Impacts of phosphate fertiliser application on soil acidity and aluminium phytotoxicity

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Abstract

New Zealand's agricultural production systems are based largely on legume-based pastures which require a high soil phosphorus (P) status to achieve optimum production. Although application of P fertilisers undoubtedly leads to increased agricultural production and a direct economic benefit to New Zealand, concerns are growing about possible harmful side effects of long-term application of high rates of P fertilisers. These side effects can arise through contaminants contained in the fertilisers and through the direct or indirect effects of the P fertilisers on soil acidity.

The general objective of the present study was to investigate the effect of long-term application of P fertilisers on soil acidity and aluminium (Al) phytotoxicity. Particular emphasis was placed on the possible role of fluoride (F), contained in the fertilisers as a contaminant, on the chemistry and phytotoxicity of soil Al.

A field study was carried out to investigate the effects of long-term annual applications of six types of P fertilisers on soil acidity under legume-based pastures. The results from this study indicated that in a marginally acidic soil ($pH(H_2O)$ 5.4-5.8), irrespective of the rate or form of P fertiliser used, the soil became increasingly acidic over a period of seven years. However, the rate of acidification varied with the type of P fertiliser used. By year 8, the application of North Carolina phosphate rock (NCPR) gave higher pH, exchangeable Ca and Ca saturation but significantly lowered exchangeable and soluble Al than the control plots. In contrast, diammonium phosphate (DAP) application gave significantly lower soil pH, exchangeable Ca and Ca saturation and increased soluble Al and exchange acidity. In comparison to the control plots, single superphosphate (SSP) in general had similar soil pH and exchangeable Al but increased exchangeable Ca and Ca saturation at higher rates of application. The results suggested that continuous use of certain reactive phosphate rocks such as NCPR can significantly slow down the rate of acidification of pastoral soils.

Using the same field trial, changes in soil solution composition and Al speciation were investigated. Application of DAP and high rates of SSP increased total Al concentrations in the soil solution even though SSP had no effect on soil pH. The increased Al concentration in the SSP treatments could be due to high concentrations of F (added as a contaminant in the fertilisers) complexing Al, and hence bringing more Al into the soil solution. Application of NCPR decreased total Al concentrations, presumably by increasing pH. Application of DAP increased the predicted concentrations of toxic Al species- Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{1+}$. In contrast application of SSP decreased the toxic Al concentration, despite higher solution Al concentration compared with control treatment. The concentration of toxic Al species in NCPR-treated soil was also lower than in the control treatment.

A short-term bioassay was carried out using barley (*Hordeum vulgare* L.) to study the effects of long-term (20 years) inputs of Ca, F, and sulphate (SO_4) from P fertilisers and changes in soil pH on Al phytotoxicity. Results of this glasshouse experiment showed that the relationships between soil Al indices and barley root growth were different for soils with different P fertiliser history. The inability of total monomeric Al, and 0.02 M $CaCl_2$-extractable Al to explain the variation in root growth in the combined data for fertilised and unfertilised soils indicated that the relative proportions of the phytotoxic Al were different for fertilised and unfertilised soils. These differences were due to the higher proportions of the less-toxic Al-F complexes in the fertilised soil and also due to the high concentrations of Ca in the soil solution. The ability of the activity ratio of Al^{3+}/Ca^{2+} to predict Al toxicity most consistently across soils with different P fertiliser histories indicated that soil solution Ca should be taken into account together with toxic Al species in the assessment of Al phytotoxicity.

A short-term bioassay was carried out to develop a chemical test to predict the potential toxicity of Al for early root growth in widely different soil types. The results from this study showed that, in soils with similar physical properties, mineralogy and low organic matter content, short time pyrocatecol violet (PCV)-Al determination in soil solution can be used as a simple and reliable method to predict Al toxicity. However, the direct use of

short-time colorimetric procedures to predict critical Al toxicity levels for different soil types could be limited by the variations in organic Al and other factors such as ionic strength, cation and anion types and concentrations. Among the Al toxicity indices studied, as observed in the trial with similar parent materials, the activity ratio of Al^{3+}/Ca^{2+} is again the best predictor of Al toxicity but now in widely different soil types.

The interactive effects of soil acidity and F were also studied using the short-term bioassay method. Increasing rates of F additions to soil significantly increased the soil solution concentrations of Al and F irrespective of the initial soil pH. However, the rate of increase was much higher at low pH than at high pH.

There was a significant interaction between soil acidity and F on root growth of barley. High rates of F addition severely reduced root growth and the effect was more pronounced in the strongly acidic soil. Speciation calculations predicted that increasing rates of F additions increased Al-F complexes in the soil solution. Results also indicated that Al-F complexes are not toxic at lower concentrations but they are toxic at high concentrations and the relative toxicity depended on the type of Al-F complexes present.

Results from this study suggest that it is unlikely that in a marginally acidic soil (pH (H_2O) 5.4-5.8) long-term F inputs via P fertilisers will have any detrimental effects on plant growth. Rather it will reduce the free Al concentration while keeping the Al-F species concentration below the toxic threshold level in the soil solution, thereby reducing the occurrence of Al phytotoxicity.

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Chapter 1

Introduction

New Zealand's agricultural production systems are based largely on legume-based pastures which require a high soil phosphorus (P) status to achieve optimum production. This, combined with the fact that

(a) most New Zealand soils had naturally low P status initially, and

(b) many New Zealand soils (particularly in the North Island) have minerals which adsorb large quantities of P,

means that application rates of P fertilisers/unit of production tend to be very high by world standards.

Although application of P fertilisers undoubtedly leads to increased agricultural production and a direct economic benefit to New Zealand, concerns are growing about possible harmful side effects of long-term application of high rates of P fertilisers. These concerns include pollution of surface waters and indirect effects on the soil itself. It is the purpose of this study to consider some aspects of the latter issue.

Phosphate fertilisers obviously increase the P status of soil. But they can also affect other soil properties through contaminants contained in the fertiliser or by their effect on soil acidity. One contaminant of P fertilisers that has received widespread publicity is cadmium. A second contaminant which is much less widely acknowledged is fluorine (F). For example in the year ended 30th June 1994, 1.4 million tons of single superphosphate (SSP) had been applied to approximately 13.5 million ha of farm lands in New Zealand (New Zealand Year Book, 1996). Assuming an average of 1.2 % F in SSP (Evans et al., 1971), approximately 17,000 tons of F was added to fertilised agricultural soils in New Zealand in that year. This equated to approximately 1.3 kg ha^{-1}. Therefore, assuming similar rates of fertiliser application over the last 50 years, nearly 850,000 tons of F have been added to farmed land. This could increase the F concentration in the soil surface (0-

75 mm) by about 80 mg F kg^{-1} soil assuming that plant uptake and downward movement of F is very low.

Given these high rates of F application, it is prudent to consider whether there are likely to be any possible harmful effects. To date, there is little evidence to suggest that F uptake by plants poses any health risks to human or animals, or indeed that plant growth has been in any way affected. Fluorine is however known to interact strongly with aluminium (Al) in soils and this leads to a possible interaction of F addition with another effect of long-term P fertiliser addition-namely soil acidification.

In recent years there has been considerable debate on the acidifying effects of various fertilisers added to soils, especially phosphate fertilisers. These acidifying effects can be indirect, arising from changes in nutrient cycling and nitrogen fixation as a result of improved soil fertility, or can be directly attributable to the fertiliser. For example unacidulated fertilisers such as reactive phosphate rocks (RPR) could be expected to exercise a significant liming effect relative to acidulated fertilisers such as SSP after long-term application, because of differences in their chemical composition. However published data on the liming effect of RPR's under field conditions is very limited (Chien, 1977; Hammond, 1979). In particular, there is little (Sinclair et al., 1993) published information on the liming effect of RPR used as a maintenance P fertiliser for temperate pastures. Yet, such information is important as liming becomes an increasingly costly input into New Zealand hill country and upland farming systems.

One mechanism by which excessive soil acidity can affect plant growth is through its effect on Al availability. In strongly acidic soils throughout the world the impacts of Al toxicity on plant growth are spectacular and severe. In the moderately acidic pasture soils of New Zealand however, the role of Al toxicity is less clear. But given the continuing inputs of P fertilisers to New Zealand pasture soils, along with the doubtful economics of lime application, especially in hill country soils, there is an urgent need for more detailed information on the impact of long-term P fertiliser application on the chemistry of our soils.

The objectives of the study reported in this thesis were to:

1. Examine the effects of long-term application of different types of P fertilisers on soil acidity under pasture

2. To determine the changes in soil solution composition and Al speciation after long-term application of P fertilisers to pasture

3. To compare conventional soil tests such as pH, $CaCl_2$-extractable Al and various soil solution Al indices for their usefulness in predicting plant growth in soils which have received P fertiliser for a long time.

4. To evaluate a range of soil testing approaches to predict Al phytotoxicity in widely different soil types.

5. To investigate the interactive effects of pH and F addition on solution Al species and to determine which Al-F complexes, if any, are toxic to plants.

Chapter 2

Literature Review

2.1 Introduction

Soil acidity is a serious agricultural problem in many parts of the world, possibly affecting 40 % of the world's arable soils (Taylor, 1988). Soil acidification occurs very slowly when the soil is in its natural state. However, with the establishment of crops and pastures, the process of acidification has been accelerated. The problem can be well developed before pastures or crops show the effects of soil acidity. As acidification progresses, it moves down to the subsoil. In the long term, extreme acidity can cause accelerated mineral dissolution and breakdown of soil structure. Because of this slow acidification of soil and sudden release of Al below a soil pH of about 4.2 with resulting damage to terrestrial and aquatic organisms, it has been categorised as a chemical time bomb (Stigliani, 1991).

In legume-based pastures, symbiotic nitrogen (N) fixation coupled with leaching losses of N and net crop removal are acidifying the soil (Helyar and Porter, 1989). There is evidence, particularly in Australia where liming is not widely practised, that pastoral soils are becoming increasingly acid (Helyar and Porter, 1989). The total area of acid soils (defined as soils with pH ($CaCl_2$) less than 4.8) in Australia is about 29 million ha, of which some 24 million ha are used for agriculture (Bureau of Rural Resources, 1991). Parfitt and McDonald (1992) reported that large areas of New Zealand have soils which are potentially acid and contain at least one soil horizon with pH (H_2O) <5.0 within 60 cm of the soil surface. The total area of land in this category is nearly 6.3 million ha in the North Island and 11 million ha in the South Island (Fig 2.1 a b). These large areas clearly indicate the seriousness of the potential soil acidity problem in New Zealand soils.

KEY

■ Strongly acid soils

▨ Moderately acid soils

▨ Slightly acid soils

Water, snow and ice,
sand and rock, urban
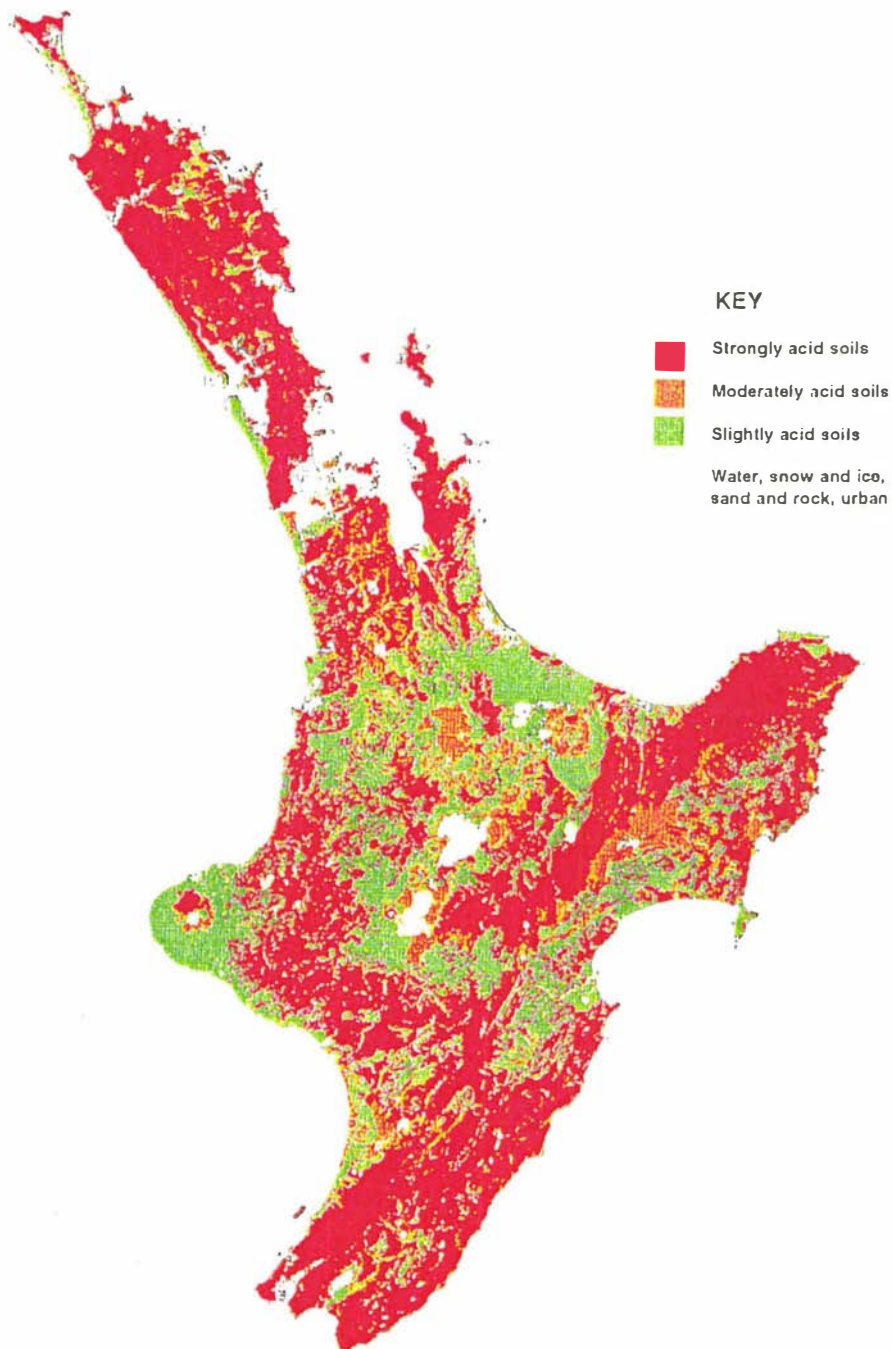
Fig 2.1a. Susceptibility of land to soil acidification,
North Island (Parfitt and McDonald, 1992).

