetric and AAS techniques.

To investigate the nature of the large quantities of Al extracted from the acid unlimed soils, the results above were compared with Al-release curves obtained from a sequential extraction procedure.

3.5.2 Methods

3.5.2.1 Aluminium release curves

Soil samples (4 g) were shaken with 20 mL of M KCl for 1 h. They were then centrifuged and filtered through a Whatman No.542 filter paper. The extraction procedure was repeated to give a total of 8 x 1 h extractions. At the conclusion of each extraction, the pH of the soil suspension was measured prior to centrifuging and filtering. Although the supernatant solution from each extraction was always passed through the original filter paper, the 8 extractions were analysed separately, using the oxine method.

3.5.2.2 Determination of M KCl-extractable aluminium: Extraction procedures

Al was extracted from unlimed and selected limed soils (Table 3.5) by 5 different extraction procedures. Each extract was diluted to 50 mL using M KCl and the Al content determined using 4 different analytical methods. All extractions were done in duplicate.

(a) Short-term shaking (Pratt and Bair, 1961)

Soil samples (4 g) were shaken by hand with 20 mL of M KCl solution in 50 mL polythene centrifuge tubes for 5 s. The solutions were then filtered through a Whatman No.542 filter paper. The whole extraction process lasted for approximately 2 min.

(b) Long-term shaking

This procedure was similar to that described in section 3.5.2.2 (a) above except that the samples were shaken, end-over-end, for 16 h at $20 \pm 2^{\circ}\text{C}$. The samples were then centrifuged at 3000 rpm for 2 min and filtered as described above.

(c) Long-term standing (Yuan, 1959)

Soil samples (4 g) were placed in separate conical flasks, 20 mL

Table 3.5 pH of unlimed and limed soils used in the
standardisation of the M KCl extraction procedure.

Soil	pH	
	Unlimed	Limed
Koronivia	4.2	4.4
Nadróloulou	4.0	4.5
Batiri	4.9	5.3
Seqaqa	4.5	5.1

M KCl solutions were added and the samples swirled gently for approximately 5 s and allowed to stand for 16 h. The suspension was then filtered through a Whatman No.542 filter paper and the residue washed onto the filter paper with 15 ml of M KCl.

(d) Leaching (Black, 1965)

Each soil sample (4 g) was placed on double Whatman No.542 filter papers and leached with 40 mL of M KCl solution for a total of 2 h at a rate of 15-20 mL h⁻¹.

(e) Sequential extraction

Soil samples (4 g) were shaken with 20 mL of M KCl for 1 h. They were then centrifuged and filtered as described above. The extraction procedure was then repeated. The supernatant solution from the second extraction was passed through the original filter paper and Al was determined in the combined extract.

3.5.2.3 Analytical procedures

3.5.2.3.1. Colorimetric methods

(a) Oxine. An aliquot of the extracts (0.2 to 3 mL) was analysed for monomeric and total Al by adapting the modified (Lee et al., 1985) oxine method of Bache and Sharp (1976b). This analysis was done immediately after extraction in an attempt to limit any problems associated with the depolymerization of Al (Bache and Sharp, 1976b). This procedure requires specialised flow cells in the spectrophotometer to ensure stable readings.

(b) Aluminon. Suitable aliquots (0.5 to 10 mL) of the extracts were analysed for Al by the aluminon method described by Hsu (1963). However, instead of heating the solutions at 80°C for 30 min to facilitate the breakdown of Al-organic and Al-polyhydroxy complexes (Hsu, 1963) the solutions were left overnight for colour development. A comparison of the heating method with the overnight standing technique using M KCl extracts of selected soils showed no difference between the 2 methods.

3.5.2.3.2 Titration (Yuan, 1959)

A suitable aliquot (10 to 20 mL) was titrated with 0.01M NaOH, using phenolphthalein as an indicator, until a permanent pink colour was obtained. One drop of 0.01M HCl was added to remove the pink coloration and then 5 ml of 4% NaF were added. The return of a pink coloration indicated the presence of extractable Al, and the solution was back titrated

until the pink colour disappeared. A similar titration of M KCl was used as the reagent blank.

3.5.2.3.3 Atomic absorption spectrophotometry

Al in the original extract was determined by a standard AAS technique (Blakemore et al., 1981) using a nitrous oxide-acetylene flame.

3.5.2.4 Recovery tests

The recovery of added Al in all procedures except oxine was investigated by adding 1 mL of a solution containing $4 \mu\text{g mL}^{-1}$ Al to suitable volumes of M KCl extracts of soil obtained using the short-term shaking procedure, described above. For the oxine technique an aliquot equivalent to $1.5 \mu\text{g mL}^{-1}$ Al was added to suitable volumes of the M KCl extracts. The percentage recovery of added Al was calculated from the difference between Al in the original M KCl extract and Al in the extract with added Al.

3.5.3 Results and discussion

3.5.3.1 Aluminium-release curves

Different amounts of Al were removed with M KCl in 8-sequential extractions from the 4 unlimed soils (Table 3.6). In general, the largest amount of Al was extracted from the Nadroloulou soil and the smallest amount from the Batiri soil. The Koronivia and Seqqa soils released moderate amounts of Al in comparison to the other soils.

Contrasting Al-release patterns were also obtained (Fig. 3.2). Generally the curves showed a gradually decreasing release of Al with increasing extraction number. This suggested a possible concurrent dissolution of exchangeable and non-exchangeable Al, rather than the sharp decrease expected with a well-defined exchangeable Al fraction (Bache and Sharp, 1976a). In contrast, Sivasubramaniam and Talibudeen (1972) obtained extraction curves characterised by a rapid initial release followed by a slower linear release. They suggested that this allowed them to distinguish between exchangeable and non-exchangeable Al. However, their results could have been influenced by the pH of the M KCl solution which was adjusted to the pH of the soil suspension (Bache and Sharp, 1976a). In the studies of Bache and Sharp (1976a), the pH of the soil suspension increased from about 4 to about 5 during progressive leaching of the soils. In the present study, the pH of the soil suspension of the Nadroloulou,

Table 3.6 Cumulative amounts of Al removed during eight sequential extractions.

	Soil			
	Koronivia	Nadroloulou	Batiri	Seqaqa
	mmol kg^{-1}			
Al	9.3	45.6	0.6	8.2

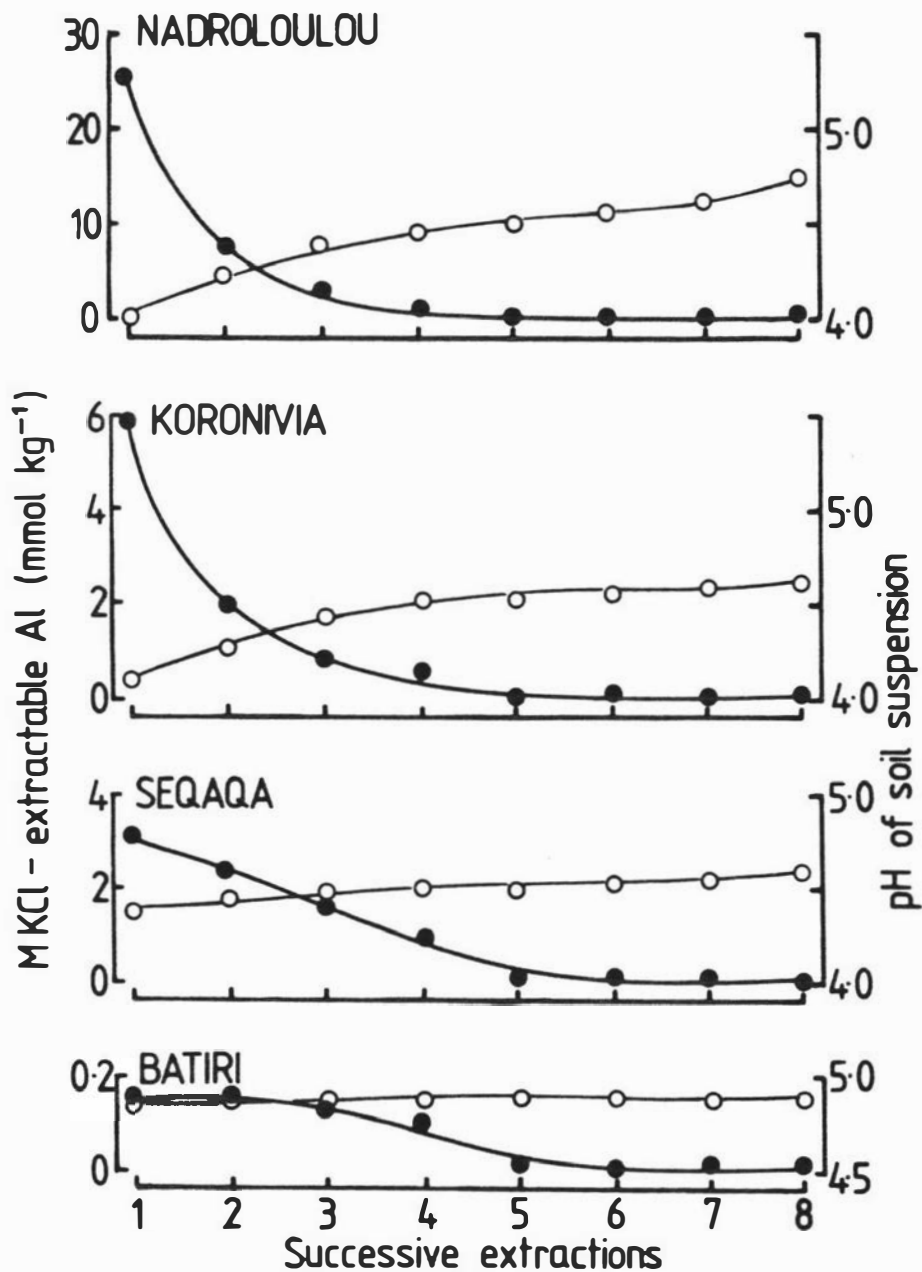


Fig. 3.2 Amounts of extractable Al (●) released and pH (○) of the soil suspension during eight sequential extractions of the unlimed soils with M KCl.

Koronivia, and Seqaqa soils also increased (Fig. 3.2) from about 4 to about 5 during the extractions, presumably due to progressive removal of H^+ and Al^{3+} ions.

On average, 60% of total extractable Al was released in the first M KCl extraction of the Nadroloulou and Koronivia soils. The Batiri and Seqaqa soils, however, showed a more gradual release with only 28 and 30%, respectively of the total amount of Al extracted being removed in the first extraction. The relatively rapid release of Al from the Nadroloulou and Koronivia soils (Fig. 3.2) is presumably due to a lower soil pH (Table 3.5) and possibly to the presence of vermiculite (Table 3.3). Aluminium interlayers in vermiculite have been reported (Wilson, 1973; McLean 1976) as a source of extractable Al. The relatively sharp decrease in the amount of Al removed during the course of the extractions is probably a reflection of the collapse of the interlayer spacing in vermiculite (Lee et al., 1985). Although both of these soils have a similar mineralogy, the reason why the Nadroloulou soil releases larger amounts of Al during the sequential extraction (Table 3.6) is probably due to its lower pH and significantly higher vermiculite and clay content.

The Al-release curve for the gibbsitic Batiri soil (Fig. 3.2) is similar to that obtained by Amedee and Peech (1976) for similar soils with a pH higher than 4 and which were also dominated by gibbsite.

The high organic matter (16.6%) and disordered aluminosilicate (oxalate-extractable Al, Table 3.3) content of the Seqaqa soil is probably responsible for the slow release of Al in this soil as a considerable proportion of the Al may be present as mono or multidentate organic complexes. Both organic Al complexes and disordered aluminosilicates (Mitchell and Farmer, 1962) have been cited as sources of slowly released Al. Because Al is generally considered to be retained strongly by organic matter (Coleman and Thomas, 1967; Bloom et al., 1979; Lee et al., 1985) its extraction from an organic-rich soil could be expected to be slower in comparison with soils containing considerably less organic matter.

3.5.3.2 Comparison of extraction procedures

There was a significant ($P < 0.01$) variation in the amounts of Al extracted by the 5 methods, with similar trends being obtained for both unlimed and limed soils. Because the differences in the amounts of Al extracted by the 5 different methods were generally similar, regardless of the analytical technique used to determine Al, only the results for

unlimed soils using the oxine methods are presented (Fig. 3.3).

The amounts of Al released by these methods (Fig. 3.3) increased in the order: short-term shaking < long-term shaking < long-term standing followed by washing < 2 x 1 h shaking < 2 h leaching. However, the time of shaking only became important when there was a large amount of extractable Al present in the soil. For example, in the Batiri soil which was low in extractable Al, there was no significant difference between the short- and long-term shaking extraction procedures, indicating that the short-term extraction was sufficient to remove the bulk of the extractable Al from this soil. However, such comparisons could partly be influenced by the detection limits imposed by the analytical techniques.

Leaching of the soils usually released 2 to 3 times more Al than short-term shaking and at least 1.5 times more Al than the overnight standing methods (Fig. 3.3). With the exception of the leaching technique, the cumulative amount of Al removed during 8-sequential extractions was always higher than that extracted by the other methods (Fig. 3.3). Surprisingly, the leaching technique extracted more Al than 8-sequential extractions from the Koronivia and Nadroloulou soils (Fig. 3.3). This illustrates the drastic action of the leaching technique and the likelihood of it removing non-exchangeable forms of Al.

The trends observed for the extraction of Al (Fig. 3.3) are possibly expected when the modes of action of the extraction procedures are considered. While the shaking methods represent a closed system in which equilibrium is established between solution and soil Al, the leaching method is an open system in which continual addition of M KCl solution drives the equilibrium towards further release of Al. Moreover, leaching of soils exposes the ion exchanger to a virtually constant concentration of electrolyte (Sivasubramaniam and Talibudeen, 1972), in contrast to the other methods in which the concentration decreases after a period of extraction, thus decreasing the efficiency of extraction. Skeen and Sumner (1967a,b) and Amedee and Peech (1976) have shown that the efficiency of the extraction depends on the concentration of the electrolyte. The long-term standing method released more Al than shaking for the same period, probably because of the washing step which followed the former extraction.

Based only on the results of the present study, it would not be possible to propose a method which would exclusively remove exchangeable Al from the soils as the M KCl extracts would be contaminated by varying amounts of non-exchangeable Al. Nevertheless, a comparison of the cumulative amount

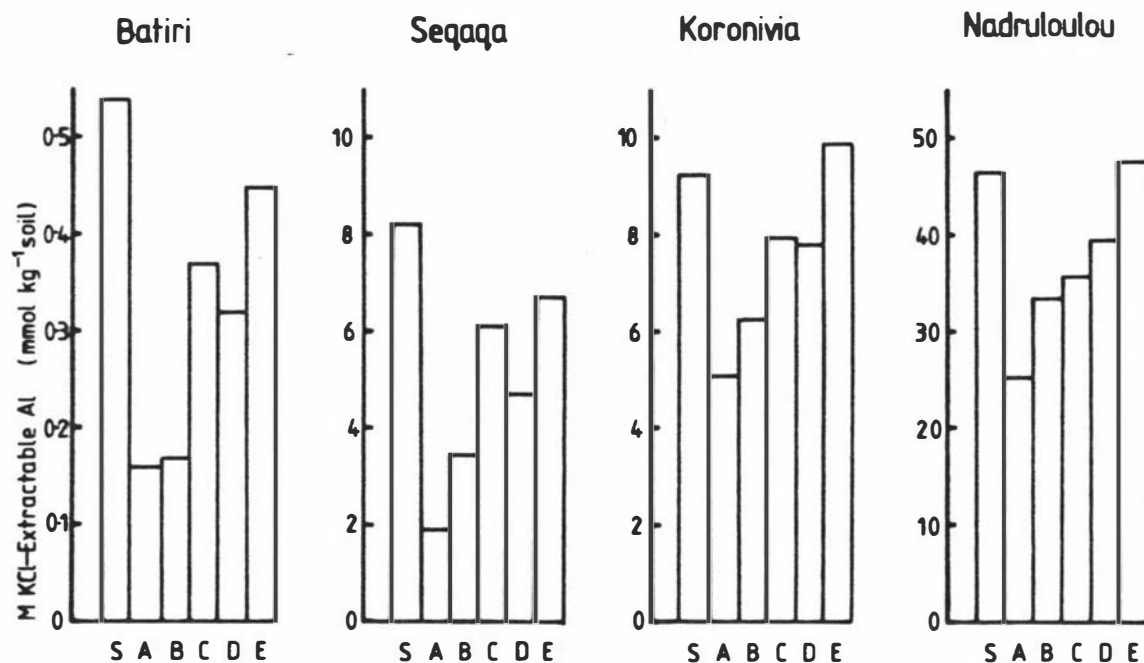


Fig. 3.3 Amounts of Al extracted from unlimed soils by the M KCl extraction procedures, short-term shaking, (A); long-term shaking, (B); 2 x 1 h shaking, (C); long-term standing, (D); and 2 h leaching of soils, (E); relative to the cumulative amount removed during 8 successive extraction, (S). LSD (5%) of results for comparison between extraction procedure within a soil = 0.06.

of Al extracted during 8-sequential extractions with the extraction methods showed that the leaching method possibly removes some non-exchangeable Al. The long-term standing method would also be unsuitable because of the short washing (i.e. leaching) step, which follows the extraction. The short-term extraction would probably be inefficient for soils high in extractable Al. In view of these considerations, either the long-term shaking or the 2 x 1 h shaking methods should provide reasonable estimates of extractable Al in the Fijian soils. However, for routine analyses the latter method is preferable due to the rapidity with which samples can be analysed.

3.5.3.3 Analytical techniques

Because the differences between the analytical techniques were generally similar, regardless of the extraction methods used, only the 2 x 1 h extraction results of the unlimed soils are presented. The results in Fig. 3.4 show that there is a significant ($P < 0.01$) difference in the amounts of Al measured by these methods. In general, the aluminon Al values are somewhat larger than titration, whereas AAS and oxine measurements are intermediate. These results confirm the observations of Webber (1974) who determined Al using AAS, oxine (8-hydroxy quinoline), and aluminon methods in M KCl extracts of a range of Canadian soils. However, the significant difference observed between AAS and the titration technique in the present study is not in agreement with the results of Bruce and Lyons (1984) who recorded no significant difference between these techniques.

The titration method failed to detect Al in the unlimed Batiri soil (Fig. 3.4) although very dilute solutions of HCl (0.01M) and NaOH (0.01M) were used. This soil contained less than $0.30 \text{ mmol Al kg}^{-1}$ soil. In all cases, the amount of Al measured by the titration method was less than that measured by the other techniques although there was good agreement between the replicates in extracts containing high levels of Al.

The colorimetric (oxine and aluminon) and AAS methods (Fig. 3.4) detected Al in all the samples, including those of the Batiri soil. However, in the AAS method there was a wide variation between the replicates, particularly those low in Al. A comparison of the AAS technique with the oxine method indicated that there was at least twice the variability among the replicates with the AAS method (C.V. = 8.3%) than with the oxine method (C.V. = 3.1%). This variability in AAS measured values may be attributed to the rather low levels of Al in the extracts and the high salt concentration which tended to

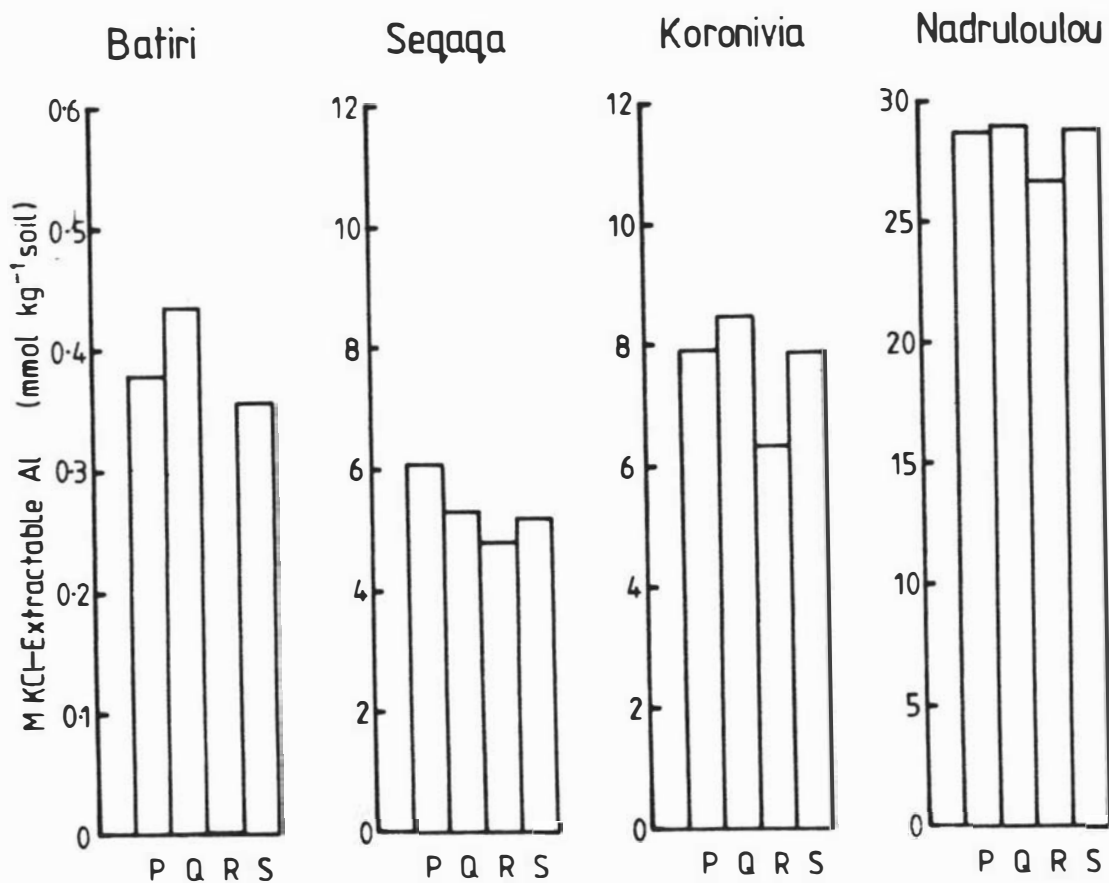


Fig. 3.4 Amounts of Al in M KCl extracts of unlimed soils estimated by the oxine, (P); aluminon, (Q); titration, (R); and AAS techniques, (S). LSD (5%) of results for comparison between analytical techniques within a soil = 0.06.

clog the burner, thereby varying the solution uptake rate. However, the oxine technique gave good reproducibility in soil extracts containing both low and high levels of Al. This is probably due to the solvent extraction step which separates the Al from the M KCl extract prior to development of colour using the oxine reagent. These results confirm the observations of Øien and Gjerdingen (1972) who reported almost identical variability among the replicates in the AAS (C.V. = 8.1%) method relative to the 8-hydroxy quinoline (C.V. = 3.1%) method. In agreement with the present observations, these investigators also found poor reproducibility at low levels of Al. Moreover, they found that at an Al level of $1.85 \text{ mmol kg}^{-1}$ soil, it was of advantage to carry out a solvent extraction to concentrate the Al and to remove KCl, as is done in the oxine technique.

Determination of Al by the aluminon method was complicated by the presence of high levels of Ca and K. Interference problems due to the presence of Ca have long been known (Frink and Peech, 1962; Page and Bingham, 1962) and it was observed that Ca concentrations exceeding 0.02 M suppressed optical density at low levels of Al and intensified it at high levels of Al. Further study showed interference from high levels of K. The curve in Fig. 3.5 shows that K concentrations exceeding 0.05 M intensified optical density at low levels of Al and suppressed it at high levels of Al. Turbidity was also observed at high levels of Al. These problems would be common in M KCl extracts of unlimed and limed soils which, in addition to high levels of K, also contain varying amounts of Ca. Such problems may be overcome by appropriate dilution, use of a range of calibration curves (Skeen and Sumner, 1967a), or by solvent extraction (Øien and Gjerdingen, 1972) of Al. However, dilution of M KCl extracts of limed soils, which contain low levels of Al, may result in loss in sensitivity.

3.5.3.4 Recovery tests

There was reasonable agreement (Table 3.7) between the amounts of Al added to the soil extracts and the amounts recovered, particularly in the unlimed soil. Between 96–100% of added Al was recovered from the soil extracts. However, the percentage recovery was variable in the extracts of the limed soils. The highest amount was recovered by the oxine method and this illustrates the sensitivity of this method. The rather low recovery by the aluminon method from the M KCl extracts of limed soils may be due to interference problems associated with high levels of Ca and K.

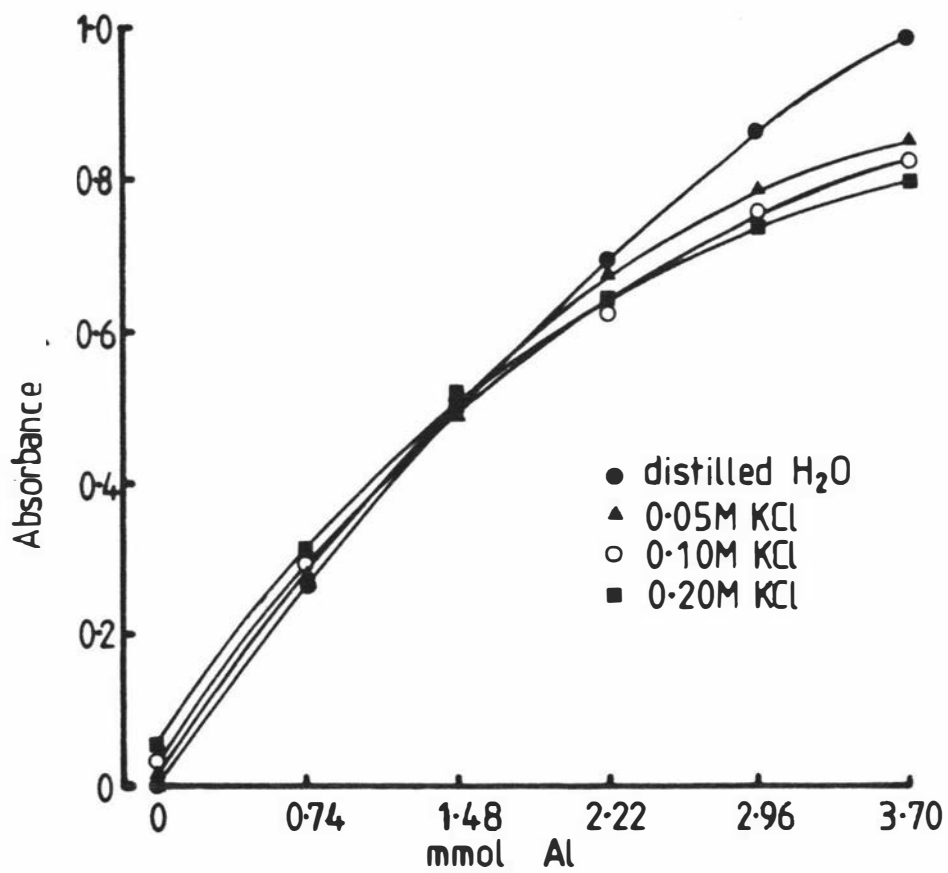


Fig. 3.5 Effect of increasing the solution concentration of K on the intensity (absorbance) of colour developed by the aluminon reagent.

Table 3.7 Percentage recovery of Al added to M KCl extracts by four analytical techniques.

Soil	pH (M KCl)	Analytical technique	Recovery %
Nadroloulou (unlimed)	4.0	Titration	96.2
	4.0	AAS	98.1
	4.0	Aluminon	98.1
	4.0	Oxine	100.0
Koronivia (limed)	4.4	Titration	96.0
	4.4	AAS	95.2
	4.4	Aluminon	92.7
	4.4	Oxine	98.5
Seqaqa (limed)	5.1	Titration	94.3
	5.1	AAS	94.8
	5.1	Aluminon	88.4
	5.1	Oxine	98.5

Furthermore, studies by Hsu (1963) have shown that the intensity of colour and the recovery of added Al from extracts by aluminon can vary with the Trade Brand of the aluminon reagent.

Thus, the oxine method would appear to be the most suitable for determination of Al in M KCl extracts of both unlimed and limed soils. However, the other methods could equally well be used to measure Al in M KCl extracts of unlimed soils which contain high levels of extractable Al.

3.5.4 Conclusions

Significantly different amounts of Al are extracted from the soils by different extraction procedures. Generally, the amount of Al removed by M KCl was in the order of short-term shaking < long-term shaking < long-term standing followed by washing < 2 x 1 h shaking < 2 h leaching.

A reasonable estimate of extractable Al may be obtained by shaking soils twice for 1 h with M KCl. This was deduced by comparing the amounts of Al extracted by the different extraction procedures with the cumulative amount released in 8 x 1 h-sequential extractions.

Significantly different amounts of Al were detected by the titration, AAS, aluminon, and oxine methods. The titration procedure was found to be the least sensitive, particularly for extracts low in Al.

The AAS and aluminon values were influenced by high salt concentrations and the presence of Ca and K, respectively.

The results of the recovery test showed that of the 4 methods tested, oxine was the most sensitive analytical technique for measuring Al in M KCl extracts of limed and unlimed soils.

CHAPTER 4

CHAPTER 4

CHARGE CHARACTERISTICS OF ACID
SOILS AS INFLUENCED BY LIMING

4.1 Introduction

Most of the reactions which control nutrient availability in soils are dependent upon physiochemical processes that occur at the soil solution-soil particle interface (Bolt, 1979). The charge characteristics of soil components influence these processes and are thus important in soil fertility.

At present there is very little information available on the surface charge characteristics of Fijian soils. The majority of Fijian soils are highly weathered, strongly acidic, and consist predominantly of oxidic and kaolinitic minerals. Thus the soils are predominantly variable charge in nature.

Some Fijian soils have been limed to reduce soil acidity and Al toxicity problems, but there is little information on the effect that liming has had on the charge characteristics of these soils. However, there is sufficient evidence from other studies (Hingston et al., 1967; Breeuswma and Lyklema, 1971; Sawhney, 1974; Wann and Uehara, 1978) to suggest that surface charge density and therefore the cation-exchange capacity of soils with variable charge may be altered by liming and P addition. Indeed, Wann and Uehara (1978) reported a significant correlation between the point of zero charge (PZC) and the quantity of P applied to an oxisol.

Although the surface charge characteristics of variable charge soils have been assessed by a number of methods (Bell and Gillman, 1978), the ion-retention method has been used most commonly. This method involves two steps in the determination of charge. The first step consists of the removal of 'native' exchangeable ions by saturating the soil with an index electrolyte under specified conditions of ionic strength and the second step involves removal and analysis of the ions adsorbed from the index electrolyte.

The surface charge properties of variable charge soils are influenced by several characteristics of the index electrolyte, including ionic species, ionic strength, and pH (Van Raij and Peech, 1972; Wada and Harward, 1974; Bell and Gillman, 1978; Bowden et al., 1980b). According to Bell and Gillman (1978), the cation and anion of the saturating electrolyte should ideally be the same as the respective dominant ions in the soil solution. From soil solution composition studies of weathered soils of tropical and subtropical regions, it has been suggested (Le Roux and Sumner, 1967; Gillman and Bell, 1976) that either NaCl, KCl, CaCl₂ or MgCl₂ could be satisfactory as saturating electrolytes. However, at an ionic strength close to that of the soil solution, both Na⁺ and K⁺ would remove only part of the exchangeable Al (Van Raij and Peech, 1972; Gallez et al., 1976; Bell and Gillman, 1978). Failure to remove exchangeable Al, especially from acid soils, may result in an under-estimation of charge. In view of this, either Ca²⁺ or Mg²⁺ would appear to be more suitable saturating electrolytes but although saturation with Ca²⁺ would remove more Al³⁺ than would Na⁺, K⁺, or Mg²⁺, it would still extract only part of the exchangeable Al at the relatively low ionic strength of the soil solution. In view of this, many investigators have opted to remove exchangeable Al as well as other exchangeable ions by multiple, preliminary washings with solutions of high ionic strength prior to equilibration with an electrolyte of low ionic strength. Thus, Van Raij and Peech (1972) removed exchangeable ions from soils by five washings with M NaCl prior to saturation with the appropriate electrolyte.

Although removal of exchangeable ions, particularly Al, by preliminary washing of soils has been considered an integral part of the charge measurement process, the effect of this on the subsequent measurement of charge is not known. Moreover, electrolytes ranging in concentration from 0.2M (Gallez et al., 1976) to 1M (Van Raij and Peech, 1972) have been used for preliminary washing prior to saturation of soils with solutions of low ionic strength.

Widely different soil:solution ratios have also been used in the measurement of charge. For example, Van Raij and Peech (1972) used soil:solution ratios of 1:20 and 1:10, whereas Grove et al. (1982) used a ratio of 1:4 and 1:5 for the saturating and extracting solutions, respectively. The sorption of anions by soils is influenced by the soil:solution ratio (Hope and Syers, 1976; Barrow and Shaw, 1979a) but the effect has been attributed solely to a change in the rate of reaction. Because the

soil:solution ratio affects the pH of the soil suspension through dilution, as well as causing differences in the amounts of H^+ and Al^{3+} removed from solution, it would seem likely that the observed effect on anion sorption is due to differences in the surface charge of the substrate, as well as to a change in the rate of reaction, per se. There does not appear to be any published information on the effect of soil:solution ratio on the surface charge characteristics of soils.

This chapter is divided into two sections. The first section deals with the factors influencing the measurement of charge and the objectives of this section were:

- (i) to determine the effect of the concentration of prewash electrolytes on charge in a range of contrasting soils;
- (ii) to evaluate the effects of soil:solution ratio on surface charge characteristics;
- (iii) to compare the effects of the index cations, Na and Ca, on the surface charge characteristics of two soils at a range of pH values (obtained by liming).

The objectives of the second section of this chapter were to use a standardised method to determine the effect of pH (as influenced by liming) and added P on the surface charge characteristics of four acid soils from Fiji.

4.2 Materials and Methods

4.2.1 Preparation of soil samples

A detailed description of the preparation of the soils has been given in Chapter 3 (Section 3.4.1). Each of the soils was incubated with either 9 or 10 rates of $Ca(OH)_2$ under the conditions described in Chapter 3, for a period of 42 d. At the end of the incubation period, subsamples of the limed soils were reincubated with 2 rates (0 and $16.1 \text{ mmol kg}^{-1}$) of added P (as solution KH_2PO_4). After a period of 14 d the incubated soils were air dried at a temperature of $20 \pm 2^\circ C$ and stored in sealed polythene bags for further analyses.

4.2.2 Charge measurement procedures

4.2.2.1 Effect of concentration of prewash electrolytes on charge subsequently determined in 0.01M CaCl₂ solution

The amounts of negative and positive charge in an unlimed and a limed sample of each soil were determined by measuring the sorption of Ca²⁺ and Cl⁻ from 0.01M CaCl₂ solution after removal of exchangeable ions by initial washing of the soils with either 0.5M, 0.1M, or 0.01M CaCl₂ solutions. The method was essentially that of Van Raij and Peech (1972) except that the pH and Al³⁺ concentration of each equilibration extract were measured.

A 2-g (< 2 mm) sample of soil was shaken with 40 mL of either 0.5M, 0.1M, or 0.01M CaCl₂ solution in weighed centrifuge tubes for 1 h, centrifuged (15 min, 3000 rpm) after measuring the pH of the suspension, and filtered into numbered tubes. The extraction was repeated twice. Next, the soils which had been suspended in 0.5M CaCl₂ were washed by shaking once with deionized water (5 min) and twice (30 min) with 0.01M CaCl₂. The water wash reduced the concentration of CaCl₂ to about 0.01M, as indicated by the amounts of Ca²⁺ and Cl⁻ in the extract. This method was designated 0.5M CaCl₂/H₂O/0.01M CaCl₂.

The soils initially washed with 0.1M or 0.01M CaCl₂ were equilibrated with 0.01M CaCl₂ solution for a further 3 times for periods similar to those for the 0.5M CaCl₂ treated soils. These methods were designated 0.1M CaCl₂ / 0.01M CaCl₂ and 0.01M CaCl₂, respectively. After the final equilibration the tubes were centrifuged, the solutions filtered, and the tubes weighed to account for entrained solution. The residues were then extracted either 4 or 5 times, depending on the concentrations of Ca²⁺ and Cl⁻ in the final extract, with 20 mL of 0.5M KNO₃. Extracts 1 to 4 were combined whereas extract 5 was kept separate to determine the amount of Ca²⁺ and Cl⁻ extracted.