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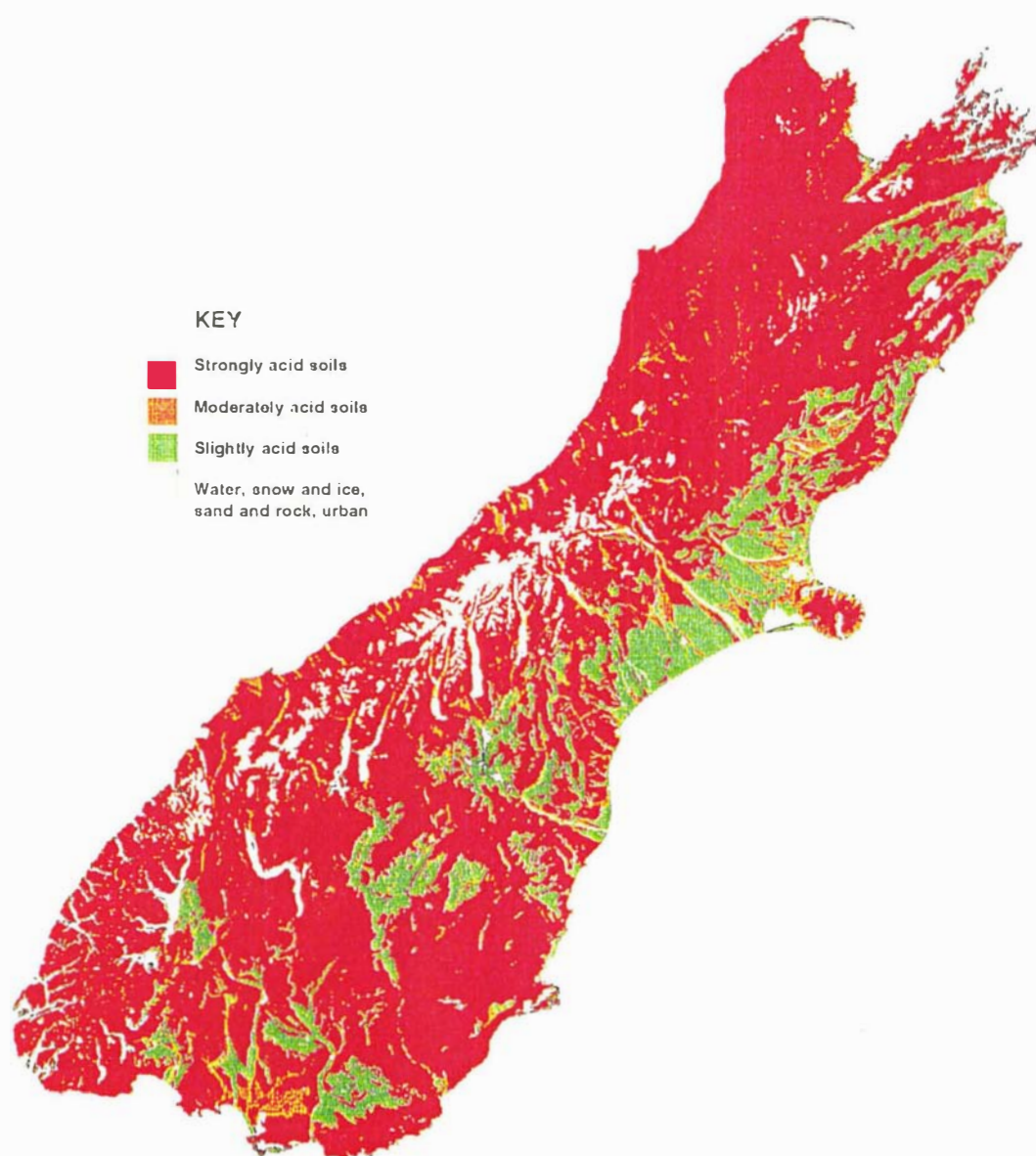
Fig 2.1b.Susceptibility of land to soil acidification,
South Island (Parfitt and McDonald, 1992).

In a comprehensive review of data obtained from a national series of field trials on lime, that covered all the major soil types in New Zealand, Edmeades and Wheeler (1985) concluded that Al toxicity resulting from soil acidity could be a factor limiting pasture production on a number of North Island hill country soils and on upland soils in the South Island. The situation is becoming more serious because liming, which is the common practice to correct soil acidity, is no longer economic on many of these hill country and upland soils which are acid (pH<5.5) (Edmeades et al., 1985a).

Acid soils commonly manifest infertility problems as a result of:

a) essential plant nutrients being rendered unavailable (phosphorus, molybdenum)

b) essential plant nutrients (basic cations) being leached below the rooting zone

c) toxic elements (aluminium, manganese) increasing in concentration to impede plant growth

d) a combination of these phenomena

There are several published reviews (Adams, 1981; Haynes, 1983; Taylor, 1988; Helyar and Porter, 1989; McCray and Sumner, 1990; Bolan et al., 1991; Foy, 1992) on soil acidification and related problems. However, they have not covered in detail the effect of long-term applications of P fertilisers on soil acidity and Al phytotoxicity and also its measurement, especially in pastoral soils.

Therefore this chapter presents a literature review on this subject with emphasis on the following areas:

(i)   the causes, rates, and amelioration of soil acidification

(ii)   the effect of P fertiliser components on the chemistry of acid soils

(iii)   the soil solution chemistry of Al, speciation methodology for Al and its implications for the measurement of Al phytotoxicity

2.2 Causes of soil acidity

In natural ecosystems, the inputs of acid are nearly balanced by the neutralising processes, such that any change in pH as a result of a dominance of acid addition must be measured over several hundred years. Accelerated acidification occurs as a result of

(a) addition of fertilisers (especially N based)

(b) accumulation of organic matter (not rich in basic-cations), largely of plant origin

(c) removal of organic anions in plant and animal products

(d) leaching of nitrate.

2.2.1 *Fertiliser addition*

Only some fertilisers acidify the soil. Table 2.1 shows the theoretical acidifying effects of different fertilisers in terms of the amount of pure lime required to neutralise the acidity produced. Superphosphate does not directly acidify the soil to any significant effect. The fertiliser itself is acidic, but it does not have any long-lasting direct effect on soil pH. After fertiliser application, the zone around each granule will be strongly acid but within a few hours soil pH will be restored close to its original level. This will be discussed in detail in section 2.5.1.

Superphosphate can indirectly cause soil acidity by promoting healthy clover growth. This adds organic matter to the soil and builds up nitrate reserves which can be lost by leaching. These factors then lead to soil acidification (Kealey, 1992).

2.2.2. *Accumulation of organic matter*

Under pasture, gains of organic matter in A horizons often exceed losses through mineralisation so that there is a net accumulation of soil organic matter. Such an accumulation is particularly marked under leguminous pastures sown on soils

initially low in organic matter content (Barrow, 1969; Watson, 1969; Williams, 1980).

Table 2.1 Lime required to counteract acidity caused by fertilisers in acid soils.

Fertiliser type	kg pure lime / 100 kg of fertiliser
Nitrogen fertilisers	
Anhydrous ammonia[1]	148
Sulphate of ammonia[1]	113
Urea[1]	83
Ammonium nitrate[1]	61
Diammonium phosphate[2]	74
Monoammonium phosphate[2]	55
Phosphorus/sulphur fertilisers	
Gold Phos[1] 0:18:0:10	26
Elemental S[2]	31
Prolong (SR-13)[1] 0:9:5:0:13	18
Single superphosphate[2]	8
Triple superphosphate[2]	15
**North Carolina phosphate rock[2]	-53
**Chatham rise phosphorite[2]	-56
**Sechura phosphate rock[2]	-47
Potassium fertilisers	
Potassium chloride[1]	0

[1] Kealey (1992); [2] Bolan (1995); **negative value indicates liming value of the fertilisers.

An increase in CEC is an important outcome that can result from the accumulation of organic matter. Such an increase in CEC, and consequently in exchange acidity, results in a concomitant decrease in soil pH (Haynes, 1983). However, Williams (1980) showed that the decrease in pH below a subterranean clover pasture occurred down to a soil depth of approximately 30 cm while organic matter accumulation was restricted to the surface 10 cm. He concluded that other factors such as cation depletion associated with NO_3 leaching, may have contributed to the pH decline.

The accumulation of organic N is an important factor causing permanent soil acidification under legume-based pastures. When fertiliser NH_4^+ is nitrified, two net H^+ ions are generated per N atom. These H^+ ions can only be neutralised if, all the NO_3^- produced is taken up and assimilated into plant organic N, and when the plant organic N is subsequently ammonified and the organic anion decarboxylated upon decomposition of the plant. Therefore, only if all the N returns to the input form (NH_4^+) will there be neutrality. Instead, if organic N accumulates (without being ammonified), the NH_4^+- fertilised system can generate in excess of 1 H^+ per atom of N accumulated (Bolan et al., 1991).

Helyar et al. (1988) reported that acid addition due to organic anion accumulation should cease once soil organic carbon levels have reached about 2.5 %. In most pasture soils in New Zealand organic carbon accumulation is very minimum as it has reached this stable level (Quin and Richard, 1981). Therefore acidification due to organic matter accumulation is expected to be low in New Zealand soils.

2.2.3. *Removal of plant and animal product*

The H^+ ions exported from the roots of a mixed sward in exchange for the accumulation of cationic charge will remain in the rhizosphere soil if the organic

anions synthesised by the plant and their basic cations are removed from the site of N_2 and CO_2 assimilation (Bolan et al., 1991). Soil acidity increases with the removal of hay, crops and, to a limited extent, animal products. Plants remove a range of nutrients from soil. When basic nutrients such as Ca, Mg and K are taken up by plants, the overall acidity of the soil increases. Removal of plant and animal products prevents return of these basic ions to the soil and this results in net acidification of the soil (Helyar et al., 1988). The acidity caused by different forms of product removal is shown in Table 2.2.

Table 2.2. Lime required to counteract acidity caused by product removal (Kealey, 1992).

Product removal (1t)	Lime requirement (kg)
Legume hay	55
Grass hay	30
Wheat grain	9
Lupin grain	20
Wool	14
Milk (1000 L)	4

Van Breemen et al. (1983) and Oenema (1990) defined soil acidification as a decrease in the acid neutralising capacity (ANC) of the soil. The ANC is the sum of all base-forming cations minus the sum of acid-forming anions in the soil. In the grasslands, the net efflux of excess cations (Ca, Mg, K, Na) over anions (H_2PO_4, Cl, SO_4 and NO_3) or excess bases (EB), gives an estimate of the decrease in ANC or increase in soil acididification. Oenema (1990) calculated EB via removal of milk and livestock and showed that it is a significant factor in acidulation of grassland soils in Netherland.

In addition, redistribution of organic anions due to camping behaviour of sheep and cattle can lower pH in some areas of the paddocks (e.g. steep slopes) and raise it at camp sites. If such paddocks are to be amended, less lime should be needed on the camping areas, and more on the remainder of the land (Davidson, 1987).

2.2.4 Leaching of nitrate

Several reviews (Haynes, 1983; Kennedy, 1986; Bolan et al., 1991) present detailed discussions of acid- and alkali- producing reactions and their role in various nutrient cycles, from the ecosystem to the plant cell level. Kennedy (1986) and Bolan et al. (1991) discussed in detail the role of the N cycle in soil acidification under legume-based pastures. Fig 2.2 shows the effects of biological nitrogen cycling on soil acidity.
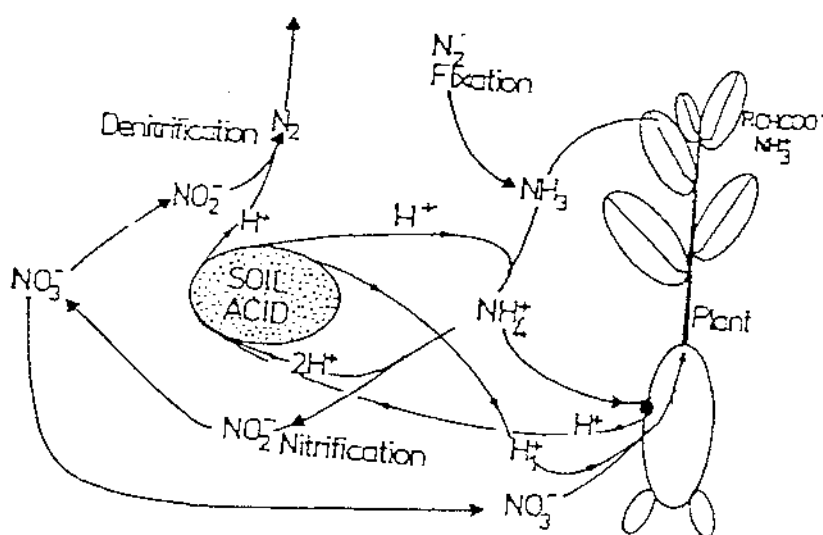
Fig 2.2 Effects of biological nitrogen cycling on soil acidity (Kennedy, 1986).

As ammonium-N is converted to nitrate, H^+ is produced. When the plant takes up nitrate, it releases OH^- (or consumes H^+) to maintain charge neutrality within the plant system. Therefore these process will not affect the soil pH. However, when

the nitrate stored in the soil is in excess of plant requirements, this excess nitrate may be leached deeper into the subsoil. Nitrate leached from the top soil carries other nutrients (eg. Ca, Mg, K) with it. The overall effect of nitrate leaching is a greater concentration of acid in the top soil.

2.3 Rate of soil acidification

Helyar et al. (1988) discussed thoroughly the rate of soil acidification under legume-based pastures and the factors accelerating the acidification processes. In this review the important factors influencing the rate of acidification will be discussed only briefly.

The rate of soil acidification depends mainly on (a) net acid or alkali addition rate and (b) soil pH buffering capacity. In a number of agricultural systems in NSW, Australia net acid addition rates to the soil profile were reported to range from near zero to rates of 3-5 kmol H^+ ha^{-1} yr^{-1} over extensive areas (Helyar et al., 1990). Higher acid addition rates, such as 10-20 kmol H^+ ha^{-1} yr^{-1}, have been measured in some exploitive systems, such as lucerne hay production. High annual rainfall may increase the rate of acidification through greater leaching of nitrate as well as increased productivity and consequently increased alkalinity removal (Helyar and Porter, 1989).

Bolan et al. (1991) compared the rate of acidification in New Zealand and Australian farms in which plants obtained most of their N requirement through N fixation. In New Zealand, a dairy farm in Waikato and a sheep farm in Canterbury were estimated to have net acidification rates of 11.36 and 8.60 kmol H^- ha^{-1} yr^{-1} respectively. In an Australian beef cattle farm in Townsville the rate of acidification was estimated to be 1.08 kmol H^+ ha^{-1} yr^{-1}. The higher rates of acidification in the two New Zealand farms compared to the Australian farm were reported to be due to higher amounts of N cycled, accumulated and leached in the New Zealand farms.

At an acid addition rate of 4 kmol H^+ ha^{-1} yr^{-1}, the soil pH can decline by one unit in the surface 30 cm within 30 years for sandy loam soils and within 120 years for clay soils (Helyar et al., 1990). The difference in the rate of decline in pH in the two soil types is due to differences in their pH buffering capacities. The clay soils have higher pH buffering capacities than the sandy soils.

Various soil constituents such as organic matter, Fe and Al oxides and $CaCO_3$ (in calcareous soils) contribute to pH buffering of soils at different pH values (Thomas and Hargrove, 1984; Bache, 1985). In many yellow brown loams in New Zealand and Xanthozems and podzolic soils in Australia, the rates of soil acidification may remain unnoticed for several years because these soils can have high short-term buffering capacities (Bolan et al., 1991).