The pH of all soil suspensions was determined following equilibration. Aluminium in all CaCl₂ washes was determined by AAS using a nitrous-oxide acetylene flame. Because of the low Al concentration and high salt concentration in the KNO₃ extracts, Al in these extracts was determined using the modified aluminon reagent (Hsu, 1963). The Ca²⁺ and Cl⁻ in the final equilibration extract and in 0.5M KNO₃ extracts were determined by AAS using an air acetylene flame and a titrimetric procedure (Vogel, 1962), respectively.

4.2.2.2 Effect of soil:solution ratio on negative and positive charge determined in 0.01M CaCl₂

The surface charge of unlimed soils was measured at 3 different soil:solution ratios (1 g:40 mL, 4 g:40 mL, and 8 g:40 mL) using the 0.01M CaCl₂ method (Section 4.2.2.1). The pH and Ca²⁺ and Cl⁻ concentrations of the final equilibration extract and the Ca²⁺, Cl⁻, and Al³⁺ concentrations in the 0.5M KNO₃ extracts were determined as described above in Section 4.2.2.1.

4.2.2.3 Effect of index cation in the determination of negative and positive charge

This was examined for limed Nadroloulou and Seqaqa soils by using either Na⁺ or Ca²⁺ as the index cation. The method was essentially the same as the 0.01M CaCl₂ method described in Section 4.2.2.1 above, except that exchangeable ions were removed by washing the soil samples twice (for 1 h) with M NaCl prior to equilibration with either 0.01M CaCl₂ or 0.03M NaCl solution.

Adsorbed ions were extracted 5 times with 20 mL of 0.5M NH₄NO₃ (Van Raij and Peech, 1972) in the case of Na⁺ and with 20 mL of 0.5M KNO₃ in the case of Ca saturated soils. NH₄NO₃ was used as the extracting electrolyte in the case of Na⁺ because it is a better exchanger (Tan, 1982) for Na⁺ than is K⁺. The Na⁺ in the final equilibration solutions and 0.5M NH₄NO₃ extracts was determined using atomic emission spectrophotometry and Ca²⁺ and Cl⁻ in the 0.5M KNO₃ and NH₄NO₃ extracts were determined as described in Section 4.2.2.1. The concentration of Al³⁺ in 0.5M NH₄NO₃ and 0.5M KNO₃ extracts was determined as in Section 4.2.2.1.

4.2.3 Effect of soil pH and added P on negative and positive charge determined in 0.01M CaCl₂

Surface charge in limed and selected limed and subsequently P-treated (16.1 mmol P kg⁻¹ soil) soils was determined using the 0.01M CaCl₂ method (Section 4.2.2.1). The Ca²⁺ and Cl⁻ in the final equilibration extract and Ca²⁺, Cl⁻, and Al³⁺ in the 0.5M KNO₃ extracts were determined as in Section 4.2.2.1.

4.3 Results and Discussion

4.3.1 Charge measurement procedures

4.3.1.1 Effect of concentration of prewash electrolytes

The washing of unlimed soils with electrolytes of different concentrations had a variable effect (Table 4.1) on charge subsequently determined in 0.01M CaCl₂.

In general, the magnitude of both negative and positive charge increased with the concentration of the prewash electrolyte. However, the increase in negative charge was dependent on pH and the M KCl-extractable Al content of the soils (Table 4.1). For example, the Batiri and Nadroloulou soils had pH values of 4.9 and 3.9, respectively and contained 0.3 and 35.6 mmol kg⁻¹ soil of M KCl-extractable Al, respectively. Measured negative charge varied from 1.9 to 2.4 and from 16.0 to 22.7 cmol(p) kg⁻¹, respectively, depending on the concentration of the prewash electrolyte. Moreover, in the limed soils (Table 4.1), where M KCl-extractable Al was reduced to zero, there was only a small effect of the concentration of prewash electrolyte on negative charge. These results suggest that the variation in negative charge is related to the amount of Al extracted during the prewashing step. The amount of Al extracted increased with the concentration of the prewash electrolyte and this was associated with a corresponding decrease in 0.5M KNO₃- extractable Al. Nevertheless, the cumulative amounts of Al extracted during the prewash, saturating, and extraction steps were essentially the same for the 3 methods.

If Al in the 0.5M KNO₃ extract balanced the negative charge as Al³⁺ then when it was included in the calculation of charge as a counterion the adjusted negative charge was almost independent of the concentration of the prewash electrolyte. This is probably the reason why there was virtually no effect of the concentration of the prewash solution on surface negative charge of limed soils when M KCl-extractable Al was reduced to zero. Slight differences in the negative charge after adjustments for Al in 0.5M KNO₃ were probably due to the differences in the pH of the soil suspension.

The use of electrolyte solutions of high ionic strength for measurement of charge has often been criticised (During, 1973; Wada and Harward, 1974; Bell and Gillman, 1978; Uehara and Gillman, 1981; Black

Table 4.1 Effect of the concentration of prewash electrolytes on the cumulative amount of Al extracted by the saturation (CaCl₂) and extracting (KNO₃) electrolytes and on the negative (Ca ads), total negative (Ca ads + Al-KNO₃) and positive charge (Cl ads) determined in 0.01M CaCl₂ in a range of unlimed and limed soils.

Soil	pH # 0.01M CaCl ₂	Method##	Al extracted by		Ca ads	Total negative charge (Ca ads + Al-KNO ₃)	Positive charge (Cl ads)
			CaCl ₂	KNO ₃			
cmol(p)kg ⁻¹ soil							
Koronivia	4.9	1	2.0	0.2	3.6	3.8	1.3
	4.9	2	1.7	0.2	3.3	3.5	1.1
	4.7	3	0.8	1.0	2.7	3.7	1.3
Koronivia (limed)	5.7	1	n.d	n.d	8.0	8.0	1.3
	5.7	2	n.d	n.d	8.0	8.0	1.3
	5.8	3	n.d	n.d	7.6	7.6	0.9
Nadroloulou	4.8	1	7.6	0.8	22.7	23.5	1.9
	4.7	2	6.7	1.5	20.8	22.3	1.5
	4.3	3	3.2	5.7	16.0	21.7	1.2
Nadroloulou (limed)	6.0	1	n.d	n.d	30.9	30.9	1.3
	6.2	2	n.d	n.d	30.7	30.7	1.2
	6.2	3	n.d	n.d	28.9	28.9	0.5
Batiri	4.7	1	0.4	n.d	2.4	2.4	4.7
	4.6	2	0.4	n.d	2.3	2.3	3.2
	4.5	3	0.1	0.3	1.9	2.2	3.0
Batiri (limed)	5.2	1	n.d	n.d	2.9	2.9	4.1
	5.2	2	n.d	n.d	2.8	2.8	3.0
	5.2	3	n.d	n.d	2.7	2.7	2.6
Seqaqa	4.7	1	2.4	0.5	8.2	8.7	3.2
	4.6	2	1.8	1.2	6.8	8.0	2.8
	4.6	3	0.8	1.7	6.5	8.2	2.6
Seqaqa (limed)	5.7	1	n.d	n.d	17.2	17.2	3.0
	5.8	2	n.d	n.d	16.9	16.9	2.7
	5.7	3	n.d	n.d	17.2	17.2	2.4

pH in sixth equilibration extract.

Method 1 = 0.5M CaCl₂/ H₂O / 0.01M CaCl₂. Method 2 = 0.1M CaCl₂ / 0.01M CaCl₂. Method 3 = 0.01M CaCl₂.

and Cambell, 1983). Recently, Grove et al. (1982) recommended an unbuffered solution, having an ionic strength which was sufficient to remove exchangeable Al, as being the most suitable.

The present study indicates that the removal of Al by electrolytes of different ionic strength has little effect on the negative charge of soils determined in 0.01M CaCl₂ provided Al removed by 0.5M KNO₃ is included in the calculation of charge. However, a high concentration of prewash electrolyte has a significant effect on the pH of the soil suspension measured in the sixth equilibration, which may be the reason for the slightly higher negative charge which was observed even after inclusion of Al in KNO₃ extracts (Table 4.1). In view of these observations, the 0.01M CaCl₂ method, with inclusion in the charge calculation of Al removed by KNO₃ is probably the most satisfactory procedure.

4.3.1.2 Effect of soil:solution ratio

Soil:solution ratio had a variable effect on the surface charge of unlimed soils (Fig. 4.1). As expected, the pH of the soil suspension was also affected (Fig. 4.2). These differences were generally related to the amount of Al extracted during the saturation process. Thus the high negative charge and high pH observed at a wide soil:solution ratio were probably due to the removal of relatively large amounts of Al and exchangeable H ions in comparison to those removed at a narrow soil:solution ratio. The increased pH (Fig. 4.2) at a wide soil:solution ratio is due, at least in part, to a dilution effect. These results further confirm the need to account for extractable Al in charge measurement procedures with acid soils.

Appreciable amounts of Al were detected in the 0.5M KNO₃ extracts of the soils but the quantities depended on the soil:solution ratio. At a narrow soil:solution ratio, relatively large amounts of Al were present in the 0.5M KNO₃ extracts, suggesting incomplete exchange during equilibration. Inclusion of this Al in the charge calculation eliminated the differences in negative charge determined at different soil:solution ratios.

Differences in positive charge are probably due to the incomplete exchange of Cl⁻ for anions such as NO₃⁻ and SO₄²⁻ on the soil surface, particularly at a narrow soil:solution ratio.

The implication of this study is that preliminary washing of soils with

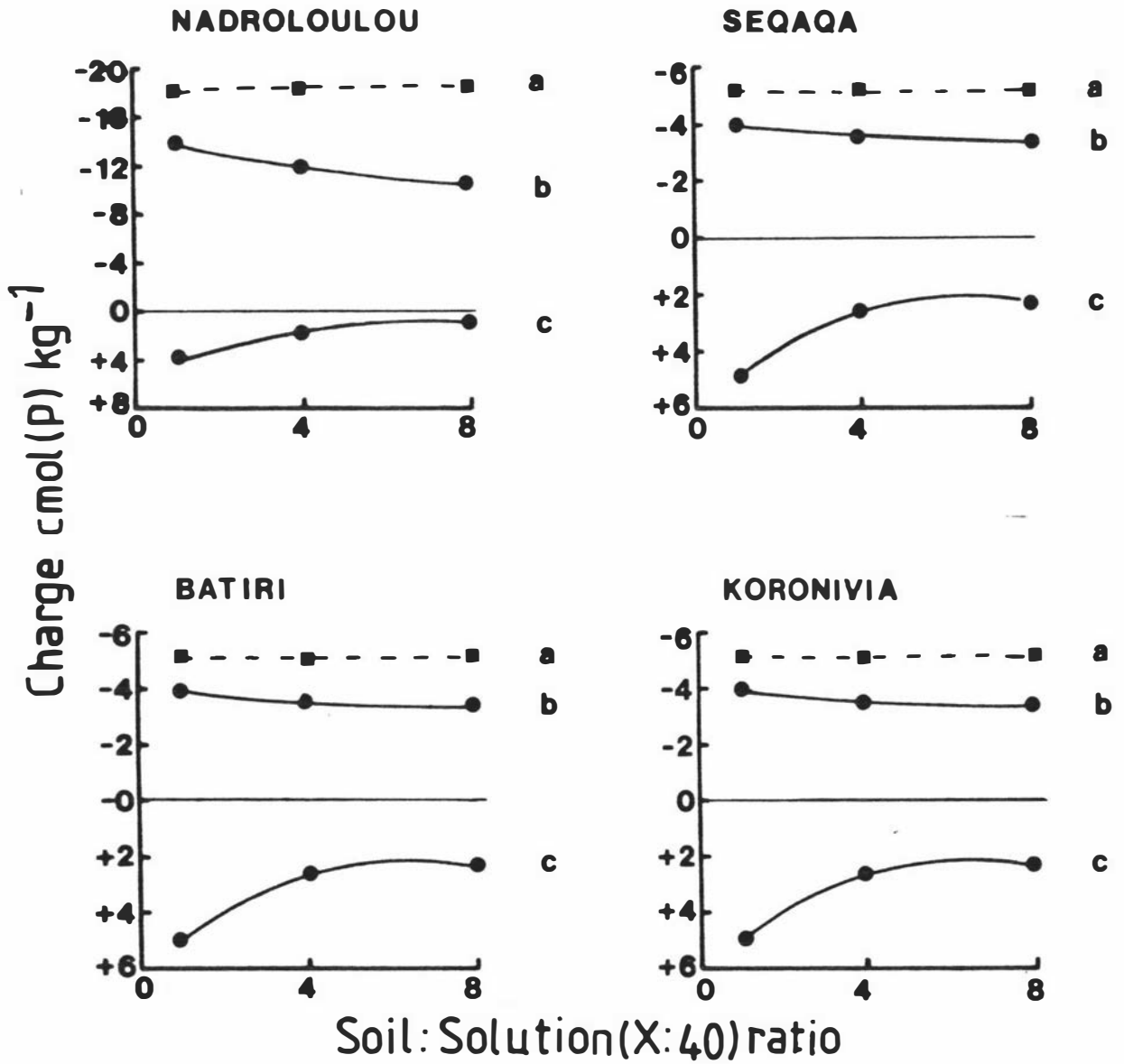


Fig. 4.1 Effect of soil:solution ratio on the distribution of (a) total negative (Ca ads + Al-KNO₃), (b) negative (Ca ads), and (c) positive charge (Cl ads) in the four soils.

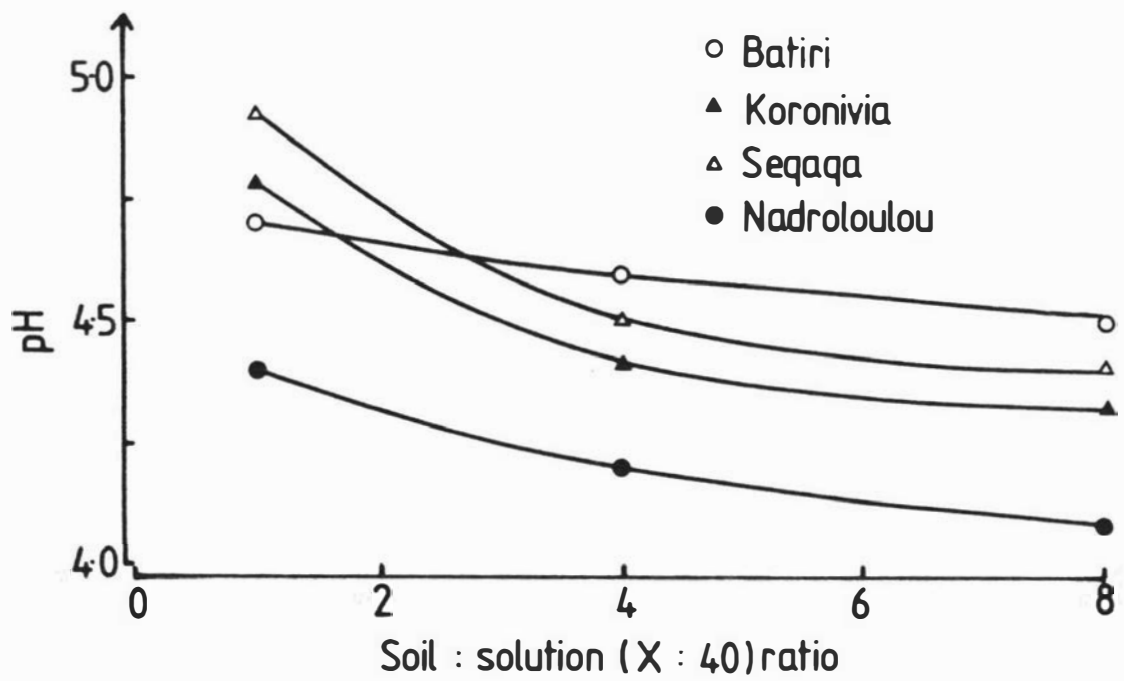


Fig. 4.2 Effect of soil:solution ratio on the pH (in the sixth equilibration) of the soil suspension.

electrolytes of high ionic strength can be dispensed with provided charge measurement is conducted at a wide soil:solution ratio with inclusion of Al in the 0.5M KNO₃ extract in the calculation of charge. Furthermore, the previously reported effects of soil:solution ratio on P sorption may satisfactorily be explained using the present results. Thus, the lower P sorption observed (Hope and Syers, 1976; Barrow and Shaw, 1979a) at a wide soil:solution ratio is possibly due to the large negative charge on soil particle surfaces relative to that at a narrow soil:solution ratio. This would affect the rate of reaction (Hope and Syers, 1976).

4.3.1.3 Effect of the index cation

Negative and positive charge measured in 0.01M CaCl₂ were both higher than values determined in 0.03M NaCl (Fig. 4.3). Similar results were obtained by Van Raij and Peech (1972) and Morais et al. (1976) and they were explained by the ion-valence effect on the potential-determining ions. Ryden and Syers (1975) suggested that increasing the valence of the supporting electrolyte increases the screening effect on surface charge, thus allowing increased sorption of H⁺ and OH⁻ ions to maintain a constant surface potential.

Correlation studies indicate a strong linear relationship between the negative charge measured in NaCl and in CaCl₂ (Table 4.2). However, negative charge measured in NaCl was always lower than that measured in CaCl₂, as indicated by the slope coefficient. This difference was more pronounced for limed soils (Fig. 4.3), and may be explained by the strong retention of Ca²⁺ compared to Na⁺ by soil colloids (Breeuswma and Lyklema, 1971, 1973; Kinniburgh et al., 1975). Stoop (1980) reported that soils containing mostly hydrous Fe and Al oxides, and thus colloids of the variable charge type retain ions through various types of adsorption mechanisms. He found that adsorbed P increased the adsorption of cations and lowered the PZC. In view of this, Ca²⁺ in the 0.5M NH₄NO₃ extracts of both Nadroloulou and Seqaqa soils was measured, in addition to Na⁺. Appreciable amounts of Ca²⁺ were detected in the extracts at pH values exceeding 5 and when these were included in the calculation of charge (line b in Fig. 4.3) the difference between the NaCl- and CaCl₂-measured values was decreased. When the adjusted charge was included in the correlation analyses both an improved correlation coefficient (Table 4.2) and a slope approaching unity were obtained. These results suggest that most of the observed variation in the NaCl- and CaCl₂-measured negative charge in

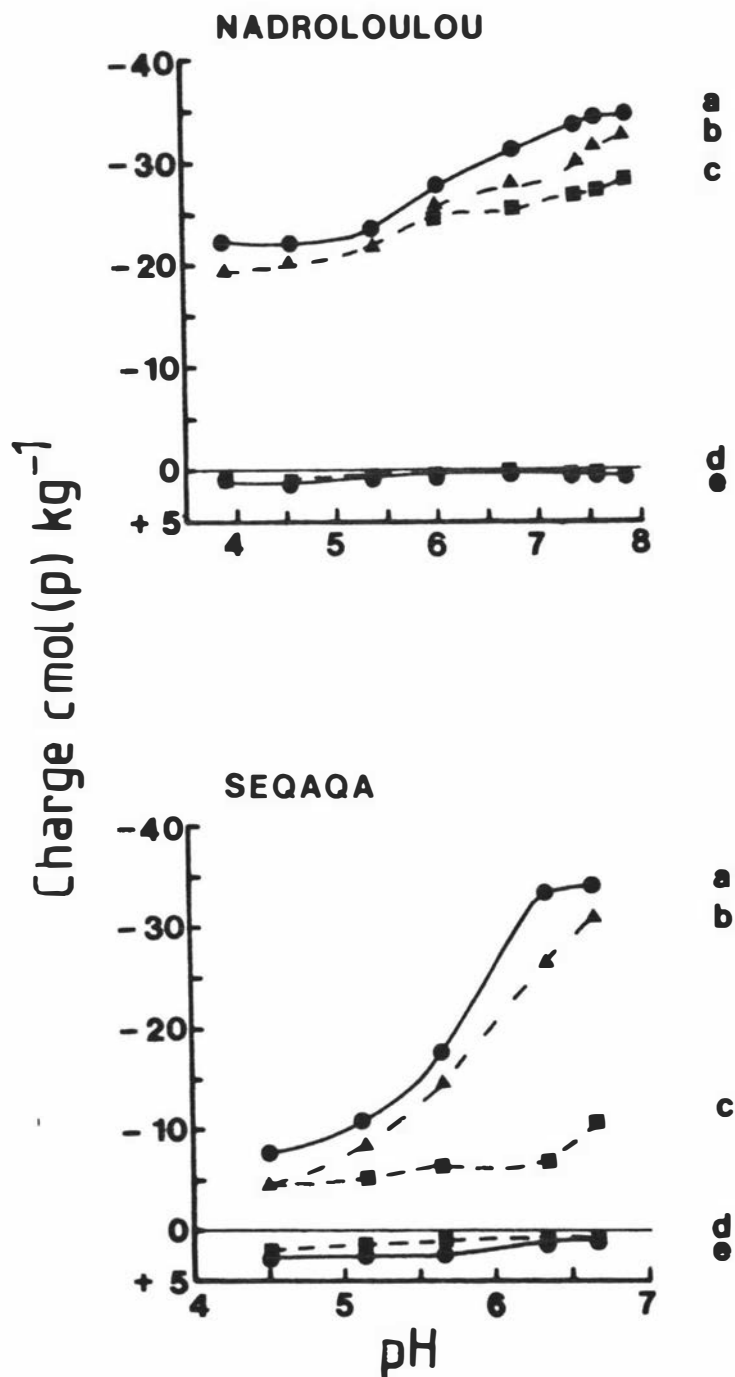


Fig. 4.3 Effect of soil pH on the distribution of negative and positive charge determined in 0.01M CaCl_2 and 0.03M NaCl .
 (a) negative charge determined in 0.01M CaCl_2 ,
 (b) total negative charge ($\text{Na ads} + \text{Ca}(\text{NH}_4\text{NO}_3)$) determined in 0.03M NaCl ,
 (c) negative charge (Na ads) determined in 0.03M NaCl ,
 (d) positive charge determined in 0.03M NaCl ,
 and (e) positive charge determined in 0.01M CaCl_2 .

Table 4.2 Correlation and linear regression coefficients between negative charge (Na ads) and total negative charge (Na ads + Ca(NH₄NO₃)) determined in 0.03M NaCl and negative charge (Ca ads) determined in 0.01M CaCl₂ solution.

Soil	Equation of line		r
Nadroloulou	Na ads	= 6.70 + 0.61 Ca ads	0.98
	Na ads + Ca(NH ₄ NO ₃)	= -0.68 + 0.93 Ca ads	0.99
Seqaqa	Na ads	= 3.26 - 0.88 Ca ads	0.85
	Na ads + Ca(NH ₄ NO ₃)	= -1.91 + 0.92 Ca ads	0.99

limed soils is due to the inability of Na^+ to exchange for Ca^{2+} at high pH values. The results further imply that for variable charge soils, such as those used in the present study, CaCl_2 should be used to measure charge.

4.3.2 Effect of soil pH on charge characteristics of soils

The amount of lime required to increase the pH varied between soils (Fig. 4.4), indicating differences in their pH buffering capacities. The buffering capacity of Batiri soil is low. Only approximately $400 \text{ kg Ca(OH)}_2 \text{ ha}^{-1}$ would be required to increase the pH to a depth of 100 mm from 4.9 to about 5.2, at which point M KCl-extractable Al would be zero. The low buffering capacity reflects the highly weathered nature of this soil. Much larger amounts of lime (Fig. 4.4) were required to adjust the pH of Koronivia, Nadroloulou, and Seqaqa soils. These soils required 4 to 14 times more Ca(OH)_2 than the Batiri soil to increase pH to about 5.2, presumably due to the high buffering capacity resulting from large amounts of M KCl-extractable Al ($9.3 - 35.6 \text{ mmol kg}^{-1}$ soil), organic matter (5.6 - 16.6%), and oxalate-extractable Fe ($63 - 94 \text{ mmol kg}^{-1}$ soil) and Al ($50 - 643 \text{ mmol kg}^{-1}$ soil) in these soils. Similar large amounts of lime ($800 - 5000 \text{ kg ha}^{-1}$) were required to increase the pH of strongly acid Hawaiian and Nigerian tropical soils to about 5.0 (Fox, 1980). Manganese toxicities may also pose a problem in these soils because the pH required to decrease soluble Mn to a sufficiently low level is relatively higher than that for Al (Fox, 1980).

All soils possessed both positive and negative charges, the amounts of which changed significantly with an increase in soil pH (Fig. 4.5). This apparent co-existence of positive and negative charge is consistent with the suggestion of Van Raij and Peech (1972), Espinoza et al. (1975), and Black and Waring, (1976) that charges are arranged on soil colloids such that they do not completely cancel each other.

The presence of negative charge at low pH values in all the soils was probably a result of different amounts of permanent negative charge arising from isomorphous substitution within the lattices of clay minerals (Robertson et al., 1954; Bolland et al., 1976). Mineralogical examination indicated that moderate amounts of kaolinite were present in all the soils, appreciable amounts of vermiculite were present in the Nadroloulou soil, and trace amounts of vermiculite were present in the Koronivia soil. The high negative charge at low pH values in the Seqaqa

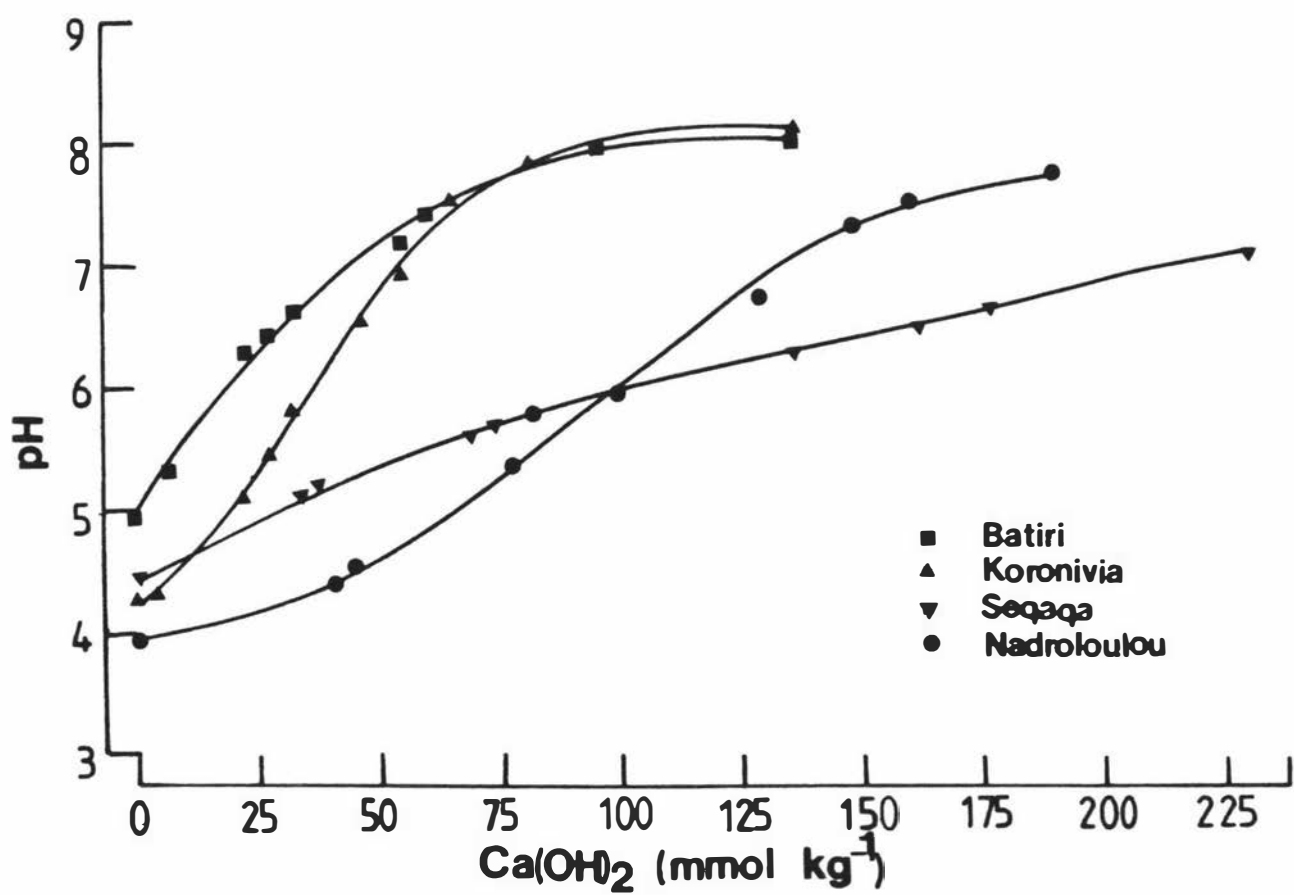


Fig. 4.4

Effect of increasing amounts of Ca(OH)_2 on the pH of four contrasting soils.

soils is probably due to the high organic matter content (16.6%) of this soil.

Liming of all soils caused a rapid increase in the negative charge (Fig. 4.5). However, the magnitude of the increase varied with the soils. For example, the negative charge in the Seqaqa soil increased from 8 to over 38 cmol(p) kg^{-1} compared to only a small increase of 2 to 10 cmol(p) kg^{-1} in the Batiri soil over the same pH range. These results suggest that the ability of these soils to retain cations should vary considerably. The Batiri and Koronivia soils, even if limed to pH 6, have a much lower cation-retention capacity than the Seqaqa and Nadroloulou soils, suggesting that losses of added cations would be substantially larger in the first 2 soils.

The effect of pH on negative and positive charge is well established and considered to be due to proton transfer mechanisms involving organic matter, Fe and Al oxides, and the edges of kaolinite (Parks, 1965; Hingston et al., 1972; Van Raij and Peech, 1972; Ryden et al., 1977a,b) and other clay minerals such as illite (Hendershot and Lavkulich, 1983).

The presence of positive charge at low pH values is consistent with the mineralogical composition of these soils. All soils contained an abundance of either gibbsite or goethite, or both (Table 3.3) and appreciable quantities of poorly-ordered material in the clay fraction. Gibbsite and goethite minerals carry net positive charge (Parks, 1965) in the normal soil pH range. However, the magnitude of positive charge can vary, depending on organic matter, which can mask positively-charged sites (Bell and Gillman, 1978).

Although positive charge decreased with increasing pH, detectable amounts were still present in all soils at pH values higher than 7. For example, the Batiri and Seqaqa soils contained in excess of 0.9 cmol (p) kg^{-1} positive charge whereas the Nadroloulou and Koronivia soils contained between 0.3 and 0.4 cmol(p) kg^{-1} . Similar observations were reported by Morais et al. (1976) and Tessens and Zauyah (1982) in a range of highly-weathered, Brazilian and Malaysian soils, respectively. The latter workers attributed this to permanent positive charge resulting from isomorphous substitution of Ti^{4+} (Quirk, 1960) and/or Mn^{4+} in the Fe oxide lattice (Sumner and Davidtz, 1965). Using the ratio of Fe to Ti and/or Mn present in citrate-dithionite-bicarbonate (CDB) extracts, the Malaysian workers were able to calculate the formula of the substituted Fe oxide mineral in the Malaysian oxisols.

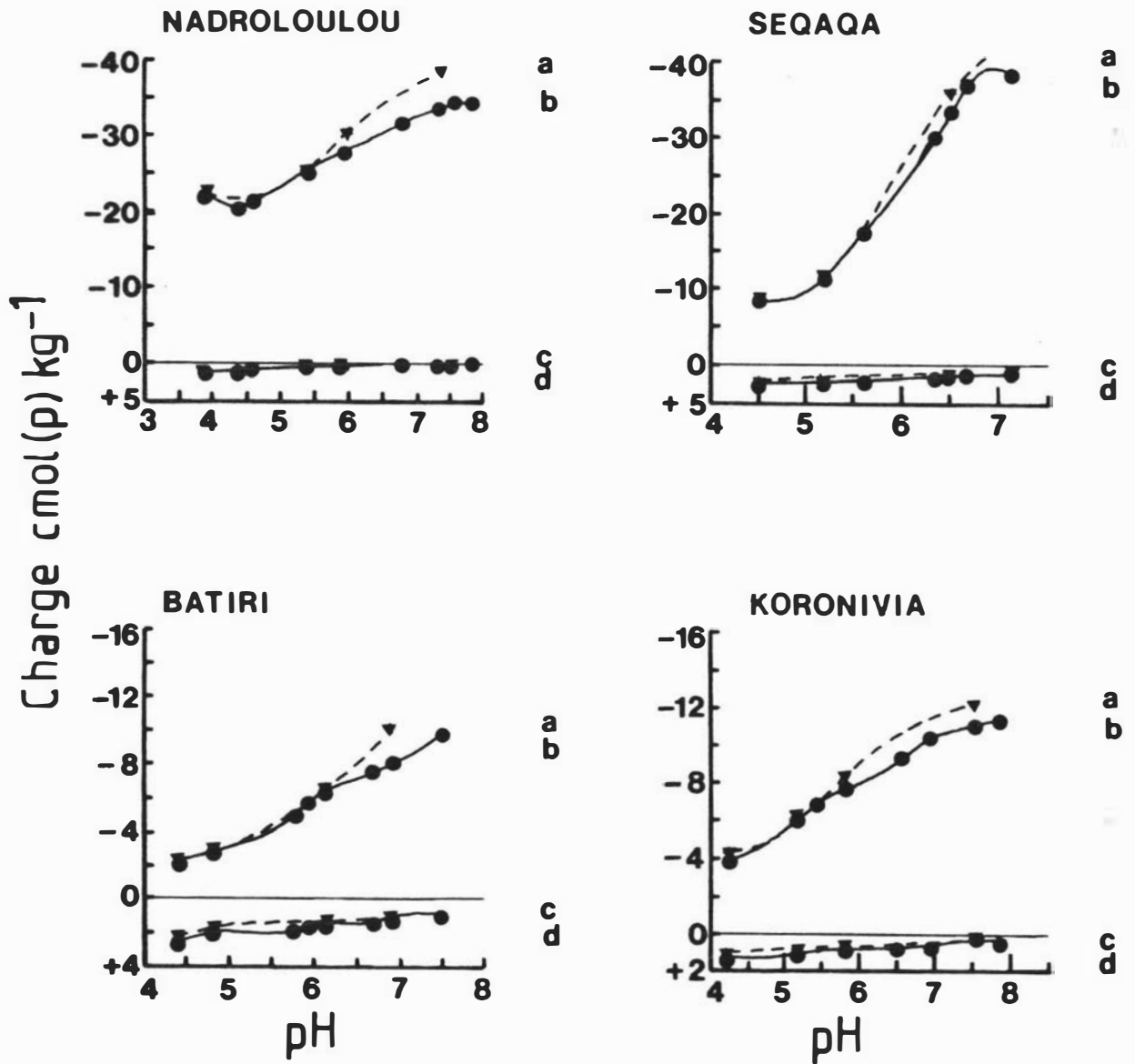


Fig. 4.5 Effect of soil pH and added P on the distribution of negative and positive charge in soils. (a) negative charge in P-treated ($16.1 \text{ mmol P kg}^{-1}$ soil) soils, (b) negative charge in untreated (0 mmol P kg^{-1} soil) soils, (c) positive charge in P-treated ($16.1 \text{ mmol P kg}^{-1}$ soil) soils, and (d) positive charge in untreated (0 mmol P kg^{-1} soil) soils.

Appreciable amounts (Table 4.3) of Fe, Ti, and Mn were detected in the CDB extracts of the Fijian soils used in this study. Using these data and calculations similar to those of Tessens and Zauyah, (1982), a theoretical, permanent positive charge was calculated (Table 4.3). A comparison between observed and calculated results shows that it was necessary to include both Ti and Mn substitution to account for the observed positive charge in all soils except Koronivia. In the Koronivia soil, the observed charge was somewhat higher than the theoretical charge.

In general, the point of zero charge (PZC) varied considerably between the soils. Three of the four soils were always negatively charged and therefore no direct measurement of the PZC could be made. The exception was the Batiri soil which had a PZC of 5.3. However, inspection of the pH-charge curves (Fig. 4.5) suggests that PZC's were in the following approximate range: Batiri (5.3) > Koronivia (~4) > Seqaqa (~3) > Nadroloulou which did not have a PZC in the normal pH range. The literature indicates that the PZC of strongly-weathered soils, such as oxisols, ultisols and alfisols, can vary from 2.7 to 6.5 (Van Raij and Peech, 1972; El-Swaify and Sayegh, 1975; Gallez et al., 1976), the lower values being obtained for surface horizons due to higher amounts of organic matter. The present values obtained are in agreement with published values.

4.3.3 Effect of added phosphate on charge

The changes in surface negative and positive charge resulting from P additions were small compared to those resulting from lime additions, described above. However, the magnitude of reduction in positive charge induced by P addition was not consistent at all pH values. A substantially larger effect of P on surface positive charge was observed at low pH values. These observations are in agreement with those of others (Hingston et al., 1967; Rajan et al., 1974; Ryden et al., 1977a). The decreased effect of P on positive charge at high pH was interpreted as being due to a higher tendency for P to sorb on neutral and negative sites (Breeuswma and Leuklema, 1973; Rajan et al., 1974; Ryden et al., 1977a). In these studies the ratio of H^+ consumed or OH^- released mol^{-1} of P sorbed increased with pH, suggesting that P was sorbed by ligand exchange with surface OH_2^+ groups in the low pH range, but displaced OH^- from neutral and negative sites at high pH. If such a ligand exchange mechanism could be accepted for P then the release of OH^- can be used to

Table 4.3 Ratio of Fe:Ti and Fe:Mn in the citrate-dithionite-bicarbonate extracts, positive permanent charge estimated from Ti(IV) and from Ti(IV) + Mn(IV) substitution in iron oxides and that determined by Cl adsorption (Cl ads) from 0.01M CaCl₂ above pH 7.

Soil	Ratio		Positive permanent charge		
	Fe:Ti	Fe:Mn	Ti# substitution	(Ti+Mn)#	Cl ads##
			————— cmol(p) kg ⁻¹ —————		
Koronivia	1220	829	0.04	0.10	0.36
Nadroloulou	1001	560	0.05	0.38	0.33
Batiri	398	752	0.62	0.92	0.91
Seqaqa	1118	229	0.13	0.70	1.05

Charge calculated by using the method of Tessens and Zauyah (1982).

Experimentally observed charge.

infer changes in surface charge in the soils.

Addition of P had a larger effect on negative charge at high pH values (Fig. 4.5). These observations are in accord with the ligand exchange mechanism discussed above. The small increase in negative charge, with a subsequent decrease in positive charge, probably have resulted in an overall decrease in the PZC following addition of P. Similar shifts in PZC were reported by Parks (1965), Mekaru and Uehara (1972), and Rajan (1978). Wann and Uehara (1978) used this decrease in PZC as an indication of the increased capacity of soils to retain cations. They showed that application of about 50 mmol P kg⁻¹ to an oxisol lowered the PZC from near 5.0 to below 3.5 in the presence of Ca, and recommended the application of P as a means of increasing the negative charge (cation retention) of soils. However, they emphasised that, in many cases, it would not be economical to apply P merely to increase the negative charge, but as variable charge soils generally require large applications of P for plant growth, the increase in negative charge comes as an added benefit. Although the amount of P added to the soils in the present study was one third of that used by Wann and Uehara (1978), the results indicate that a very large amount of P would be required to obtain an increase in negative charge which would have any long-term, beneficial effect on plant growth.

4.4 Conclusions

The effects of the concentration of prewash electrolytes, soil:solution ratio and index cation on the magnitude of surface charge were investigated using selected unlimed and limed soils from Fiji.

Preliminary washing of soils, with electrolytes of varying concentration and soil:solution ratio, had little effect on surface negative charge provided Al in the 0.5M KNO₃ extract was included in the calculation of charge. Surface charge measurements obtained in 0.01M CaCl₂ were always larger than those in 0.03M NaCl. Most of the difference was due to the inability of Na⁺ to exchange with Ca²⁺ in soils at high pH.

Based on these observations it would appear that the best method for measuring charge in limed Fijian soils is to use 0.01M CaCl₂ with inclusion of Al in 0.5M KNO₃, without a preliminary washing with an electrolyte of high concentration.

Liming of soils caused a significant increase in negative charge and a smaller decrease in positive charge. The latter was detected in all soils even at pH values higher than 7. Presence of positive charge at high pH values was explained by isomorphous substitution of Ti^{4+} and/or Mn^{4+} in the Fe oxide lattice.

The effect of added P ($16.1 \text{ mmol kg}^{-1}$ soil) on surface charge was different at different pH values but was always small relative to that due to liming.

The Batiri and Koronivia soils had a relatively low negative charge at field pH values, suggesting that losses of added cations would be substantially larger than those experienced with the less weathered soils.

CHAPTER 5

CHAPTER 5

EFFECT OF LIMING ON PHOSPHATE
EXTRACTED BY TWO SOIL-TESTING PROCEDURES

5.1 Introduction

It has generally been observed that liming of highly-weathered, acid soils increases plant growth and this has been attributed to an alleviation of Al toxicity and/or an increase in the availability of P and other nutrients (Sanchez and Uehara, 1980). However, there have been a number of reports (e.g., Sumner, 1979), based on plant P data, where liming acid soils to near neutrality appeared to decrease P availability after an initial increase in availability up to soil pH values of approximately 6. In contrast to these observations, considerable controversy exists in the literature regarding the effects of liming on the amount of P extracted by various soil-testing procedures. For example, whereas Rhue and Hensel (1983) reported an increase in Mehlich-extractable P with increasing lime rates, Griffin (1971) recorded both an increasing and a decreasing trend in Mehlich-extractable P with increasing pH depending on soil type. Furthermore, Lambert and Grant (1980) and Sorn-srivichai et al. (1984) reported a consistent decrease in Olsen-extractable P with increasing lime additions. The latter investigators attributed the decrease in Olsen P with increasing pH to an artefact in the Olsen method. This suggests that some of the conflicting reports in the literature may be explained by careful consideration of the soil-testing procedures.

With the exception of the study on the influence of pH on Olsen-extractable P by Sorn-srivichai et al. (1984) and the suggestion by Kamprath and Watson (1980) that liming may decrease the efficiency of weak acid extractants for the removal of P, there is little information in the literature on the effect of liming on the amount of P extracted by soil-testing procedures used to assess the available P status of soils. The present study was designed to investigate the effects of liming on the amount of P extracted from acid soils by two contrasting soil-testing procedures and to relate these to the amounts of isotopically-exchangeable P.

Because the soils used in this study were initially strongly acid and were subsequently limed, the two soil-testing procedures selected were those developed by Olsen (Olsen et al., 1954) and Mehlich (Nelson et al., 1953). The Olsen procedure was chosen because it was initially designed (Olsen et al., 1954) for calcareous soils and subsequently shown to be successful with acid soils (Barrow and Shaw, 1976). The Mehlich procedure was selected because it is relatively successful with highly-weathered, acid soils (Thomas and Peaslee, 1973). The determination of exchangeable P is less empirical and provides a good measure of potentially-available P (Barrow, 1983a).

5.2 Materials and Methods

5.2.1 Preparation of soil samples

Detailed descriptions of the soils, and the methods used for their preparation are given in Chapter 3, but a brief description is included below.

Lime as $\text{Ca}(\text{OH})_2$ was added to the 4 soils (Batiri, Koronivia, Nadroloulou, and Seqaqa) at either 9 or 10 rates and thoroughly mixed and incubated under the conditions specified in Chapter 3. At the end of the incubation period, the soils were air dried and subsamples were reincubated with 3 rates of added P. Following this second incubation, the soils were air dried and stored in polythene bags for chemical analysis.

5.2.2 Chemical analyses

Exchangeable P: Isotopic-exchange measurements were done by shaking soil (1 g) with distilled water (39 mL) end-over-end for 16 h, at 20°C. Carrier-free ^{32}P (1 mL, 4 μCi) was then added and the tubes shaken for a further 4 h. This method was essentially the same as that used by Le Mare (1981), except that after the addition of ^{32}P the soils were shaken for 4 h rather than 24 h. The tubes were centrifuged, the solution passed through a membrane filter ($<0.45 \mu\text{m}$), and ^{32}P activity and ^{31}P determined in the filtrate. The activity of ^{32}P was determined by liquid scintillation counting using a triton-toluene scintillation cocktail (Patterson and Green, 1965).

The method of Murphy and Riley (1962) was used to measure ^{31}P in all soil extracts.

Olsen-extractable P (Olsen et al., 1954): 1 g of soil was shaken for 30 min with 20 mL of 0.5M NaHCO₃ (pH 8.5) solution in polypropylene tubes, centrifuged, and filtered through Whatman No. 5 filter paper. Inorganic P was determined in the extract by the method of Murphy and Riley (1962).

Mehlich-extractable P (Nelson et al., 1953): 5 g of soil was shaken for 5 min with 20 mL of Mehlich reagent (0.013M H₂SO₄ + 0.05M HCl, pH 1.25) in polypropylene tubes, centrifuged, and filtered through Whatman No. 5 filter paper. Inorganic P in the extracts was determined as described above for Olsen-extractable P. The pH of the Mehlich extract after filtration was also measured.

During this study it was observed that the pH of the Mehlich reagent, following extraction of limed soils, had increased considerably above its initial value of 1.25. To determine the effect of pH increase on the amounts of P extracted by the Mehlich reagent, extractions were carried out on selected limed and unlimed samples of the Batiri, Koronivia, and Nadroloulou soils in a Radiometer Copenhagen autoburette. This maintained the pH of the extractant close to 1.25 by the automatic addition of 0.13M H₂SO₄ + 0.5M HCl, which was 10 times more concentrated than the Mehlich reagent. The use of such a strong reagent to control pH ensured only small changes in the volume of the extractant.

All results are presented as the means of duplicates.

5.3 Results and Discussion

Addition of lime to each soil resulted in samples covering a range of pH from 4.0 - 5.0 to over 7.

5.3.1 Effect of lime and phosphate additions on isotopically-exchangeable phosphate

Lime and P additions had a marked effect on the amounts of exchangeable P (Fig. 5.1). In the absence of added P the Batiri, Seqaqa, and Nadroloulou soils generally showed an increase in exchangeable P up to pH values between 6 and 7.4, above which it decreased. In contrast, in the Koronivia soil, there was a small decrease in exchangeable P between pH values 4 to 5.5, above which it increased slightly. In the high P-sorbing Batiri and Seqaqa soils, treated with low levels of lime, solution P was nondetectable and ³²P

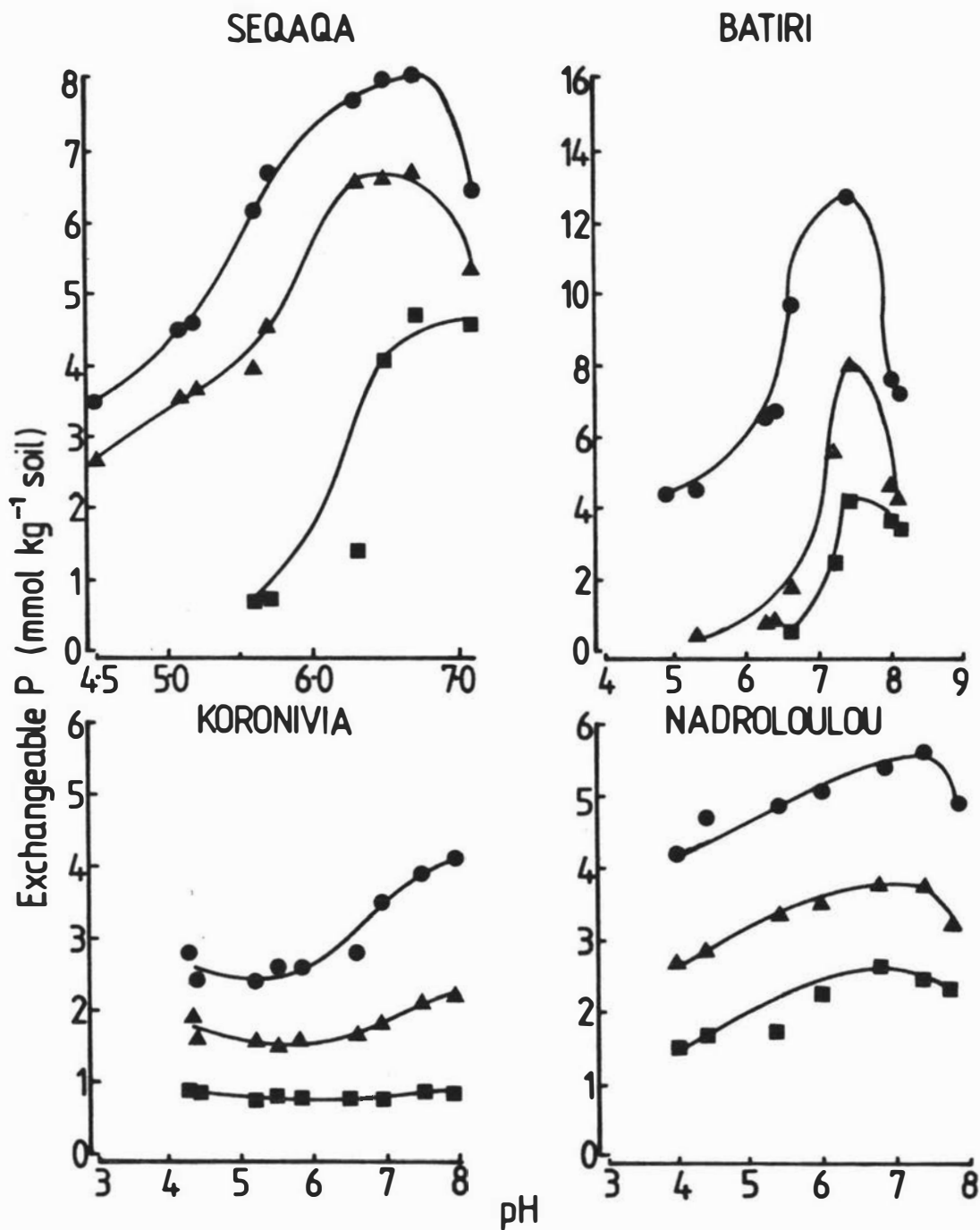


Fig. 5.1 Effect of increasing pH on isotopically-exchangeable P in 4 soils incubated with 3 rates of added P. (\blacksquare = 0; \blacktriangle = 8.1; \bullet = 16.1 mmol kg^{-1} soil).

counts were very low, so it was not possible to obtain exchangeable P values, even in soil samples treated with medium (8.1 mmol kg^{-1}) levels of P.

In soils incubated with added P, exchangeable P increased several fold, maintaining the trend with increasing pH observed for the untreated soils. However, the extent of the increase in exchangeable P with increasing lime and P additions varied between the soils. For example, in the Batiri soil, exchangeable P increased rather rapidly above pH 6.0, relative to the increase recorded for the other soils. Furthermore, whereas exchangeable P increased within each lime level in the Koronivia, Nadroloulou, and Seqaqa soils treated with increasing amounts of added P, it was not measurable at low pH values in the Batiri soil even when it was treated with medium amounts of added P (Fig. 5.1). In the Batiri soil, a marked increase in exchangeable P within each lime level at low pH values was only recorded at the highest level of added P. These results suggest that the Batiri soil contains a small number of very active P-sorbing sites which are rapidly neutralized by liming up to pH 6, or by addition of a high level of P. Subsequent to neutralization of these sites there was a rapid increase in exchangeable P.

In considering these results, the first point to note is that more than one physio-chemical process may be involved in the exchange reaction. Thus, when P is sorbed by a soil, several reaction mechanisms are possible, depending on the pH and the charge on the surface (Mott, 1970). Moreover, isotopic-exchange is a continuing process in soil systems (Barrow, 1975). Rather than having a definite end point, the added ^{32}P exchanges at a decreasing rate with an increasing proportion of the soil P, the rate of exchange being dependent in part on the strength of the bond between sorbed P and the substrate (Ryden and Syers, 1977b). Thus, the observed initial increase in exchangeable P with soil pH may be due to an increase in net surface negative charge (Chapter 4, Section 4.3.2) of the soils with liming. As a result of this the potential in the plane of sorption would become increasingly negative (Bowden et al., 1980b), thereby decreasing the binding energy between sorbed P and the surface. At high pH values, surface reactions may be complicated by precipitation reactions involving Ca and solution P. Thus, the decrease in exchangeable P at high pH values in the Batiri, Nadroloulou, and Seqaqa soils suggests the formation of a new phase, which in this case is probably Ca-P (Wild, 1953; Mattingly, 1975; Murrmann and Peech, 1969). However, the pH at which precipitation reactions occur will vary with the concentration of Ca and P in solution (Wild, 1953;

Barrow et al., 1980). This is possibly the reason why Koronivia soil, to which the lowest amount of lime was added, did not show a maximum in exchangeable P over the pH range studied, whereas in the Seqaqa soil, which received the largest amount of lime, exchangeable P reached a maximum at approximately pH 7.

5.3.2 Effect of lime and phosphate additions on Olsen-extractable phosphate

Both lime and P additions had a variable effect on Olsen-extractable P (Fig. 5.2). In general, less than $0.1 \text{ mmol P kg}^{-1}$ soil was extracted from the unlimed soils which had not been incubated with added P. When the soils were incubated with added P, the proportion of added P extracted varied from less than 1% in the Batiri and Seqaqa soils to between 12 and 35% in the Nadroloulou and Koronivia soils, respectively. These results are consistent with the mineralogical composition of the soils in that the Batiri and Seqaqa soils, which contain large amounts of either acid oxalate- or dithionite-extractable Fe and Al (Table 3.3), sorbed the largest amounts of added P.

In contrast to the results for exchangeable P, liming had little effect on the amount of P extracted by the Olsen reagent from soils which had not been incubated with added P. However, in soils treated with the medium level of added P there was a tendency for Olsen P to decrease initially with increasing soil pH and this was followed by an increase at high pH values. This trend was more pronounced in soils treated with high levels of added P such that there was a definite minimum in Olsen P between pH values 5.5 and 6.5 (Fig. 5.2).

A decrease in Olsen P with increasing pH has been reported recently (Lambert and Grant, 1980; Sorn-srivichai et al., 1984) and this was attributed (Sorn-srivichai et al., 1984) to an artefact in the Olsen procedure. The latter investigators provided good supporting evidence to suggest that P coprecipitated as a Ca-P compound in the Olsen extract. They suggested that such coprecipitation became more pronounced as soil pH increased due to the higher quantities of Ca present. Coprecipitation should also increase with an increase in the amount of added P and this was noted in the present study.

The increase in Olsen P above pH 5.5 - 6.5 does not appear to have been reported by previous workers, possibly because the soils in these studies were not limed to pH values as high as those in the present study.

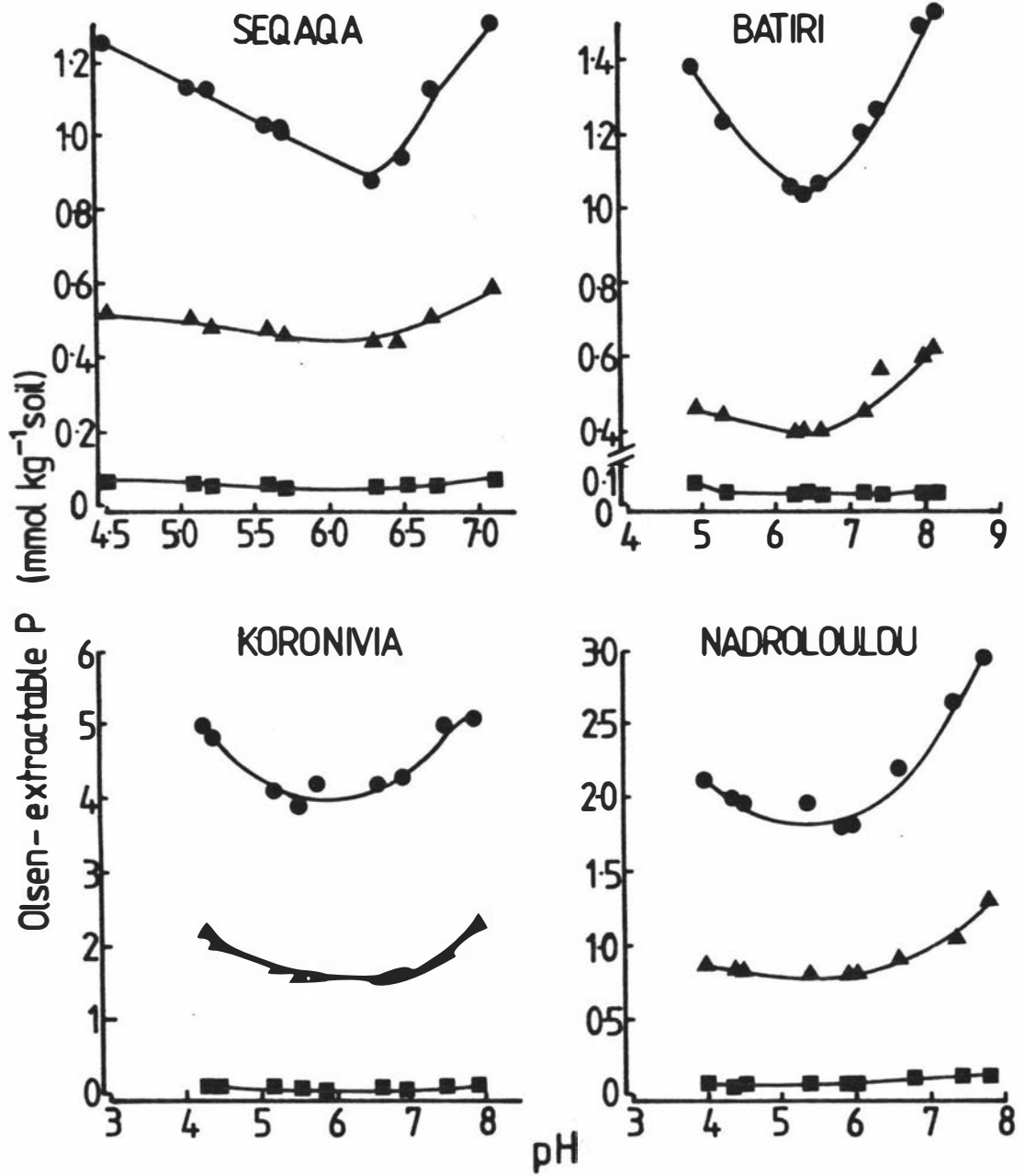


Fig. 5.2

Effect of increasing pH on Olsen P in 4 soils incubated with 3 rates of added P.

(■ = 0; ▲ = 8.1; ● = 16.1 mmol kg⁻¹ soil).

However, a similar trend in exchangeable P in limed soils was reported by Murrmann and Peech (1969) and they attributed the increase in exchangeable P above pH 5.5 to increased solubility of Al-hydroxy polymers and the release of occluded P. Such a mechanism would be less likely in the present soils because, unlike in the study of Murrmann and Peech (1969), P was added to soils subsequent to incubation with lime. Although, it is not possible to provide a definite explanation for the increase in Olsen P above pH 5.5 - 6.5, the isotopic-exchange data (Section 5.3.1) suggest that the increase was related to the rate at which P was released in the Olsen extract. Two competing solubility equilibria, presumably, operate during the Olsen extraction. There is an interaction between Ca and CO_3^{2-} , and also between Ca and released P. As shown by Sorn-srivichai et al. (1984), the rapid release of sorbed P in Olsen extracts at low and medium pH values increases the concentration of P to levels which cause precipitation of insoluble Ca-P compounds. Presumably, this process does not operate at high pH values. Results from the isotopic-exchange study (Section 5.3.1) indicate that most of the added P would be present as insoluble Ca-P compounds at high pH values. Relative to sorbed P, the release of P from precipitated compounds during the Olsen extraction would be slow, so that the only precipitation reaction would be between Ca and CO_3^{2-} . This formation of CaCO_3 would considerably reduce the concentration of Ca in the Olsen extract such that the interaction between Ca and P is minimised. Based on this mechanism, Olsen et al. (1954) recommended the Olsen test for calcareous soils.

Although Olsen P increased above pH 5.5 - 6.5, soils normally would not usually be limed above this pH in view of the observed deleterious effects on plant growth of liming acid soils to pH values in excess of 6.0 (Sumner, 1979). Also, although critical Olsen P levels are not available for the range of crops grown in Fiji, a comparison with recommended Olsen P values for acid soils on which crops of medium P requirement are grown in the United States of America ($0.2 - 0.3 \text{ mmol kg}^{-1}$; Thomas and Peaslee, 1973) indicates that at the medium or high levels of added P used in this study, all unlimed and limed soils had higher Olsen P values than those required for normal crop growth. Thus, the observed decrease in Olsen P with increasing pH may not be of much practical significance to plant growth in the short term.

5.3.3 Effect of lime and phosphate additions on Mehlich-extractable phosphate

In general, Mehlich P decreased with increasing soil pH for all soils except Koronivia, in which it behaved rather similarly to Olsen P (Fig. 5.3). However, the extent of the decrease in Mehlich P varied with both the soil and the level of added P. For example, in the absence of added P, Mehlich P was nearly constant with increasing pH in the Batiri, Koronivia, and Nadroloulou soils. In the Seqaqa soil, Mehlich P decreased slightly with increasing soil pH.

As was the case with the Olsen extraction, the amount of added P which was extracted by the Mehlich reagent varied with the P-sorption capacity of the soils. For example, in the high P-sorbing, unlimed Seqaqa soil, less than 1% of the added P ($16.1 \text{ mmol kg}^{-1}$) was extracted in comparison to the unlimed Batiri, Koronivia and Nadroloulou soils from which 3, 30, and 15% of the added P ($16.1 \text{ mmol kg}^{-1}$) was extracted, respectively.

These results are similar to those reported by Griffin (1971) who also obtained a variable trend in Mehlich P with increasing pH. According to Kamprath and Watson (1980) such trends are due to variations in soil type. In the present study, it is apparent from the pH of the Mehlich extract (Fig. 5.3) that in all except the Koronivia soil there was a significant effect of soil pH on the pH of the extractant and this may contribute to the reduced efficiency of the Mehlich reagent with increasing soil pH. This increase in pH of the Mehlich extractant could be a result of 2 factors, namely (i) soil mineralogical and chemical characteristics and their effect on P-buffering capacity of the soil and (ii) the rate of liming. For example, there was a marked difference in the pH of the Mehlich reagent before and after extraction of the unlimed soils. This difference was more pronounced in the Nadroloulou and Seqaqa soils which were also high in Al and Fe components, and organic matter and clay content. Although the Batiri soil also contains very large amounts of Al and Fe components, there was no marked effect of these on the pH of Mehlich reagent, presumably because of the lower organic matter content. The effect of increasing lime additions on the pH of the Mehlich extract is well shown by the results for the Seqaqa, Nadroloulou, and Kornivia soils. Because very large amounts of lime were added to the Nadroloulou and Seqaqa soils, a larger effect on the pH of the Mehlich extractant was observed and associated with this was a much sharper decrease in Mehlich P with increasing pH (Fig. 5.3). In contrast, relatively small amounts of lime were added to the Koronivia

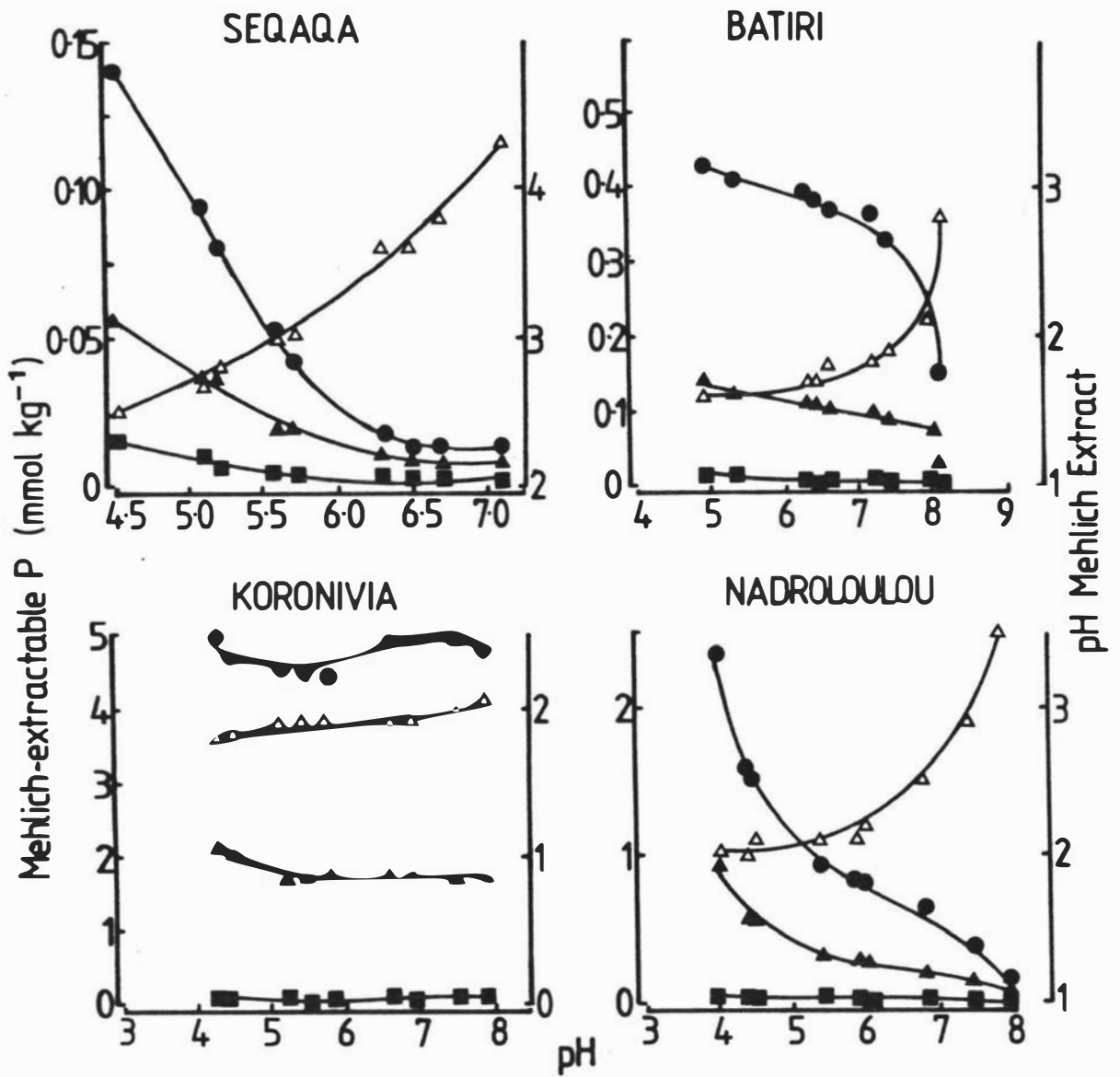


Fig. 5.3 Effect of increasing pH on Mehlich P and pH of the Mehlich extract (Δ) in 4 soils incubated with 3 rates of added P. (\blacksquare = 0; \blacktriangle = 8.1; \bullet = 16.1 mmol kg⁻¹ soil).

soil and consequently little change in pH of the Mehlich extract was recorded with increasing soil pH. This also corresponded to small changes in Mehlich P with increasing soil pH.

To further investigate the effect of pH on the amount of P extracted by the Mehlich reagent, selected unlimed and limed Batiri, Koronivia, and Nadroloulou soils were extracted at a constant pH using an autoburette (see Section 5.2.2). The results of this investigation (Table 5.1) showed that when the pH of the extractant was constant, the amount of P extracted was independent of the initial soil pH. These results confirm the suggestion of Thomas and Peaslee (1973) and Kamprath and Watson (1980) that soils dominant in Fe oxide, CaCO₃ and high clay content rapidly neutralize the acid of the Mehlich reagent, thereby decreasing its efficiency.

5.3.4 Comparison of soil-testing procedures

The amounts of P extracted by the soil-testing procedures generally increased in the order Mehlich P < Olsen P < exchangeable P. The only exception to this was the Koronivia soil which had been incubated with added P. In this soil, Olsen P values were higher than the exchangeable P values. The soil-testing procedures showed contrasting trends with pH. To explain these contrasting effects of pH on the extraction of P, the mechanisms involved during the extraction of P by each soil-testing procedure and also the nature of P constituting the exchangeable pool must be considered.

The Mehlich reagent (pH 1.25) is expected to principally dissolve P-reactive surfaces (Al and Fe hydrous oxides) and Ca-P (Thomas and Peaslee, 1973). The Olsen reagent probably desorbs loosely-held P, and some chemisorbed P (Ryden and Syers, 1977a), and dissolves P from certain Ca-P compounds (Olsen et al., 1954). Exchangeable P is believed to be mainly P which is loosely held on or in surfaces of P-reactive compounds and P-minerals (Ryden and Syers, 1977a) and some chemisorbed P, depending on the period of equilibration (Bolan, 1983). Given these mechanisms and the fact that exchangeability generally increases with an increase in negative charge (Ryden and Syers, 1977b), all the soil-testing procedures examined in this study would be expected to remove an increasing amount of P with an increase in pH. Such a trend in Mehlich P with pH for limed soils was reported by Holford (1983) and Rhue and Hensel (1983). Moreover, because the Mehlich reagent operates by a dissolution mechanism it would be expected to remove

Table 5.1

Amount of P extracted by the Mehlich reagent (pH 1.3) from unlimed and limed and subsequently phosphate treated ($8.1 \text{ mmol P kg}^{-1}$ soil) Batiri, Koronivia, and Nadroloulou soils.

Soil	Treatment	pH of soil		Mehlich P (mmol kg^{-1})
		Before extraction	During extraction	
Batiri	unlimed	4.9	1.3	0.6
	limed	8.0	1.3	0.5
Koronivia	unlimed	4.2	1.3	2.3
	limed	7.9	1.3	2.3
Nadroloulou	unlimed	4.0	1.3	1.3
	limed	7.4	1.3	1.2

the largest amount of P. However, in the present investigation the amount of P extracted by the Mehlich reagent, relative to that extracted by the Olsen reagent, depended on soil type as well as on whether the soils were limed (Table 5.2). For example, in all the limed soils Mehlich P was less than Olsen P and this must have been due to the neutralizing effect of lime on the Mehlich extractant (Section 5.3.3). In the unlimed soils, Mehlich P generally depended on the initial P-sorption capacity of the soils. Thus, whereas in the low to moderate P-sorbing Koronivia and Nadroloulou soils, Mehlich P was identical to Olsen P, it was generally less than Olsen P in the high P-sorbing Batiri and Seqaqa soils. These differences are probably due to different degrees of secondary sorption (Cajuste and Kussow, 1974) of extracted P by the soil constituents.

Although exchangeable P was generally higher than Olsen and Mehlich P, it does not necessarily indicate extensive exchange with chemisorbed P. Some of the differences in P extracted by these methods must be due to the artefact in the Olsen method and the effects of liming on the efficiency of the Mehlich extractant.

With the exception of exchangeable P, which generally increased with increasing pH, the Mehlich and Olsen extractants showed rather contrasting trends with increasing pH; these were attributed to a decrease in the efficiency of the Mehlich reagent because of the increase in pH during extraction and to an artefact (Sorn-srivichai et al., 1984) in the Olsen method. In view of these problems it is not practicable to correlate the results of the 3 soil-testing procedures.

Although lime additions affected the amount of P extracted by both soil-testing procedures, only in the case of the Mehlich procedure were the changes sufficiently large to be of concern. Thus, in 3 of the 4 soils, an increase in pH from 4.5 to 5.5 resulted in a decrease in the amount of P, sufficient to change the ranking of the soils from medium to low, particularly in the P-treated soils, based on critical P concentrations provided by Thomas and Peaslee (1973).

5.4 Conclusions

Liming of soils can have a variable effect on the amount of P extracted by the Olsen and Mehlich methods and on the amount of exchangeable P. Isotopically-exchangeable P generally increased with pH, Mehlich P generally

Table 5.2 Amounts of P extracted by the Mehlich and Olsen reagents from unlimed but phosphate treated (0, 8.1, 16.1 mmol P kg^{-1} soil) soils.

Soil	Treatment	Mehlich P	Olsen P
		mmol P kg^{-1}	
Koronivia	0.0	0.1	0.1
	8.1	2.1	2.2
	16.1	4.9	4.9
Nadroloulou	0.0	0.1	0.1
	8.1	0.9	0.9
	16.1	2.4	2.1
Batiri	0.0	<0.1	0.1
	8.1	0.1	0.5
	16.1	2.4	2.1
Seqaqa	0.0	<0.1	0.1
	8.1	0.1	0.5
	16.1	0.2	1.3

decreased with increasing pH and Olsen P decreased up to about pH 5.5 to 6.5, above which it increased.

The initial decrease in Olsen P with increasing pH was attributed to an artefact in the Olsen method (Sorn-srivichai et al., 1984), whereas the decrease in Mehlich P with increasing pH was attributed to a decrease in the efficiency of extraction caused by an increase in pH of the extractant.

In view of these problems associated with the Mehlich and Olsen procedures and the fact that plant growth generally increases in the pH range up to ~6.0 it may be difficult to relate these soil P test results to the uptake of P by plants. This aspect of soil-testing procedures will be considered in Chapter 8.