2.4 Amelioration of soil acidity

Soil acidity problems can be corrected with a range of materials. Liming is the most effective and practical way to raise surface soil pH. The main liming materials are lime, dolomite and magnesite.

However, use of surface-applied lime ($CaCO_3$) to ameliorate subsoil acidity is often ineffective in the short term, and field responses are variable (Sumner et al., 1986; Alva et al., 1988; Shainberg et al., 1989). This is especially true in highly weathered soils, even when applied at high rates to the soil surface (Reeve and Sumner, 1972; Black and Cameron, 1984). Deep placement of lime is necessary in these cases because lime moves very slowly through these soils. This is because of its low solubility, neutralisation of hydroxyl and bicarbonate ions by H and Al ions in surface horizons and greater adsorption of Ca ions at pH-dependent exchange sites generated as pH increases (McCray et al., 1991).

Yield responses to deep lime placement have been obtained (Brennan and Axley, 1983; Farina and Channon, 1988), but the power requirement for deep placement

can be a prohibitive factor. An alternative is to apply ameliorating materials such as gypsum or phosphogypsum which are more soluble than lime to the soil surface and allow leaching to move the material into the subsoil (Ritchey et al., 1980; Sumner et al., 1986).

However, variable effects have been obtained following the addition of gypsum or phosphogypsum to acid soils (Hornsnel, 1985; Alva et al., 1988; O'Brien and Sumner, 1988; Shainberg et al., 1989; Keerthisinghe et al., 1991; Smith et al., 1994). Although some of the variability may be attributable to insufficient water for leaching, a great deal of the variability could be due to the different reactions of ameliorants in soils.

Several mechanisms have been proposed for the subsoil amelioration of Al toxicity with gypsum. These include; a self-liming effect, i.e. sulfate from gypsum displacing hydroxide off soil surfaces into the soil solution (Reeve and Sumner, 1972); a decrease in Al^{3+} activity in the soil solution due to an increase in ionic strength (Ritchie, 1989); the formation of non-toxic $AlSO_4^+$ ion pairs (Pavan et al., 1982) or precipitation of Al hydroxy sulfate minerals out of the soil solution (Nordstrom, 1982); a decrease in the ratio of Al:Ca (Ritchey et al., 1980) and displacement of Al^{3+} off soil colloids and subseqent leaching of Al^{3+} from the soil (Oates and Caldwell, 1985).

Although gypsum is a neutral soluble salt, when applied to soil it has a variable effect on soil pH. A decrease in soil pH has been obtained after gypsum application to some soils. In these soils, application of soluble Ca from gypsum displaced Al^{3+} and H^+ from the cation exchange sites into soil solution which resulted in a lowering of the pH of the soil (Black and Cameron, 1984; Alva et al., 1988). In contrast on soils with variable charge Reeve and Sumner (1972) and Shainberg et al. (1989) found that addition of gypsum increased soil solution pH. The rise in soil pH was ascribed to ligand exchange, whereby the SO_4 ion replaces OH ions on the

soil colloidal surfaces as discussed earlier. The net effect of gypsum on soil pH, therefore, will depend on the balance between these two reactions.

However, a major advantage of gypsum application compared with liming, is that it markedly increases ionic strength and solution Ca^{2+} activity while resulting in only a slight increase in solution Al^{3+} concentration and this often decreases the Al^{3+} activity (McCray and Sumner, 1990).

Beneficial effects of phosphogypsum (PG) have been attributed, at least in part, to ion pairing of Al with F and SO_4 and the alleviation of Al toxicity (Alva et al., 1988, Alva and Sumner, 1988; Alva et al., 1989). In column leaching experiments, O'Brien and Sumner (1988) found that surface applications of PG reduced subsoil acidity, as evidenced by the reduced levels of exchangeable Al and increased exchangeable Ca in subsoils. They suggested that Al was detoxified as a solid phase, possibly alunite.

Anions derived from organic materials are expected to produce results analogous to gypsum or phosphogypsum for ameliorating acid subsoils. In fact, research has shown that Al can be rendered non-phytotoxic by simple organic anions such as citrate and malate (Hue et al., 1986). The benefits of organic matter applications in decreasing the activity of Al in soil solution and increasing plant growth have been demonstrated in several pot experiments (Ahmad and Tan, 1986; Bessho and Bell, 1992; Hue, 1992). Such benefits have not been tested specifically under field conditions. Hue et al. (1986) demonstrated that a given concentration of soluble Al in uncultivated forest soil (which had higher organic matter content), is less toxic than in cultivated soils probably because Al in the former is chelated in soluble but non-toxic form. Organic matter addition to a soil not only reduces the Al^{3+} activity but can also provide other plant nutrients such as Ca, Mg and P that can affect the Al toxicity threshold levels for plant growth.

Although several ameliorants have been proposed to reduce soil acidity and Al toxicity, their application under field conditions depends not only on agronomic factors but also on economic factors. Under legume-based pastures in New Zealand lime application is effective and economical on flat lands. But in hill country pastures, as mentioned earlier, lime application is often not economical. Recent studies (Easterwood, 1989; Wright et al., 1991; Sinclair et al., 1993) have shown that reactive phosphate rocks have a small liming effect and suggested that they might be used not only as a P source but also as an ameliorant of Al toxicity in the long term. In addition some P fertilisers such as SSP, contain high amounts of SO_4 and F. These components can also affect Al phytotoxicity. These aspects of P fertilisers and Al phytotoxicity will be discussed in detail in the following sections.

2.5 Effect of P fertiliser application on the chemistry of acid soils

Most P fertilisers used in New Zealand contain Ca, PO_4, and SO_4 as their main constituents and also contain significant quantities of F. These components can affect soil acidity and Al phytotoxicity directly or indirectly due to their interactions with the soil-plant system. Since SO_4 has been discussed in detail in the previous section, it will not be discussed any further.

This section is subdivided into 3 parts.

(i)   Effect of PO_4 on soil acidity and Al phytotoxicity

(ii) Interaction of F with acid soils and its effect on Al phytotoxicity

(iii) Solution chemistry of Al and its implication to Al phytotoxicity

2.5.1 *Effect of PO₄ on soil acidity and Al phytotoxicity*

In non-agricultural ecosystems, soil solutions generally contain too little P to affect solution Al concentrations. However, P fertiliser application at high rates can be an effective means of lowering soil solution Al to non-toxic levels, by forming insoluble precipitates such as $Al(OH)_2H_2PO_4$. It has been recognised since the 1920's that high rates of SSP can alleviate symptoms of Al phytotoxicity (Adams,

1981). The amount of P required to detoxify Al temporarily depends upon the level of exchangeable Al. In a study of 60 acid subsoils, Coleman et al. (1960) found a high correlation (r=0.84) between the exchangeable Al concentration and the amount of P converted to a variscite-like mineral ($Al(OH)_2H_2PO_4$). Because the solubility of Al phosphate follows the equation

$$Al(OH)_2H_2PO_4 \Leftrightarrow Al^{3+} + 2OH^- + H_2PO_4^-$$
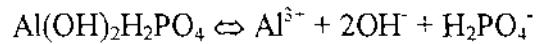
increasing amounts of $H_2PO_4^-$ will lower solution Al to satisfy the solubility product of amorphous $Al(OH)_2H_2PO_4$ (Adams, 1981).

Sloan et al. (1995) in an incubation study using an acid soil with $NaH_2PO_4.2H_2O$ as the P source have shown that soil solution Al^{3+} decreased and Al-orthophosphate complexes increased after P addition. Large decreases in Al concentration occurred when P was added at the rate of 30 kg P ha^{-1}, but further additions of P fertiliser decreased the total monomeric Al concentration only slightly. They also found significant reductions in exchangeable Al with increasing P rates and concluded that banded P fertiliser is a viable alternative method to reduce toxic forms of Al in strongly acidic soils. However, they did not support their conclusions with any plant growth measurements

In contrast some workers have observed increased Al toxicity in the vicinity of P fertiliser bands and have attributed this in part to low pH in the vicinity of the fertiliser bands. If SSP is added to water, an acidic pH is developed, as a result of the hydrolysis of monocalcium phosphate (MCP), leading to the formation of less soluble dicalcium phosphate (DCP) with a release of phosphoric acid close to the fertiliser granule.

$$Ca(H_2PO_4)_2 .H_2O + H_2O \Rightarrow CaHPO_4.2H_2O + H^- + H_2PO_4^-$$
(MCP)   (DCP)
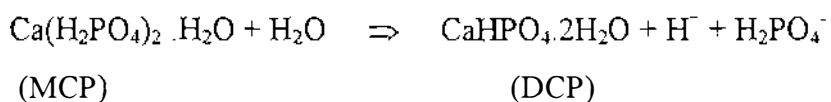
Phosphoric acid subsequently dissociates into phosphate ions and hydrogen ions. Part of this acidity is neutralised by the hydroxyl ions released during the adsorption of the phosphate ions by soil particles.

Such effects will occur immediately in the vicinity of fertiliser granules in soil. However, over a period, these effects will disappear as diffusion and neutralising reactions occur (Lindsay and Stephenson, 1959). Eventually, phosphate will be either utilised by plants in the monovalent form, leached in this form from acid soil or immobilised by sorption or precipitation. Barrow (1989) reported that fertilisation with phosphate is not necessarily acidifying, because adsorption of one divalent phosphate ion (HPO_4^{2-}) on the average releases about one OH^- ion from the soil colloidal surface. If the pH is not too high, the released OH^- is neutralised by an H^+ derived from the dissociation of a monovalent phosphate ion ($H_2PO_4^-$) and therefore there is no change in solution pH.

However, despite the absence of long-term effects on soil pH, it does appear that in the short-term the osmotic effect or low pH near the fertiliser band can affect root growth if the soil is not buffered enough to resist the pH change. Moody et al. (1995) studied band application of MCP with and without gypsum ($CaSO_4.2H_2O$) in a short-term root growth experiment with soybean (*Glycine max*) using samples from six acidic soils (Kurosols, Ferrosol, Vertisol, Kandosol). Their results showed that banding of MCP and MCP plus $CaSO_4.2H_2O$ caused Al toxicity in all soils and Mn toxicity in all soils except one of the Kurusols. They concluded that banding MCP and MCP plus $CaSO_4.2H_2O$ can reduce root elongation through a combination of osmotic effects, and H, Mn and /or Al toxicities as a consequence of the low pH in proximity to the fertiliser band.

Long-term application of SSP may not alter the soil pH directly but can decrease the pH indirectly via increased clover growth resulting in increased NO_3 leaching and increased OM accumulation as discussed in section 2.2.

In contrast to soluble P fertilisers such as SSP, RPRs contain free $CaCO_3$ and structural CO_3 which, on dissolution, consume soil acidity. In addition, when RPR dissolves it consumes 2 moles of H^+ for every mole of P dissolved. Therefore it is theoretically possible that application of RPR could decrease or prevent soil acidification (Chien, 1977; Hammond, 1979; Easterwood et al., 1989; Wright et al., 1991; Sinclair et al., 1993). There has been however, only one known study carried out in a legume-based pastoral system to quantify the long-term effects of RPR application on soil acidity (Sinclair et al., 1993). This study showed that application of different forms of P fertilisers over a 6-year period, reduced soil pH (0-75 mm soil depth) by an average of 0.16 units in the unfertilised control and SSP treatments. There were no significant differences in soil pH between the various SSP application rates (average rates of 13.5, 20, 27, 54 kg P ha^{-1} yr^{-1}). Application of RPRs reduced the decrease in pH and the decrease in pH was virtually eliminated at the highest RPR application rate of 54 kg P ha^{-1} yr^{-1}.

In addition to the liming effect described above, RPR contains a higher concentration of F than SSP. Long-term application of F will increase the total F concentration in the soil and will eventually increase solution F concentrations. Under certain conditions, F in soil solution can reduce the toxic effects of free Al by forming Al-F complexes. This will be discussed in section 2.6.2. However, in order to explain the effect of F application on Al toxicity, it is important to know the basic chemistry of F reactions with soil constituents and this will be discussed in the next two sections.

2.5.2 Interaction of F with acid soils and its effect on Al toxicity

There have been several reviews of the effects of F on soils and plants (Marier and Rose, 1971; Rose and Marier, 1977; Weinstein, 1977; Weinstein and Alscher-Herman, 1982; Pickering, 1985; McLaughlin et al., 1996). This review, provides a brief description of soil F distribution, reactions of F in soils and plant responses

to F and then discusses in more detail the interaction between soil acidity and F and also the solution chemistry of F species.

This section is subdivided into 3 parts:

(i)   Fluorine distribution in soils and plants

(ii) Reactions of F with soil

(iii) Effects of F on plants

2.5.2.1 *Fluorine distribution in soils and plants*

The main natural sources of F in soils are minerals such as apatite ($CaF_2.3$ $Ca_3(PO_4)_2$), cryolite (Na_3AlF_6), fluorite (CaF_2) and topaz (Al-silicate containing F) (Pickering, 1985). Soil typically contains 20-500 μg F g^{-1} (Weinstein, 1977) although concentrations may be higher where there are deposits of minerals such as fluorspar (Cooke et al., 1976), where fertilisers containing F have been added (Robinson and Edgington, 1946; Oelschlager, 1971; Omueti and Jones, 1977a) or near major industrial emission sources (Thompson et al., 1979; Haidouti, 1991). If SSP (containing 1 % F) is applied at the rate of 250 kg ha^{-1} yr^{-1} for 50 years it can increase the soil F level by 250 mg F kg^{-1} soil in the surface 0-7.5 cm layer (bulk density 1000 kg m^{-3}) assuming low F uptake by plants and no leaching of F.

A few plant species such as *Camellia* can accumulate leaf concentrations in excess of 50 μg F g^{-1} from unenriched soils, but in the majority of species, F concentrations are much lower than 20 μg F g^{-1} (Weinstein, 1977). In most agricultural situations where the airborne F is sufficiently high to make forage unacceptable for animal feeding, the contribution from soil F is relatively small. But it may become more significant as the 40 μg F g^{-1} dry matter dietary limit for the farm animals is approached, especially in areas where soils are acidic and organic, and where there has been long-term deposition of F (Davison, 1982).

2.5.2.2 Reactions of F with soil

Fluoride is the most chemically reactive halide and compared with other halides, it is strongly adsorbed by soils. It is consistent with the generalisation of Bowden et al. (1980) that ions with high affinity for protons (eg: phosphate, molybdate) are strongly adsorbed by soils. Like phosphate F is adsorbed specifically on soils by displacing OH from the soil colloidal surface and the initial adsorption is followed by a diffusive penetration into the soil particles (Barrow, 1986; Barrow and Ellis, 1986). The average plane of adsorption of F is even closer to the surface than that of phosphate.

When columns of some fine sandy Florida soils were treated with F solutions (CaF_2, HF, H_2SiF_6) and then leached regularly with the equivalent of 25 mm of rainfall per day, 55% of the added F remained in the columns after six weeks of leaching, irrespective of the initial form of added F (Specht and MacIntire, 1961). In a lysimeter study, treatment of four Tennesse loams with HF, followed by leaching with water indicated that between 75.8% and 99.6% of the F input was firmly retained in the soils (MacIntire et al., 1955). The ability of these loams to fix the majority of the added F was attributed to interaction of F with the Ca, Al and Fe compounds in the soils (Specht and MacIntire, 1961).