CHAPTER 6

CHAPTER 6

EFFECT OF LIMING ON PHOSPHATE SORPTION BY ACID SOILS

6.1 Introduction

In addition to reducing Al toxicity, liming affects the amount of P sorbed by acid soils, and these effects are variable. For example, liming of soils has been shown to decrease (Woodruff and Kamprath, 1965; Lopez-Hernandez and Burnham, 1974; Ryan and Smillie, 1975), increase (Lucas and Blue, 1972; Mokwunye, 1975; Sims and Ellis, 1983) or not affect (Woodruff and Kamprath, 1965) the sorption of added P by soils.

Various reasons have been advanced to explain these contrasting effects. For example, Haynes (1982) attributed the contrasting effects to inconsistencies in the soil incubation procedures, suggesting that the intervening drying process between the addition of lime and P could have a significant effect on the P-sorption characteristics of soils. However, Barrow (1984) attributed the variable effects of liming to 4 further factors, viz: the pH over which sorption is measured, the background electrolyte, the amount of desorbable P in the soil, and the relationship between pH and the potential on the soil surface. From these studies it is apparent that the experimental conditions used may substantially influence the results obtained.

As discussed in Chapter 1, highly-weathered, acid soils are relatively common in Fiji and large areas have low production potential mainly due to acidity, Al toxicity, and P deficiency problems. A clear understanding of the effect of soil acidity and liming on P availability is required prior to the development of these infertile soils. To this end the effect of soil pH on the sorption of P by four soils from Fiji was investigated. Sorption was also studied using selected limed soils which had also previously been treated with added P. Attempts were made to explain the trends obtained in terms of the interactions of Al, Ca, and P.

6.2 Materials and Methods

6.2.1 Preparation and preliminary analysis of soils

Detailed descriptions of the soils used and their preparation have been given in Chapter 3. Each of the 4 soils, Batiri, Koronivia, Nadroloulou, and Seqaqa were incubated with either 9 or 10 rates of lime to obtain a range of pH values up to 7 (Fig. 4.4). After the incubation period, which lasted 42 d, the limed soils were air dried at a temperature of $20 \pm 2^{\circ}\text{C}$ and subsamples of the Koronivia and Seqaqa soils were reincubated with 8.1 and 16.1 mmol kg^{-1} soil, respectively of added P. These soils were selected for incubation with P because they represented the lowest and the highest P-retention capacities of the group of soils in this study.

Selected samples of the limed soils in the pH range ~4 to ~7, were subsequently chosen for this study (Table 6.1).

6.2.2 Incubation of soils with KOH

During the course of the sorption studies it was observed that in all the soils the equilibrium solution P concentration tended to decrease at high pH values. To investigate whether this was due to the presence of Ca or due to the formation of X-ray amorphous Al-hydroxy polymers of high reactivity (Amarasiri and Olsen, 1973), samples of Nadroloulou soils were incubated with KOH as described below. The Nadroloulou soil was chosen because it contained very large amounts of M KCl-extractable Al.

Subsamples of the Nadroloulou soil were thoroughly mixed with varying rates of KOH and incubated for 28 d under conditions similar to those used for lime addition (Chapter 3, Section 3.4.1). At the end of 28 d, the incubated soils were air dried, passed through a 2-mm sieve, and stored in polythene bags for further analyses. The incubation period was decreased from 42 d to 28 d because of the more reactive nature of KOH.

6.2.3 Phosphate sorption studies

Sorption was investigated at 2 rates of P addition (Table 6.2); one rate was common to each of the 4 limed soils whereas the second rate varied depending on the P-retention capacity of the soil. Sorption of P was determined by weighing duplicate 1.0-g samples of soil into centrifuge

Table 6.1 pH values of the soils selected to investigate
the effect of pH on P sorption.

Soil	L0	L1	L2	L3	L4	L5
Koronivia	4.2	4.4	5.2	5.8	6.6	7.5
Nadroloulou	4.0	4.4	5.4	6.0	6.8	7.4
Batiri	4.9	5.3	6.5	6.6	7.4	-
Seqaqa	4.5	5.2	5.6	6.5	7.1	-

Table 6.2 Initial solution P concentration in the background electrolyte during the investigation of the effect of pH on P sorption.

Soil	Initial solution P concentration	
	P1	P2
	mmol L ⁻¹	
Koronivia	0.43	1.08
Nadroloulou	1.08	1.61
Batiri	1.08	1.47
Seqaqa	1.08	3.23

tubes together with 15 mL of 0.02M CaCl_2 solution containing a few drops of toluene to prevent microbial action. After the addition of an appropriate quantity of P (as KH_2PO_4 solution) the solutions were made up to 30 mL with deionized water to give a final CaCl_2 concentration of 0.01M. The tubes were then shaken for 72 h at $20 \pm 2^\circ\text{C}$. A separate set of control tubes containing the soils and the background electrolyte, but with no added P, were shaken at the same time. At the end of the shaking period, the pH of the suspension was measured. The tubes were then centrifuged and the supernatant solution filtered through a Whatman No.5 filter paper. The Ca and P concentrations in the solution were determined using AAS and the colorimetric method of Murphy and Riley (1962) respectively.

The above procedure was repeated to investigate the effect of pH on the sorption of P at 1 rate of added P by samples of the Koronivia and Seqaqa soils which had been limed and subsequently incubated with P. The rates of added P used in the sorption study were 0.27 and 2.15 mmol L^{-1} for the Koronivia and Seqaqa soils respectively.

The effect of pH on the sorption of P by Nadroloulou soil, incubated with lime or KOH, was also investigated using either H_2O , 0.01, 0.05, 0.1, or 1M KCl as the background electrolyte. The method used was as described above, except that only one rate (1.61 mmol L^{-1}) of added P was used. At the end of the shaking period, the pH of the suspension was measured. The Ca and P concentrations of the supernatant solutions were determined as described above. The concentration of K in the supernatant solutions of KOH-incubated soils was also determined using a Gallenkamp flame photometer.

6.3 Results and Discussion

6.3.1 Effect of liming on pH, extractable aluminium, and Olsen-extractable phosphate

All soils were initially strongly acid (Table 6.1), with pH (M KCl) values varying in the relatively narrow range of 4.0 to 4.9. The amounts of Al extracted by M KCl varied considerably between the soils, ranging from 0.3 mmol kg^{-1} in the Batiri soil to 35.6 mmol kg^{-1} in the Nadroloulou soil. The ratio of oxalate- to dithionite-extractable Al and Fe varied

from 0.06 to 0.63 and < 0.01 to 0.14, respectively (Table 6.3), reflecting the wide variation in the nature of the metal oxides present in the soils.

Incubation with lime generated a series of samples for each soil with pH values ranging from about 4 to 7.5 (Table 6.1). As soil pH increased there was a sharp decrease in M KCl-extractable Al values (Fig. 6.1). The amounts of P extracted by the Olsen reagent were low (0.01 - 0.1 mmol kg⁻¹) in the soils which had not been incubated with added P (Chapter 5, Section 5.3.2).

When the Koronivia and Seqaqa soils were incubated with added P there was a small change in the pH of the soils and also the amount of M KCl-extractable Al. However, Olsen-extractable P increased at equivalent lime levels in each soil (Chapter 5, Section 5.3.2).

6.3.2 Effect of pH on phosphate sorption

The soils differed markedly in their ability to sorb P at all pH values (Fig. 6.2). In general, sorption decreased in the order Seqaqa > Batiri >> Nadroloulou > Koronivia. These differences are most likely due to the large variation in the amount and nature of Fe and Al components present in the soils (Table 6.3). The high sorption observed in the Seqaqa soil was probably due to the presence of large amounts of oxalate- and dithionite-extractable Fe and Al. The active component in the Batiri soil is likely to be free crystalline Fe oxide minerals which are present in abundance (>13%) and which result in a net surface positive charge (Chapter 4, Section 4.3.2) at the natural soil pH.

There was little effect of pH on the amount of P sorbed at low initial solution P concentrations particularly in the high P-sorbing Batiri and Seqaqa soils (Fig. 6.2). This was surprising because even at the lowest P additions the amount added during sorption studies was at least 10 times higher than that usually added to these highly-weathered soils in the field. However, in all the soils, at very high initial solution P concentrations (Table 6.2) the amount of P sorbed decreased, passed through a minimum between pH 5.5 - 6.5, and then increased again (Fig. 6.2). This trend was most pronounced in the low P-sorbing Koronivia soil. The pH at which minimum sorption occurred varied between the soils. A similar effect of pH on P sorption was reported by Marsh (1983) for a range of limed volcanic ash soils from New Zealand and more

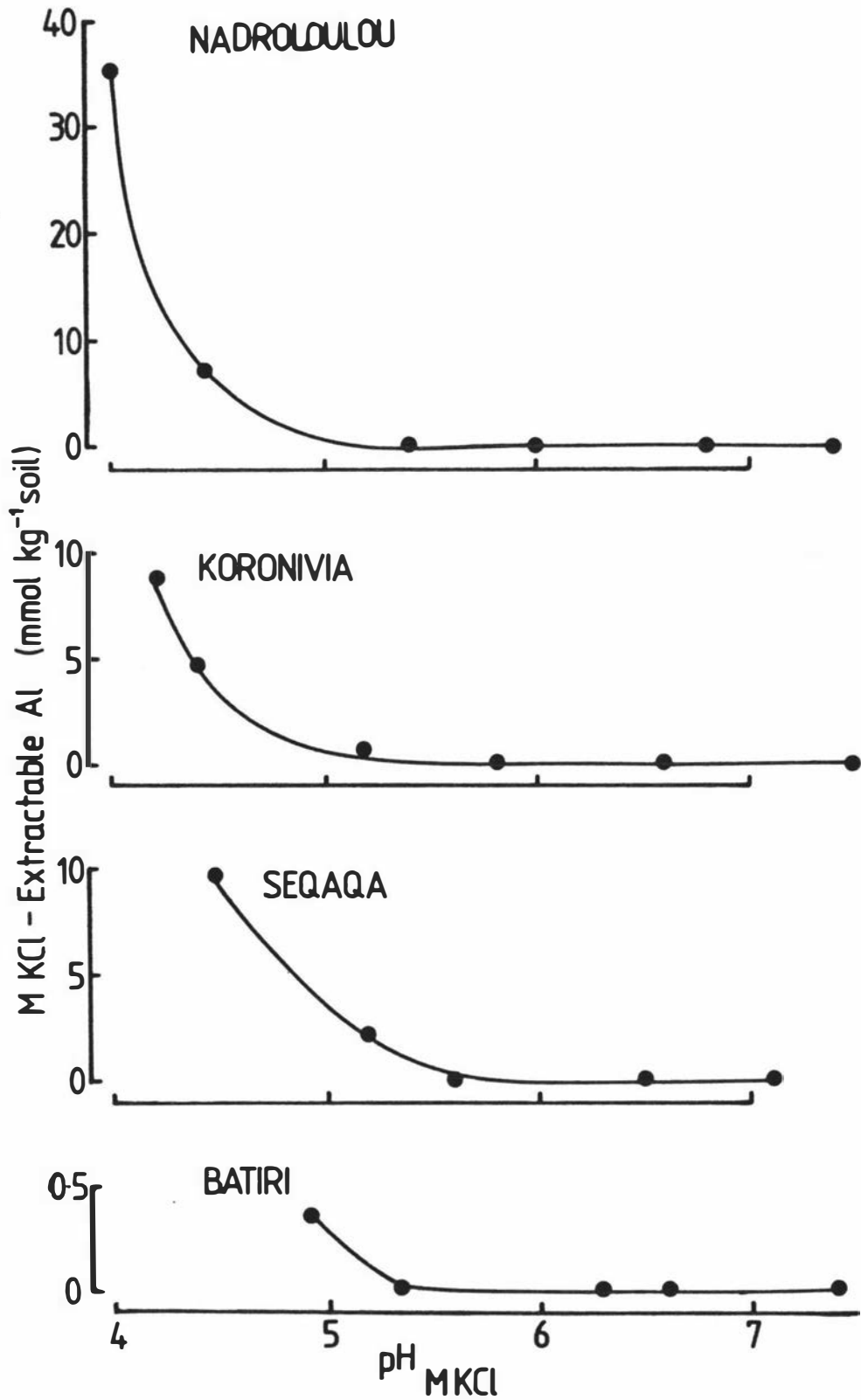


Fig. 6.1

Effect of soil pH on the amounts of Al extracted from limed soils by M KCl solution.

Table 6.3 Amounts of crystalline free Fe and Al, and short-range order Fe and Al extracted by citrate-dithionite-bicarbonate and acid ammonium oxalate reagents, respectively, and the ratio of oxalate- to dithionite-extractable Al and Fe.

Soil	Oxalate-extractable		Dithionite-extractable		Oxalate:dithionite-extractable	
	Al	Fe	Al	Fe	Al	Fe
	———— mmol kg ⁻¹ soil ————					
Koronivia	49.5	68.1	193	472	0.26	0.14
Nadroloulou	111.9	62.9	288	951	0.39	0.07
Batiri	50.0	10.7	820	2399	0.06	<0.01
Seqaqa	643.4	94.4	1025	1487	0.63	0.06

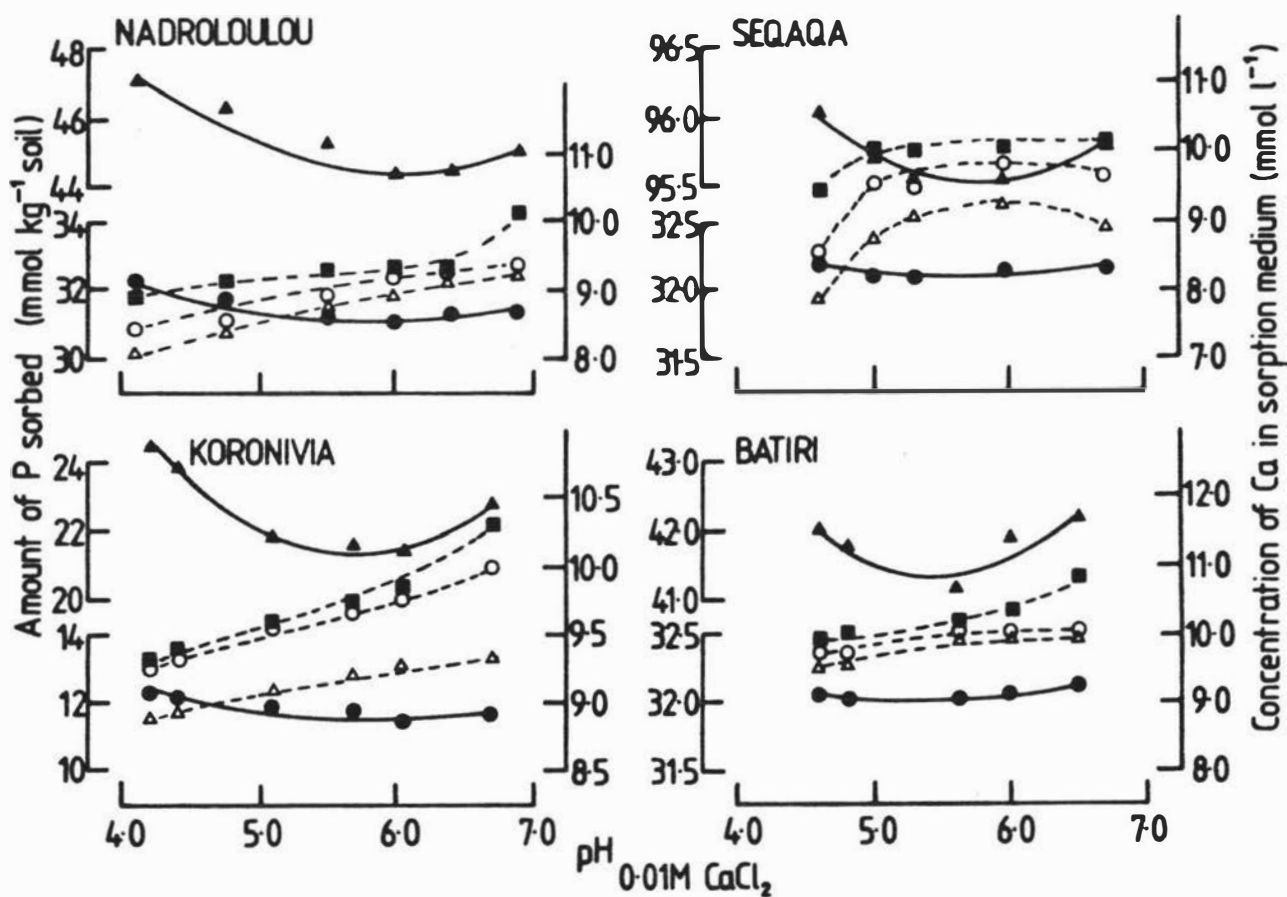


Fig. 6.2 Effect of soil pH on the amount of P sorbed (—) at 2 initial solution P concentrations (P1 = ● and P2 = ▲, Table 6.2) and the concentration of Ca (---) in the control samples (■) and in the presence of added P (P1 = ○ and P2 = △, Table 6.2).

recently by Barrow (1984) for CaCO_3 -treated Australian soils.

Although the differences in P sorption were small, they were sufficient to produce a significant increase in equilibrium P concentration with increasing pH. For example, at an initial solution P concentration of 1.08 mmol L^{-1} , the equilibrium solution P concentration increased from $0.003 \text{ mmol L}^{-1}$ in the unlimed, high P-sorbing Seqaqa soil to $0.005 \text{ mmol L}^{-1}$ at pH 5.2 where minimum P was sorbed. Because the concentration of P in the soil solution is usually very low, this ~70% increase in equilibrium solution P may have a beneficial effect on plant growth. Results relating to this effect are reported in Chapter 7. A similar but somewhat larger increase in equilibrium solution P concentration was observed for the other soils.

The variation in the amount of P sorbed with increasing pH was apparent regardless of whether the soils had been incubated with added P (Fig. 6.3) after the initial incubation with lime. However, the amount of P sorbed by soils which had been incubated with both lime and P was lower than that sorbed by soils incubated with lime only. These results indicate that some of the previously added P was probably occupying P-sorption sites, blocking them from further reaction (Barrow, 1984).

The observed initial decrease (Fig. 6.2 and 6.3) in the sorption of P was probably due to a combination of factors. These would include the neutralization of Al^{3+} and hydroxy Al as Al hydroxide during liming resulting in a decrease in the number of P-sorption sites (Syers et al., 1971; Sanchez and Uehara, 1980). Bowden et al. (1977) have suggested that an increase in soil pH, such as occurs on liming, causes the surface to become increasingly negative, resulting in a decrease in the electrostatic potential in the plane of adsorption. This would result in a decrease in the strength of sorption of P with increasing pH.

The increases in sorption on the higher pH side of the observed minima, although reported by several workers, are more difficult to explain. Bowden et al. (1977) suggested that with increasing pH, the concentration of HPO_4^{2-} would increase 10 fold with each unit rise in pH and this ion may be sorbed preferentially, but in a later study (Bowden et al., 1980b) it was suggested that this increase in concentration of the divalent HPO_4^{2-} ion with increasing pH would only be sufficient to slow down the rate of decrease in sorption and not cause an increase. In a recent review, Haynes (1985) has suggested that the addition of high rates of lime may increase the ionic strength and the concentration of Ca in the sorption

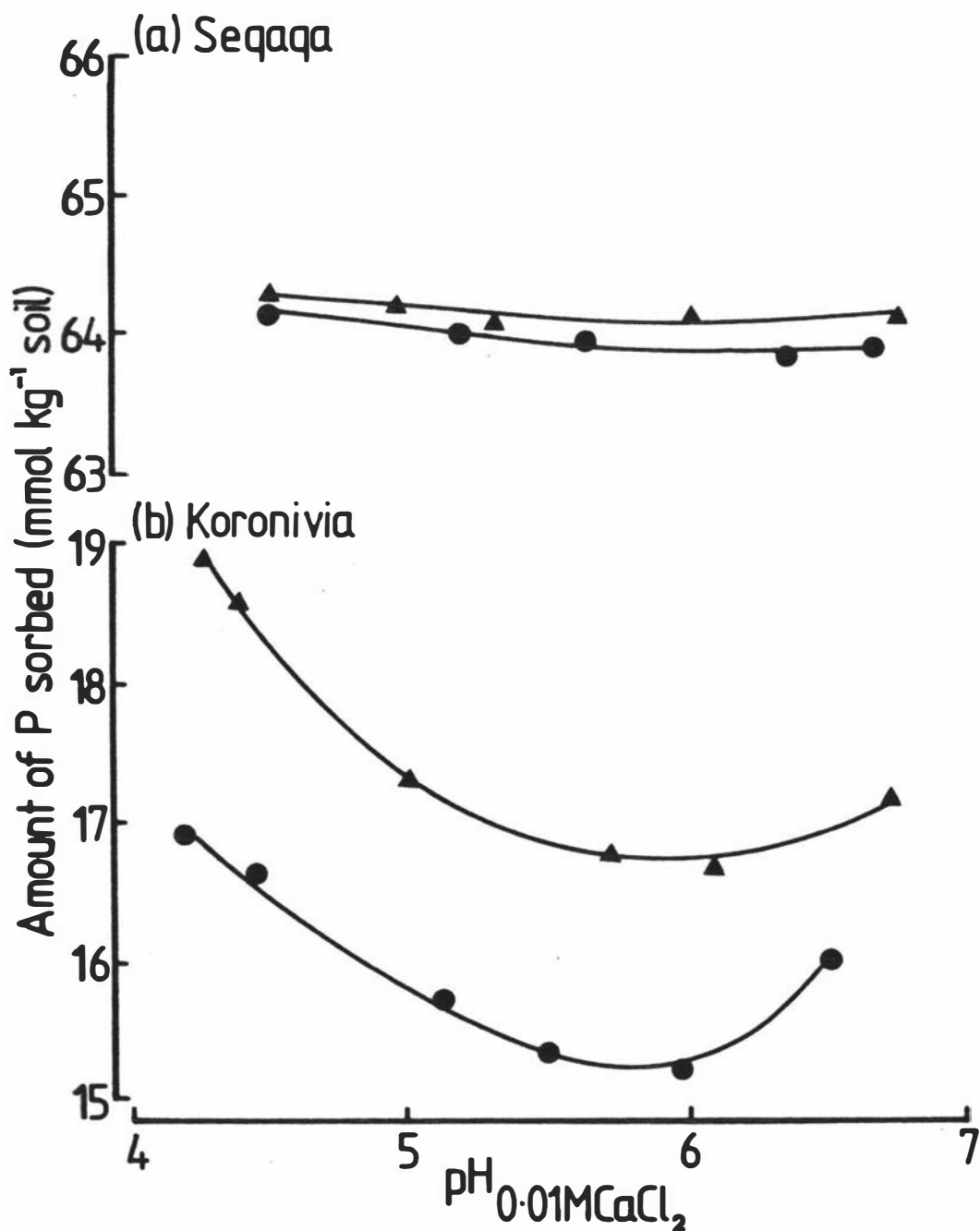


Fig. 6.3

Effect of pH on the amount of P sorbed by untreated (▲) and P-incubated (●) Koronivia and Seqaqa soils at initial solution P concentrations of 0.69 and 2.15 mmol L⁻¹, respectively.

medium and that this, in turn, may have an effect on P sorption. The results shown in Fig. 6.2 indicate that the concentration of Ca in the control samples (no added P) increased by a factor of about 1.1 when soil pH was increased from 4 to about 7, indicating a small increase in the ionic strength of the sorption medium. A similar increase in Ca concentration was noted for the systems containing added P.

A survey of the literature suggests that whenever an increase in P sorption has been observed at high pH values, either Ca was used as the liming material or was present in background electrolyte. This had led authors (Fox et al., 1974; Parfitt, 1979; Barrow et al., 1980; Sanchez and Uehara, 1980) to propose the precipitation of calcium phosphate (Ca-P) as the mechanism responsible for the decrease in solution P concentration at high pH values. Thus, using the method of Clark and Peech (1955), Barrow et al. (1980) showed that the decrease in P concentration at high pH values during the sorption of P by goethite could be due to the formation of insoluble Ca-P compounds. However, in a more recent study, Barrow (1984) found that sorption increased at high pH values even when the concentration of Ca was too low for precipitation to occur. Helyar et al. (1976a,b) related the increase in sorption by gibbsite at high pH values to the presence of Ca and proposed surface complex formation between sorbed P and solution Ca and P.

When the values for pH, Ca concentration, and P concentration from the section of the graph where sorption increased (Fig. 6.2) were plotted (Fig. 6.4) using the method of Clark and Peech (1955) and Barrow et al. (1980), they fell close to the lines representing both octa-calcium phosphate and hydroxyapatite. From these results, it seems possible that the increased sorption above about pH 5.5 - 6.0 was probably due to the formation of insoluble Ca-P compounds. However, conformity of solution concentration data to solubility equilibria does not necessarily prove that precipitation has occurred because kinetics, including the time required for nucleation, are ignored. Nevertheless, further evidence for the formation of insoluble Ca-P compounds at high pH values was presented in the isotopic-exchange study reported in Chapter 5.

6.3.3 Effect of background electrolyte on phosphate sorption by Nadroloulou soil incubated with calcium or potassium hydroxide

To further investigate the apparent increase in P sorption at high pH described above, samples of the Nadroloulou soil were incubated with KOH to

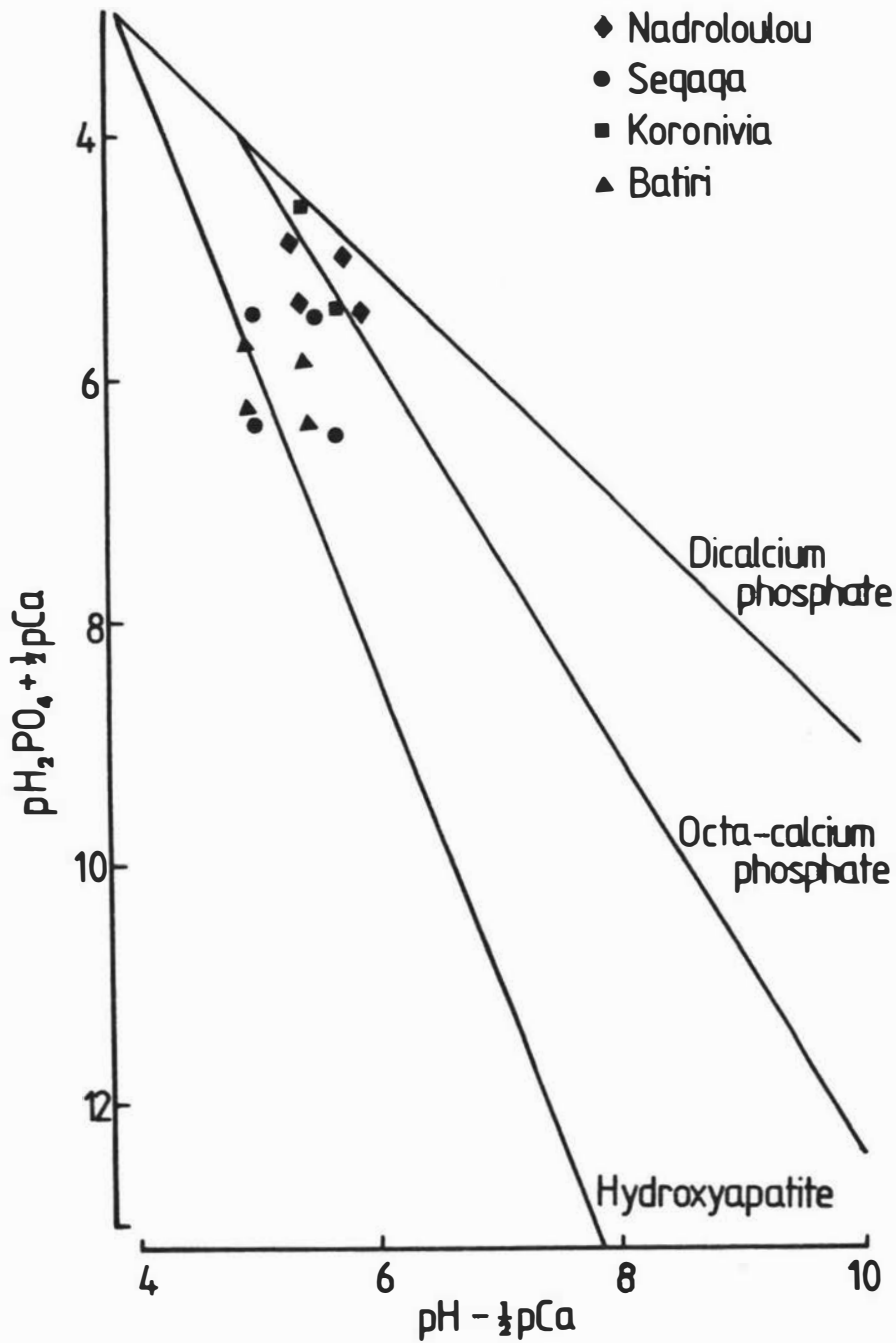


Fig. 6.4 Values for pH and Ca and P concentrations from the section on the pH-P sorption curve where sorption increases, plotted according to the method of Clark and Peech (1955).

give a range of pH values comparable to that obtained earlier by incubation with $\text{Ca}(\text{OH})_2$ (Section 6.2.1). Both the $\text{Ca}(\text{OH})_2$ and KOH-treated soils were then used to investigate P sorption from a variety of background electrolytes.

When P sorption by the KOH-incubated soils was studied, using KCl as the background electrolyte (Fig. 6.5), the amount of P sorbed decreased steadily with increasing pH, irrespective of the concentration of the electrolyte; there was no evidence of a tendency for sorption to increase at high pH. The lowest amount of P was sorbed when water was used as the support medium (background electrolyte) and the highest amount from the 0.05M KCl medium.

In contrast, when sorption was conducted with soils which had been incubated with $\text{Ca}(\text{OH})_2$ (Fig. 6.6) and H_2O was used as the background electrolyte, the amount of P sorbed passed through a minimum at about pH 6.9 above which it increased again. Interestingly, the rate of increase in sorption of P above pH 6.9 decreased consistently with the increase in the concentration of the background electrolyte (Fig. 6.6), such that this effect was not observed in M KCl.

This apparent increase in sorption above pH 6.9 may be due to one or more of the three reasons advanced previously, viz: the precipitation of insoluble Ca-P compounds (Barrow et al., 1980; Sanchez and Uehara, 1980); the formation of a surface P-Ca-P complex (Helyar et al., 1976a,b) or an increase in ionic strength at high rates of lime addition (Haynes, 1985). To investigate the last possibility, K and Ca concentrations were measured, in the H_2O extracts of the KOH- and $\text{Ca}(\text{OH})_2$ -incubated soils, respectively. When sorption was conducted in H_2O using the $\text{Ca}(\text{OH})_2$ -incubated soils, the concentration of Ca ranged from undetectable amounts to 0.3 mmol L^{-1} . In contrast the concentration of K in the KOH-incubated soils ranged from <0.01 to over 4.5 mmol L^{-1} at the highest pH. Thus there was a much larger increase in ionic strength in the presence of KOH than there was in the presence of $\text{Ca}(\text{OH})_2$. Therefore the increase in P sorption at high pH values is unlikely to be due to an ionic strength effect. It would appear that the increase in sorption is due either to insoluble Ca-P or surface complex formation, as suggested by Helyar et al. (1976a,b). However, Parfitt (1978) has commented that the surface complex mechanism of Helyar et al. (1976a,b) would suggest interaction on the (001) face of gibbsite which was not likely from infra-red studies. Furthermore, if there was a complex formation of the type proposed by Helyar et al. then exchangeable P would be expected to increase steadily even at the

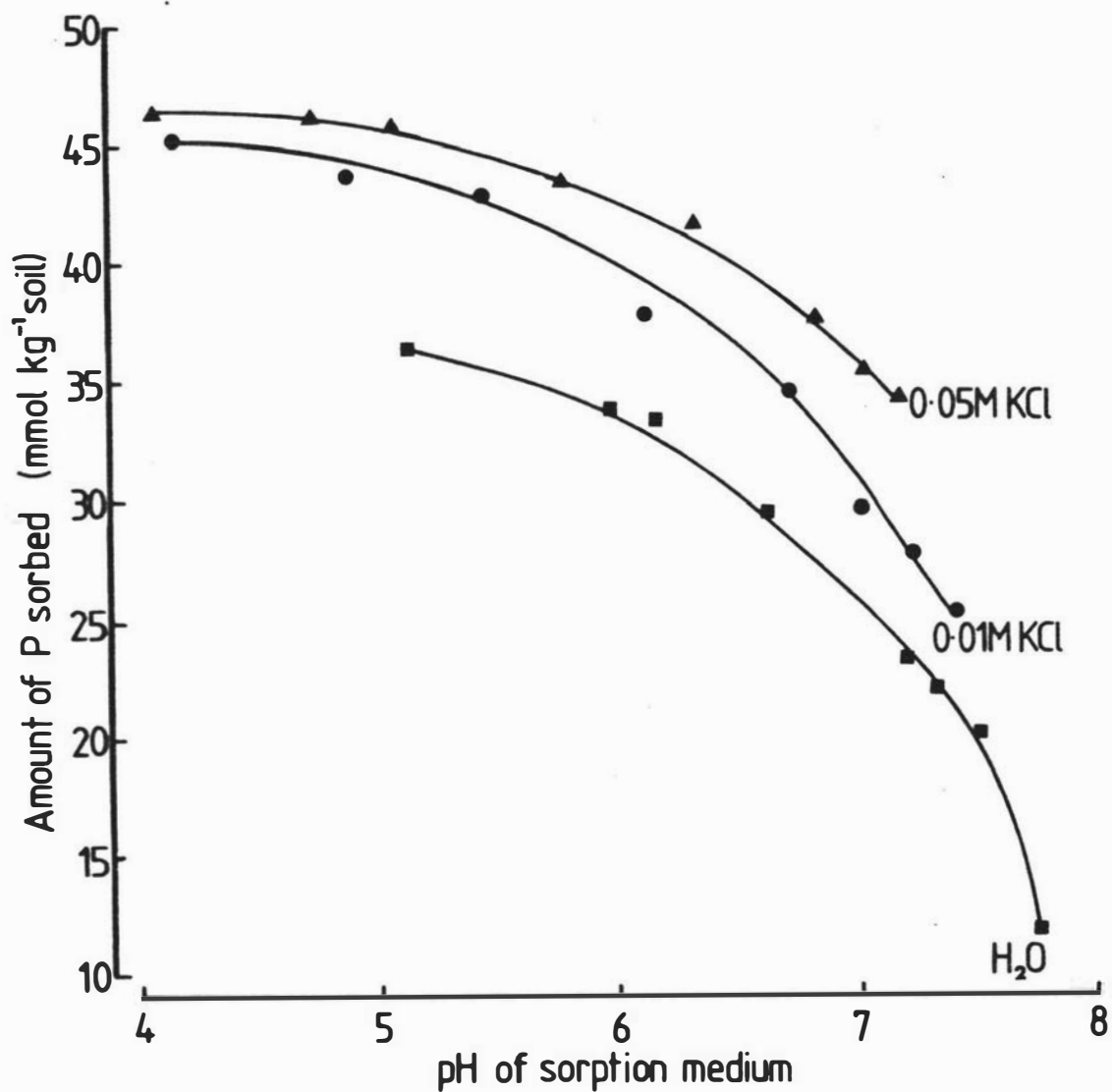


Fig. 6.5 Effect of background electrolyte concentration on the amount of P sorbed by Nadroloulou soils incubated with KOH at an initial solution P concentration of 1.61 mmol L^{-1} .