Retention of F is favoured, in soils of high clay content and with high concentrations of amorphous Al oxides and hydroxides (Omueti and Jones, 1977b; Pickering, 1985).

Soil pH is the major variable controlling F sorption and therefore F availability to plants. Sorption is greatest at pH 5.5-6.5 (Larsen and Widdowson, 1971; Omueti and Jones, 1977b; Barrow and Ellis, 1986). The decrease in F sorption at pH values below 5.5 appears to be caused by the formation of complexes between F and Al in solution. The decrease in F sorption at high pH can be explained by decreases in the electrostatic potential of the variable charge soil colloids (Barrow and Ellis, 1986).

Fluoride can also react with soil organic matter. Studies by Polomski et al. (1982) have shown that F-containing solutions (10 to 200 mg l^{-1}) induce substantial leaching losses of total organic carbon, Al, and Fe and the losses from acid soils were higher than those from calcareous soils. Hani (1978) showed that F can dissolve the aluminium-organic matter complexes present in clay soils, with more Al being extracted from an acid soil than from a limed soil. This could cause increased Al-F complexes in the soil solution, making them more available for plant uptake.

The above studies indicate that with the continuous application of F to soils, F can accumulate in the surface soil over a time due to its high adsorption. Whether this accumulation of F in the soil is a beneficial or deleterious factor to plants has not been studied in detail under moderately F-polluted soils, such as P fertilised pasture systems, although a number of studies have been carried out on highly F- polluted soils (Braen and Weinstein, 1985; Haidouti, 1991). These studies will be discussed in Chapter 7.

2.5.2.3 *Effects of F on plants*

In their review of physiological responses to F, Weinstein and Alscher-Herman (1982) stated that F is one of the most phytotoxic of the common pollutants. In addition F also has a peculiar effect that it is accumulated in plants from both the atmosphere and soils.

In the vicinity of a F-emitting industry, direct uptake by plant foliage of airborne F would mask any accumulation from the soil. In areas having high concentrations of F in the soil but low concentrations of airborne F, soilborne F may be a major source of F to plants.

Soluble soil F has been highly correlated with plant F content in sodic soils, but the relationship is not so clear in acid soils (Davison, 1982). This could be possibly due to the interaction of F with solution Al in the acid soils, thereby affecting its plant availability. For example, in a solution culture study, Takmaz-Nisancioglu and Davison (1988) showed that exposing bean roots to NaF led to F concentration in the roots and first leaves of 47 and 17 times respectively those of the control (no F) treatment. In contrast the same concentration of F given as AlF_3 gave concentration in roots and leaves 83 and 68 times respectively those of the controls. Results from this study indicate that F uptake depends on the form of F present in the solution and the F complexed with Al is more readily taken up by plants than free F ions such as in the NaF treatment.

However, Weinstein (1977) in their review on F and plant life stated that in most studies, soil amendments of relatively insoluble forms of F, including fluorapatite, calcium fluoride or cryolite, had no important effects on F uptake or injury in vegetation even at high rates of application. But application of soluble F salts increased F uptake by vegetation with the amount of accumulation depending upon the amount added, the soil type, and the crop.

2.6 Soil solution Al chemistry, Al speciation methodology and its implications to the measurement of Al phytotoxicity

This section is subdivided into 3 main parts.
(i)   soil solution chemistry of Al
(ii) aluminium species and phytotoxicity
(iii) aluminium speciation methodology

2.6.1 Soil solution chemistry of Al

The soil and soil solution chemistry of Al has been discussed by numerous workers (Thomas and Hargrove, 1984; Huang, 1988; Driscoll, 1989; Lindsay and Walthall,

1989; Ritchie, 1989; Van Breemen, 1991; Wolt, 1994). Aluminium is the most abundant metallic element in soils and the associated environment. Aluminium comprises from 1 to 30 % (mean 7.1%) of the soil (Bowen, 1966), where it is found predominantly as a component of a variety of aluminosilicates, oxyhydroxides, and other minerals (Barnhisel and Bertsch, 1982). Despite its prevalence in the soil environment, biochemically active Al is principally of concern only in acid environments where the concentration of Al^{3+} may reach toxic levels (Wolt, 1994). Aluminium concentrations in soil solutions from temperate regions are typically <0.4 μmol L^{-1} (Bohn et al., 1979), but concentrations ranging from 23 to 410 μmol L^{-1} have been reported for acid, highly weathered surface soils of tropics (Kamprath, 1984).

Aluminium biogeochemistry is environmentally significant because Al, in its bioavailable form, exhibits considerable phytotoxicity as well as aquatic ecotoxicity. Aluminium can be released from minerals to soil solutions and natural waters through chemical and biochemical weathering reactions. The Al released to soil solutions and natural waters undergoes a series of reactions including hydrolysis, polymerization, complexation, precipitation, and crystallization. These reactions are bound to be very significantly influenced by prevalent ionic factors (pH, ionic strength and type and concentration of ions) in the systems (Huang, 1988). Transformation products of Al as influenced by ionic factors have an important bearing on soil acidity and liming (Jackson, 1963a,b; Hsu, 1977; Thomas and Hargrove, 1984).

2.6.1.1 *Forms and distribution of Al in soil solution*

In soil solutions, Al can form complexes with a series of organic and inorganic ligands (Huang, 1980; Campbell et al., 1985; Huang and Violante, 1986; Huang, 1987). The extent of complexation will depend on the ionic strength and pH of the soil solution and the relative concentrations and complexing abilities of the soluble ligands (Sposito, 1981).

The important hydrolytic reactions of monomeric Al in an acid system can be represented as (Lindsay, 1979):

$$Al^{3+} + H_2O = Al(OH)^{2+} + H^+ \qquad pK=5.0$$

$$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+ \qquad pK=10.1$$

$$Al^{3+} + 3 H_2O = Al(OH)_3^0 + 3H^+ \qquad pK=16.8$$
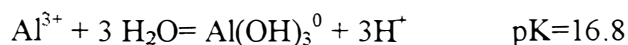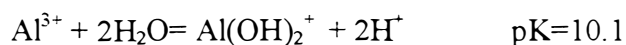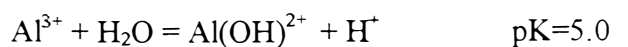
where pK is the negative logaritham of the stability constant. These relationships indicate that Al hydroxy monomers will be the dominant Al species in slightly acid soil solution, while Al^{3+} will increasingly dominate at pH <5. Fig 2.3 shows the aqua and hydroxy Al species changes with solution pH.

In addition to Al-hydroxy monomers, a number of hydrolytic reactions involving the formation of Al-hydroxy polymers have been postulated (Bache and Sharp, 1976; Tsai and Hsu, 1984). Baes and Mesmer (1976) concluded that the polymeric species formed by hydrolysis of Al^{3+} are $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$. Direct NMR evidence indicates that the Al_{13} polymer exists in partially neutralised solutions ranging widely in Al concentration and the methods of synthesis (Bottero et al., 1980; Bertsch et al., 1986).
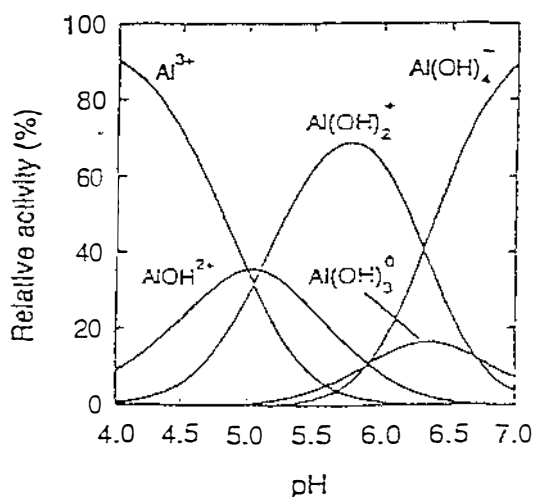
Fig 2.3. Relative activities of Al species as affected by pH of solution (Kinraide, 1991).

The precise differentiation of polynuclear and mononuclear Al species has been difficult. Indirect methods of differentiation include conductometry, light scattering, ultracentrifugation, ion exchange, dialysis, and kinetic methods based on the interaction of Al with a complexing agent (Huang, 1988). Ion speciation models can be useful for partitioning Al among hydrolytic species; but again, the lack of reliable thermodynamic data for the stability constants of these species is a problem.

2.6.1.2 *Aluminium complexation with inorganic ligands*

The nature and concentration of inorganic ligands play an important role in influencing the hydrolysis and polymerisation of Al (Marion and Thomas, 1946; Ross and Turner, 1971; Nordstrom, 1982; Violante and Huang, 1984, 1985). Anions such as Cl, ClO_4 and NO_3 which do not have strong affinity for Al (Hsu, 1966; Ross and Turner, 1971), produce highly soluble salts and yield clear solutions (Hsu, 1977). Furthermore, polynuclear Al ions continue to hydrolyze and polymerize into larger units during prolonged ageing unless a high concentration of a counter anion such as F is present (Huang, 1988). In the presence of ligands that have strong affinity for Al, such as SO_4 (Hsu, 1973), PO_4 (Hsu, 1975), H_4SiO_4 (Luciuk and Huang, 1974), CO_3 (White and Hem, 1975; Serna et al., 1977), and F (Violante and Huang, 1985), the further hydrolysis of polynuclear Al species is prevented or at least retarded.

Formation of ion pairs between Al^{3+} and SO_4^{2-} and F^- can reduce Al^{3+} activity in soil solutions substantially. Stability constants for Al-sulphate ion pairs are smaller ($AlSO_4^+$, pK 3.2- Lindsay, 1979) than those for Al-fluoride ion pairs (AlF_3, pK 16.7; AlF_2^{1+}, pK 12.6; AlF^{2+}, pK 6.9-Lindsay, 1979) (Roberson and Hem, 1969), but the greater abundance of SO_4^{2-} in unpolluted soil environments may increase the occurrence of Al-sulphate over Al-fluoride ion pairs (Burrows, 1977).

In F-polluted environments, such as soils close to Al smelters, Al-F species dominated in the soil solution (Wenzel and Blum, 1992a b). Recent investigations on acid Haplorthod soil solutions and natural waters draining forested watersheds in the northeastern USA indicate that F is responsible for complexing large fractions of total Al, despite the greater concentrations of SO_4 relative to F in solution (Johnson et al., 1981; David and Driscoll, 1984; Driscoll and Newton, 1985). However no known studies have been carried out on pastoral lands that have received continuous inputs of F and SO_4 via P fertilisers to find out the relative effects of solution F and SO_4 on Al speciation. Although soil solution F concentration may be low in the pH range of 5.5-6.0 generally observed in pasture soils due to high adsorption of F, Al concentration is also low in this pH range. Therefore, even a small amount of solution F may be sufficient to change the Al speciation substantially.

2.6.1.3 *Aluminium complexation with organic ligands*

Aluminium can also form soluble complexes with organic anions depending on the type and concentration of organic ligand, pH, ionic strength and the presence of competing cations (Rashid, 1974; Kwong and Huang, 1977; Ritchie et al., 1982; Stevenson, 1982; Young and Bache, 1985). Humic materials appear to complex considerable Al at pH 4.5 to 5.0, but as pH decreases, so does complexation (Krug and Frink, 1983).

Low molecular-weight organic acids also complex Al. The stability of complexes formed is in the approximate order citric>oxalic>malic>tannic>aspartic>p-hydrobenzoic>acetic (Ng Kee Kwong and Huang, 1979a b; Wang et al., 1983; Hue et al., 1986). The sources of low-molecular weight organic acids in soil environments include root exudates, canopy drip, decay of plant and animal residues, and microbial metabolites. The kinds and amounts of these organic acids in soil solution are likely to be greatly influenced by microbial activity, and will exhibit wide temporal fluctuation. This temporal variation in dissolved organic

matter is a factor which greatly influences the Al chemistry of soil solutions (Nilsson and Bergkvist, 1983). Since living plants can modify the root environment by release of root exudates (Rovira and McDougall, 1967), it is likely that Al speciation in the rhizosphere may be different from that in the bulk soil solution. There is however no detailed information available on Al speciation in the rhizosphere of different plant species.

2.6.1.4 *Mixed ligand systems*

The behaviour of Al in soil solutions may vary greatly compared with that in pure solutions because of multiple ligands present in the soil solution system forming complexes with Al with different stabilities. For example, Al-fluoride ion pairs are more stable than Al-sulphate ion pairs (Roberson and Hem, 1969). Aluminium complexes with dissolved organic carbon are in general stronger than those with inorganic ligands (Ritchie et al., 1988); and Al complexes with humic or fulvic acid appear to be stronger than Al complexes with simple carboxylic acids (Plankey and Patterson, 1987; Ritchie et al., 1988; Sikora and McBride, 1989). Further detailed research in this area will allow us to better understand the complex Al reactions in soil solutions.

2.6.2 Aluminium species and phytotoxicity

Aluminium toxicity is probably the most important growth-limiting factor for plants in acidic soils (Kamprath and Foy, 1985; Foy, 1988). The relationships between aqueous Al chemistry and phytotoxicity are still not fully understood (Parker et al., 1989). The efforts to relate phytotoxicity to levels of Al in soil solution have met with varying degrees of success (Adams and Lund, 1966; Brenes and Pearson, 1973; Pavan et al., 1982; Adams and Moore, 1983; Adams and Hathcock, 1984). This may be partly ascribed to an insufficient understanding of the various Al species present in soil solution and their relative contribution to biological toxicity (Parker et al., 1989).

It is generally agreed that some measure of Al activity in soil solution is more indicative of potential Al toxicity than concentrations of water soluble Al, exchangeable Al or percentage Al saturation of soil CEC (Adams and Lund, 1966). There have been several investigations of Al speciation and phytotoxicity, but most of these studies have been carried out in controlled nutrient solutions (Pavan and Bingham, 1982; Pavan et al., 1982; Blamey et al., 1983; Wagatsuma and Ezoe, 1985; Alva et al., 1986a, b; Cameron et al., 1986; Hue et al., 1986; Tanaka et al., 1987; Kinraide and Parker, 1987a b; Wagatsuma and Kaneko, 1987; Wright et al., 1987; Parker et al., 1988, 1989). Much of this earlier work has been summarised in reviews by Bertsch (1990), Parker et al. (1989) and Kinraide (1991). Therefore emphasis in this section will be placed on more recent work.

The most striking symptom of Al toxicity is its rapid inhibition of root growth (Foy, 1992). Short-term root elongation is thus the most commonly used growth parameter in Al toxicity studies. Many investigators have attempted to relate the predicted activities of hexaaqua-, hydroxo-, sulfato-, and fluro-complexed Al to observed toxicities and have correlated an observed biological response (usually root length) to the activities of one or more specific Al complexes. The results of these studies have not been consistent, some suggesting that the Al-hydroxy species may be relatively more phytotoxic than Al^{3+} (Adams and Moore, 1983; Blamey et al., 1983; Alva et al., 1986b c; Noble et al., 1988a b), with others suggesting the opposite (Bartlett and Riego, 1972; Pavan et al., 1982; Cameron et al., 1986). Likewise, a number of studies have suggested that sulphate complexes are relatively more toxic than Al^{3+} (Blamey et al., 1983; Alva et al., 1986c), whereas others have suggested that these complexes are much less toxic or nontoxic to plants (Cameron et al., 1986; Tanaka et al., 1987; Kinraide and Parker, 1987a; Noble et al., 1988a b). Generally, most studies have indicated that the Al-F complexes are either much less toxic than Al^{3+} or are nontoxic (Cameron et al., 1986; Tanaka et al., 1987; Noble et al., 1988a, Parker et al., 1989; MacLean, et al., 1992). Nutrient studies

have also shown that organic complexes of Al are not phytotoxic (Bartlett and Riego, 1972; Hue et al., 1986; Harper et al., 1995).

Bertsch (1990) reported that the above mentioned discrepancies could be due to (1) differences in the composition of nutrient solutions of varying complexity, often containing organic chelators that were not accounted for during speciation calculations, (2) differences in speciation models having different thermodynamic databases, (3) collinearity between Al species, (4) differences in the methods of measurement of inorganic monomeric Al which is an important input in speciation calculations and (5) the toxicity being influenced by some other factor not considered in the study, such as cation (eg. Ca) amelioration of Al toxicity.

As noted above, free Al^{3+} activity alone may not be diagnostic of plant growth reduction in acid soils and the toxic effect of Al may sometimes be better expressed in terms of the ratio of soil solution Al^{3+} activity to the activities of some other soil cations (for example Ca^{2+}) that may influence plant growth response (Adams, 1984; Alva et al., 1986a). In a more recent study by Menzies et al. (1994) using a short-term (mungbean root growth) bioassay it has been shown that the most effective diagnostic criterion for Al toxicity study was a Ca-Al balance (CAB), defined as 2 log (Ca^{2+})-6 log(Al^{3+}). Slattery et al. (1995) reported that the combination of Ca activity and the sum of the activities of Al monomers, together with organic carbon content, may provide a better description of the responsiveness of acid soils to lime applications than the conventional Al toxicity indices.

However, the relative efficacy of other cations in ameliorating Al toxicity has been little studied. Magnesium has been shown to effectively ameliorate Al toxicity and appeared to be as effective as Ca (Rhue and Grogan, 1977; Kinraide et al., 1985; Rengel and Robinson, 1990). Limited data available for monovalent cations suggest that K and Na can ameliorate toxicity, but much less so than Ca and Mg (Kinraide et al., 1985) and it is uncertain whether this entails more than an ionic strength effect.

2.6.3 Aluminium speciation methodology

Understanding chemical speciation in soil solutions and on the surfaces of soil particles is important because speciation determines both the mobility and the biological effects of chemical elements. For example, the aqueous chemical species Al^{3+} is highly toxic to plant roots and is of limited mobility in soils, whereas Al^{3+} bound to soluble organic molecules is not toxic and is very mobile. Accurate estimation of the speciation of the various Al forms will aid our understanding of the complexities imparted by acidification of soil and provide better information on management techniques for agricultural systems.

Only a few comprehensive reviews have been published of Al speciation methods (Bertsch, 1990; Bloom and Erich, 1989). These reviews indicate that there is considerable controversy concerning the determination of Al species using different methods. Certainly, numerous techniques have been employed in an effort to partition mononuclear and polynuclear, organic and inorganic Al (Driscoll, 1984; Seip et al., 1984; Hodges, 1987; Jardine and Zelazny, 1987; Bertsch and Anderson, 1989; Willett, 1989; Browne et al., 1990; Hawke and Powell, 1994; Hawke et al.,1996).

Three general approaches to Al speciation can be identified. The first is essentially computational, where an analytically determined total dissolved Al determination, in combination with the analytically determined concentrations of all other important dissolved components, are utilised in thermodynamically-based geochemical models (Pavan and Bingham, 1982). The second involves the analytical separation of various Al species based on differential reaction kinetics with complexing agents, and/or the physicochemical separation of Al species based on size or charge (Campbell et al., 1983; James et al., 1983; Driscoll, 1984; LaZerte, 1984; Buffle et al, 1985; Kerven et al., 1989a b; Hawke and Powell, 1994; Hawke et al.,1996). The third general approach involves the combination of one or more analytical

separation techniques with the geochemical speciation model (Driscoll et al., 1980; Johnson et al., 1981; Cambell et al., 1983; James et al., 1983; Driscoll, 1984; LaZerte, 1984; Seip et al., 1984; Tanaka et al., 1987; Wagatsuma and Kaneko, 1987; Wright et al., 1987).

However, among these various analytical techniques available for the speciation of Al, the most frequently used procedures are those based on rates of reaction with complexing agents such as 8-hydroxyquinoline (8-HQ) (Barnes, 1975; Bloom et al., 1978; James et al., 1983), pyrocatechol violet (PCV) (Morrison, 1990; Samaritan et al., 1993), or ferron (Jardine and Zelazny 1986).Another commonly used method of Al speciation is the use of F-ion selective electrode.

2.6.3.1 *Speciation using F-ion selective electrode.*

As stated in the previous section F has received attention as a potential tool in the study of Al chemistry because of the high stability of Al-F complexes (Lindsay, 1979). In most natural waters, the only metal ion that binds a significant fraction of F is Al. If Al is the only component that binds F, determination of the free F (F^-) activity and the total F concentration is sufficient for the calculation of Al^{3+} activity (Hodges, 1987). The method utilises an approximate decomplexation buffer (converts all Al-F complexes into free F) to determine total F and direct free F activity measurements using an F ion selective electrode. The assumptions in this method are that Ca, Mg, Si, and Fe fluoride complexes are negligible and that the system is at thermodynamic equilibrium. For calculating Al activity (Al^{3+}) from total F concentration [F] and F ion activity (F), Munns et al. (1992) used the following expressions:

$$[F\text{-}bound] = [F] - (F)/G_1$$

$$(Al^{3+}) = [F\text{-}bound]/\{K_1 (F)/G_2 + 2K_2(F)^2/G_2 + 3K_3(F)^3 \}$$

where [F-bound] = total concentration of F complexed with Al, G_1 and G_2 are monovalent and divalent ion activity coefficients, and K_1, K_2 and K_3 are formation constants for the Al-F complexes.

However, there are several problems associated with this method when applied to soil solutions. Among these are the potential interferance in the F measurements by dissolve organic matter and the assumptions that the system is in equilibrium and that no other important-fluoro complexes are present (Bertsch, 1990). Munns et al. (1992) compared Al^{3+} activity determined in soil solution by the F ion selective electrode method with that determined by PCV+Geochem and 15 s 8 HQ methods and reported that the F-ion selective electrode method increasingly overestimated Al^{3+} as pH increased. They were not able to find any reasons for this overestimation.

2.6.3.2. *Speciation using ion-exchange resins*

Cation-exchange resins are the most common methods used to separate inorganic monomeric Al from other forms of Al in natural waters and soil solutions. Two types of methods have been used. One method utilises a short-term batch reaction with a chelating resin such as Chelex 100 (Campbell et al., 1983; Hodges, 1987; Miller and Andelman, 1987), whereas the other utilises the reaction of solutions with a strong acid resin in a cation exchange column (Wright and Skogheim, 1983; Driscoll, 1984; Rφgeberg and Hendrickson, 1985; Fairman and Sanz-Medel, 1993). In both methods, inorganic monomeric Al reacts much more rapidly with the resin than the other Al components, and monomeric Al can be estimated from the differences in measured Al concentration before and after reaction with the resin. Driscoll (1984) used a cation-exchange column technique for the fractionation of Al in surface waters in combination with other procedures (PCV or 8-HQ or Ferron). The combination of these procedures is probably the most widely used method for determining inorganic monomeric Al in acidic waters and soil solutions. The

method is convenient, reproducible, can be readily automated and can also be used in the field. Driscoll (1984) distinguished three forms of Al by using a series of Al determinations via combination of a colorimetric method with an ion exchange separation step (Fig 2.4).

In the fractionation scheme outlined in Fig 2.4, an acid-reactive Al fraction was determined by acidification of the sample to pH 1 and keeping it for 1 hr, followed by Al determination employing the 8-HQ method of Barnes (1975), the PCV method of Dougan and Wilson (1974) or the ferron procedure of Smith (1971).

Total Reactive Al, Acid Digested		
Al in solution before passing through the column measured by Rapid Reaction with PCV,8-HQ or Ferron (Total monomeric Al)		
Al in Column effluent measured by rapid reaction with PCV, 8HQ or Ferron.		
Organic monomeric Al (nonlabile)	Inorganic monomeric Al (labile)	Colloidal, polymeric and strong organic complexes (acid soluble)
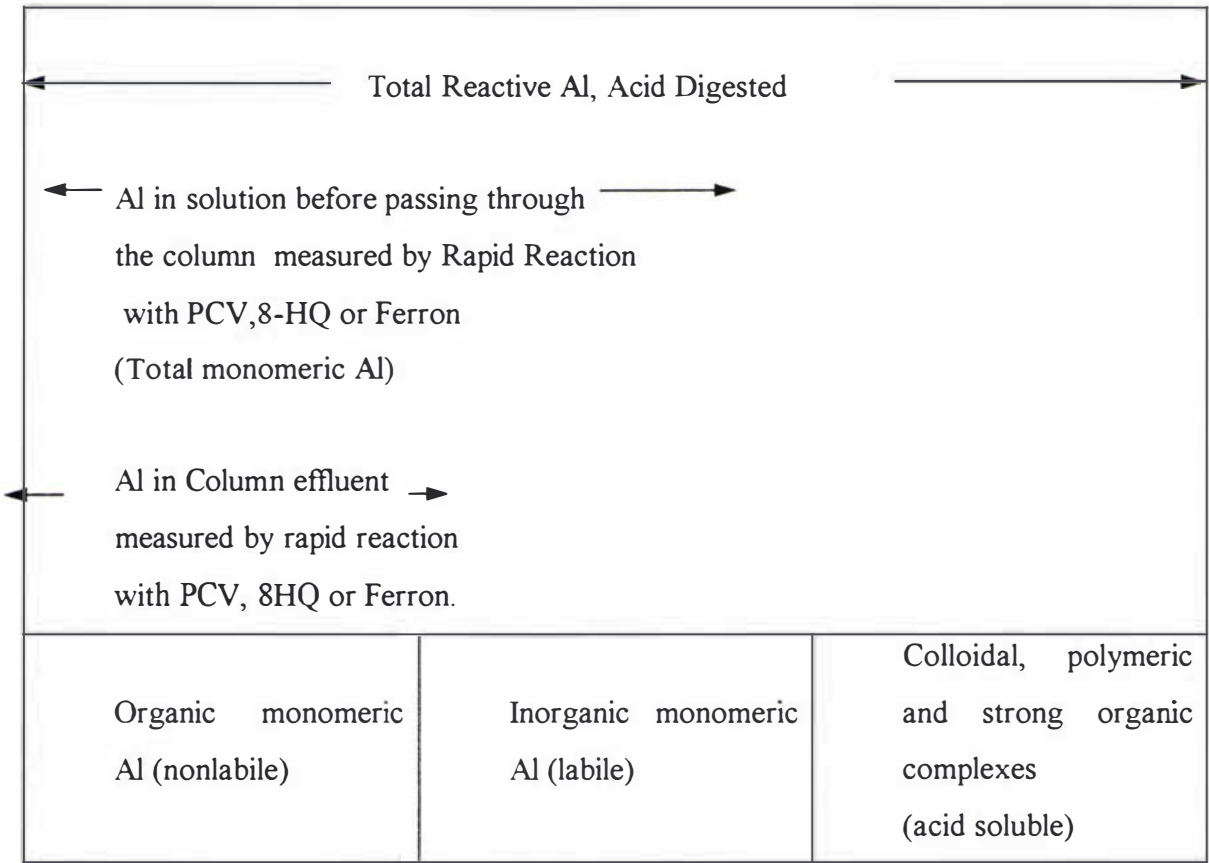
Fig 2.4. Schematic representation of the Al fractionation procedure of Driscoll (1984), using a strong acid-resin column to separate inorganic monomeric Al.

The methods used for determining total monomeric Al (organic + inorganic) are based on short-term reactions with complexing reagents. The methods include the ferron method of Smith (30 s), the PCV method (4 min) of Dougan and Wilson (1974), or the 8-HQ method at pH 5.0 (15 s) of Bloom et al. (1978).

Differentiation of organic monomeric and inorganic monomeric Al was achieved by passing a sample through a highly charged cation exchange resin, adjusted to comparable ionic strength and pH as the sample to minimise reeqilibration in the column environment, followed by Al determination in the eluent, again according to the Ferron method (30 s) of Smith (1971) or the PCV method (4 min) of Dougan and Wilson (1974) or the 8 HQ method (15 s) of Bloom et al. (1972). It is assumed in this method that the reactive Al in the eluent is primarily composed of organically complexed forms. Cation-exchange methods preferentially adsorb the positively charged inorganic monomeric Al rather than the negatively charged organic Al fraction. The concentrations of inorganic monomeric Al forms are then calculated by taking the concentration difference in Al between an aliquot that has passed through the exchange column and a measurement of total monomeric Al in a sample that has not passed through the column (Campbell., 1983; Driscoll, 1984).

Because of the differences in the reaction rates of these complexing agents with the various Al fractions in natural waters and soil solutions, these different procedures could be expected to yield somewhat different results. Cation-exchange methods are only applicable at pHs below approximately 6.5-7.0, as they depend upon the adsorption of the positively charged monomeric Al on to the negatively charged resins. At pHs greater than 7, $Al(OH)_4^-$ becomes increasingly dominant (May et al., 1979).

2.6.3.3 Ion chromatographic methods

Recently ion chromatographic methods have been developed to determine Al species in synthetic solutions, natural water samples and soil solutions (Bertsch and

Anderson, 1989; Willett, 1989; Whitten et al., 1992). In these methods Al species are separated according to their charges. In solutions containing Al and F the concentrations of mono-, di- and tri-valent Al as determined by ion chromatography corresponded closely with those predicted from stability constant data for AlF_2^{1+}, AlF^{2+} and Al^{3+} respectively except the peak corresponding to Al^{3+} also contained Al hydroxy species and $AlSO_4^+$ (Willett, 1989).

Among the advantages of ion chromatography, one could mention very small sample volume used (ca 100-200 μL), the speed of analysis (ca. 5 min) and the possibility of making a direct measurement of inorganic monomeric Al. It may also be possible to determine some F complexes (eg: AlF^{2+}) separately (Willett, 1989), which is difficult with most other methods.

However it is questionable whether ion chromatography is generally suitable for measuring Al species in soil solutions. This is mainly because of the presence of high concentration of dissolve organic carbon in soil solution which would affect the column, by adsorbing to the packing material and possibly blocking the column.

2.6.3.4 *Comparison of speciation methods*

Driscoll (1984) compared the organic monomeric Al (Al_o) values estimated by the resin column method against those determined by the F electrode technique and found adequate agreement only at low organic monomeric Al concentrations. At high organic monomeric Al concentrations the column method underestimated organic monomeric Al, suggesting that some dissociation of Al-organic complexes may be occurring while passing through the exchange column. However, because of the indirect nature of the F- ion electrode method, and its inherent assumptions, it is not really known whether F-ion electrode method overestimated organic Al or the cation-exchange method underestimated organic Al.