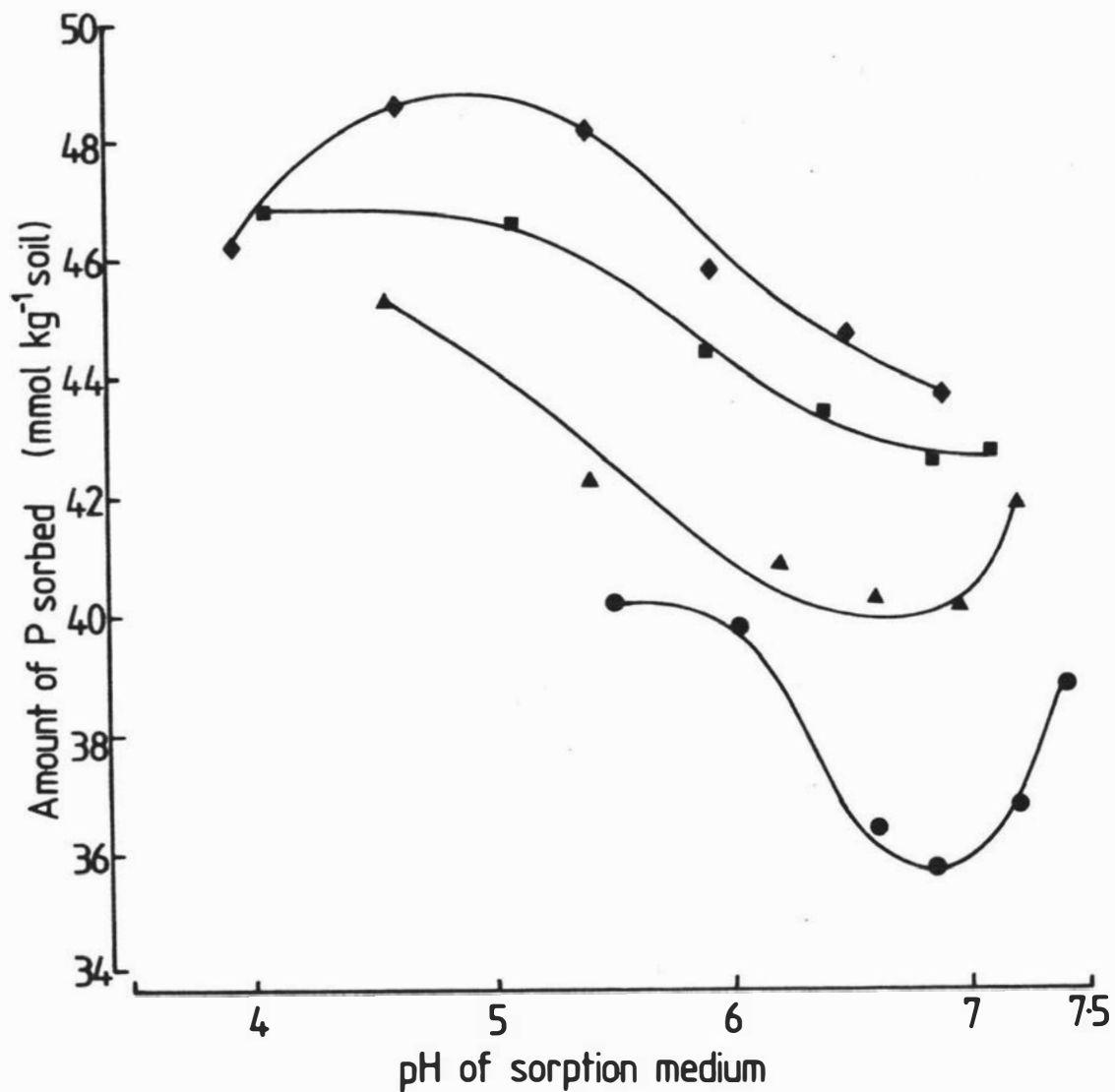


Fig. 6.6

Effect of background electrolyte concentrations on the amount of P sorbed by Nadroloulou soils incubated with $\text{Ca}(\text{OH})_2$ at an initial solution P concentration of 1.61 mmol L^{-1} .

($\text{H}_2\text{O} = \bullet$; $0.01\text{M KCl} = \blacktriangle$; $0.1\text{M KCl} = \blacksquare$; $1\text{M KCl} = \blacklozenge$).

highest pH, and not decrease as reported for the soils in the present study.

Inspection of Fig. 6.7, shows that the pH of the sorption medium differs considerably between the various background electrolytes. Interestingly for the cases where a minimum in sorption was not observed, the pH of the sorption medium for the soil with the highest rate of $\text{Ca}(\text{OH})_2$ addition was less than 6.9.

To verify whether the decrease in solution P concentration at high pH values was a pH effect, a separate sorption study was conducted by increasing the pH of the background electrolyte in which a minimum in sorption was not observed to values higher than 6.9. This was achieved by the addition of dilute NaOH solution. The results of this study showed (dotted line, Fig. 6.8) an increase in sorption even when M KCl was used as the background electrolyte, provided the pH was higher than 6.9. This investigation together with those reported earlier on KOH- and $\text{Ca}(\text{OH})_2$ -incubated Nadroloulou soils suggest that the observed decrease in solution P concentration at high pH values was probably due to an interaction between pH, Ca, and P, such that an insoluble Ca-P compound was formed. This is consistent with the results of the isotopic-exchange study reported in Chapter 5 (Section 5.3.1), which showed an initial increase in exchangeable P at low pH which was followed by a sharp decrease at high pH values. Such a sharp decrease in isotopic exchange at high pH was interpreted (Murrmann and Peech, 1969) as being due to the formation of insoluble Ca-P compounds.

6.4 Conclusions

Liming of soils had a variable effect on P-sorption capacity. In general, P sorption decreased with an increase in the rate of liming up to about pH 5.5 - 6.0, above which sorption increased. However, the rate of initial decrease in sorption varied markedly between soils, such that in the high P-sorbing Batiri and Seqqa soils, the decrease was insignificant relative to the amount of P added. Nevertheless, an appreciable increase in equilibrium solution P concentration was observed with all of the soils up to the pH of minimum sorption.

As would be expected, incubation of soils with added P following liming resulted in a larger decrease, with increasing pH, in the amounts of P subsequently sorbed as compared to the soils with no previously added P.

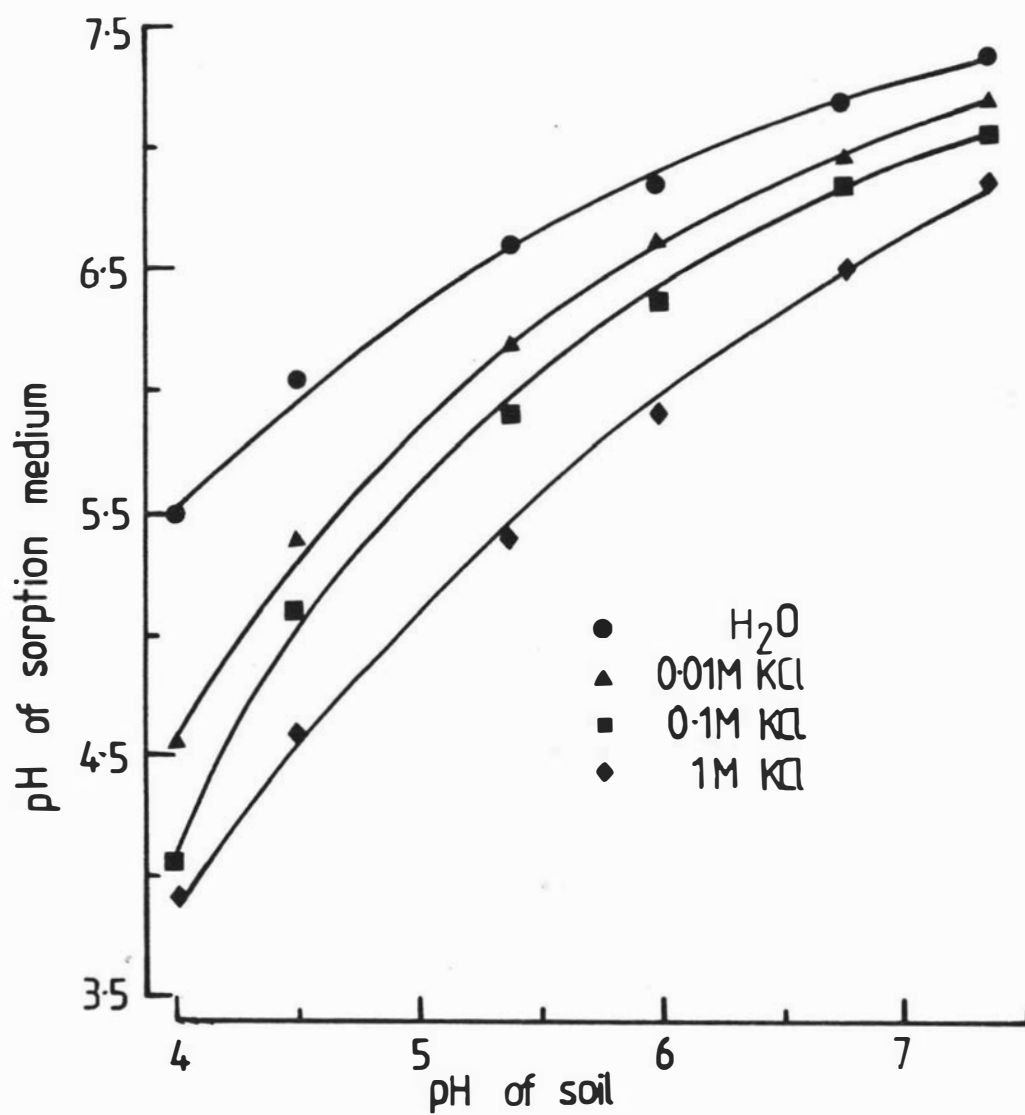


Fig. 6.7

Effect of electrolyte concentration on pH of the sorption medium in the Nadroloulou soils incubated with $\text{Ca}(\text{OH})_2$.

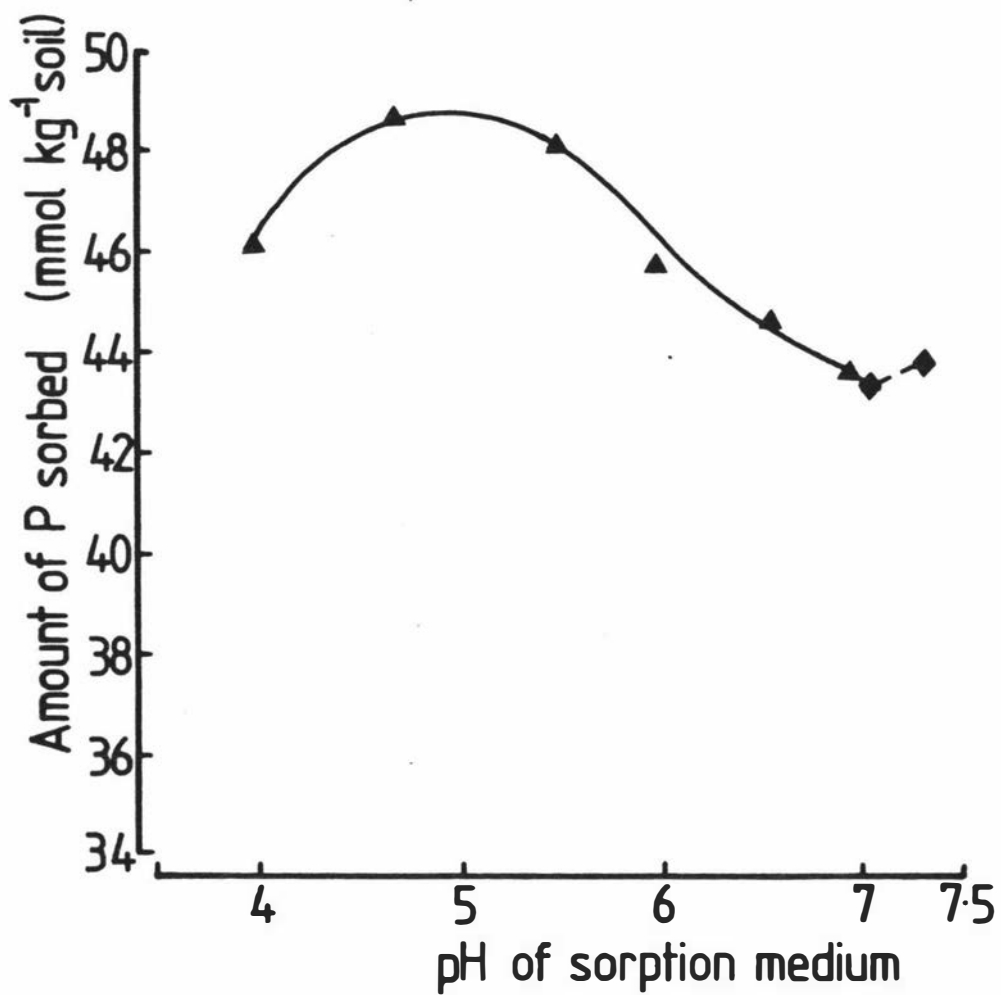


Fig. 6.8

Effect of increasing the pH by additions of dilute NaOH to soils previously limed to pH 6.9 on the amount of P sorbed by Nadroloulou soil suspended in M KCl.

The observed initial decrease in sorption was probably related to the decrease in reactive Al and also to an increase in surface negative charge resulting from increased soil pH. The increase in surface negative charge would result in a decrease in the electrostatic potential in the plane of adsorption, thereby decreasing the sorption of P (Bowden et al., 1977).

From a sorption study of soils incubated with KOH and Ca(OH)_2 and using a variety of electrolyte concentrations, it was concluded that the presence of Ca was associated with the increase in P sorption at high pH values. These investigations also showed that, at the solution P and Ca concentrations similar to those encountered in the present study, it was essential for the pH of the sorption medium to be higher than 6.9 for a decrease in solution P concentration to be obtained.

CHAPTER 7

CHAPTER 7

LIME-ALUMINIUM-PHOSPHATE INTERACTION AND
THE GROWTH OF LEUCAENA LEUCOCEPHALA

7.1 Introduction

Low crop yields in much of the humid tropics are associated with high soil acidity and/or acute P deficiency. These two factors are not independent and one of the primary reasons commonly proposed for liming acid soils is to increase P availability to plants (Sanchez and Uehara, 1980). The mechanisms by which an increase in P availability occurs are far from clear but are known to involve the soil and plant components of the system.

Acid soils frequently contain phytotoxic levels of soluble and exchangeable Al (McLean, 1976; Foy and Fleming, 1978; Webber et al., 1982). A major characteristic of Al toxicity is an inhibition of the uptake and translocation of P by plants (Foy and Fleming, 1978; Jones and Fox, 1978). Thus, liming acid soils often increases P uptake by plants by decreasing Al toxicity rather than by an effect on soil P availability, per se (Vickers and Zak, 1978; Haynes and Ludecke, 1981).

Conflicting views are held as to the effects of liming on P availability in highly-weathered, acid soils and these have been discussed in Chapters 5 and 6. Nevertheless, liming has generally been found to increase plant growth up to pH values where M KCl-extractable Al is reduced to very low levels. Lime in excess of this amount has been reported to decrease plant growth (Amarasiri and Olsen, 1973; Janghorbani et al., 1975; Juo and Uzu, 1977; Sumner, 1979; Farina et al., 1980a,b).

Several contrasting reasons have been put forward to explain the decrease in plant growth at high pH values. For example, Fox et al. (1964) attributed the decrease to a reduction in available P caused by the formation of insoluble Ca-P compounds in the soil. In contrast, Friesen et al. (1980b) attributed the decrease to induced Zn deficiency. Farina et al. (1980a,b) related the decrease to the presence of high levels

of Al in the plant tissue at soil pH values where growth was depressed. In view of this, it appears that there is a need for further studies of:

- (i) the interaction between lime, Al and P in acid soils and
- (ii) how this interaction affects the availability of P as assessed by plant uptake.

In this study, four Fijian soils were incubated with different amounts of lime and P, in a factorial design, to produce soils covering a range of pH and P status, and the effect of these treatments on the growth of the tropical legume Leucaena leucocephala was investigated.

7.2 Materials and Methods

7.2.1 Soils

The 4 soils used in this study have been described previously (Chapter 3). Each soil was incubated with a range of lime (Fig. 7.1) and P (Table 7.1) additions. The experimental design used with 3 of the 4 soils was a replicated 5 x 3 lime ($\text{Ca}(\text{OH})_2$) x P complete factorial. With the fourth soil (Koronivia) only 4 rates of lime were applied because of the limited supply of this soil. The lime rates were chosen so as to obtain approximately 0, 30, 70, and 100% reductions in the amounts of M KCl-extractable Al originally present in the soil. Three rates of P were added. One was common to all soils and, of the other 2 rates, 1 was very low and the other depended on the P-sorption capacity of the soil (Table 7.1).

Lime was incorporated into replicate (4) samples of soil by thoroughly mixing in Analytical Grade $\text{Ca}(\text{OH})_2$ and incubating at field capacity at $20 \pm 2^\circ\text{C}$ for a period of 42 d. Distilled water was added every second day to compensate for evaporative losses. After each addition of water, the soils were remixed thoroughly. At the end of the incubation period, the soil samples were air dried at a temperature of $20 \pm 2^\circ\text{C}$ and passed through a 2-mm sieve. The replicates at each lime level were then bulked, thoroughly mixed, and reweighed. Subsamples of the limed soils were reincubated with various levels of P (Table 7.1) under the same conditions. After 14 d, the lime-P treated soils were air dried at a temperature of $20 \pm 2^\circ\text{C}$, passed through a 2-mm sieve and samples at each treatment level were bulked and mixed thoroughly. Subsamples of these soils were used for chemical analyses and plant growth studies.

Table 7.1 Amounts of P added to limed soils prior to incubation and growth of Leucaena leucocephala.

Soil	P applied		
	P ₁	P ₂	P ₃
	mmol kg ⁻¹ soil		
Koronivia	0.40	2.42	4.84
Nadroloulou	0.80	4.84	9.68
Batiri	1.61	4.84	14.52
Seqaqa	1.61	4.84	14.52

7.2.2 Plant growth study

The plant growth study was conducted in a controlled-climate laboratory, at average day and night temperatures of 30 and 20°C, respectively, and relative humidities of 70 and 85%, respectively.

Lime- and P-treated soils (500 g) were placed in 100mm x 100mm-plastic containers, with polythene bag liners to contain any leachate. Each treatment was replicated 4 times. The potted soils were moistened to field capacity with distilled water. Three seeds of the tropical legume Leucaena leucocephala, which had been soaked in distilled water for 24 h, were planted in each pot. The pots were covered to minimize evaporation and the seeds allowed to germinate. After 14 d the pots containing more than one plant were watered and then thinned to one plant per pot. Where no seeds germinated, seedlings were transplanted from a separate pot containing 14-d old plants. Where possible, seedlings were transplanted from replicate pots of the same treatment. Thereafter the pots were watered to field capacity daily. Solutions (20mL) containing all major and minor nutrients except P (Middleton and Toxopeus, 1973) were added every second day to each pot, prior to addition of distilled water. Plants were checked daily and intact, dying leaves were examined, removed, and stored in labelled bags (Jones and Jones, 1979). These leaves were later included in the yield determinations. Twelve weeks after germination the plants were harvested. The roots were carefully separated from the soil, washed free of adhering soil, and the herbage (tops and roots) oven dried for 48 h at 65°C, weighed, and ground for subsequent chemical analysis.

7.2.3 Chemical analyses

7.2.3.1 Soils

The pH (Appendix 2) of incubated soils before and after cropping was determined in M KCl at a soil:solution ratio of 1:2.5 after equilibration for 16 h. Prior to cropping, subsamples of the soils were extracted with M KCl using the method described in Chapter 3 (Section 3.5.2.3, b). Al in the extract was determined by the modified aluminon method (Hsu, 1963), as described in Chapter 3, (Section 3.5.2.2, b).

Available P was determined by the Olsen- (Chapter 5, Section 5.2.2) and resin-extraction procedures (Cooke and Hislop, 1963). The resin-extraction

procedure was chosen because it is generally believed to act like a plant root, in that it provides a continuing sink for available P (Amer et al., 1955). In this procedure soil samples were shaken with a Cl-exchange resin ('Dowex' 2-XB, 20-50 US mesh) and 35 ml of deionized water for 16 h, following which the bags containing resin were washed free of adhering soil using deionized water. The resin bags were then shaken for 1 h with 25 ml of M NaCl solution and P was determined in suitable aliquots using the colorimetric procedure of Murphy and Riley (1962).

7.2.3.2 Plants

Plant material (20-100 mg of roots or tops) was ashed at 480 C for a period of 4 h in borosilicate tubes (15mm x 70mm), cooled, and dissolved with 7 ml of 2M HCl (prepared from redistilled Analytical Grade acid). The samples were then analysed for major and minor elements by Plasma Emission Spectroscopy (ICP, Lee, 1981).

7.3 Results and Discussion

7.3.1 Effect of liming on pH, extractable aluminium, and extractable phosphate

As discussed previously (Chapter 4, 5, and 6), all the soils were strongly acid (Table 3.3), with the initial pH falling in a relatively narrow range of 4.0 - 4.9. However, M KCl-extractable Al values varied considerably among the soils (Table 3.3). Available P, measured using the Olsen-extraction procedures, ranged from $<0.1 \text{ mmol kg}^{-1}$ in the Batiri, Nadroloulou, and Seqqa soils to approximately 0.2 mmol kg^{-1} soil in the Koronivia soil (Fig. 7.3). In contrast to Olsen P, resin P was $<0.1 \text{ mmol kg}^{-1}$ in all 4 soils (Fig. 7.4).

With increasing additions of lime, pH values increased from 4.0 - 4.9 to over 6.0 (Fig. 7.1). There was a corresponding decrease in M KCl-extractable Al (Fig. 7.2) such that in each soil it was undetectable at or above pH 5.2.

Incubation of limed soils with added P resulted in a several-fold increase in both Olsen P (Fig. 7.3) and resin P (Fig. 7.4) at equivalent lime levels in all soils. However, there was considerable variation in extractable P with increasing soil pH. Thus, in each of the soils,

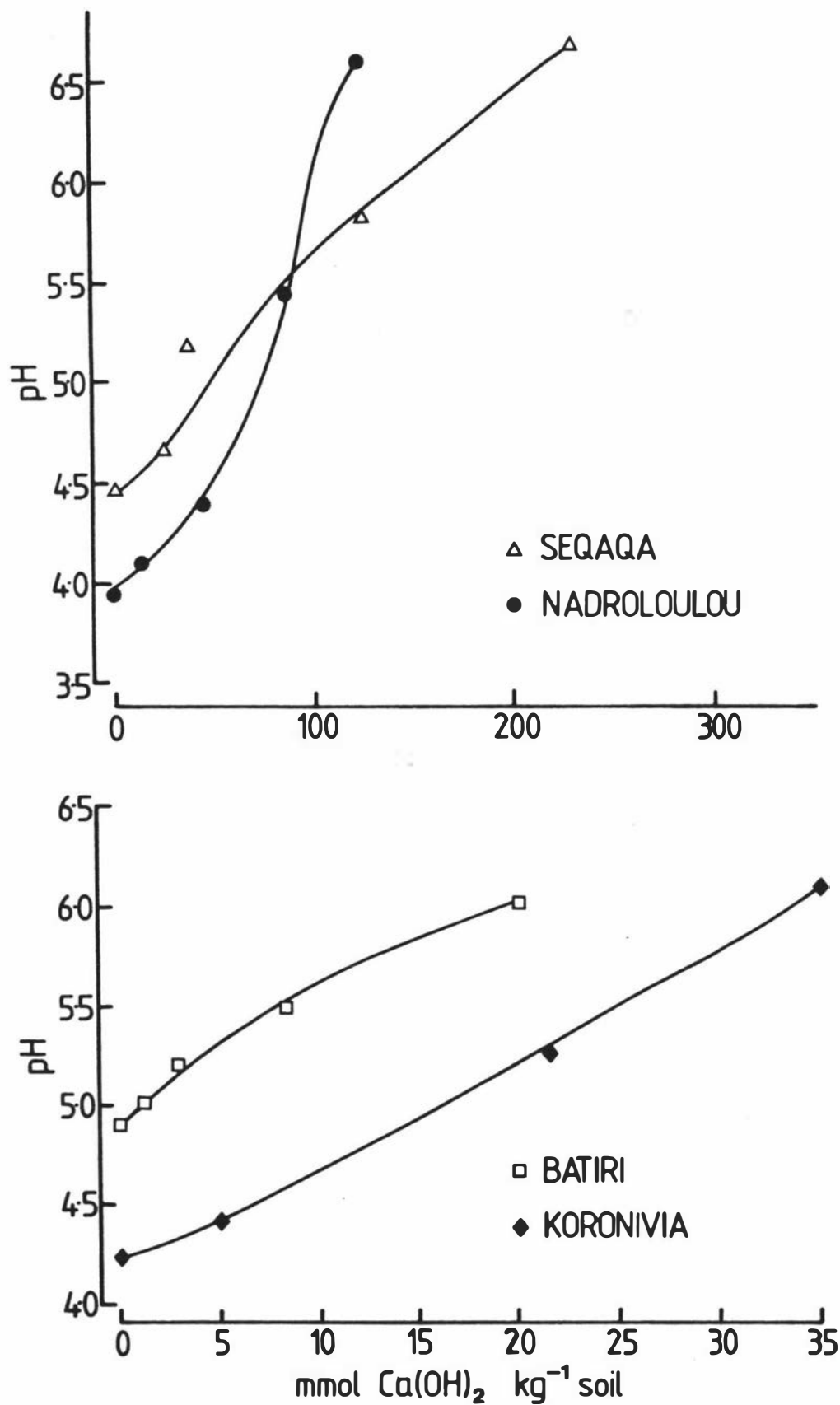


Fig. 7.1

Effect of increasing additions of Ca(OH)_2 on the pH of soils.

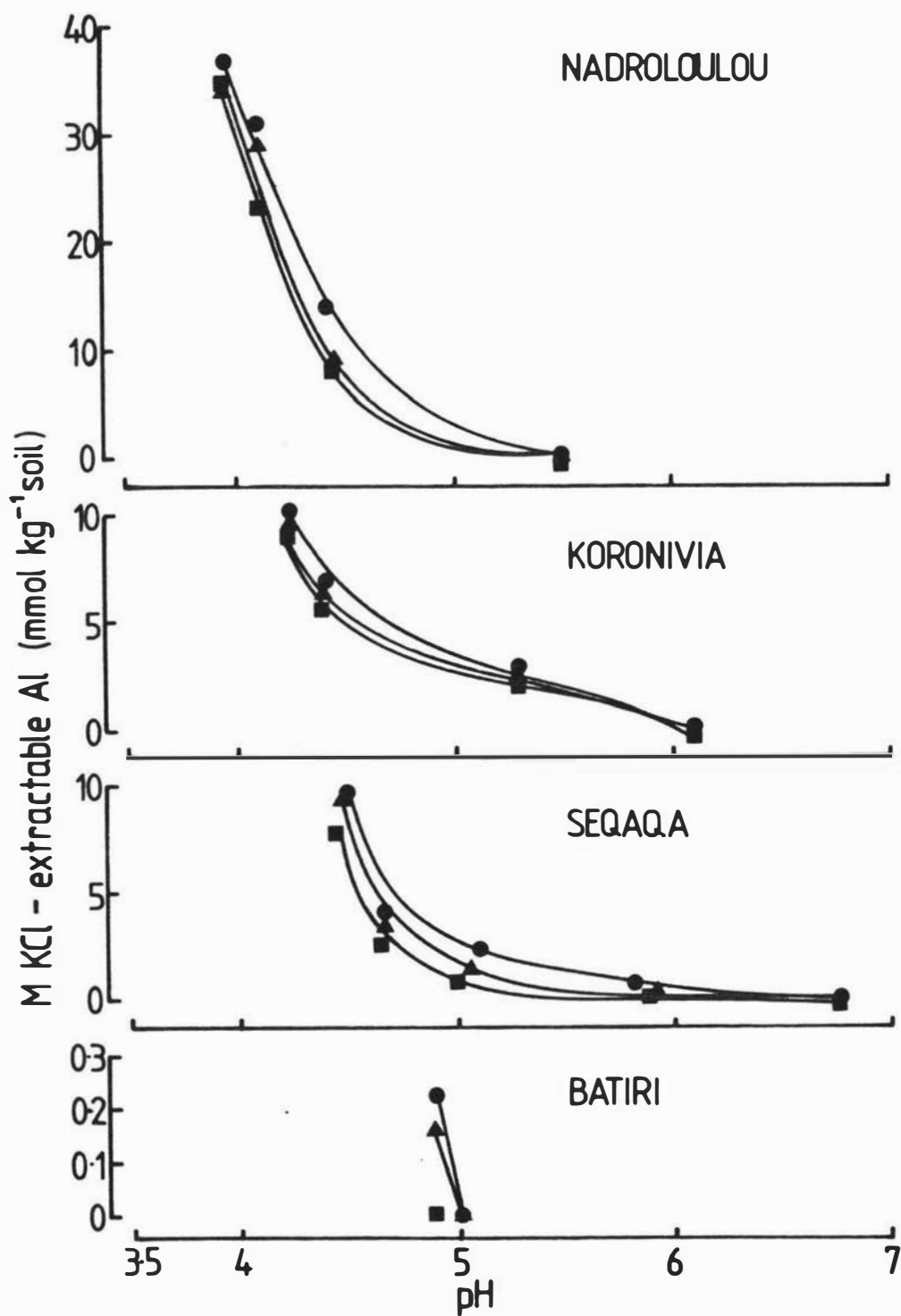


Fig. 7.2 Effect of soil pH on the amounts of Al extracted by M KCl from soils treated with 3 rates of added P (Table 7.1). (● = P1, ▲ = P2, and ■ = P3).

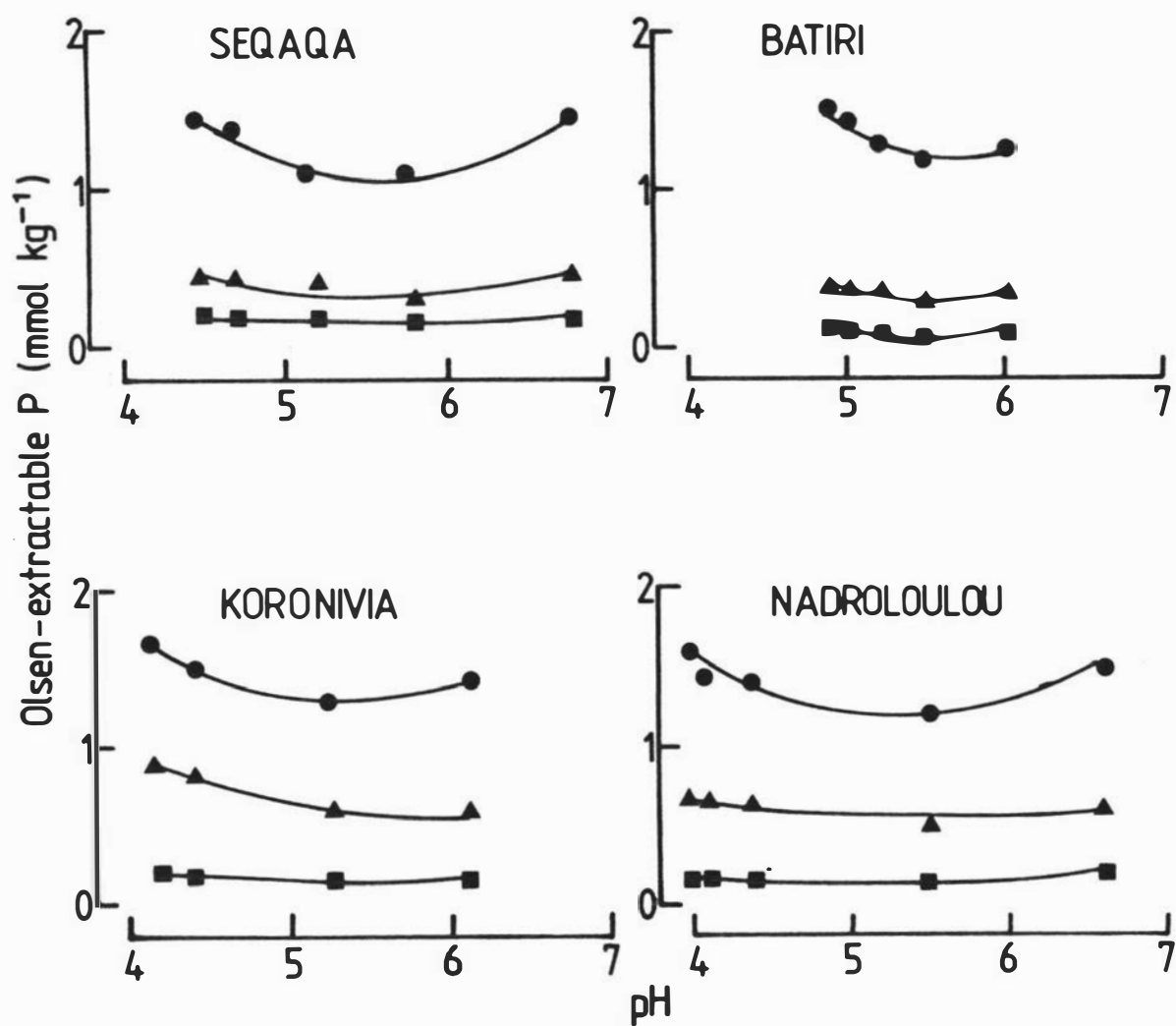


Fig. 7.3 Effect of soil pH on the amount of P extracted by the Olsen reagent from soils treated with 3 rates of added P (Table 7.1). (■ = P1, ▲ = P2, and ● = P3).

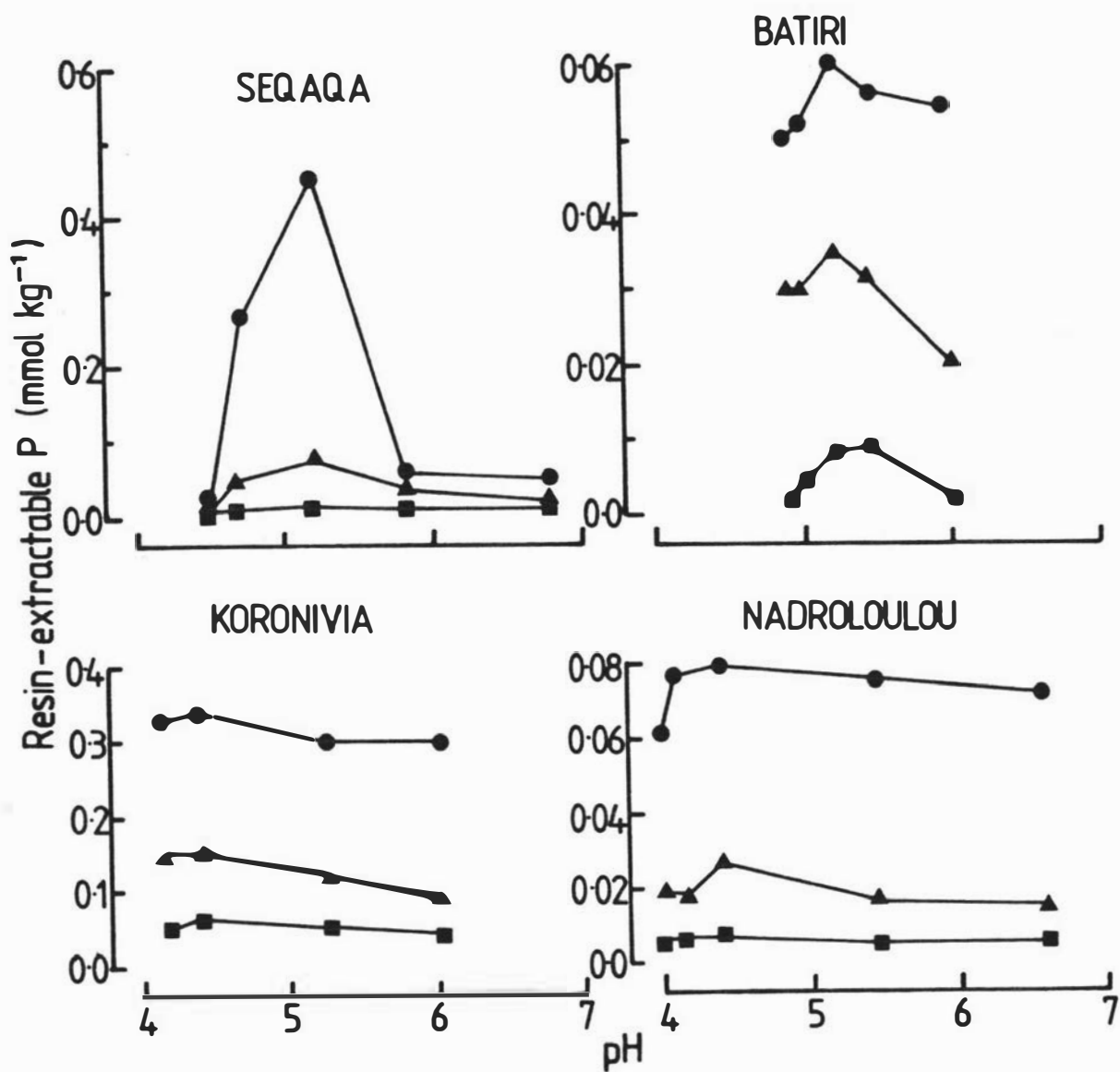


Fig. 7.4 Effect of soil pH on the amount of P extracted by anion-exchange resin from soils treated with 3 rates of added P (Table 7.1). (■ = P1, ● = P2, and ▲ = P3).

resin P increased to a maximum value between pH 4.4 to 5.5, above which it decreased. This trend was most pronounced in the Seqaqa soil which had been incubated with either medium or high levels of added P.