Hodges (1987) evaluated five speciation methods (8-HQ and ferron, ion-exchange column, batch chelating resin and the F-ion selective electrode procedures) and concluded that some dissociation of Al-organic complexes occurred during the passage through the ion exchange column for the soil and synthesised solutions he investigated. However, he also reported that strongly chelating organic ligands such as citrate could desorb inorganic Al separated from previously-processed samples, producing anomalously high organic monomeric Al estimates. Driscoll (1984) suggested that the flow rate of the solution through the ion exchange column did influence the measurement of nonlabile monomeric Al and proposed a flow rate of 3.7-4.2 ml min^{-1} per ml of resin bed volume to minimise these effects.

LaZerte et al. (1988) compared an automated, modified, sulfonic ion exchange column method with a manual dialysis method for estimating the organic monomeric Al and inorganic monomeric Al fractions. The comparison demonstrated remarkable agreement for the 267 dilute natural water samples they investigated, with only a 6% deviation observed. However, an almost identical comparison by Backes and Tipping (1987) for isolated naturally occurring humic materials indicated a much larger deviation; up to 25 %, and the discrepancy increased with the increase in the relative amount of Al associated with the organic fraction.

Sullivan and Seip (1986) compared fractionation methods of the Barnes/Driscoll MIBK (methyl isobutyl ketone) extraction method and the PCV method, for surface water samples from southern Norway. They found that the results for inorganic monomeric Al, which is biologically most important, were in very good agreement, although there were systematic differences particularly for the organic monomeric Al fraction. A similar observation was made by McAvoy et al. (1992), when comparing 8-HQ (10 s) and PCV (4 min) methods in natural soil solution samples. They found good agreement between inorganic monomeric Al concentrations measured by PCV and 8-HQ methods.

The main advantage with the PCV method lies in its suitability for automation compared with the 8HQ method in which the organic solvent extraction step is necessary; which is difficult to automate. The automated PCV method needs much smaller sample volumes compared with the 8 HQ method and also can increase the sample turn over and improve precision. Another advantage is that the PCV method is insentitive to F up to a level of 500 μM (Dougan and Wilson 1974).

In a more recent study, Hawke and Powell (1994) compared complexing agents Chrome azarol (CAS), eriochrome cyanin R (ECR) and PCV for the estimation of kinetically labile Al (includes Al^{3+} + $Al(OH)_n^{3-n}$ and Al that can rapidly dissociate from complexes of Al with natural organic matter) in a series of complexes with model ligands and in soil solutions. Their results showed that PCV reacted more rapidly than CAS although CAS complexed more Al than PCV under equilibrium conditions. CAS also provided greater sensitivity than ECR and PCV and they therefore recommended that a short reaction time of 10 s with CAS in a flow injection system (FIA) be used to measure kinetically labile Al^{3+} in soil solutions and natural waters.

The fraction of interest to most investigators is inorganic monomeric Al because this fraction includes most of the toxic Al species. The most rapid but least satisfactory method of determining inorganic monomeric Al is to measure the Al that reacts rapidly with complexing reagents. This is mainly because of their high reactivity with the organic Al complexes which may lead to overestimation of the inorganic monomeric Al. Although F- ion selective electrode has the potential to be used in the measurement of Al^{3+} in soil solutions and natural waters, due to the difficulties in electrode calibration at very low F activities, interference with dissolved organic matter and the several assumptions implicit in this method, the use of this method can be limited to only selective samples.

The ion-exchange method appears to be the best method available for the determination of inorganic monomeric Al, although this method also has its own

limitations. Since this method has been widely accepted and used, it allows direct comparison of results with those from other investigators. In addition this method has the advantage of being easily automated and can even be used in field studies (Rϕgeberg and Henriksen, 1985).

Although ion chromatographic methods have been developed recently to speciate Al, they have not been sufficiently tested in soil solution studies to accept them as standard routine methods. Blocking of the chromatographic column by dissolved organic carbon in soil solution is a major problem. In addition, these methods involve high technical skills, special sample preparation and expensive instruments. Therefore their usage may be limited to certain laboratories.

2.7. Summary and Conclusions

This review shows that in New Zealand, large areas of hill country and upland soils under legume based pastures are acidic. This is mainly due to the accumulation of organic matter and NO_3 leaching in these soils. Aluminium toxicity could therefore be an important factor limiting pasture growth in these acid soils. As liming is no longer economic on many of these hill country and upland soils it is important to improve our understanding of how acidification and its effects on soil Al are affecting pasture productivity.

Phosphate fertilisers are the main input to pastoral soils. There is no adequate information in the literature on the effects of these fertilisers on soil acidity and Al toxicity. This review suggests that SSP application does not directly acidify the soil in the highly buffered pastoral soils of New Zealand to any significant degree in the long-term. But it can decrease the pH indirectly via increased clover growth resulting in increased NO_3 leaching and increased organic matter accumulation. Laboratory studies have shown that in contrast to soluble fertilisers such as SSP, the RPRs may have significant liming effects on soils. However, there appears to

have been only one field study (Sinclair et al., 1993) carried out on the long-term liming effects of RPRs used on legume-based pastures. Research in this area is important for the sustainable management of these pasture soils.

This review also indicated that P fertiliser application can have a significant effect on Al toxicity, due to the interaction of P fertiliser components such as PO_4, SO_4 and F with Al in acid soils. These interactions will affect the types and concentrations of Al species in the soil solution which is an important factor determining Al toxicity in plants. However, this concept has not been investigated specifically under field conditions where P fertilisers have been applied over a long-period of time.

Both soil and nutrient solution studies have shown that the main phytotoxic Al species are Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^{+}$. Nutrient solution studies have also shown that Al-F complexes are less-toxic than Al^{3+}. However, there is no detailed information available on whether high concentrations of these Al-F complexes, formed under acidic soil conditions can have some toxic effects on plants. This is important because with increased acidification and the ongoing addition of F in P fertilisers Al-F complex concentrations may increase beyond the toxic threshold levels. The practical difficulty of keeping Al concentrations constant in soil solutions (as opposed to nutrient solutions) with increasing F additions may be the reason for the scanty information available on soils in this subject. There is a need for further research on soil acidity and F interactions and their effects on plant growth.

Behaviour of Al in soil solutions may vary greatly compared with that in pure solutions because of multiple ligands present in the soil solution system. Also, it is likely that Al speciation in the root rhizosphere may be different from that in the bulk soil solution due to the active microbiological processess and the production of root exudates. There is no detailed information available on Al speciation in the

rhizosphere of different plant species. Further detailed research in this area would allow us to better understand the Al tolerance of different plant species.

Reviews of recent studies indicated that exchangeable Al or the concentration of total soluble Al may not be suitable as a soil test, because they do not consider the activity and forms of phytotoxic Al in solution. Studies also indicate that the toxic effect of Al may sometimes be better expressed in terms of the ratio of soil solution Al^{3+} activity to the activities of some other soil cations (for example Ca^{2+}) that may influence the plant growth response to Al. Since the application of P fertilisers can affect the types and concentrations of anions and cations in the soil solution, they may have a significant effect on Al toxicity threshold levels in pasture soils. However, there are no detailed studies available related to this hypothesis. Further investigation of this aspect will allow us to improve prediction of Al toxicity in pasture soils.

The brief review of Al speciation methodology indicated that a continuing process of method development and inter-comparison is needed to more accurately characterise the fractions of monomeric Al determined with these methods, and to assess the phytotoxicity of the various Al species.

Chapter 3

Effects of long-term application of phosphate fertilisers on soil acidity under pasture in a Central Yellow Grey Earth[1]

3.1 Introduction

Modelling of nutrient cycles, particularly the nitrogen cycle , in pasture soils suggests that there is slow but continuing soil acidification in New Zealand legume-based pastures (Bolan et al., 1991). Changes in soil pH in most soils over a decade are small, because of the inherent large buffering capacity of New Zealand soils. In Australian soils, however, which have lower buffering capacities, the effects of increasing soil acidification in legume-based pastures have been seen in the short term (Williams, 1980). The problem there has been so bad that in many areas pasture production has been severely inhibited or cereal growth, in cereal-pasture rotations, has failed (Lee, 1980).

In flat land pastures in New Zealand, soil acidity is easily remedied by lime application. However, with the lower productivity and profit margins of hill country soils, lime use is often uneconomic and phosphate and sulphur fertilisers may be the only economic soil amendments. On these hill country soils it may be possible to apply phosphate fertiliser in a less acidulated form than fully acidulated superphosphate to help control soil acidity. Most reactive phosphate rocks (RPR) have significant liming action due to the presence of carbonate in apatite (francolite) and in accessory minerals (calcite, dolomite) and because when RPR dissolves it consumes 2 moles of H^+ for every mole of P dissolved.

$$Ca_{10}(PO_4)_6F_2 + 12\ H^+ \rightarrow 10Ca^{2-} + 6\ H_2PO_4^- + 2\ F^-$$
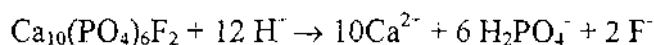
Easterwood et al. (1989) and Wright et al. (1991) have shown in laboratory incubation studies, that application of very high rates of RPR to cropped soils with low buffering capacities has significantly reduced soil acidity. However to our knowledge only one

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[1] Manoharan et al. (1995). In Plant-Soil Interactions at Low pH: Principles and Management. (Eds). R.Date et al. Kluwer publishers. p.85-91.

published paper (Sinclair et al., 1993) is available on the effect of RPR on soil acidity in New Zealand pastoral soils. Sinclair et al.(1993) studied the effects of annual applications of triple superphosphate (TSP), single superphosphate (SSP), Sechura phosphate rock (SPR) and North Carolina phosphate rock (NCPR) on soil pH over 6 years in 10 field trials under clover/grass pasture. Their results showed that over the 6-year period, soil pH (0-75 mm soil depth) in control, SSP and TSP treatments fell by an average of 0.16 units. RPR's reduced the fall in pH and this effect increased with increasing RPR application rates, the fall in pH being virtually eliminated at the highest RPR application rate.

This chapter presents the results of an investigation of the effects of seven years of annual applications of six types of P fertiliser on soil acidity under pasture in New Zealand.

3.2 Materials and Methods

3.2.1 Soil sample collection

Soil samples were collected from a long-term mowing/grazing trial established in 1985 in the Manawatu area of the North Island of New Zealand. The trial tested the effects of various forms of P fertilisers on pasture. It consisted of 10 treatments (Table 1) replicated 5 times and the plots were arranged according to a randomised complete block design. The plot size was 3 m $\times$ 3 m with 1 m between replicates. The soil is classified as Tokomaru silt loam, a Central Yellow Grey Earth (Aeric Fragiaqualf). The site had a pH (H_2O) of 5.70, a P sorption capacity (Saunders, 1965) of 22 % and an Olsen P level of 10 $\mu g\ g^{-1}$ at the start of the trial in 1985. The pH (H_2O) of the site had been measured earlier and in 1981 was 5.85. Fertiliser treatments were applied annually (during March/April), starting in 1985. The 1992 application was carried out on 7 April, 1992. Plots were cut about 6 times a year for pasture yield determinations. Immediately after each cut sheep were let in for two to three days to graze the entire experimental area. Soil samples were collected on 31 March, 1992 by taking a composite of 12, 25-mm diameter cores per

plot. Two sets of samples, one to a depth of 30 mm and the other to a depth of 75 mm, were collected from each plot. Air-dried soil samples, ground to pass through a 2 mm sieve, were used for chemical analysis. Soil samples were collected again on 20 January 1993 from depths of 0-30, 30-75, 75-120, and 120-200 mm. pH(H_2O) was measured on these samples to determine the depth to which the fertiliser treatments had affected soil pH.

Table 3.1. Fertiliser treatments

	Fertiliser treatments	Abbrev.	Total P (%) in fertiliser 1985-1988	Total P (%) in fertiliser 1989-1991	Total F (%)	Rate of Application[b] kg P ha^{-1} yr^{-1}
1	Control (no added P)	Cont	-		-	0
2	Single superphosphate	SSP-15	9.5	9.9	0.98	15
3	Single superphosphate	SSP-30	9.5	9.9	0.98	30
4	Single superphosphate	SSP-45	9.5	9.9	0.98	45
5	Single superphosphate	SSP-60	9.5	9.9	0.98	60
6	Jordan phosphate rock	JPR	14.1	14.2	3.40	30
7	North Carolina phosphate rock	NCPR	13.1	13.4	3.16	30
8[a]	Jordan PAPR (30 % acidulation)	JPAPR	16.2	17.4	n.d	30
9[a]	North Carolina PAPR (30% acidulation)	NCPAPR	14.8	15.3	n.d	30
10	Diammonium phosphate	DAP	20.0	20.4	1.20	30

n.d., Not determined
[a]From 1989 onwards 20% acidulated PAPR was applied
[b]Sulphur in the form of gypsum was applied annually to plots to make the S rate of addition similar to treatment 5; basal K was applied annually in the form of KCl (50 kg K ha^{-1}) to all plots.

3.2.2 Soil analyses

Soil pH was determined in water and 1 M KCl at 1:2.5 soil to solution (w/w) ratio. Exchangeable bases were determined by extraction with neutral 1 M NH_4OAc and measuring K and Na in the extracts using atomic emission spectrophotometry and Ca and

Mg using atomic absorption spectrophotometry. Exchangeable acidity was determined by sequentially extracting 5 g soil with three 30 ml aliquots of 1 M KCl for 30 min each and titrating the combined extracts with standard NaOH using phenolphthalein indicator (Yuan, 1959). pH buffering capacity was determined on the 0-75 mm samples by equilibrating soil with varying rates of $CaCO_3$ at a moisture content approximating field capacity at room temperature for 2 months. The amount of $CaCO_3$ required to raise the soil pH from 5.0 to 6.0 was calculated from the regression equation relating pH and rates of $CaCO_3$. This value expressed as kmol H^+ ha^{-1} (soil depth 75 mm, bulk density 1.1 g cm^{-3}) was taken as the buffering capacity of the soil (0-75 mm) in the pH range 5.0-6.0.

Exchangeable Al was determined by agitating 5 g soil with 50 ml 1 M KCl for 30 min and determining the Al in the soil extract by the aluminon method (Barnhisel and Bertsch, 1982). $CaCl_2$-extractable Al was determined by extracting Al from the soil with 0.02 M $CaCl_2$ at a 1:2 soil to solution ratio and 1 hr shaking (Edmeades et al., 1983; Hoyt and Nyborg, 1972). The Al in the extracts was measured using the aluminon method. $CuCl_2$-extractable Al was determined by 3 successive 30 min extractions of 10 g soil with 30 ml 0.5 M $CuCl_2$ solution (Juo and Kamprath, 1979). The Al in the extract was measured by atomic absorption spectrophotometry.

3.2.3 Phosphate rock dissolution

The amount of phosphate rock dissolved was determined by subtracting the amount of phosphate rock remaining in the soils (0-75 mm) from the total amount of phosphate rock added over the 7 yr period. The amount of phosphate rock remaining undissolved was measured by extraction of P from the soils with 1 M HCl following extraction with 0.5 M NaOH (Bolan and Hedley, 1989).