In contrast to resin P, Olsen-extractable P generally decreased in soils treated with either low or medium amounts of added P (Fig. 7.3). At the highest level of added P there was a tendency for Olsen P to increase at high pH values (Fig. 7.3).

M KCl-extractable Al decreased slightly with each level of added P (Fig. 7.2).

7.3.2 Effect of lime and phosphate additions on plant growth

For all 4 soils, increasing amounts of added lime caused an increase in dry matter yield to a maximum value and then a decline (Fig. 7.5). The pH at which maximum yield occurred varied between the soils (Fig. 7.5). For the Batiri and Seqaqa soils maximum yields were obtained at about pH 5.2 and for the Koronivia and Nadroloulou soils they occurred at about pH 4.4. However, the limited number of lime levels in this study, does not permit an accurate definition of the pH at which maximum growth is possible. The magnitude of these changes in dry matter yield was strongly dependent on P status. Thus, at the lowest level of added P, the effects of lime additions were small and in each of Batiri, Nadroloulou, and Seqaqa soils, the only significant ($P < 0.01$) increase in yield occurred at L2. In contrast, increasing lime additions to the Koronivia soil had a larger effect on crop yield even at the lowest level of added P (Fig. 7.5).

Further additions of P accentuated the effect of lime on crop growth (Fig. 7.5). However, the magnitude of this effect varied between soils. For example, liming had a marked effect on crop yield at the medium level of added P in the Koronivia and Seqaqa soils but it showed a pronounced effect on yield only at the highest level of added P in the Batiri soil. Interestingly, although both the Batiri and Seqaqa soils were incubated with the same amounts of P and had an identical pH at which maximum growth was recorded, liming had a much more pronounced effect on crop growth in the latter soil, particularly at L1 and L2. This increased effect of liming on crop growth in Seqaqa soil was also similar to the increased availability of P as measured by the resin-extraction procedure (Fig. 7.4).

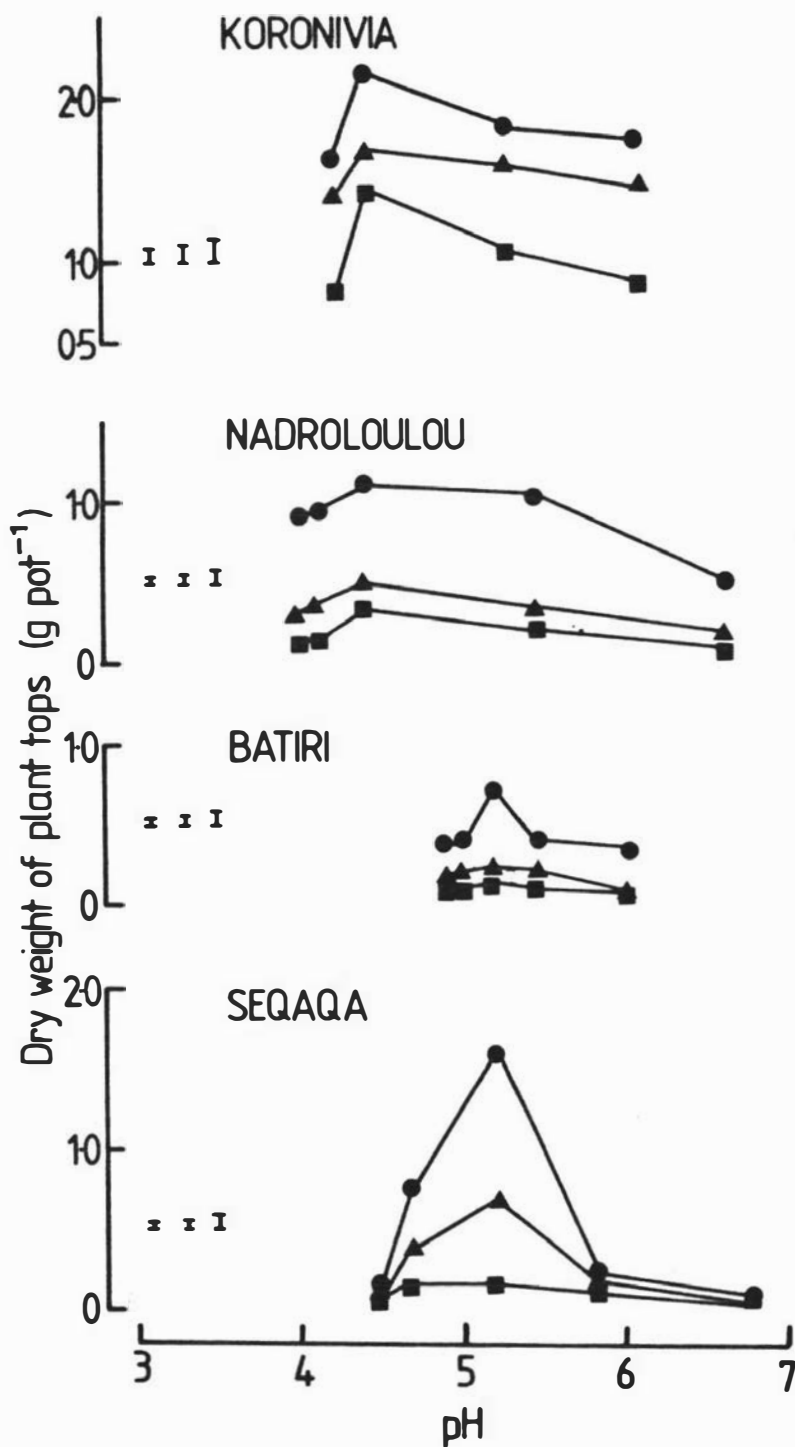


Fig. 7.5

Effect of soil pH and added P (Table 7.1) on dry matter top yield. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance. (■ = P1, ▲ = P2, and ● = P3).

In contrast, liming did not have any major effect on crop growth in the Nadroloulou soil (Fig. 7.5), even with the highest level of added P.

Although the pH at which maximum yield occurred varied between soils (Fig. 7.5), the M KCl-extractable Al content of the soils was either zero or rather small (Fig. 7.2) at lime levels at which maximum growth occurred. Lime in excess of this amount caused a depression in plant growth, as reported above. These observations confirm the findings of Woodruff and Kamprath (1965), Friesen et al. (1980b), and Farina et al. (1980a,b), all of whom observed a positive response of plants to lime at or less than pH values at which exchangeable Al was reduced to zero. In these studies, lime in excess of this amount caused a depression in plant growth.

Although crop growth increased to a maximum with all 4 soils, there is some doubt as to whether the rates of P addition were sufficient to ensure that optimum growth was achieved. To investigate this further, the concentration of P in plant tops was compared with that reported in previous studies (Gonzalez et al., 1980; Manibool, 1982). From this comparison, it appears that P was not limiting in the Koronivia and Seqaqa soils when the highest amount of P was added but the P concentrations in plants grown in the Batiri and Nadroloulou soils were always less than the critical concentration (50 mmol kg^{-1} , Gonzalez et al., 1980; Manibool, 1982). This was surprising as the amounts of P added were considerably above those commonly used in the field and the amounts of Olsen-extractable P (Fig. 7.3) in the soils did not suggest P deficiency in the soils treated with medium and high amounts of P. As will be discussed in Section 7.3.4, herbage P concentration was strongly influenced by lime additions and it is possible that, in these 2 soils, lime rates were such that none of the soil pH values obtained in this study were close enough to the pH for optimum growth. Thus it is possible that if slightly different lime rates had been used considerably higher yields and herbage P concentrations might have been obtained.

Somewhat different results have previously been reported for the growth of Leucaena leucocephala in limed, acid soils (Fox and Whitney, 1981; Fox et al., 1981; Hu and Wei-Er, 1981). In contrast to the present observations, liming of Hawaiian acid soils (Fox and Whitney, 1981; Fox et al., 1981) resulted in an increase in yield, even at pH values as high as 7. This increase in yield was attributed to improved Ca nutrition through liming (Munns et al., 1977; Fox and Whitney, 1981). However, in the present study, optimum levels of Ca were added with basal nutrients to

all treatments so that Ca was not limiting plant growth at low pH values. Although there was an increase in the concentration of Ca in plant tops with increasing pH through liming (Appendix 3a-3d), the concentration of Ca in plants grown at low pH was not deficient (Gonzalez et al., 1980), suggesting that the increased growth was not due to increased Ca, per se. However, previous studies on Leucaena leucocephala have been conducted in the field (Munns and Fox, 1976) and there are indications that lime-induced yield depressions in some crops are not as pronounced under field conditions as they are in pot experiments, particularly because of the limited volume of soil in pot experiments.

Although incubation of soils with added P generally resulted in a significant ($P < 0.05$) increase in yield within each lime level (Fig. 7.5), it did not eliminate the depression in yield at high pH values. Sumner (1979) related a similar yield depression to P deficiency and the initial extractable Al content of soils. He proposed that the initial level of exchangeable Al, at a given pH, reflected the reactivity of aluminous surfaces which, in turn, governed the solubility of P. From a review of literature and from his studies, Sumner (1979) concluded that plant growth was reduced at high pH only in those soils in which extractable Al exceeded 1.4 mmol kg^{-1} soil before liming. He was able to correct the yield depression by the addition of high levels of P. Except for the Batiri soil, the M KCl-extractable Al values in this study are higher than the critical value reported by Sumner (1979). However, the amounts of P used by Sumner at the highest rate of application were 2 to 3 times higher than those used in the present study. It therefore seems possible that the depressions in yield observed in the present study could have been corrected if very high additions of P had been used.

7.3.3 Effect of lime and phosphate additions on root growth

Lime and P additions had similar but less pronounced effects on root yield than they had on the yield of tops (Fig. 7.6). Thus, in the low and medium P-treated Batiri, Nadroloulou, and Seqqa soils, lime additions had only a small effect on root yield. In contrast to these soils, there was an appreciable increase in root yield at L1 in the low and medium P-treated Koronivia soils. Above L1, liming caused a decrease in root yield, as was also observed for top yield. With further additions of P, liming caused an increase in root yield up to the pH at which maximum plant

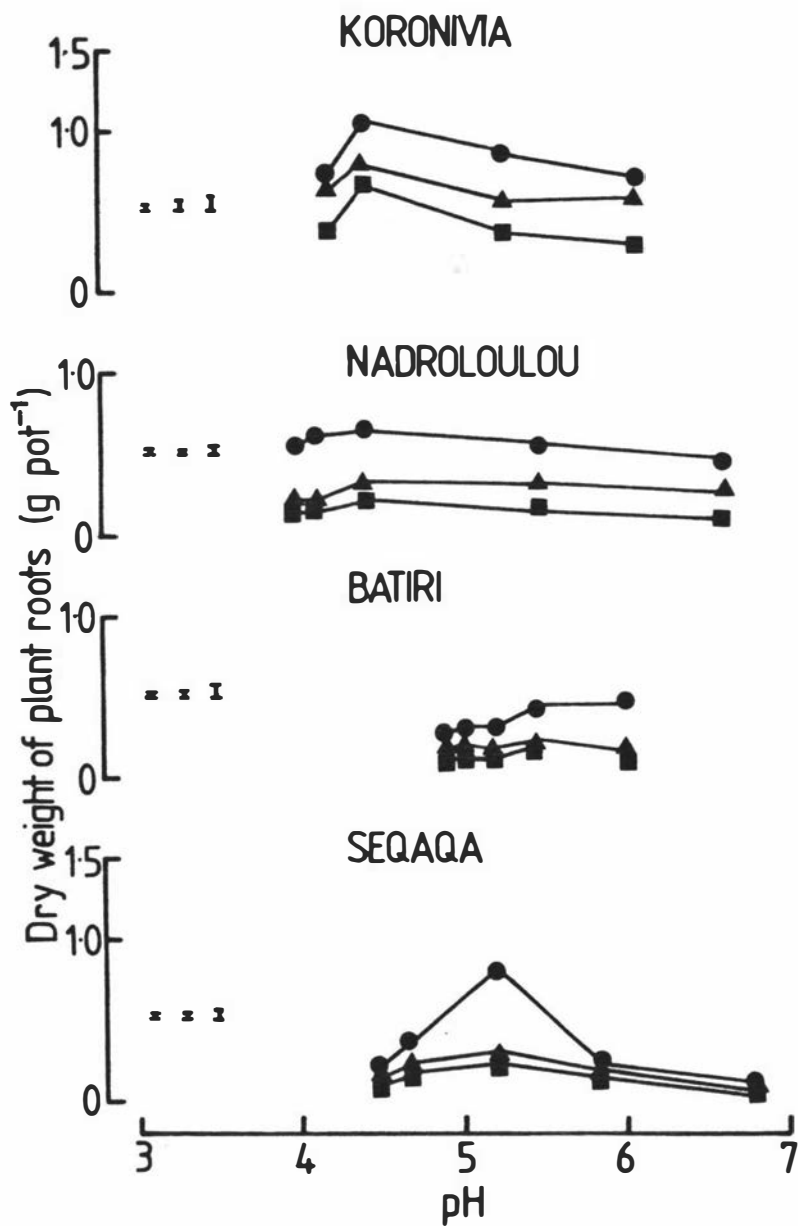


Fig. 7.6

Effect of soil pH and added P (Table 7.1) on dry matter root yield. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance. (■ = P1, ▲ = P2, and ● = P3).

top growth occurred, above which it decreased in all soils except Batiri. In the Batiri soil liming resulted in small but consistent increases in yield with increasing pH values.

The morphology of the roots also differed among the lime treatments. Generally, the plant roots at pH values where maximum growth was obtained had many more secondary or lateral roots than those grown in unlimed soils. Whereas the unlimed soils produced roots which were stunted and thickened, overliming limited the development of both secondary and lateral roots.

7.3.4 Effect of lime and phosphate additions on the chemical composition of *Leucaena leucocephala*

In general, the P concentrations in plant tops followed trends very similar to the yield response curve (Fig. 7.7). Thus, on either side of the pH at which maximum growth occurred, the P concentration in plant tops in all soils, except Koronivia, decreased markedly. The Koronivia soil showed a similar trend but the decrease was not as pronounced. Similar effects have previously been reported for *Leucaena leucocephala* (Fox et al., 1964) and other legumes and this decrease in the concentration of P was cited as a probable cause of yield reduction at high pH values (Fox et al., 1964; Lanyon et al., 1977; Sumner, 1979). Although the concentration of P in plant roots varied with pH the trend was not consistent between soils (Fig. 7.8). In general, however, the concentration of P was lowest at high pH.

In contrast to the data for P, the Al concentration in plant tops was at a minimum at the pH where maximum growth occurred, on either side of which it increased (Fig. 7.9). This increase was most pronounced in the tops of plants grown in the Nadroloulou and Seqaqqa soils. It is apparent that crop growth was severely depressed at Al concentrations exceeding approximately 1.3 mmol kg^{-1} DM tops (Fig. 7.10a) and, moreover, the concentration of P in tops when this Al concentration was exceeded was very low (Fig. 7.10b). These results appear to confirm the findings of Fox et al. (1964) and Farina et al. (1980a,b) in that plants can take up Al at soil pH values where it might be expected to be in the form of an insoluble hydroxide. Interestingly, the Al concentration in the plant tops in the Nadroloulou soil at the highest pH was higher than that in the unlimed soils at pH 4.0 (Fig. 7.9). Such an observation was also

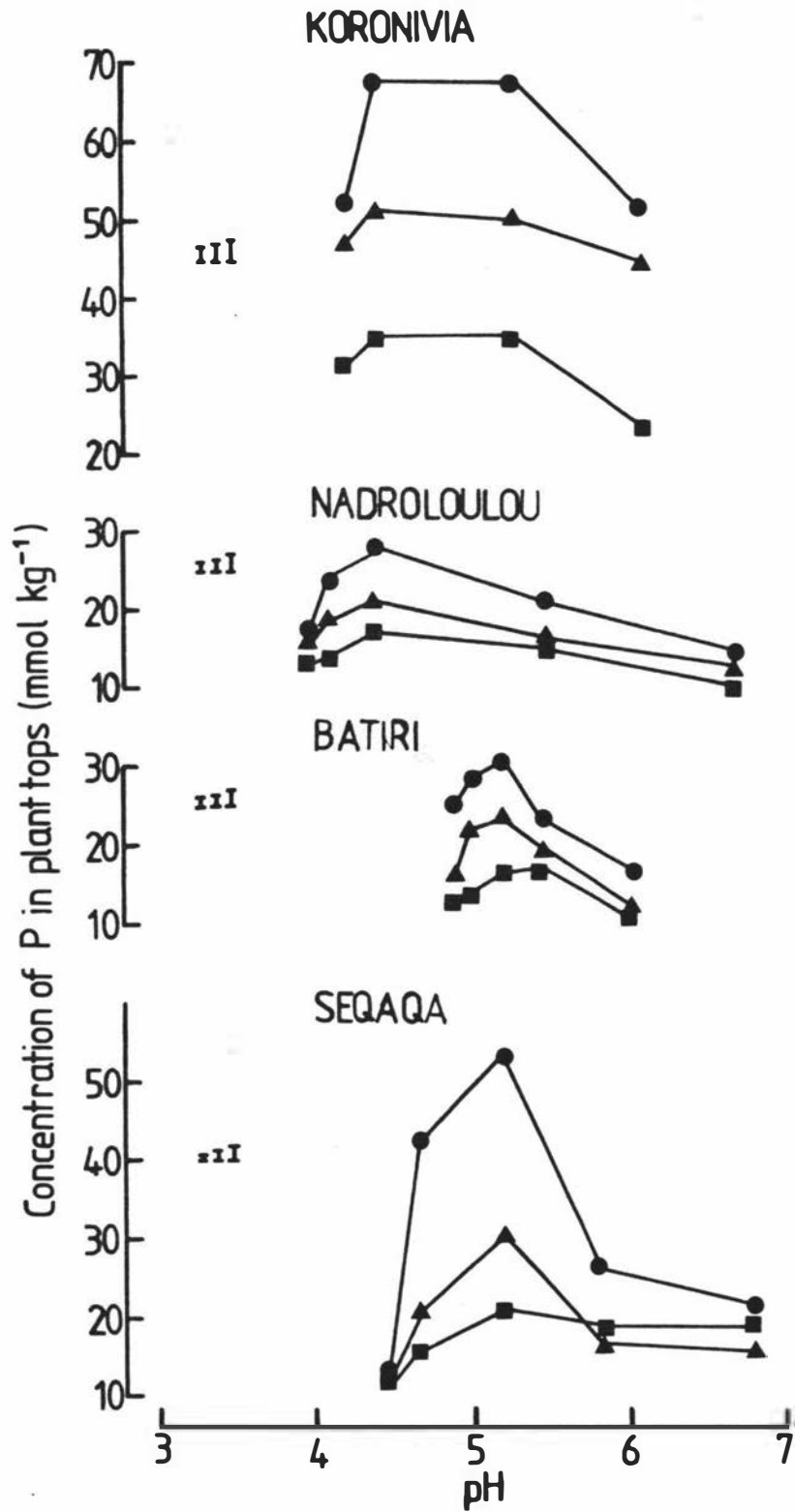
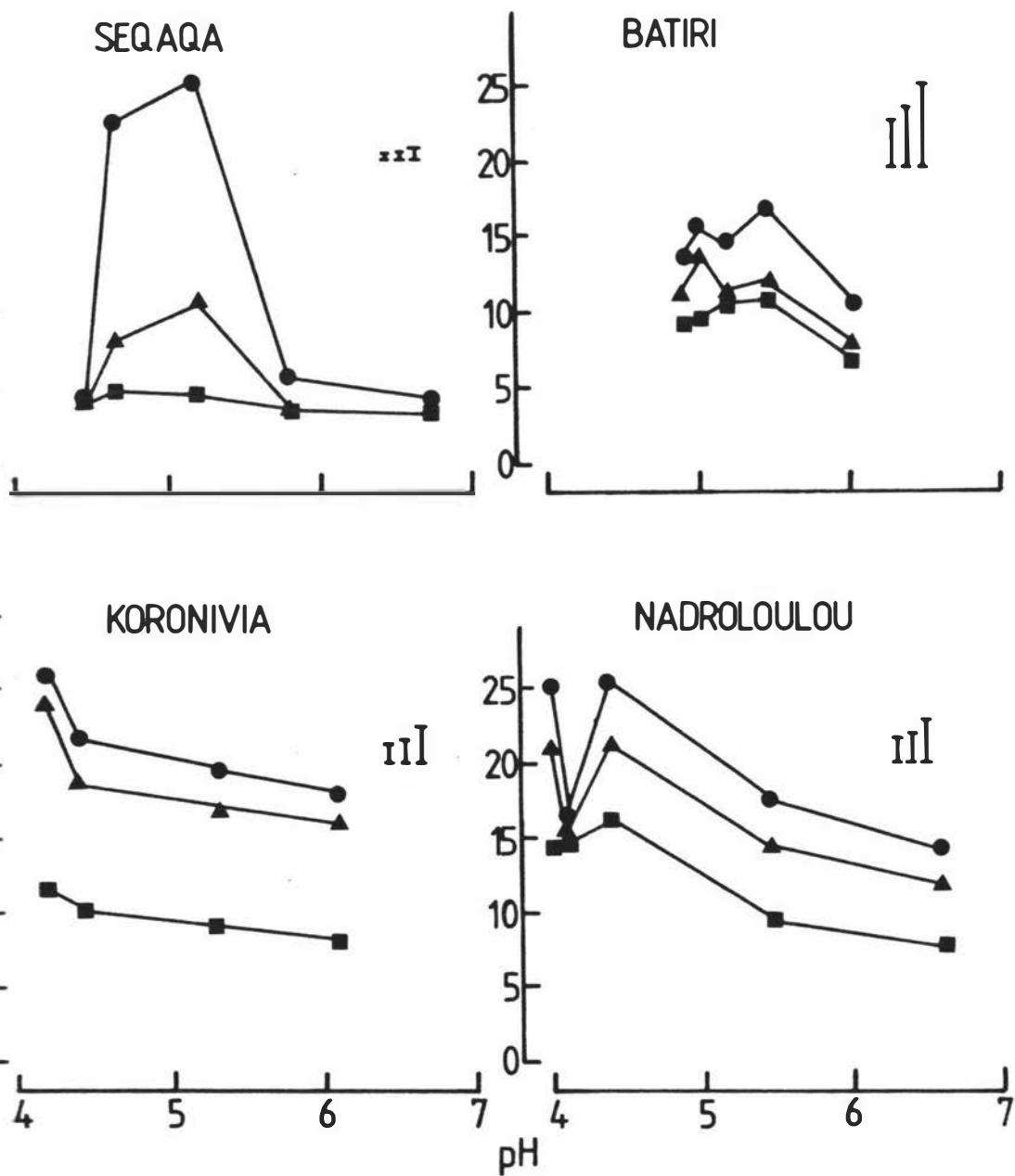


Fig. 7.7

Effect of soil pH and added P (Table 7.1) on the concentration of P in plant tops. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance. (■ = P1, ▲ = P2, and ● = P3).



7.8

Effect of soil pH and added P (Table 7.1) on the concentration of P in roots. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance. (■ = P1, ▲ = P2, and ● = P3).

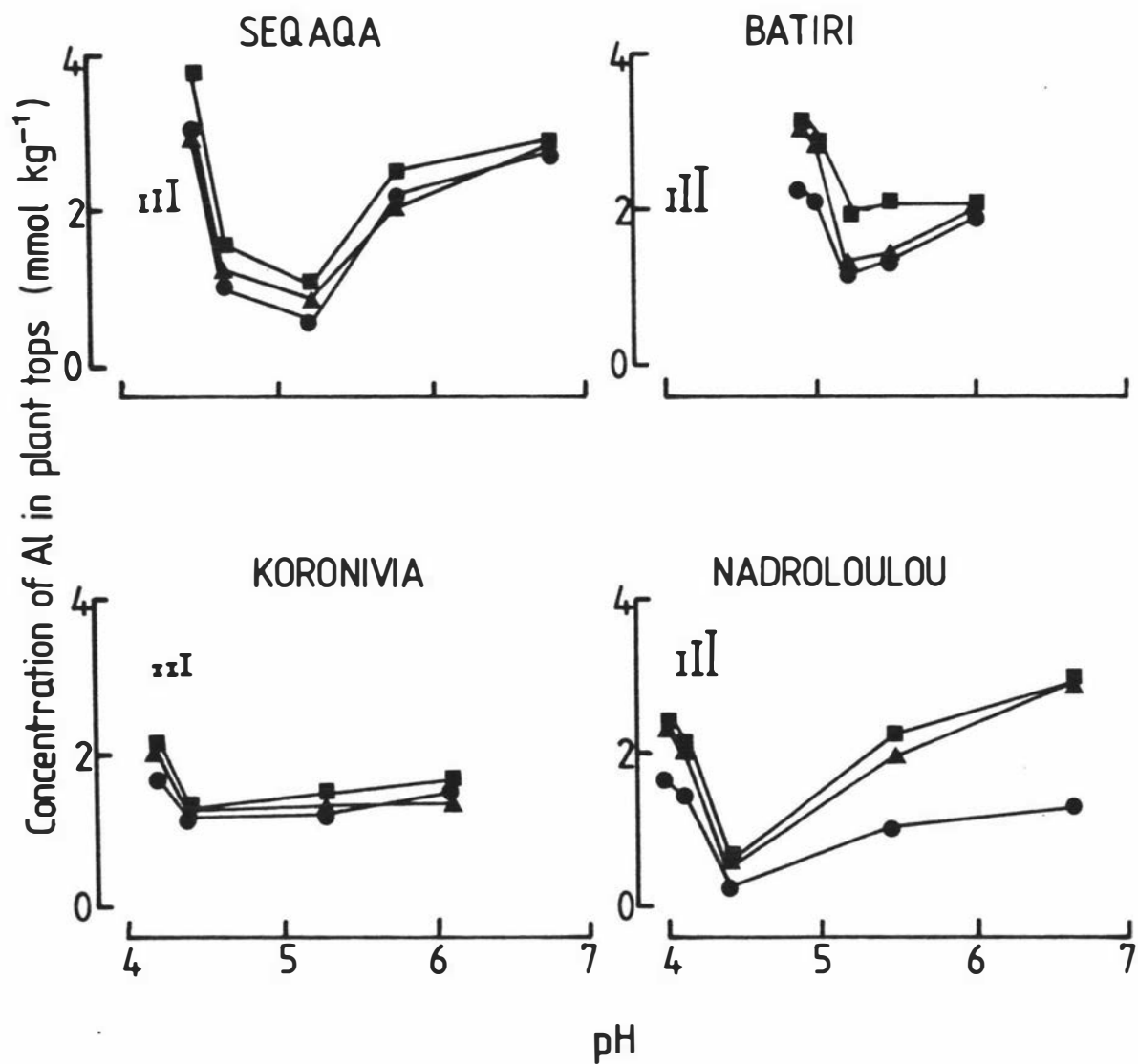


Fig. 7.9

Effect of soil pH and added P (Table 7.1) on the concentration of Al in plant tops. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance. (■ = P1, ▲ = P2, and ● = P3).

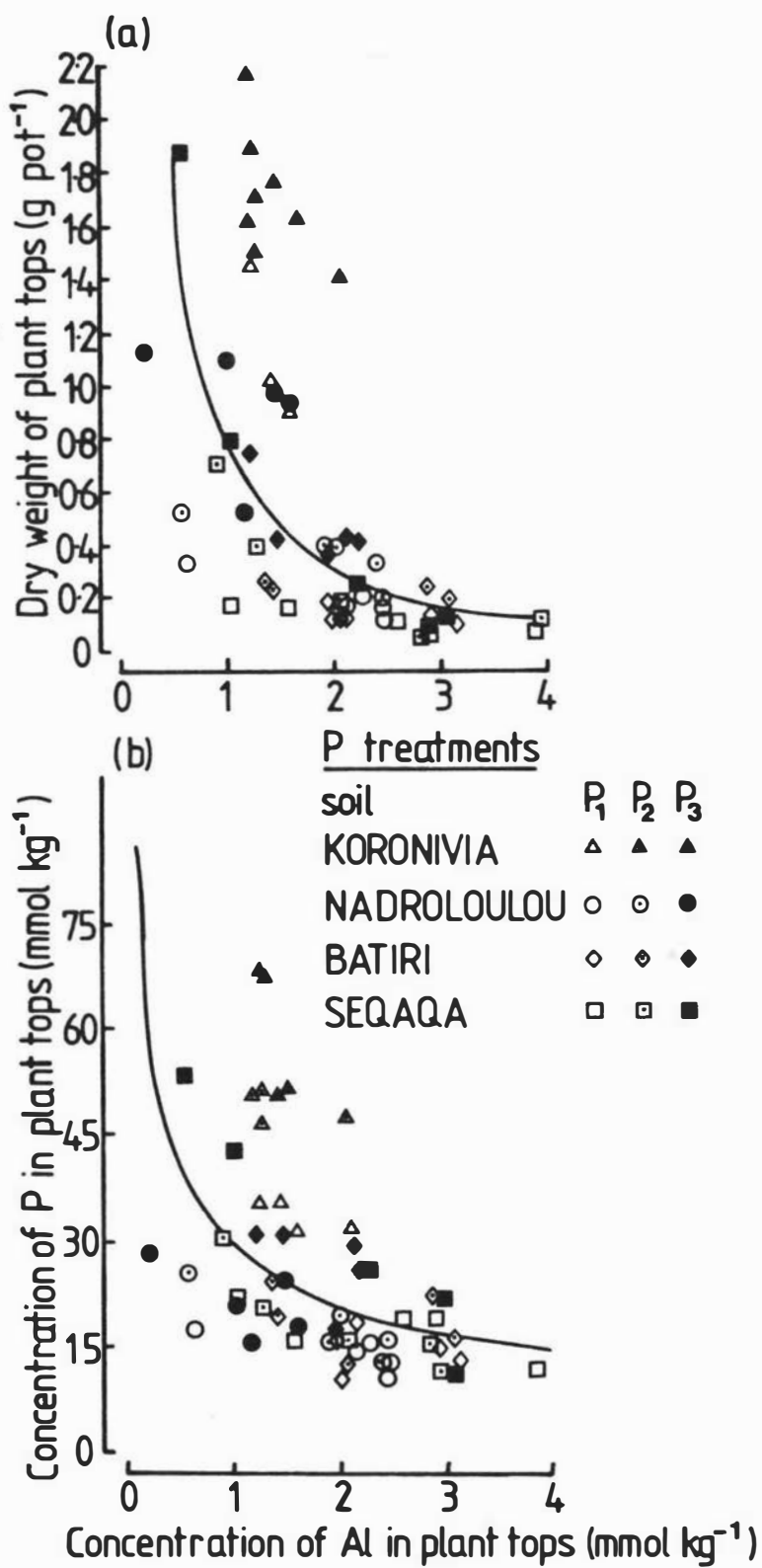


Fig. 7.10

Relationship between the concentration of Al in plant tops and
 (a) dry matter top yield, and
 (b) concentration of P in the tops.

recorded by Farina et al. (1980a) in leaf tissue of corn plants grown in acid soils treated with lime. In the present study, an increase in the amount of added P resulted in a small decrease in Al concentrations in plants grown in all soils.

In contrast to the trends in Al concentration described above for plant tops, the Al concentration in roots decreased with lime additions until the pH at which maximum growth occurred and then remained constant (Fig. 7.11). In addition, the Al concentration in the roots was always 10 to 20 times higher than in the tops. This is not surprising because Al is known to accumulate in the roots of Al-sensitive plants (Foy et al., 1978; Helyar, 1978). Although the Al concentration of the plant roots may have been influenced by some contamination from adhering soil particles, this would alter only the absolute values measured and not the trends observed.

Fox et al. (1964) attributed high plant Al concentrations at high soil pH values to the localized effect of $\text{Ca}(\text{OH})_2$ resulting in zones of high pH such that aluminate ions formed. If this mechanism was operative then it would be expected to influence the Al status of plants grown in soil, regardless of exchangeable Al content. The findings of Sumner (1979), that yield depression was observed only in soils in which exchangeable Al exceeded 1.4 mmol kg^{-1} , casts some doubt on the reason proposed by Fox et al. (1964). Furthermore, all the soils in the present study were thoroughly mixed during the lime incubation period. Studies by Kwong et al. (1978) and Young and Bache (1985) suggest that active Al could be present in soils at a pH >5.5 in the form of soluble organic complexes. Perhaps it is these soluble Al-organic complexes which are taken up by plants at high pH values. Of the soil properties considered in previous chapters and in the present study, only pH 4.8 NH_4OAc -extractable Al increased at high pH values (Appendix 1). However, these pH values were much higher than those at which growth depression first occurred.

Although the concentration of Al in the plant tops increased markedly at high pH, it is interesting to note that there was no clear trend with pH in the total amount of Al taken up into the plant tops (Fig. 7.12). Indeed, the uptake by the roots (and the whole plants) declined steadily with increasing pH (Fig. 7.13). This suggests that the increased Al concentration in plant tops at high pH values may be due, at least in part, to the concentrating effect of reduced growth which has resulted from factors

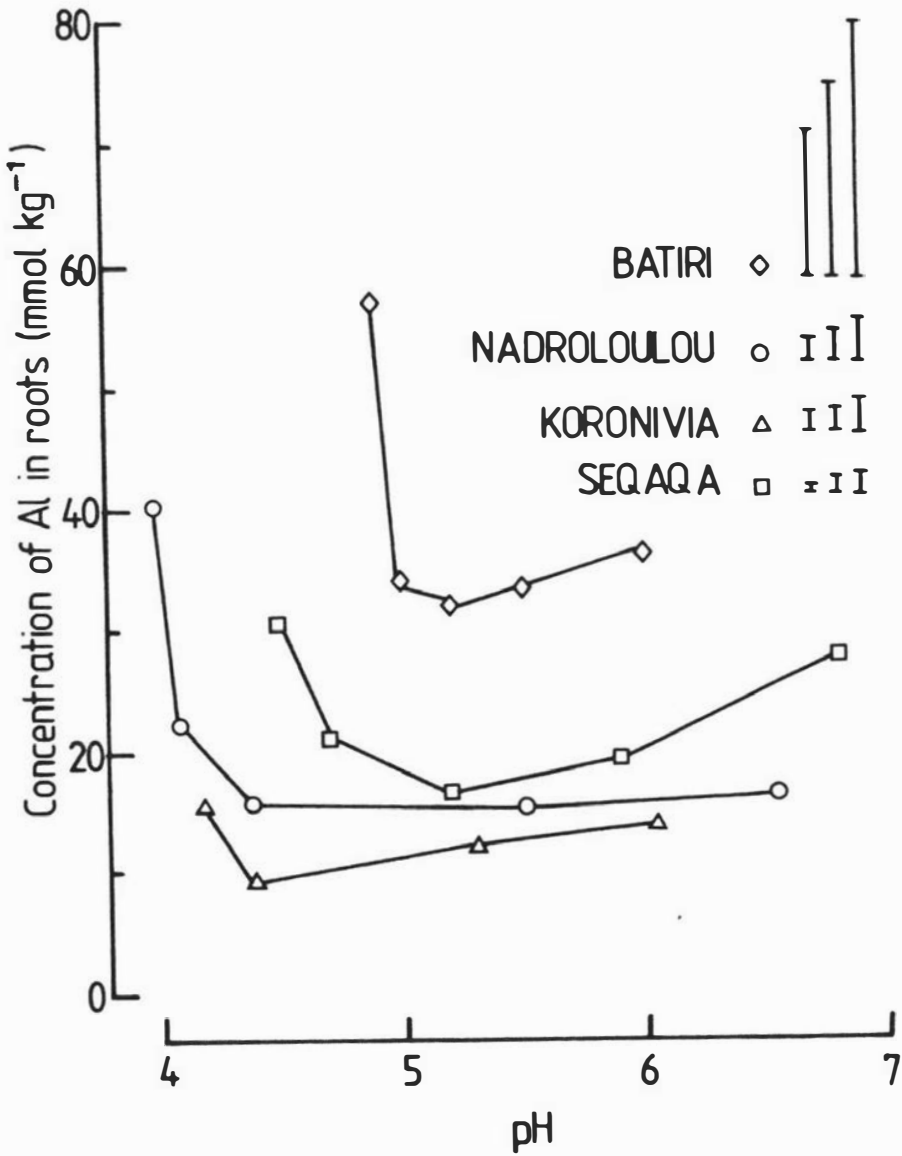


Fig. 7.11

Effect of soil pH on the concentration of Al in roots of plants grown in soils treated with $4.84 \text{ mmol P kg}^{-1}$. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance.

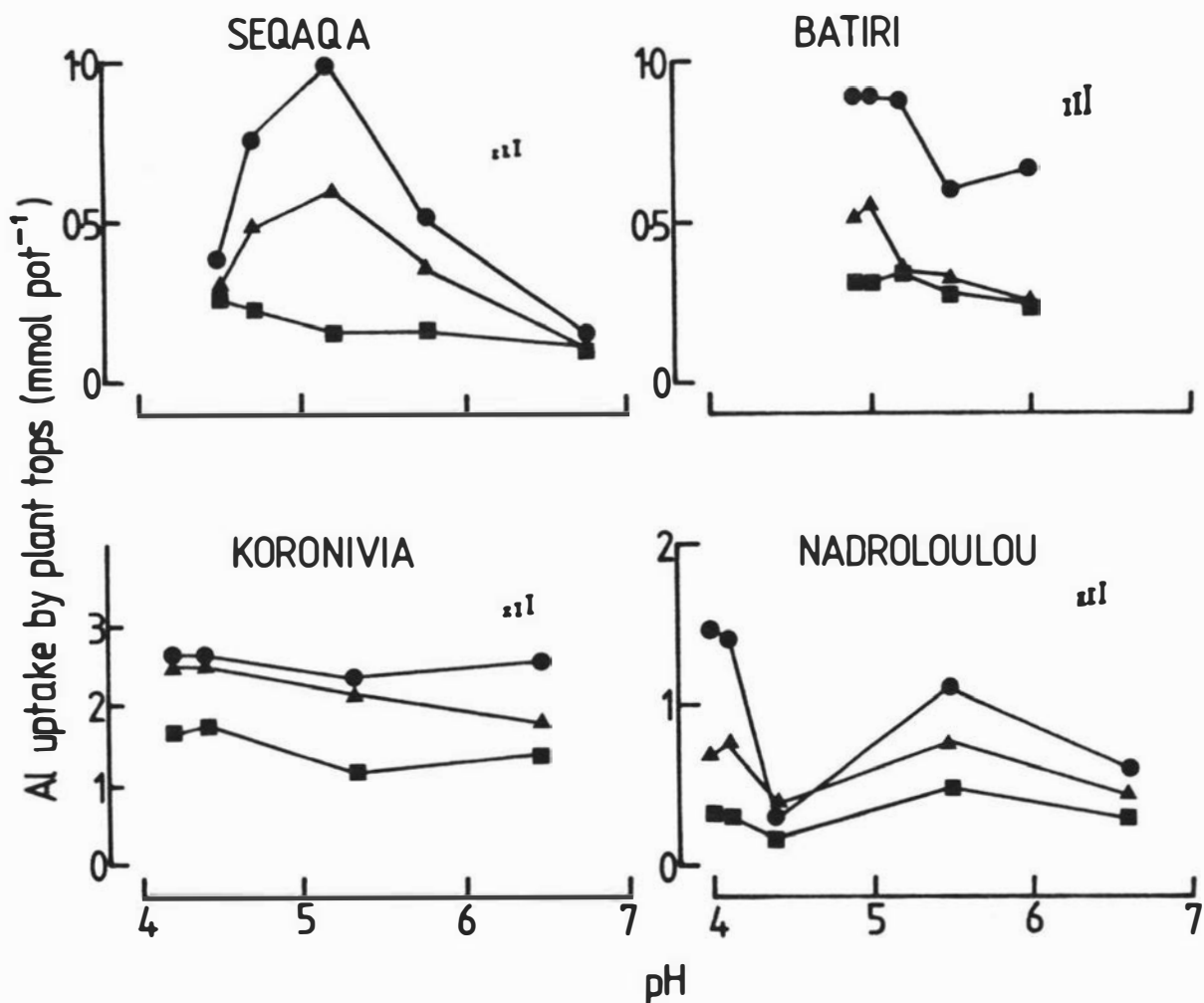


Fig. 7.12

Effect of soil pH and added P (Table 7.1) on the uptake of Al by plant tops. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance. (■ = P1, ▲ = P2, and ● = P3).

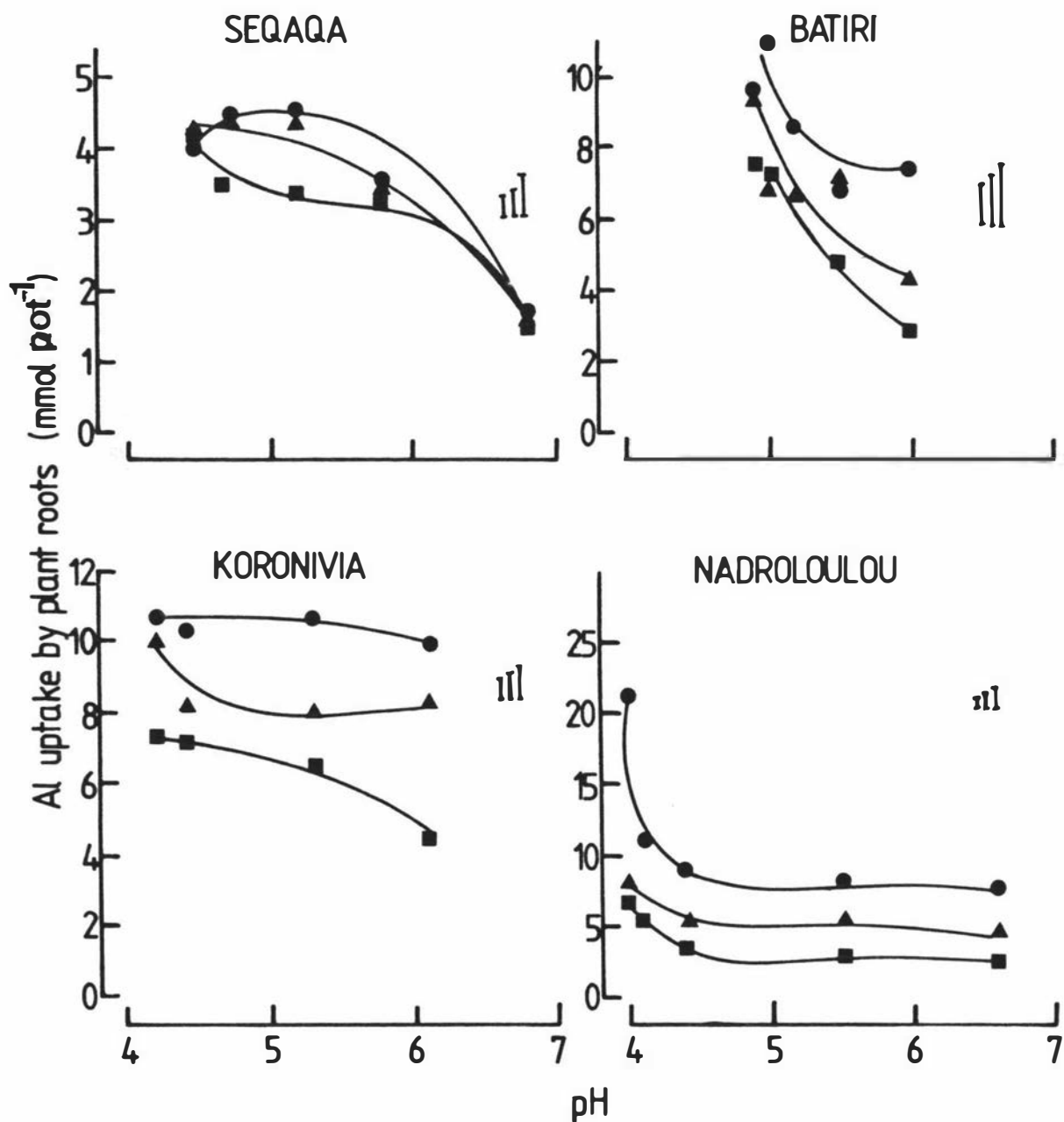


Fig. 7.13

Effect of soil pH and added P (Table 7.1) on the uptake of Al by plant roots. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance. (■ = P1, ▲ = P2, and ● = P3).

other than increased Al uptake.

The results for other major and minor nutrients are presented in Appendix 3a-3d. Although complete major (except P) and minor nutrients were added regularly there was some variation in the uptake of nutrients with pH. The plants grown at both low and at high pH values showed a range of symptoms, although nutrient concentrations generally did not fall below the critical concentrations (Gonzalez et al., 1980) and none of the symptoms could be associated with a specific element.

7.3.5 Lime-aluminium-phosphate interactions in soils and plants

The initial, positive response to lime by plants at medium and high levels of added P was probably associated with a decrease in M KCl-extractable Al and to enhanced availability of added P. In all soils, lime additions caused a decrease in M KCl-extractable Al (Fig. 7.2) and a corresponding increase in resin-extractable P up to pH values of 4.5 to 5.5 (Fig. 7.4). This is consistent with the general finding that the initial response of plants to liming is due to enhanced availability of added P (Fox et al., 1964; Woodruff and Kamprath, 1965) and a decrease in M KCl-extractable Al.

The reasons for the depression in plant growth at high pH values are less clear and many conflicting mechanisms have been proposed (Kamprath, 1971; Amarasiri and Olsen, 1973; Summer, 1979; Friesen et al., 1980b; Farina et al., 1980a,b). In this study, the observations that the concentration of P at extreme pH values was below the critical concentration required for normal growth coupled with the elevated ratio of P in roots to P in roots + tops (Fig. 7.14) suggests P deficiency at these pH values. However, the pattern of Al uptake by plant roots (Fig. 7.13), together with the results for the concentration of P in roots (7.8), suggests that different mechanisms were responsible for the cause of P deficiency in plants at low and high pH values. Thus, at low pH values, P deficiency appears to result largely from the blocking of P movement from the roots to the tops by the presence of high concentrations of Al in the roots (Fig. 7.11). Phosphate deficiency at high pH values has been related to a decrease in solution P concentration by the formation of insoluble Ca-P compounds (Kamprath, 1971; Fox et al., 1964). Support for this mechanism in the present study comes from the resin P results which decreased at high pH values. Further evidence to support this

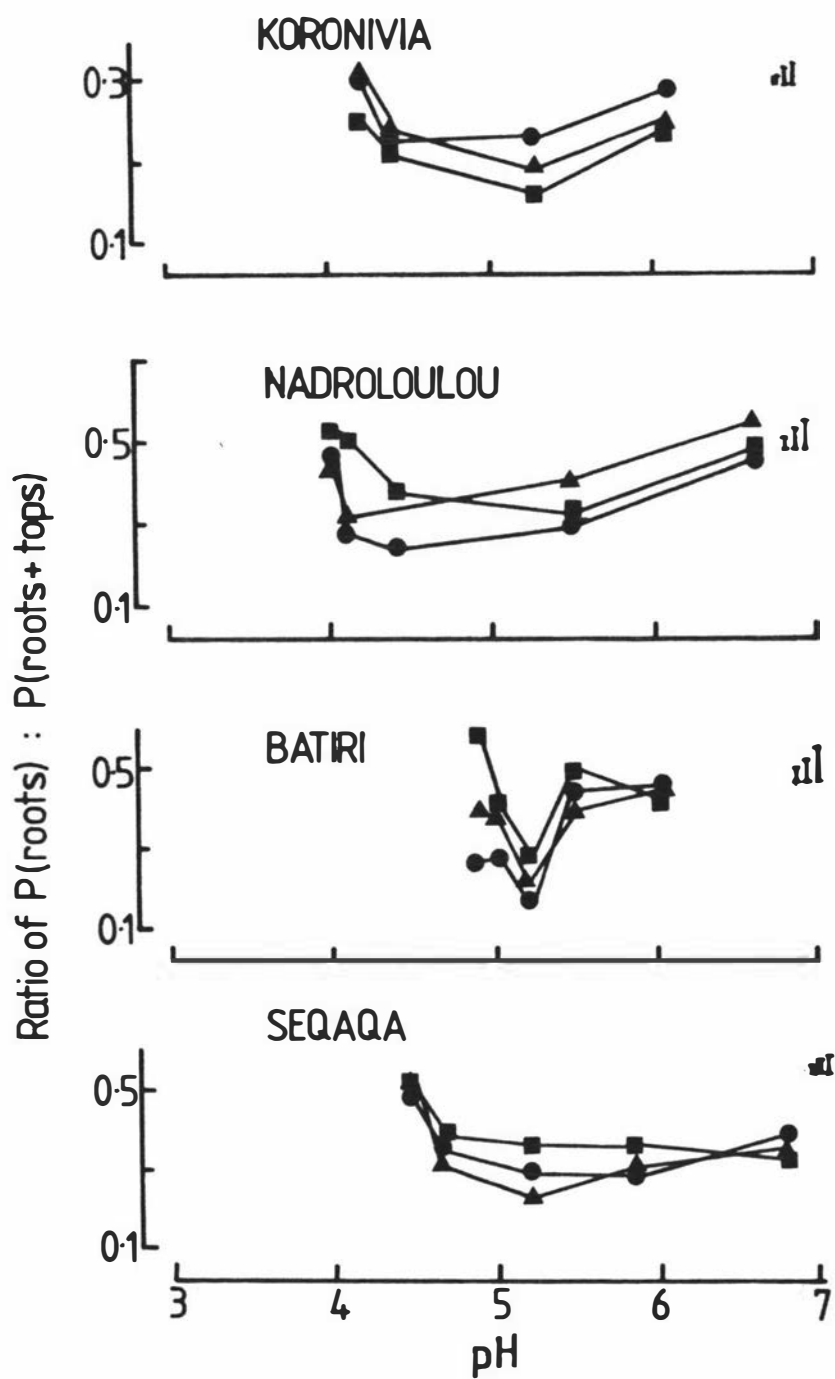


Fig. 7.14

Effect of soil pH and added P (Table 7.1) on the ratio of P roots to P (roots + tops) in plants. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance. (■ = P1, ▲ = P2, and ● = P3).

hypothesis is presented by the work of Murrmann and Peech (1969) and by observations on isotopic exchange and P sorption presented earlier in this study (Chapter 5 and 6, respectively). Reduced availability of P at high pH values has also been related to an increased sorption of added P by freshly precipitated Fe and Al hydroxides in limed soils (Amarasiri and Olsen, 1973).

However, Farina et al (1980a) reported that P deficiency, per se, may not explain the depression in yield at high pH values. In subsequent studies, Farina et al (1980b) reported that as much as 70% of the variation in the yield of corn at high pH values was explicable in terms of leaf Al content and that inclusion of P did not improve the variance accounted for. A similar treatment of the data from this study revealed that when yield and P concentration data from plant tops in which Al concentration exceeded approximately 1.3 mmol kg^{-1} (Section 7.3.4) were regressed together, P concentration accounted for 69% of the variability in yield. Inclusion of Al in the multiple regression analysis improved the variance accounted for to 74%. However, when the regression was conducted by taking results of the plants grown at high pH values only, where growth was depressed, P concentration alone accounted for 82% of the variability in yield. Inclusion of Al improved the relationship such that over 92% of the variability in yield was accounted for. The concentration of Al alone accounted for 55% of the variability in yield. Thus, the present results suggest that the variability in yield at high pH values can largely be explained by the concentration of P and to a smaller extent by the concentration of Al in the plant tissue.

7.4 Conclusions

Liming had a variable effect on the growth of Leucaena leucocephala in all soils. In general, plant growth was severely affected at both low and high pH values and this effect persisted even with additions of P. The pH at which maximum yield occurred varied between the soils but was generally in the range 4.4 - 5.2. Incubation of soils with P resulted in a significant ($P < 0.05$) improvement in yield within each lime level in all soils.

The response of plants to lime varied with both the amount of added P and soil type. Thus, although yield increased with added P in the

Nadroloulou soil, there was no obvious interaction between lime and P. This effect of lime and P in the Nadroloulou soil could have arisen from the fact that the lime rates were such that the pH values achieved were either too high or too low for optimum growth. In contrast to the Nadroloulou soil, a positive lime X P interaction was obtained in medium and high P-treated Batiri, Koronivia, and Seqaqa soils. This highly significant lime X P interaction is typical of P-deficient, highly-weathered, acid soils (Munns, 1965a,b; Friesen et al., 1980b).

From the P concentration data and yield response curves, it is apparent that near maximum growth was attained only in the Koronivia and Seqaqa soils treated with the highest level of added P. It is also apparent from the P concentrations of plants growing in Batiri and Nadroloulou soils, that poor growth in these soils is largely related to a deficiency of P.

The initial increase in yield with increasing pH was probably due to enhanced availability of added P and also to a decrease in active Al. The depression in plant growth at high pH values appears to be largely related to P deficiency and to a smaller extent to the presence of excess Al.

Although the ratio of P in roots to P in roots + tops indicates deficiency of P at both low and high pH values, the data for the Al and P concentrations in the roots also indicate Al-induced P deficiency in plants grown at low pH values.

The observed increase in Al concentration in plants at high pH values is due, at least in part, to the concentration effect of reduced growth on Al concentration. This contrasts with the situation at low pH where, despite lower growth, the uptake of Al by plant roots was higher.

CHAPTER 8

CHAPTER 8

ASSESSMENT OF PLANT-AVAILABLE PHOSPHATE
USING SEVERAL SOIL-TESTING PROCEDURES

8.1 Introduction

There is an increasing awareness of the need to limit application of fertilizer P to rates which are adequate for plant growth. However, to determine optimum application rates, soil-testing procedures are required to assess soil P status. Two of the basic criteria of a soil-testing procedure are that it requires a minimum amount of calibration and, once calibrated, it should successfully predict the response of plants to added P (Thomas and Peaslee, 1973). The soil-testing procedure should also be convenient for the routine analysis of large numbers of samples.

In Fiji, a single soil-testing procedure involving extraction with 0.025M H₂SO₄ is currently used to assess the P status of soils (Fiji SCEP, 1984). However, the extent to which this acid extractant is successful over a range of soil types, which vary widely in chemical and mineralogical properties, is not known. Because the relationships between 0.025M H₂SO₄-extractable P and plant response to P has not been evaluated there is a need to standardise soil-testing procedures for the range of soils in Fiji (Fiji SCEP, 1984).

Although only four Fijian soils were studied in Chapter 7, the performance of a number of soil-testing procedures can be assessed using the results obtained for the effect of liming on the growth of Leucaena leucocephala. However, in assessing the usefulness of soil-testing procedures, it is necessary to ensure that plant growth is not limited by other factors. As discussed in Chapter 7, there was a considerable growth limitation in Batiri, Nadroloulou, and Seqaqa soils because of Al toxicity, particularly at low pH values, such that some doubt existed as to whether available P was completely exhausted.

To investigate this further, subsamples of the soils which had initially been planted with Leucaena leucocephala, were grown with perennial ryegrass (Lolium perenne L) using the procedure of Stanford and

Dement (1957). This test is designed to be highly exploitive of the nutrient under study. Ryegrass was chosen as the crop because it is known to be less sensitive to Al toxicity than Leucaena leucocephala.

Thus, in this chapter, a range of soil-testing procedures was used to assess the plant-available P status of soils which had been treated with lime and added P. The soil-testing procedures chosen were Olsen (Olsen et al., 1954), Colwell (Colwell, 1963), Bray (I and II) (Bray and Kurtz, 1945), Mehlich (Nelson et al., 1953), Cl-exchange resin (Cooke and Hislop, 1963), and isotopic exchange (Chapter 5). The Mehlich soil-testing procedure was used in preference to the procedure used in Fiji because it has been shown to successfully predict the P requirements of plants in highly-weathered soils (Thomas and Peaslee, 1973).

8.2 Materials and Methods

8.2.1 Soils

The soils used in this study and their preparation have been described in detail in Chapter 7 (Section 7.2.2). Each of the 4 highly-weathered, acid soils were limed at either 4 or 5 rates to obtain a range of soils with pH values up to 7. Subsamples of the limed soils were incubated subsequently with 3 rates of P. The rates of P were such that all soils received 1 common P treatment and the other 2 rates were low or high, depending on the P-sorption capacity of the soils. These treatments are listed in Table 7.1. Following incubation, the soils were air dried at a temperature of $20 \pm 2^{\circ}\text{C}$ and stored in polythene bags for chemical analysis and plant growth studies.

At the completion of the Leucaena leucocephala growth study (Chapter 7), all soil samples were air dried at a temperature of $20 \pm 2^{\circ}\text{C}$, passed through a 2-mm sieve, and again stored in polythene bags for the ryegrass growth study.

8.2.3 Extractable Phosphate

Mehlich- and Olsen-extractable P in the treated soils were determined by the methods described in Chapter 5 (Section 5.2.2), while resin-extractable P was determined using the method described in Chapter 7 (Section 7.2.3.1).

Colwell-extractable P (Colwell, 1963) : 0.2 g of soil was shaken for 16 h with 20 mL of 0.5M NaHCO₃ (pH 8.5) solution in polypropylene tubes, centrifuged, and filtered through Whatman No. 5 filter paper. Inorganic P was determined in the extracts by the method of Murphy and Riley (1962).

Bray (I)-extractable P (Bray and Kurtz, 1945) : 1 g of soil was shaken by hand for 60 s with 7 mL of the Bray reagent (0.025M HCl + 0.03M NH₄F) in polypropylene tubes and filtered through Whatman No. 5 filter paper. Inorganic P was determined in the extracts, as described above for Colwell-extractable P.

Bray (II)-extractable P (Bray and Kurtz, 1945) : 1 g of soil was shaken by hand for 40 s with 7 mL of the Bray reagent (0.1M HCl + 0.03M NH₄F) in polypropylene tubes, and filtered through Whatman No. 5 filter paper. Inorganic P was determined in the extracts as described above for Colwell-extractable P.

Isotopically-exchangeable P : 1 g of soil was shaken with 30 mL of deionized water for 16 h, following which, 1 mL of carrier-free P solution (2 to 4 μ Ci) was added to the soil suspension. The tubes containing the soil suspension were shaken for a further 2 h, centrifuged, the supernatant solution passed through a millipore membrane ($< 0.45 \mu\text{m}$), and ³¹P and ³²P determined in the filtrate. The contact time was decreased from the 4 h used in Chapter 5, to 2 h to ensure exchange with the fraction of P which would be most easily exchangeable. The procedure used for the determination of ³²P is described in Chapter 5 (Section 5.2.2).

8.2.3 Determination of buffer capacity

To determine the P-buffer capacity of soils, sorption studies were conducted by shaking soil samples (1 g) with 0.02M KCl (30 mL) solution containing varying amounts of P (Holford, 1979). The buffer capacity of each of the soils was then determined by 3 different methods, which included

- (i) the maximum slope of the Langmuir isotherm, as described by Holford (1979),
- (ii) the slope of the sorption isotherm (Peaslee and Phillips, 1981), and
- (iii) the amount of P required to increase the solution P concentration to 0.008 mmol L⁻¹ (0.25 $\mu\text{g mL}^{-1}$; Jones and Fox, 1977).

In addition, the P retention of unlimed soils was determined by the method of Saunders (1965).

8.3 Plant Growth Studies

A modified Stanford and Dement (1957) procedure was used to assess the amount of available P remaining after the growth of Leucaena leucocephala (Chapter 7).

A plastic pot, with the bottom removed, was placed inside a second pot and subsequently filled with 300 g of washed river sand. A solution containing complete major and minor nutrients was added to each pot. Perennial ryegrass (Lolium perenne L) was used as the test plant and approximately 50 seeds were sown per pot. The pots were watered regularly to the required moisture content until the seeds germinated.

After 6 weeks of plant growth, when the roots of the plants had formed a dense mat at the bottom of the pot, the plants were cut to a level of 200-300 mm above the sand surface. The inner pots, containing the sand and the roots, were then transferred into another intact pot containing 20 g of the treated soils which had earlier been used to grow Leucaena leucocephala. Six pots containing ryegrass growing in sand were kept as control plants. These pots were watered regularly to the required moisture content. All major and minor nutrients, except P, were added twice each week in addition to the regular watering.

At the end of 28 d, the tops were harvested, the roots washed free of adhering sand and soil particles, and the herbage dried at 65°C for 48 h. Dried herbage (roots and tops) was weighed to obtain the yield, ground, and P concentration determined by the method of Twine and Williams (1971). Aluminium in the tops of plants grown in Seqaqa soil was determined after digestion in perchloric acid using the modified aluminon method (Hsu, 1963).

8.4 Results and Discussion

8.4.1 Plant growth studies

For all but the Koronivia soil, there was an increase in growth with increasing lime rate up to either L1 or L2 and this was followed by a depression in growth at higher pH values. With the Koronivia soil, yield was almost constant up to L1, above which it declined. Only the results for the common P treatments are presented because lime additions had similar effects at all P levels. These trends are similar to those

reported earlier for the growth of Leucaena leucocephala on these soils. Interestingly, the majority of the plants grown in Batiri and Seqaqa soils at either low or high pH gradually died. This occurred after about 3 weeks, during which time the initially healthy roots of ryegrass (in sand culture) gradually became spotty in appearance. This contrasted with the plants in the control treatment which continued to grow slowly even without any addition of P. Thus, the yield of plant tops grown at low and high pH values was generally less than that in the control pots (Fig. 8.1).

In Chapter 7 it was suggested that the major factor limiting plant growth in soils at low pH values was Al toxicity and/or Al-induced P deficiency and at high pH values was soil P supply and to a smaller extent the increased concentration of Al in the plant tissue. In the present study, the concentration of P in plant tops was low at both low and at high pH values (line b, Fig. 8.2). Only the results for the medium P-treated Seqaqa soils are presented because the plants growing in this soil were the most severely affected. In contrast, the concentration of Al was at a minimum at the pH of maximum growth, on either side of which it increased (line a, Fig. 8.2). Although reduced plant growth in soils at high pH values could have been due to a decrease in plant-available P, comparison with the control plants would suggest that this alone could not have caused the death of plants. This probably arose from the increased concentration of Al in the plants and provides compelling evidence for some Al toxicity effects at high pH.

8.4.2 Relationship between plant uptake of phosphate and soil-test results

The relationship between uptake of P by plants (Leucaena + ryegrass) and P extracted by the seven soil-testing procedures is illustrated in Fig. 8.3 a-g. With the exception of the results for isotopic exchange, all procedures gave results which were correlated with plant P uptake data. However, only for resin P was the relationship a close one. The slope coefficient (0.97) for the regression equation, together with a very low intercept, suggested an almost, 1:1 relationship between resin-extractable P and P uptake. This high correlation between resin P and plant P supports the findings of a number of workers who have observed that the resin-extraction procedure is a good indicator of P availability in a wide range of soils (Bache and Rogers, 1970; Walmsley and Cornforth, 1973; Le Mare, 1981).

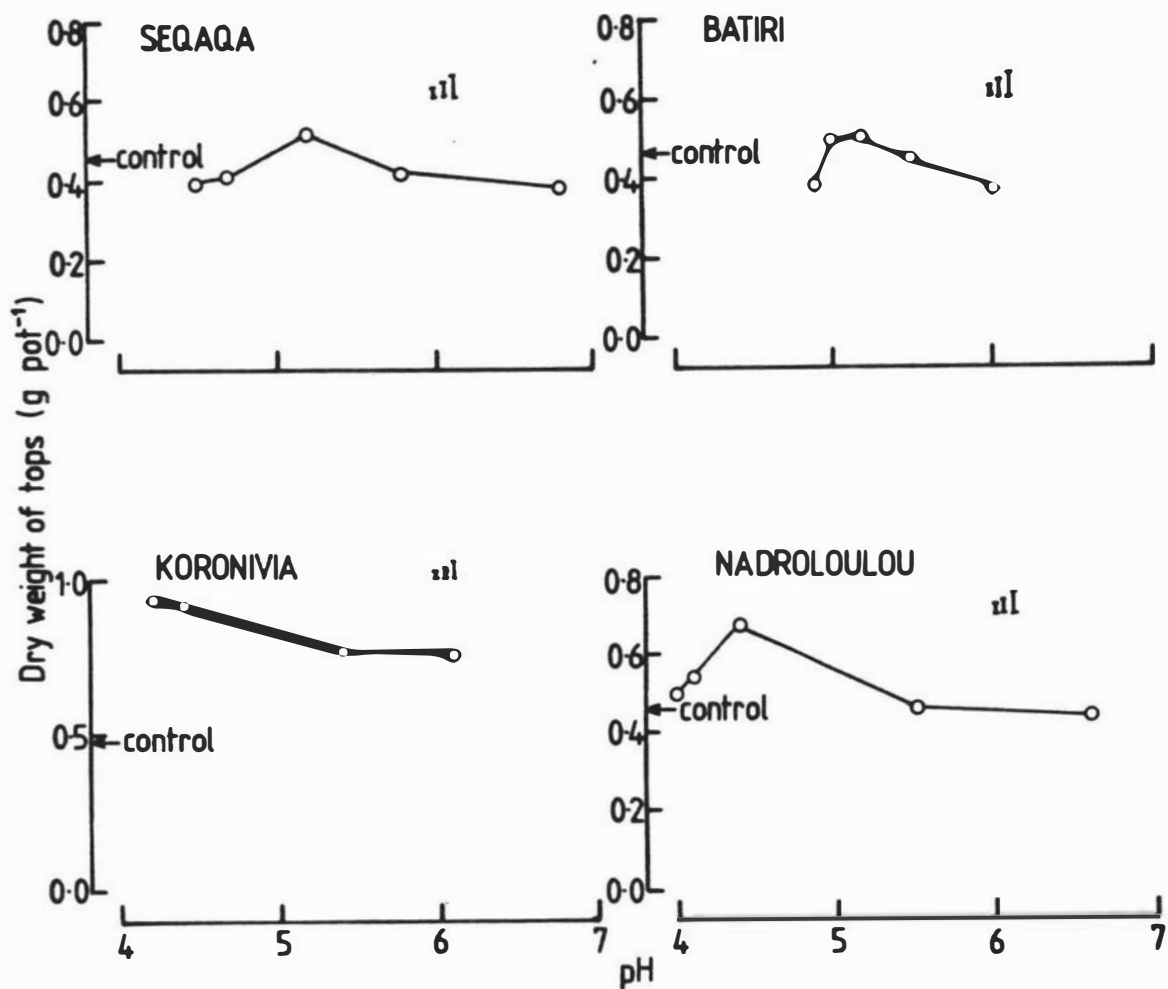


Fig. 8.1 Effect of soil pH and added P ($4.84 \text{ mmol kg}^{-1}$) on the dry weight of ryegrass tops. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance.

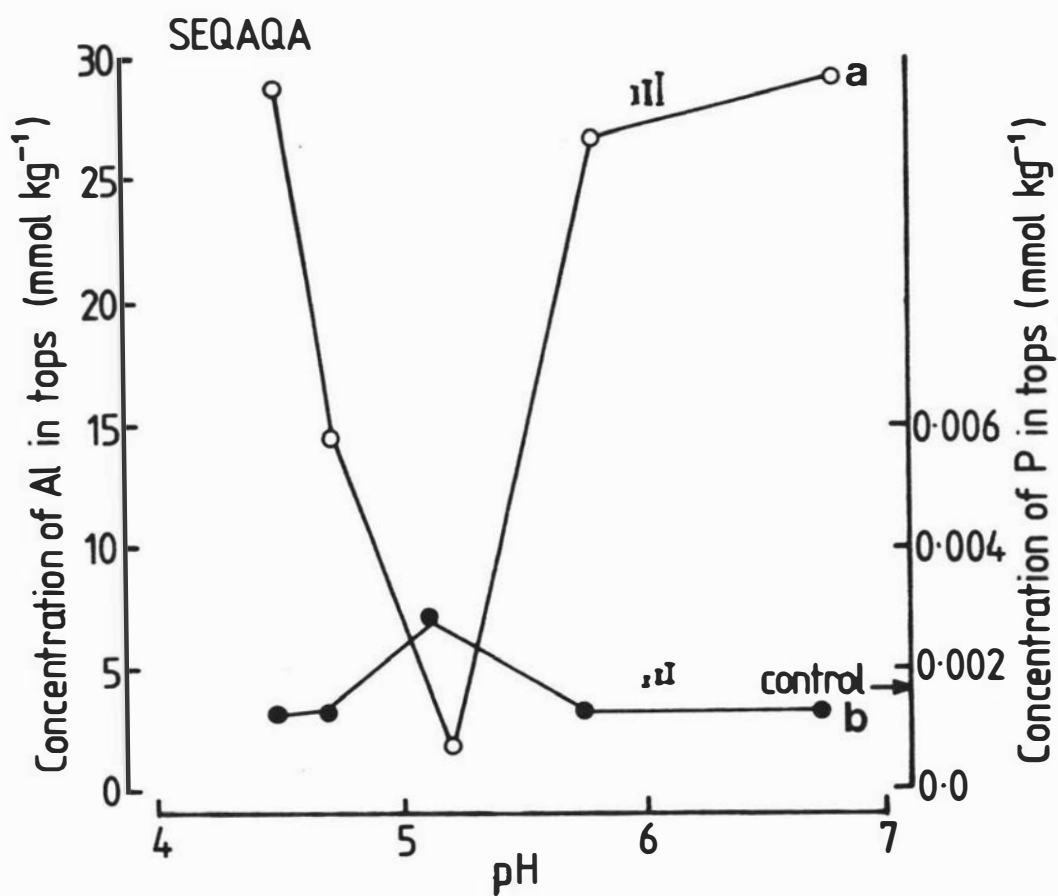


Fig. 8.2

Effect of soil pH and added P ($4.84 \text{ mmol kg}^{-1}$) on the concentration of (a) Al and (b) P in ryegrass tops. Vertical bars (I) represent LSD (pH) at 5, 1, and 0.1% level of significance.

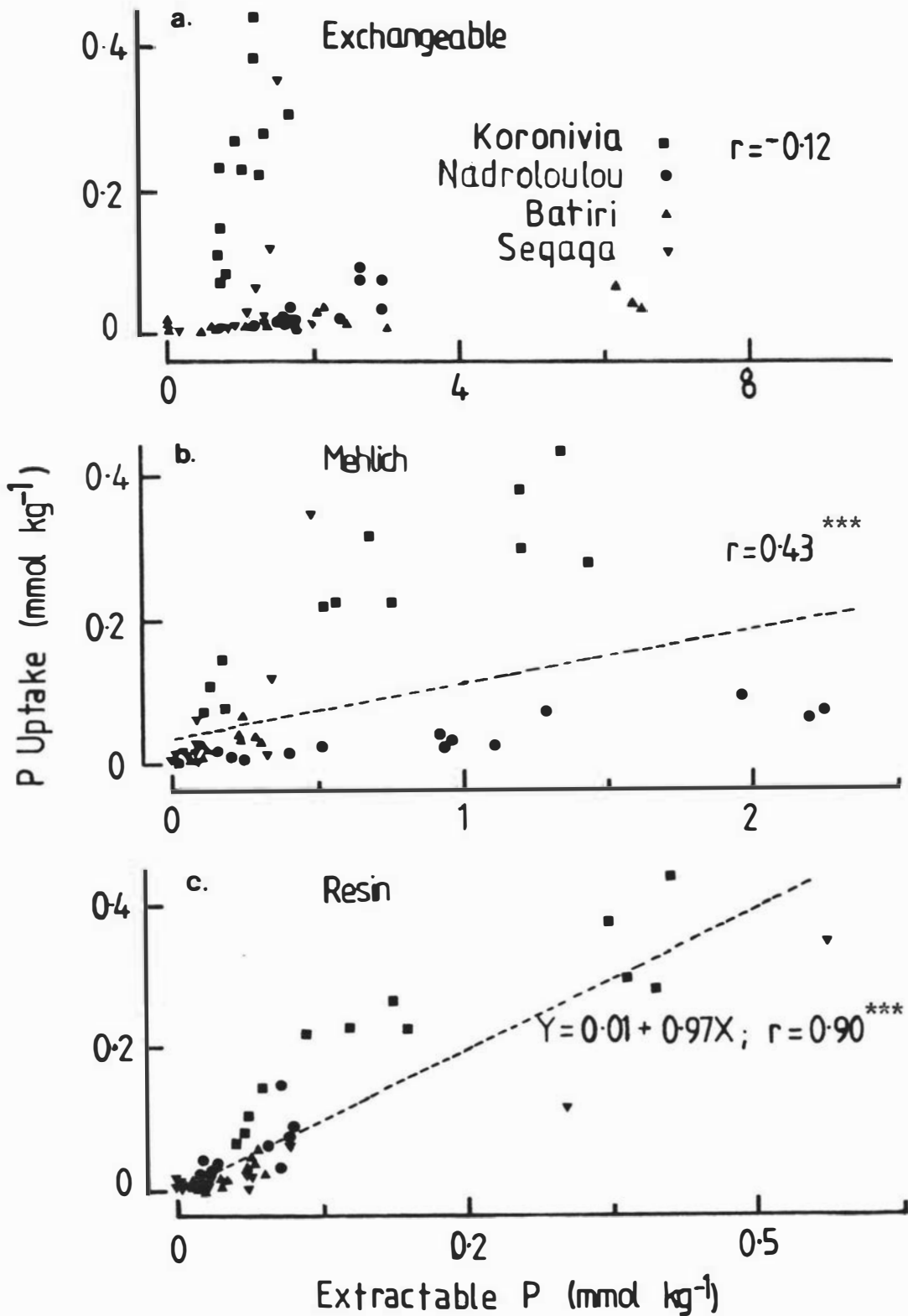


Fig. 8.3
(contd.
p.133)

Relationship between uptake of P by plants (*Leucaena leucocephala* and ryegrass) and amounts of isotopically-exchangeable P (a) Mehlich- (b), resin- (c), Bray(I)- (d), Bray(II)- (e), Olsen- (f), and Colwell-extractable P (g).