3.3 Results and Discussion

3.3.1 Soil pH

Results from this study indicated that in a marginally acidic soil (pH(H_2O) 5.5-5.8) irrespective of the rate or form of P fertiliser used, the soil became increasingly acidic with time (Table 3.2 and Fig 3.1). Soil pH values, in both H_2O and KCl, of samples collected in 1992 after 7 years of fertiliser application were generally lower in the 0-75 mm soil depth than in the 0-30 mm depth, the difference being greater for pH in KCl (Figs. 3.1 and 3.2). McLaughlin et al. (1990) also observed a higher pH in the 0-20 mm layer than in 20-40 and 40-60 mm layers in Australian soils under a subterranean clover pasture. McLaughlin et al. (1990) explained this pH stratification as due to the return of organic anions (organic acids having pK_a values above the soil pH) and bases in plant material and animal faeces to the surface layers, a higher rate of oxidation of organic anions at the surface producing an increase in pH and the increased production of protons by clover roots in the subsurface layers compared to surface layers. Another possible reason could be that the surface soil has a higher buffering capacity due to high organic matter content and thus a lower reduction in pH compared with the subsurface soil.

Table 3.2. Changes in soil pH with time

pH (H_2O) (0-75 mm soil depth)				
Year	Control	SSP (30)	NCPR (30)	DAP (30)
[a]1981	5.85	5.85	5.85	5.85
[b]1985	5.70	5.70	5.70	5.70
[c]1992	5.48	5.50	5.65	5.39

[a] Before the trial; [b] At the start of the trial; [c] After the trial
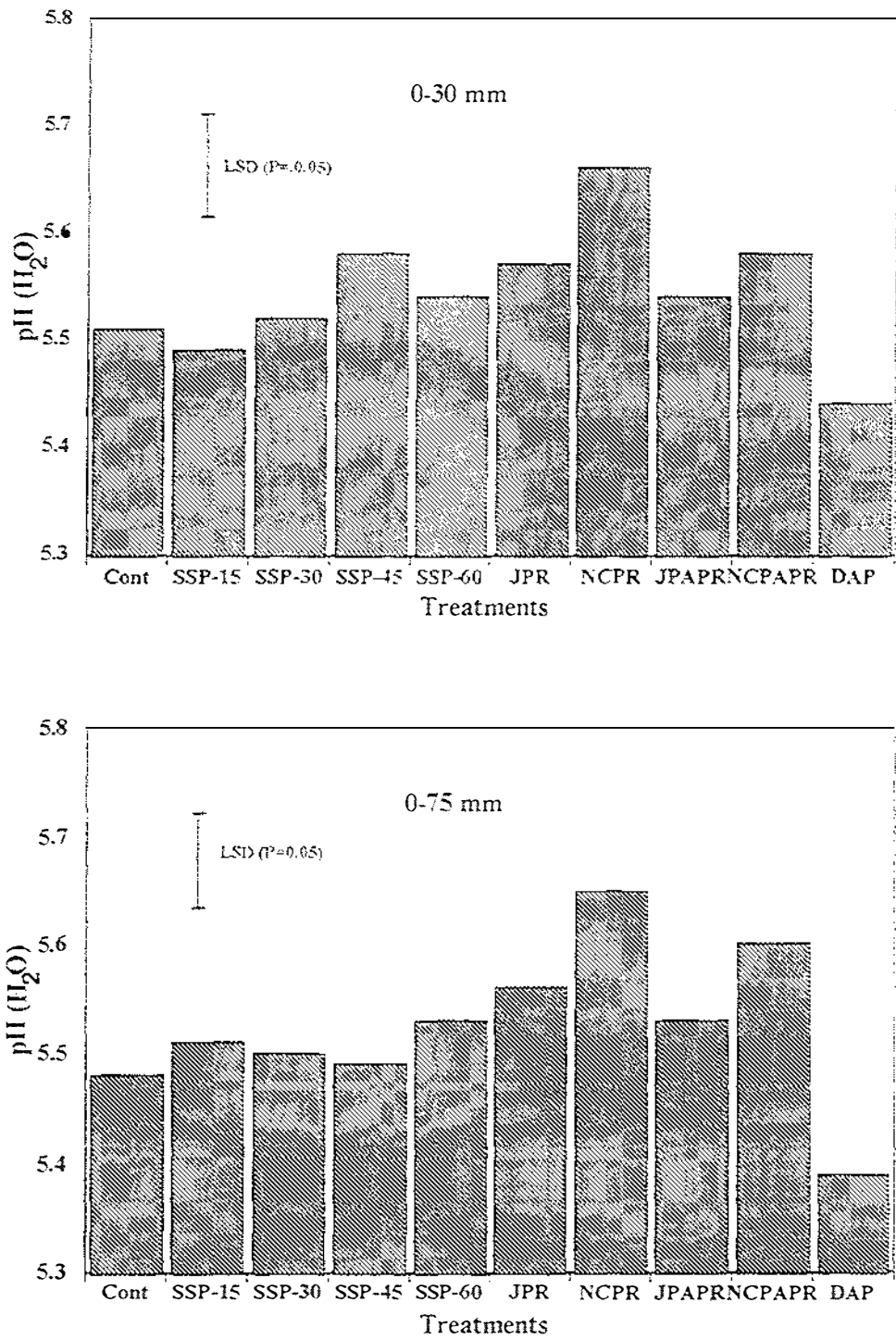
Fig 3.1. Effect of P fertiliser application on soil pH (H_2O) at 0-30 mm and 0-75 mm soil depths.
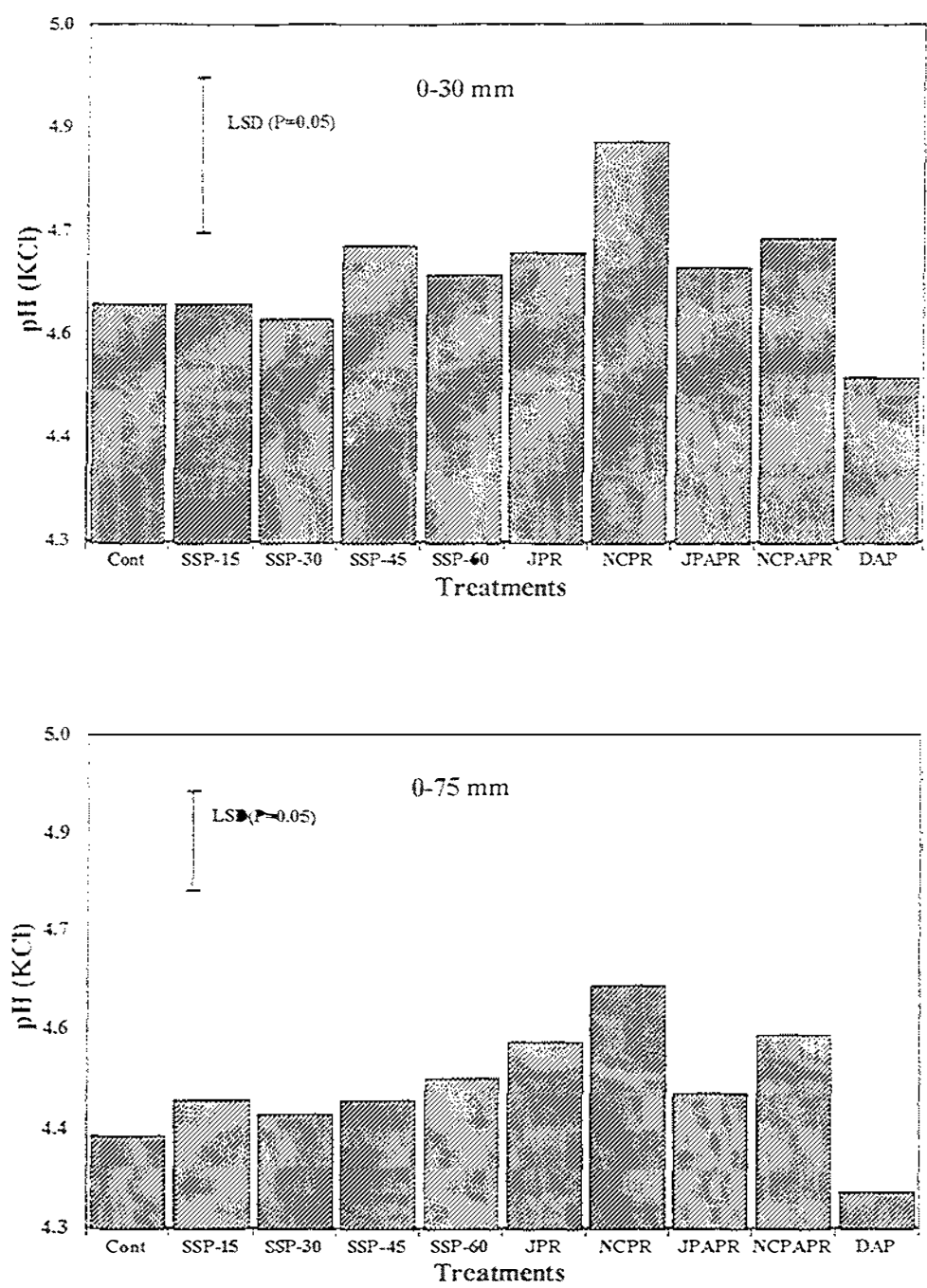
Fig 3.2. Effect of P fertiliser application on soil pH (KCl) at 0-30 mm and 0-75 mm soil depths.

At both depths, the NCPR treatment had significantly higher pH in water and KCl than control and DAP treatments. The Jordan PR (JPR) and NCPAPR treatments had significantly higher pH (KCl) than the control in the 0-75 mm depth only. Superphosphate had no significant effect on soil pH relative to the control at either soil depth. In general the effect of fertiliser addition on pH increase relative to the control was in the order NCPR>NCPAPR>JPR. The greater effect of NCPR than Jordan PR on soil pH was probably due to the former's higher reactivity and carbonate content (NCPR has a carbonate content equivalent to 12 % $CaCO_3$ and Jordan PR has 8% $CaCO_3$; Syers et al., 1986). The differences in pH between the control plots and those receiving RPR or PAPR were however small, not more than 0.22 pH units. Hammond (1979) also reported that the effect of phosphate rock on soil pH varied from no effect to a slight increase in pH of 0.2 to 0.4 units, depending on the rate of P added and the reactivity of the phosphate rock . In a glasshouse study with an Oxisol from Colombia, incubated for 90 days, he observed a soil pH increase from 4.63 when no P was added to 4.97 when 400 mg P kg^{-1} of Sechura phosphate rock was added. The less reactive Pesca rock and TSP appeared to have no effect on soil pH.

In contrast however, a phosphate rock that contains a significant amount of free carbonates (calcite and dolomite) has been shown to have a significant effect on soil pH. In an incubation study with acid soil under flooded conditions, Chien (1977) found that the pH in the soil solution equilibrated with Huila rock, which contained 10 % free carbonates, increased from 4.8 to 6.2 in 1 week, unlike the pH of soil equlibrated with other rocks, including NCPR, which rose from 4.8 to a maximum of only 5.1.

The DAP treatment produced the lowest soil pH. The difference in soil pH in water between control and DAP treatment was statistically significant in the 0-75 mm depth. The lower soil pH in the DAP treated plots is probably due to the release of protons from the nitrification of the ammonium ions in DAP.

3.3.2 Exchangeable acidity

Exchangeable acidity was lowest for the NCPR treatment, as expected from the effects of this treatment on soil pH, but it was not statistically different from that of the control treatment (Fig 3.3). The DAP treatment had significantly higher exchangeable acidity than the control treatment at both depths due to its lower soil pH.

3.3.3 Calculation of rate of soil acidification

The buffering capacity of the soil (0-75 mm) calculated from the buffer curve was 44.5 kmol H^+ ha^{-1} pH $unit^{-1}$. The average rate of soil acidification in the control plots, calculated (for two periods, 1981-1985 and 1985-1992) using this buffering capacity value and pH values of 5.85, 5.70 and 5.48 in the years 1981, 1985 and 1992 respectively was 1.54 kmol H^+ ha^{-1} yr^{-1} (Appendix 1). Similarly, the rates of acidification in the NCPR, SSP (30) and DAP treatments were calculated to be 0.32, 1.27 and 1.97 kmol H^+ ha^{-1} yr^{-1} respectively (Appendix 1). At these rates of acidification the approximate times for the control, NCPR, SSP (30) and DAP plots to reach a pH (H_2O) of 5.00 in the 0-75 mm soil depth would be 15, 91, 18 and 9 years respectively (Appendix 2). This suggests that use of reactive phosphate rocks might markedly slow down the rate of soil acidification. This calculation suggests that the acid consumption by NCPR in the 0-75 mm soil depth is 1.54 minus 0.32 or 1.22 kmol H^+ ha^{-1} yr^{-1}.