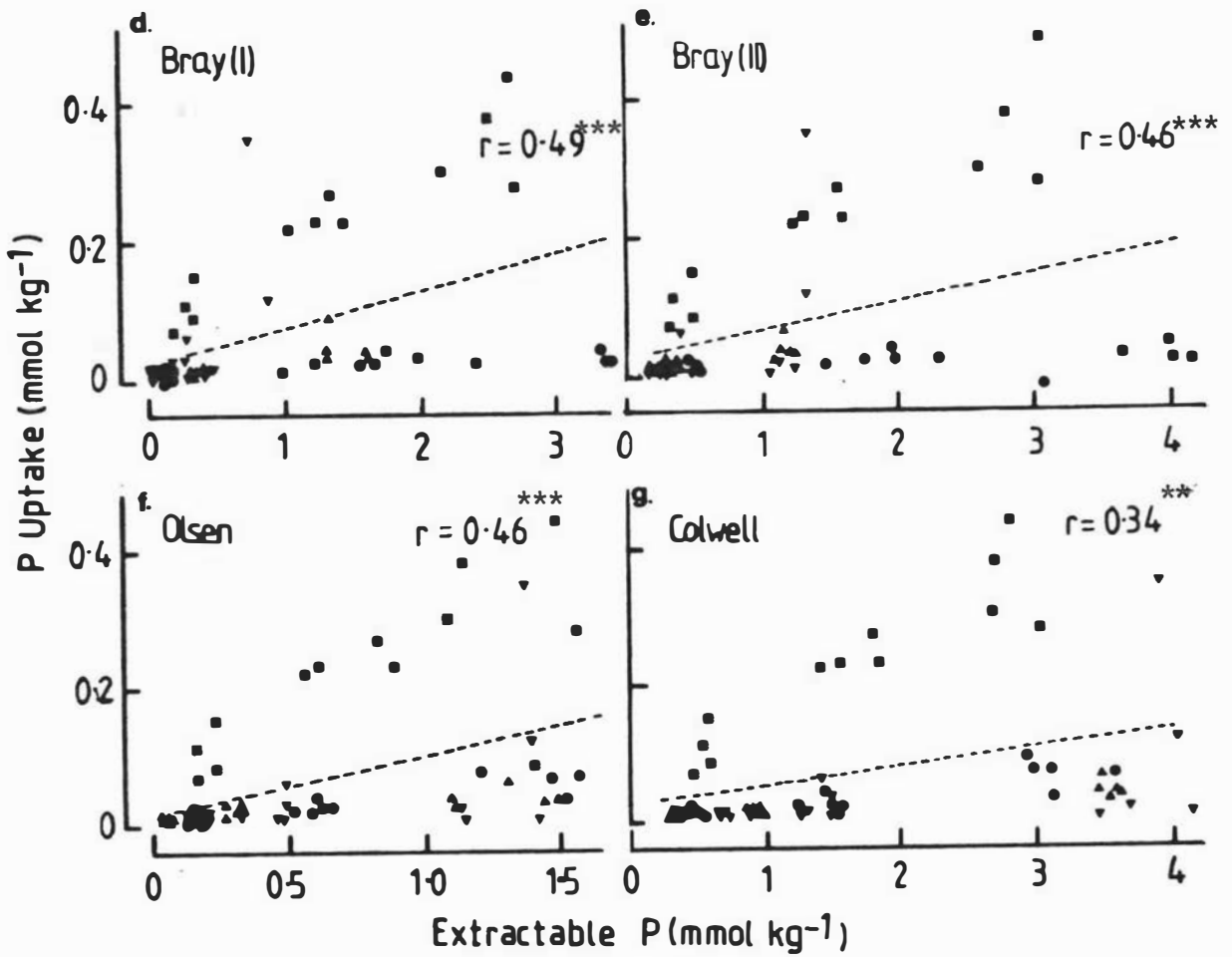


Fig. 8.3
(contd.
from
p.132)

Relationship between uptake of P by plants (*Leucaena leucocephala* and ryegrass) and amounts of isotopically-exchangeable P (a), Mehlich- (b), resin- (c), Bray(I)- (d), Bray(II)- (e), Olsen- (f), and Colwell-extractable P (g).

The superiority of the resin soil-testing procedure over the other methods in predicting plant P uptake is probably due to two reasons. Firstly, a weak anion-exchange resin, such as Cl, does not alter the surface properties of the soil as do the other reagents and, moreover, it acts principally by removing solution P and by desorbing loosely-held P (Amer et al., 1955). Secondly, but more importantly, the continuing sink provided by the Cl resin makes it function rather like a plant root with a very high capability for P uptake.

The relationship between isotopically-exchangeable P and plant P uptake was very poor. These results agree with the findings of a number of investigators (McConaghy et al., 1966; Amer et al., 1969; Dalal and Hallsworth, 1977) who reported that isotopic-exchange measurements generally over estimated plant-available P in soils of high P-sorption capacity. This is because the concentration of P in the soil solution depends not only on the amount of P on the surface, which is measured by isotopic exchange, but also on the number of vacant sites. Dalal and Hallsworth (1977) also observed that in soils with high P-sorption capacity, the relationship between isotopic-exchange and P uptake by plants depended to a large extent on the reliability of measuring solution P. A similar difficulty in measuring solution P in the soils used in this study was discussed in Chapter 5.

The results in Fig. 8.3 show that for all the soil-testing procedures, except the resin procedure, the P uptake values relative to extractable P for the Batiri, Nadroloulou, and Seqaqa soils were generally clustered together, whereas those for the Koronivia soil were segregated for all but resin P. The Koronivia soil differs from the other soils in having a relatively lower P-sorption capacity. However, even exclusion of this soil did not improve the relationship between soil-test results and P uptake.

To account for the variation in soil properties, several investigators (e.g. Holford and Mattingly, 1976) included a buffer capacity term in the multiple regression analysis between P uptake and extractable P. Because there is no agreed method of determining buffer capacity, 4 different indices of buffer capacity were used in the multiple regression studies in the present study. These indices included the maximum slope of the Langmuir sorption isotherm (HBC), measured over an equilibrium concentration range of 0 to 0.16 mmol L^{-1} ($0-5 \text{ } \mu\text{g mL}^{-1}$) in 0.02M KCl (Holford, 1979);

the slope of the P-sorption isotherm (SBC); the quantity of P needed to increase the solution P concentration to $0.008 \text{ mmol L}^{-1}$ ($0.25 \text{ } \mu\text{g mL}^{-1}$ FBC), which is considered by Jones and Fox, (1977) to provide optimum plant growth; and P-retention (PR) values of the unlimed soils (Saunders, 1965).

When the buffer capacity indices were included in multiple regression analyses between P uptake and extractable P there was only a small improvement in R^2 values, particularly with the HBC, FBC, and SBC indices (Table 8.1). In contrast, there was an appreciable improvement in R^2 values when PR was included in the correlation studies. Nevertheless, even when the PR term was included, none of the soil-testing procedures, except the resin accounted for more than 50% of the variation in P uptake. The resin procedure accounted for over 80% of the variation in P uptake, even without the inclusion of a buffer capacity term.

A number of investigators have suggested that the relationship between plant P uptake and soil-test results may be influenced by the density of soil (Mengel and Kirby, 1982) and also by soil texture (Novais and Kamprath, 1978). For example, Mengel and Kirby (1982) have suggested that organic soils have a low bulk density and the expression of results on a weight basis can be misleading. Furthermore, such factors will not be accounted for by buffer capacity terms. Of the 4 soils used in the present study, the Koronivia and the Seqaqa soils differed from the other 2 in having a low clay and a high organic matter content, respectively. When either of these soils was excluded from the correlation studies there was only a small improvement in the R^2 value. These results contrast with those presented by Holford (1980) and Dalal and Hallsworth (1976) who recorded a significant improvement in R^2 values when buffer capacity terms were included. However, unlike the soils used by these investigators, the soils used in the present study were limed. Quoting the work of Fitts (1956), Kamprath and Watson (1980) suggested that liming may influence the amount of P extracted by chemical extractants, thereby affecting the relationship between plant P uptake data and extractable P. Thus, it is likely that the difficulty in relating plant P uptake data to extractable P arises from the problems associated with the extraction of P from limed soils.

It has been shown that the amount of P extracted by the Olsen (Sorn-srivichai et al., 1984) and Mehlich (Chapter 5) reagents is affected

Table 8.1 Proportion of variation in plant P uptake (R^2) accounted for by extractable P alone and in combination with various indices of buffer capacity, as determined by multiple regression analyses.

Phosphate parameter	R^2				
	Extractable P alone	Extractable P + Buffer Capacity			
		HBC	SBC	FBC	PR [#]
Olsen	0.21	0.21	0.26	0.28	0.44
Colwell	0.12	0.17	0.21	0.25	0.43
Mehlich	0.18	0.12	0.15	0.20	0.30
Bray (I)	0.24	0.20	0.24	0.25	0.34
Bray (II)	0.21	0.18	0.23	0.24	0.33
Resin	0.81	0.80	0.83	0.84	0.90
³² P	0.01	0.17	0.19	0.27	0.29

[#] HBC = maximum slope of the Langmuir isotherm as described by Holford (Holford, 1979).

SBC = slope of sorption isotherm.

FBC = amount of P required to increase the solution P concentration to 0.008 mmol L⁻¹.

PR = phosphate retention values of the unlimed soils.

by the concentration of Ca in the extract and by the pH of the soils, respectively. The curves in Fig. 8.4 show that the amount of P extracted by the Bray (I) reagent also decreased with an increase in soil pH, contrary to the trends observed for plant growth. The decrease in Bray-extractable P was probably due to a decrease in F-activity in the suspensions of higher pH samples due to complex formation between F and Ca^{2+} (Syers et al., 1972).

8.5 Conclusions

The plant availability of P in 4 soils limed to varying pH values and varying widely in P-sorption capacity and P status, was assessed by the growth of ryegrass subsequent to the growth of Leucaena leucocephala, in a controlled-climate laboratory, using a modified Stanford and Dement (1957) procedure. Generally, liming caused an increase in plant growth at low rates of application and this was followed by a marked decrease in growth at high pH values. A comparison of plants grown on soils with those in control pots (sand culture only) showed that poor growth at both low and high pH values was due in part to a toxicity effect rather than simple P deficiency. It was proposed, that toxicity could have resulted from increased Al concentration in the herbage.

Among the soil-testing procedures examined, resin-extractable P most closely approximated the plant-available P status of the soils. Generally, the amount of P extracted by this test was small and almost equivalent (slope = 0.97; $r = 0.90$) to the amount of P taken up by plants.

In contrast to resin P, isotopically-exchangeable P showed no correlation with plant P uptake data. This was attributed to the difficulty in measuring solution P in soils with a very high P-sorption capacity and also that although isotopically-exchangeable P measures the amount of P on surface it does not reflect the concentration of P in soil solution.

All chemical extractants were only weakly correlated with plant P uptake. Inclusion of 4 different indices of P-buffer capacity did not markedly improve the correlation. This was attributed to the effect of lime on the effectiveness of soil-testing procedures.

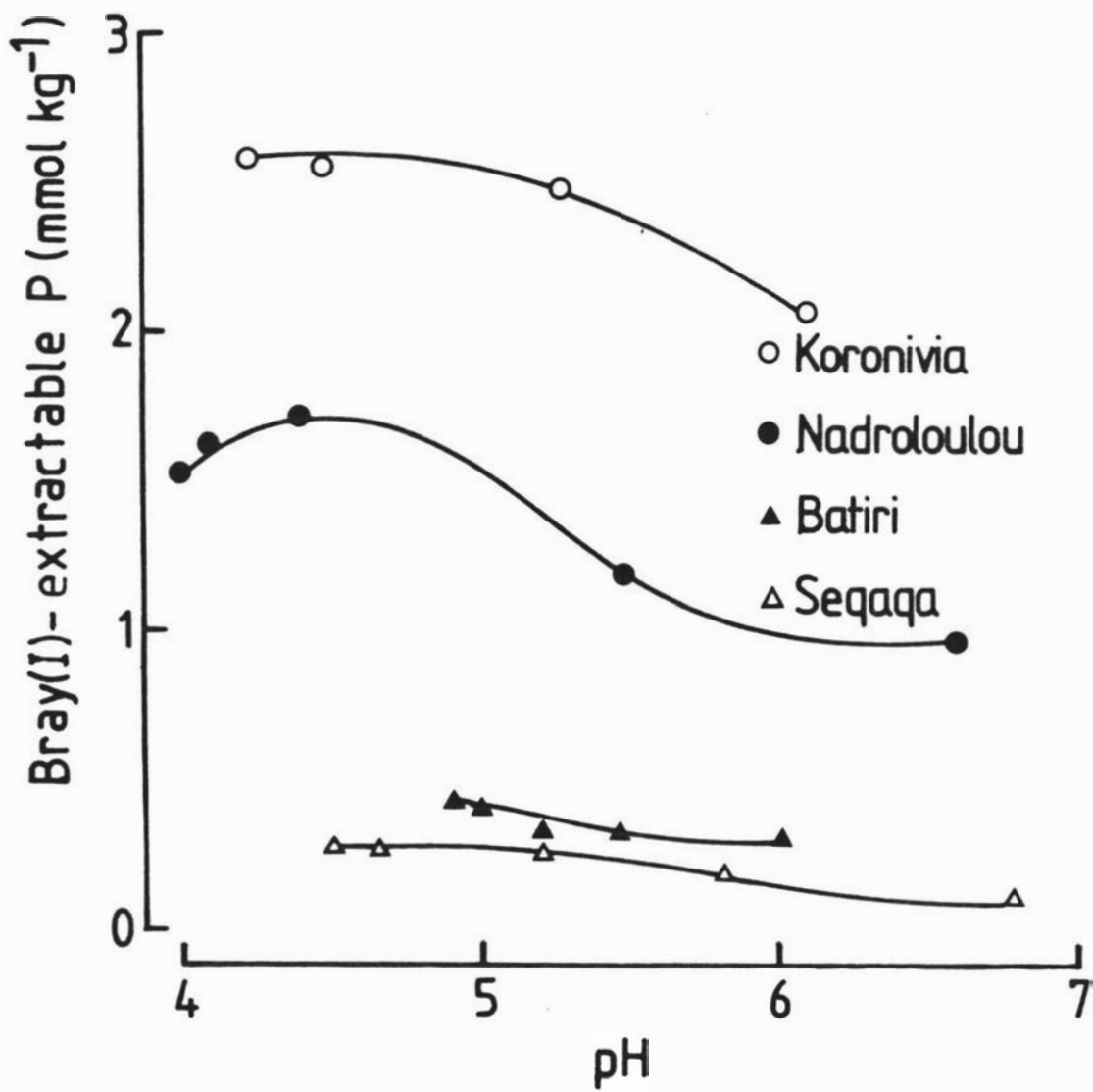


Fig. 8.4

Effect of soil pH and added P ($4.84 \text{ mmol kg}^{-1}$) on the amount of P extracted by the Bray(I) reagent.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

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

- (1) A review of the literature indicates that, although liming acid soils generally increases plant growth, there is considerable controversy regarding the effects of liming on the extractability and/or retention of P by soils. It is also apparent that if the amount of added lime exceeds that needed to neutralize exchangeable Al, a depression in plant growth is likely. The conflicting views regarding the effects of liming on extractable P, P sorption, and plant growth appear to arise because investigations were confined either to laboratory studies or to plant growth studies only.
- (2) In Fijian soils acidity, Al toxicity, and/or P deficiency problems limit agricultural production. Lack of suitable soil-testing procedures and a poor understanding of lime-Al-P interactions limit improved utilization of these acid soils. Following preliminary investigations, 4 contrasting Fijian soils were chosen for a lime-Al-P interaction study.
- (3) An investigation was conducted to compare exchangeable Al extraction and determination methods. The results of this study showed large differences in the amounts of Al removed from any soil depending on the method of extraction and determination. This observation has important implications for liming of soils because in recent years there has been an increasing tendency to base application rates on the level of exchangeable Al in soils. From this investigation, it appears that the most suitable method of extracting Al from Fijian soils would involve 2 X 1-h shaking of soil followed by the determination of Al in M KCl extracts using the oxine technique.
- (4) Results of a preliminary lime incubation study showed that there was considerable variation in the pH buffering capacity of the soils.

The M KCl-extractable Al content of all soils was reduced to near zero at soil pH values exceeding 5.2.

- (5) The ion-retention method is commonly used to assess the surface charge characteristics of soils. The method involves an initial washing of soils with an electrolyte (prewash electrolyte) of high concentration to remove exchangeable ions, equilibration of the washed soils with an electrolyte of appropriate concentration, and subsequent extraction of the saturated soils. In an initial study, the effect of the concentration of the prewash electrolytes on the magnitude of surface charge of unlimed and selected limed soils was investigated. Results showed that the amount of Al removed during the prewash and the equilibration step had a marked effect on surface negative charge. However, when the Al released in the extracting solution was included in the calculation of charge, the differences in the measured negative charge obtained with varying concentrations of prewash electrolyte were reduced. As with the concentration of the prewash electrolytes, the soil:solution ratio also had a marked effect on the negative charge but the differences were largely related to the amount of Al removed during the equilibration step. These results suggest that it is important to include the Al content of the extracting solutions in all calculations of charge.
- (6) A study of the effect of different index cations on the surface charge of limed soils showed that surface charge measured in 0.01M CaCl_2 is always higher than that determined in 0.03M NaCl. Interestingly, the differences in surface negative charge increased with increasing soil pH values. Subsequent studies showed that the differences between the 2 methods arose largely from the inability of Na to effectively exchange with adsorbed Ca at high pH values.
- (7) Following the investigations reported in (5) and (6) it was concluded that a suitable method for measuring the surface charge of limed soils would use 0.01M CaCl_2 as the equilibration electrolyte and include in the calculation of charge the amount of Al released in the 0.5M KNO_3 extracting solution. This method consisted of 6 equilibrations of soils with 0.01M CaCl_2 at a soil:solution ratio of 1:20, and either 4 or 5 extractions of the equilibrated soils with 0.5M KNO_3 solution.

- (8) Liming had a marked effect on the surface negative and positive charge of the soils. With increasing pH there was a marked increase in the surface negative charge and a smaller decrease in surface positive charge of the soils. However, the magnitude of the increase in surface negative charge varied considerably between soils. In all soils, surface positive charge was detectable at pH values as high as 7 and this was thought to be due to the presence of permanent positive charge arising from isomorphous substitution of Ti^{4+} and/or Mn^{4+} in the Fe oxide lattice.
- (9) In contrast to liming, incubation of soils with added P resulted in only small changes in both surface negative and positive charge.
- (10) The results of an isotopic-exchange study suggested that there was an increase in the amount of surface P up to a pH of approximately 7. At higher pH values exchangeable P decreased, possibly because of the precipitation of Ca-P compounds. In contrast, Olsen-extractable P was at a minimum between pH values 5.5 - 6.0, on either side of which it increased, particularly in soils treated with high amounts of P. The initial decrease in Olsen P was attributed to an artefact in the Olsen procedure. The increase at high pH values was thought to be due to the slow release of P from precipitated Ca-P compounds. There was a consistent decrease in Mehlich-extractable P with increasing soil pH. In a series of extractions the pH of the Mehlich extractant was kept constant using an autoburette and the decrease in extractable P was shown to be largely due to the neutralizing effect of lime on the Mehlich extractant.
- (11) Results of a sorption study conducted in 0.01M $CaCl_2$ demonstrated that P sorption decreased with increasing pH up to pH 5.5 - 6.0 and then increased again. At low initial solution P concentrations (1.61 mmol L^{-1}) the effects were small in the Batiri, Nadroloulou, and Seqaqa soils although they were sufficiently large to cause pronounced changes in the equilibration solution P concentration. The effects were always larger in the Koronivia soil, and also in the other soils if higher initial solution P concentrations were used. The initial decrease in P sorption with pH appears to result from an interaction between added P, negative charge, and the electrostatic potential in the plane of sorption. Results of a

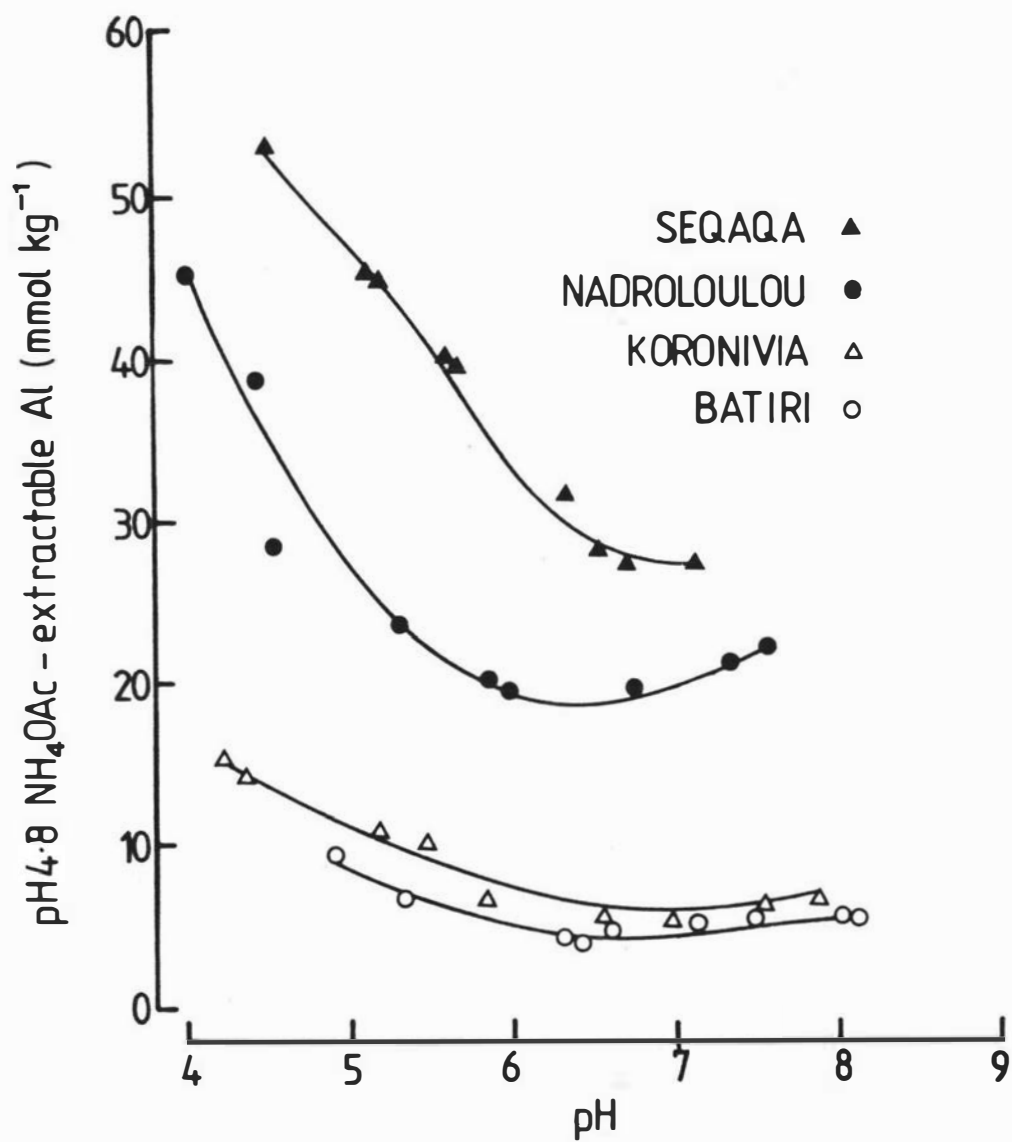
comparative sorption study, involving KCl and CaCl₂ of varying concentrations as the background electrolyte and using Nadroloulou soil incubated with KOH or Ca(OH)₂, suggested that the increase in sorption at high pH values was due to the formation of insoluble Ca-P compounds. This is consistent with the results of the isotopic-exchange study. Sorption studies conducted using soils which had been incubated with P after liming showed a marked reduction in the amount of P sorbed.

- (12) Results of a controlled-climate, plant-growth study using the tropical legume Leucaena leucocephala showed marked differences in plant growth between the 4 soils. For all 4 soils, liming and P addition caused an initial increase in plant growth which was followed by a marked reduction in growth at high pH values. This trend was most pronounced in the Seqaqa soils. The pH at which maximum growth occurred varied between the soils but was determined by the level of lime needed to reduce M KCl-extractable Al to low values. Additions of P caused a significant ($P < 0.01$) increase in plant growth within each lime level in all soils and in the Batiri, Koronivia, and Seqaqa soil there was a positive interaction between lime and added P. Although Nadroloulou soil was P deficient, a significant interaction between lime and added P was not observed.
- (13) For all 4 soils the concentration of P in the Leucaena tops followed trends similar to the yield response curve. In contrast, the concentration of Al was lowest at the pH corresponding to maximum growth, and on either side of this, Al concentration increased. The increased Al in tops at low pH values was attributed to the increased availability of Al under acid conditions. At high pH values the increased Al concentration appears to be due, at least in part, to the concentrating effect of reduced growth which has resulted from factors other than increased Al uptake. From the elevated ratio of P in roots to P in roots + tops and low P concentrations in plant tops it appeared that poor growth at extreme pH values was due to reduced availability of P. However, consideration of the pattern of Al uptake by the roots together with the concentration of P in roots indicated that Al within the plant induced P deficiency at low pH values. At high pH values

P deficiency was probably related to a decrease in soil P supply. This seemed consistent with results of the isotopic-exchange study.

- (14) A glass house study was conducted using soils which had been initially planted with Leucaena leucocephala. The study involved an initial growth of ryegrass in sand culture and subsequent transfer of these plants onto the soils. When the initially healthy ryegrass plants were transferred onto the soils most of the plants grown at low and high pH values gradually died. A comparison with control plants grown in a similar manner but not transferred onto the soil showed that the reduced growth at extreme pH values was due, in part, to a toxicity effect rather than simple P deficiency. It was proposed that Al was responsible.
- (15) Comparison of the data obtained by resin extraction and plant P uptake gave a close 1:1 relationship. In contrast, Olsen-, Colwell-, Bray(I)-, Bray (II)-, and Mehlich-extractable P were only weakly correlated with P uptake. Inclusion of 4 different indices of P-buffer capacity did not improve the relationship between P uptake and extractable P. The difficulty in relating plant P uptake data to extractable P levels was attributed to the problems associated with extracting P from limed soils. There was no useful relationship between P uptake and isotopically-exchangeable P.

APPENDICES



APPENDIX 1.

Effect of soil pH on the amounts of Al extracted from limed soils by pH 4.8 NH_4OAc solution.

APPENDIX 2

pH of lime- and phosphate-treated soils
before and after growth of Leucaena leucocephala.

Soil		pH					
		before			after		
		P1#	P2	P3	P1	P2	P3
Seqaqa	L1#	4.5	4.5	4.5	4.5	4.5	4.5
	L2	4.7	4.7	4.6	4.7	4.7	4.8
	L3	5.2	5.1	5.0	4.8	4.9	4.9
	L4	5.8	5.9	5.9	5.8	5.8	5.8
	L5	6.8	6.8	6.8	6.5	6.6	6.6
Batiri	L1	4.9	4.9	4.9	4.9	4.9	4.9
	L2	5.0	5.0	5.0	5.1	5.0	5.0
	L3	5.2	5.2	5.2	5.1	5.1	5.1
	L4	5.5	5.5	5.4	5.4	5.4	5.6
	L5	6.0	6.0	6.0	5.9	5.9	6.1
Nadroloulou	L1	4.0	3.9	3.9	4.0	3.9	3.9
	L2	4.1	4.1	4.1	4.1	4.1	4.1
	L3	4.4	4.4	4.4	4.5	4.5	4.4
	L4	5.5	5.5	5.5	5.3	5.4	5.4
	L5	6.6	6.6	6.6	6.5	6.5	6.5
Koronivia	L1	4.2	4.2	4.2	4.2	4.2	4.2
	L2	4.4	4.4	4.4	4.4	4.5	4.4
	L3	5.4	5.4	5.4	5.3	5.3	5.3
	L4	6.1	6.1	6.1	6.1	6.3	6.2

rates of added lime and P are discussed in Chapter 7 (Section 7.2.1).

APPENDIX 3a Effect of soil pH and phosphate addition on the concentration of nutrients in
Leucaena leucocephalatos grown in Koronivia soil.

Amount of added P mmol kg ⁻¹	pH (M KCl)	Ca	Fe	K	Mg	Mn	Na	S	Zn
		mmol kg ⁻¹ DM tops							
0.40	4.2	96.2	1.0	298.9	65.2	1.6	20.4	20.1	0.3
0.40	4.4	126.0	1.0	278.9	48.8	1.1	19.9	26.7	0.3
0.40	5.3	219.2	1.1	276.5	41.7	0.8	17.5	35.6	0.2
0.40	6.1	244.1	0.9	265.8	38.2	0.6	20.1	36.1	0.2
2.42	4.2	95.4	1.0	389.9	63.4	1.6	20.1	34.7	0.4
2.42	4.4	127.1	0.9	374.4	56.8	1.1	20.4	36.5	0.3
2.42	5.3	217.8	1.0	374.6	44.9	0.7	19.2	46.0	0.2
2.42	6.1	238.3	0.9	365.0	47.2	0.5	17.7	47.9	0.2
4.84	4.2	94.5	1.0	401.5	63.8	1.4	15.6	36.0	0.4
4.84	4.4	126.7	1.0	390.0	54.9	1.1	13.2	38.1	0.3
4.84	5.3	184.6	1.0	392.9	50.4	0.7	17.3	48.9	0.3
4.84	6.1	220.1	1.0	373.3	34.3	0.5	12.6	51.7	0.2
LSD (5%, pH)		7.2	0.1	9.3	2.4	0.1	NS	1.6	0.1
(5%, P)		6.2	0.1	8.0	2.1	0.1	1.7	1.4	NS

APPENDIX 3b

Effect of soil pH and phosphate addition on the concentration of nutrients
in Leucaena leucocephala tops grown in Nadroloulou soil.

Amount of added P mmol kg ⁻¹	pH (M KCl)	Ca	Fe	K	Mg	Mn	Na	S	Zn
		mmol kg ⁻¹ DM tops							
0.80	4.0	44.0	1.4	116.9	69.0	0.9	30.4	13.9	0.5
0.80	4.1	48.0	0.5	159.7	59.9	0.7	14.6	16.0	0.4
0.80	4.4	115.1	0.8	176.8	56.6	0.5	8.1	23.5	0.3
0.80	5.5	140.6	1.2	207.7	43.8	0.4	10.4	35.1	0.2
0.80	6.6	233.2	1.0	172.0	38.2	0.6	14.0	29.0	0.2
4.84	4.0	32.6	1.4	135.3	68.1	0.8	19.8	17.9	0.6
4.84	4.1	46.2	1.2	164.9	51.2	0.7	3.6	20.1	0.4
4.84	4.4	95.1	0.8	181.2	49.9	0.5	7.7	25.7	0.3
4.84	5.5	121.3	1.1	215.2	46.0	0.4	8.0	34.0	0.2
4.84	6.6	218.7	0.9	206.8	38.2	0.5	14.9	13.7	0.2
9.68	4.0	37.4	1.1	147.8	67.8	0.7	14.2	17.8	0.4
9.68	4.1	46.6	1.0	150.9	52.3	0.7	1.8	21.0	0.3
9.68	4.4	92.9	0.7	184.0	50.7	0.5	4.7	25.3	0.2
9.68	5.5	124.4	1.1	259.8	45.9	0.5	7.7	32.6	0.2
9.68	6.6	210.1	0.8	215.4	35.8	0.6	16.4	25.6	0.2
LSD (5% pH)		5.9	0.2	7.8	1.9	0.1	1.3	1.5	0.1
(5% P)		4.6	NS	6.1	1.4	0.1	1.0	1.2	NS

Effect of soil pH and phosphate addition on the concentration of nutrients in Leucaena leucocephala tops grown in Batiri soil.

Amount of added P mmol kg ⁻¹	pH (M KCl)	Ca	Fe	K	Mg	Mn	Na	S	Zn
1.61	4.9	49.5	1.8	372.3	50.0	1.4	10.7	31.0	0.3
1.61	5.0	57.7	1.7	324.3	40.3	1.1	10.3	30.2	0.3
1.61	5.2	84.4	1.3	289.3	36.7	0.7	10.4	31.7	0.3
1.61	5.5	130.2	1.1	277.8	37.1	0.7	10.0	32.7	0.2
1.61	6.0	134.8	1.3	262.6	31.5	0.5	6.6	38.6	0.2
4.84	4.9	38.7	1.6	418.0	47.6	1.3	40.6	32.6	0.3
4.84	5.0	52.5	1.5	347.6	38.4	1.0	8.4	37.8	0.3
4.84	5.2	66.2	1.1	343.5	37.0	0.7	10.4	40.3	0.2
4.84	5.5	122.4	0.9	332.8	28.5	0.6	6.9	42.4	0.2
4.84	6.0	129.8	1.0	301.8	30.0	0.5	6.4	40.8	0.2
14.52	4.9	27.2	1.7	667.6	47.3	0.8	27.3	36.3	0.2
14.52	5.0	41.0	1.3	576.2	37.2	0.8	9.9	38.7	0.2
14.52	5.2	63.2	1.3	508.2	37.7	0.6	5.2	40.2	0.1
14.52	5.5	114.0	1.2	391.8	37.8	0.6	7.0	43.7	0.1
14.52	6.0	120.0	0.9	355.4	35.7	0.4	4.1	17.0	0.1
LSD (5%, pH)		5.1	0.1	12.8	1.4	0.1	1.3	1.6	0.1
LSD (5%, P)		4.0	0.1	9.9	1.1	0.1	1.0	1.2	0.1

APPENDIX 3d

Effect of soil pH and phosphate addition on the concentration of nutrients in Leucaena leucocephala tops grown in Seqqa soil

Amount of added P mmol kg ⁻¹	pH (M KCl)	Ca	Fe	K	Mg	Mn	Na	S	Zn
1.61	4.5	38.9	2.0	79.4	69.8	13.3	58.8	9.6	0.2
1.61	4.7	145.6	1.6	220.5	33.0	2.1	22.9	23.2	0.2
1.61	5.2	162.5	1.2	250.7	30.0	1.9	21.0	29.0	0.2
1.61	5.8	270.0	0.9	280.4	14.5	1.5	27.0	31.2	0.1
1.61	6.8	291.5	1.4	269.3	22.2	1.2	18.9	41.0	0.1
4.84	4.5	36.7	1.4	128.1	52.5	12.8	60.0	11.8	0.2
4.84	4.7	142.1	1.2	272.3	34.7	1.8	19.9	23.6	0.2
4.84	5.2	168.2	1.0	277.3	33.8	1.5	17.5	29.8	0.2
4.84	5.8	245.6	1.4	274.1	27.0	1.2	28.3	32.9	0.1
4.84	6.8	270.6	3.4	289.8	20.4	0.8	17.9	43.4	0.1
14.52	4.5	31.4	1.6	197.0	37.9	10.7	60.0	12.8	0.2
14.52	4.7	142.0	1.2	352.2	37.5	1.5	18.2	24.5	0.2
14.52	5.2	155.1	0.8	326.7	39.8	1.2	15.8	30.6	0.2
14.52	5.8	246.8	2.4	243.9	27.5	1.1	27.9	36.9	0.1
14.52	6.8	262.0	1.8	316.7	23.6	0.9	17.2	48.5	0.1
LSD (5%, pH)		4.7	0.3	20.1	1.5	0.6	2.1	1.0	0.04
(5%, P)		3.6	0.2	15.5	NS	0.5	1.6	0.7	0.03

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