pH measurements made on samples of soil below 75 mm showed that the pH (H_2O) values of the NCPR-treated plots were higher than the control plots even below 75 mm, though the difference was not statistically significant (Fig. 3.4). A calculation similar to the one used for the 0-75 mm soil depth using appropriate measured bulk densities but assuming the same buffering capacity as for the 0-75 mm depth showed that the acid consumption by NCPR at the soil depth of 75 to 200 mm is 0.66 kmol H^+ ha^{-1} yr^{-1}. Therefore the total acid consumption by NCPR to a soil depth of 0-200 mm is calculated
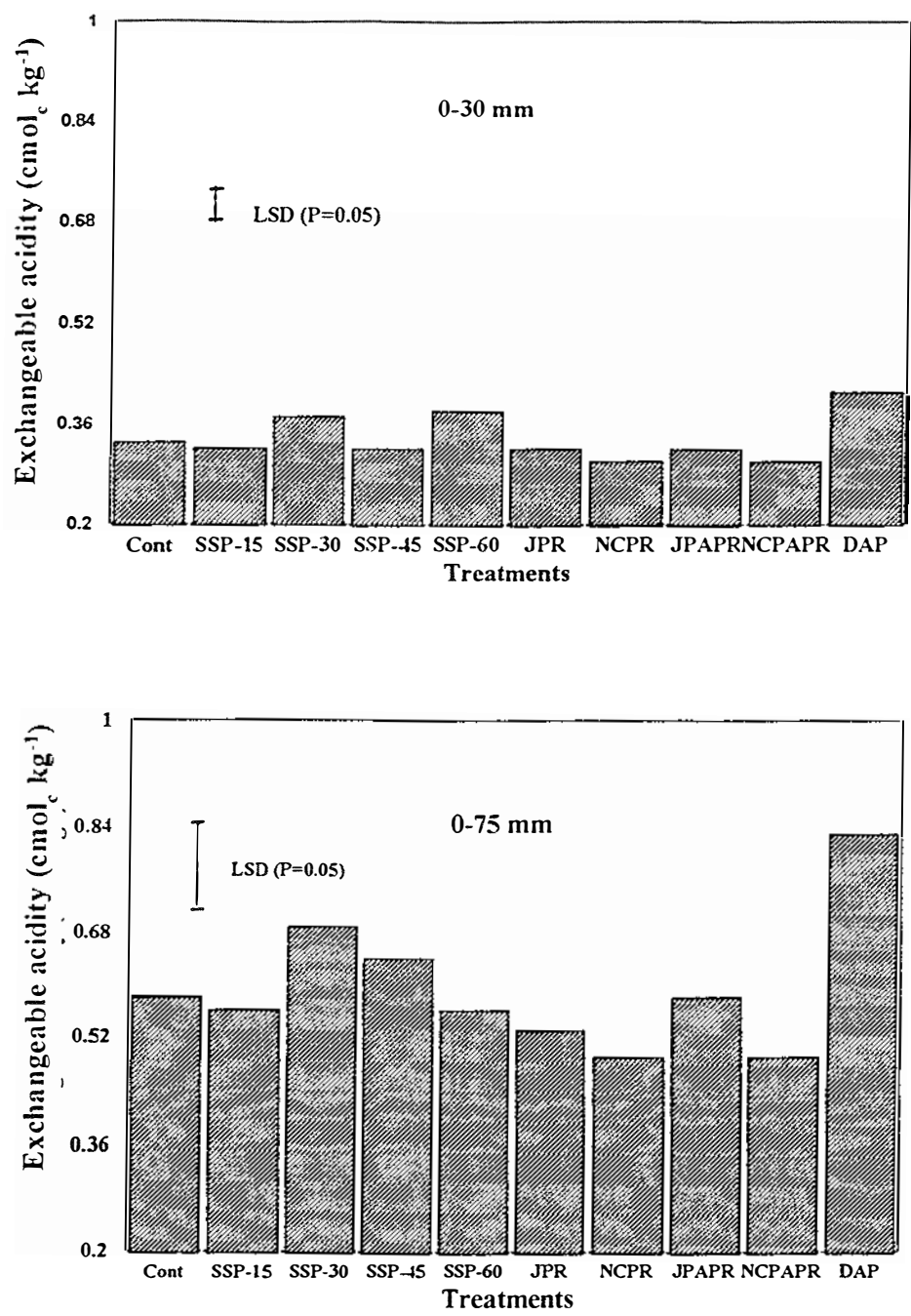
Fig 3.3. Effect of P fertiliser application on exchangeable acidity at 0-30 mm and 0-75 mm soil depths.
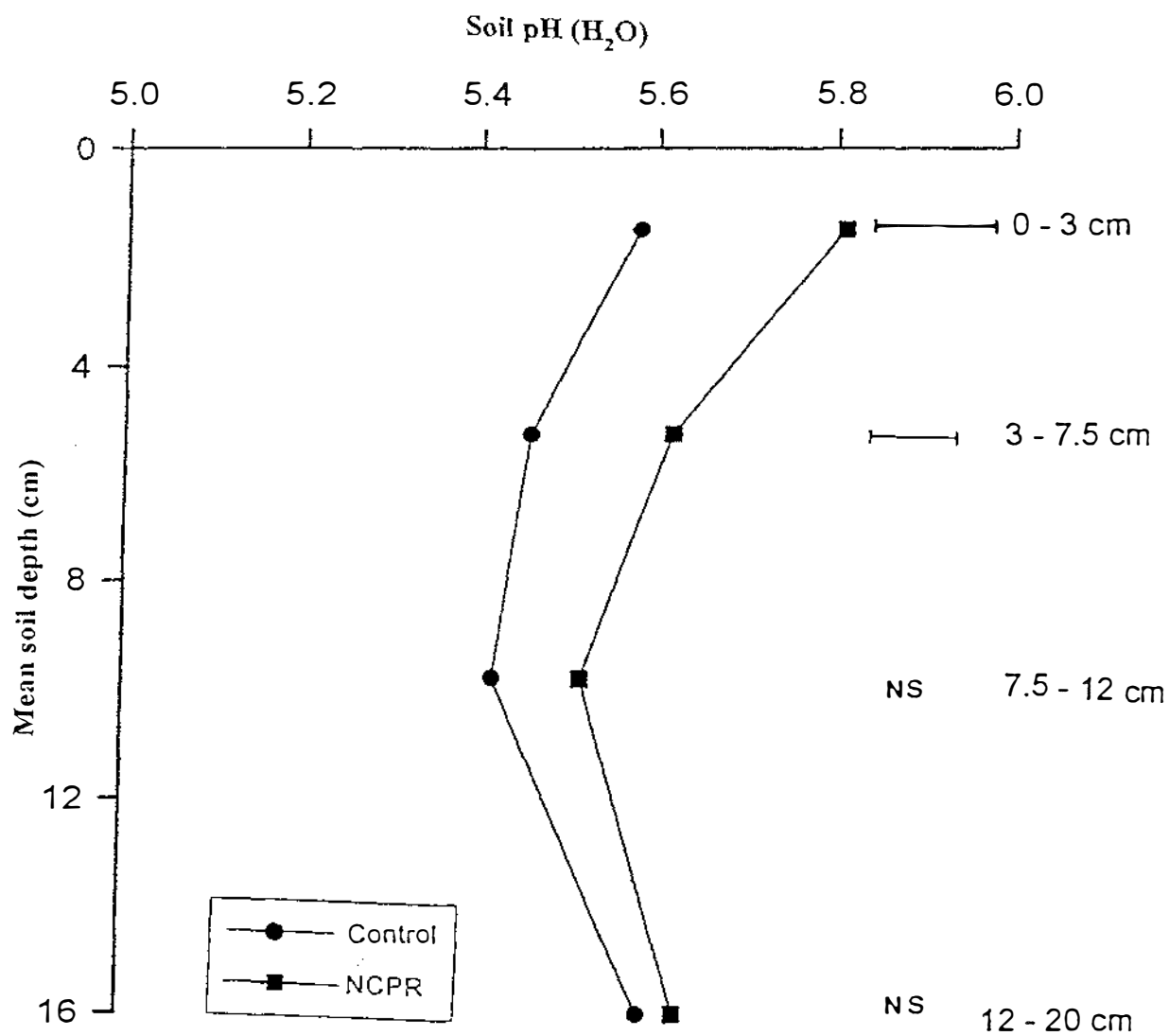
Fig 3.4. Effect of NCPR on pH (H₂O) at various soil depths. Horizontal bars indicate LSD at p=0.05 between treatment mean.

as 1.88 kmol H^+ ha^{-1} yr^{-1}. This may be a slight overestimate of the true value because the buffering capacity at lower depths is expected to be less than that in the surface layer due to lower organic matter content at lower depths.

3.3.4 Calculation of acid consumption based on RPR dissolution rate

The NCPR had been applied at the rate of 227.3 kg ha^{-1} yr^{-1} from 1985 to 1991 (a total of 1591 kg ha^{-1}). The NCPR dissolution analysis showed that 68 % of this amount dissolved in the 0-75 mm soil depth. This amounts to a dissolution of 1082 kg NCPR ha^{-1} (227.3×7×0.68). Dissolution of this amount of NCPR would theoretically have consumed 11.8 kmol H^+ ha^{-1} or 1.69 kmol H^+ ha^{-1} yr^{-1} (Appendix 3). This is similar to the value calculated in the previous section based on the difference in soil pH values of NCPR and control plots. This good agreement between the theoretical acid consumption value and the observed value, indicates that the theoretical value of 54.6 % potential lime ($CaCO_3$) equivalent (Appendix 3) used for NCPR explains very well the observed pH increase in the NCPR- treated soils relative to the untreated soils.

3.3.5 Comparison of the liming effect of RPR with long-term lime trials

Phosphate rock dissolution analysis showed that 68 % of all NCPR added to the soil was dissolved in the seven year period. Thus after seven years of annual application at the rate of 30 kg P ha^{-1} yr^{-1} , the net effect of the dissolved NCPR and the carbonate in NCPR, assuming complete dissolution of the latter, would be equivalent to 652 kg $CaCO_3$ ha^{-1} (Appendix 4). Thus at the rate of 30 kg P ha^{-1} yr^{-1}, a difference in pH between SSP and NCPR treatments equal to the effect of 652 kg $CaCO_3$ ha^{-1} would be predicted. Edmeades et al. (1984) reported an average increase of 0.42 pH units following the application of 2.5 t lime ha^{-1} in 27 field trials on silt loams. On this basis, and assuming 90 % $CaCO_3$ equivalent in the lime used in those trials, the predicted pH differences between SSP and NCPR after seven years of annual applications at the rate of 30 kg P ha^{-1} yr^{-1} is 0.12 pH units. The observed difference of 0.15 pH units between SSP and

NCPR at the rate of 30 kg P ha^{-1} yr^{-1} in seven years is thus close to the predicted value. These calculations confirm that relative to SSP, NCPR has a liming effect, which is probably due to proton consumption during the dissolution of P in the apatite mineral with a small contribution also being made by its free carbonate content.

3.3.6 Soil Al

As expected from the pH values (Figs. 3.1 and 3.2), KCl-exchangeable Al was higher in the 0-75 mm depth than in the 0-30 mm depth (Fig 3.5, Table 3.3). In the 0-30 mm depth, only NCPR-treated soil had significantly lower KCl-Al than the control. In the 0-75 mm depth, both the phosphate rocks (NCPR and JPR) and their partially-acidulated products (NCPAPR and JPAPR) had significantly lower KCl-Al than the control - the extent of reduction in these values was in the order, NCPR>JPR>NCPAPR>JPAPR. CaCl$_2$-extractable Al was significantly reduced only by the NCPR treatment. Loganathan et al. (1995) and Wright et al. (1991) have also reported that application of NCPR significantly reduced KCl-Al and 0.02 M CaCl$_2$-extractable Al in laboratory incubation studies.

In contrast to the NCPR treatment, the DAP treatment had significantly higher CaCl$_2$-extractable Al than the control. This was expected from the lower pH values of the DAP treatments compared to the control treatment.

The 0.02 M CaCl$_2$-extractable Al (1.08 to 2.64 mg kg^{-1}) and exchangeable (KCl-Al) Al (0.09 to 0.25 cmol$_c$ kg^{-1}) in the samples (Fig 3.6, Table 3.3) were generally lower than the critical levels of 3-5 mg kg^{-1} (Edmeades et al., 1983; Hume et al., 1988) and 1-2 cmol$_c$ kg^{-1} (Edmeades et al., 1983) respectively, reported for Al toxicity in white clover. The 0.02 M CaCl$_2$-extractable Al in DAP-treated soils was however very close to the critical concentration.
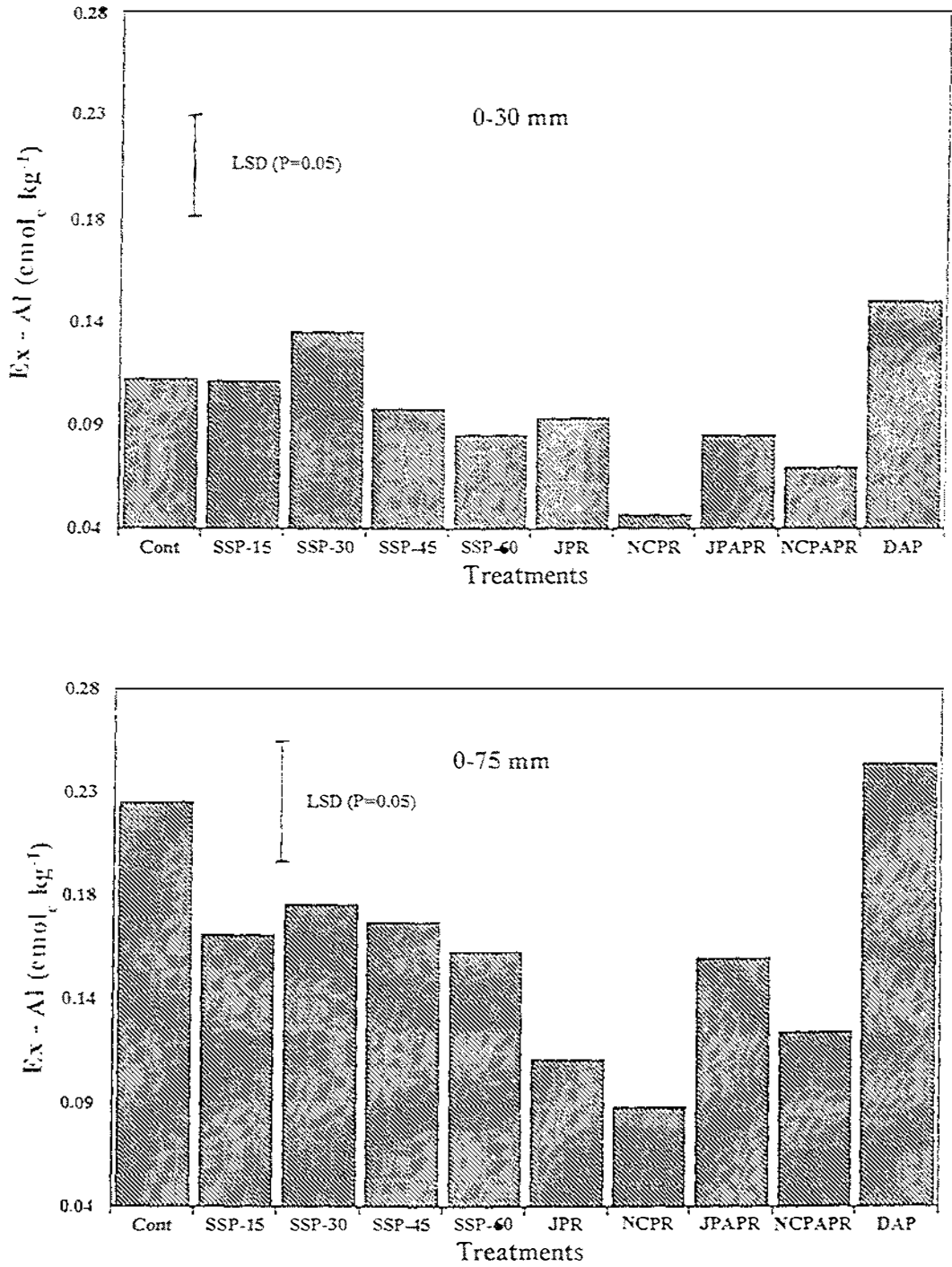
Fig 3.5. Effect of P fertiliser application on KCl-exchangeable Al at 0-30 mm and 0-75 mm soil depths.

Table 3.3. Effect of P fertilisers on forms of soil Al, exchangeable Ca and Ca saturation

	KCl-Al (cmol$_c$ kg^{-1})	CuCl$_2$-Al (cmol$_c$ kg^{-1})	Exch. Ca (cmol$_c$ kg^{-1})	ECEC[a] (cmol$_c$ kg^{-1})	Ca saturation[b] (%)	0.02 M CaCl$_2$-Al (mg kg^{-1})
0-30 mm soil depth						
Control	0.11	3.31	7.87	10.6	74.2	
SSP-15	0.11	3.43	8.54	11.0	77.7	
SSP-30	0.13	3.53	8.42	10.9	77.7	
SSP-45	0.10	3.35	8.71	11.2	77.6	
SSP-60	0.08	3.26	8.93	11.3	79.1	
JPR	0.09	3.02	8.43	10.7	78.1	
NCPR	0.05	2.88	8.94	11.4	78.8	
JPAPR	0.08	3.34	8.59	11.1	77.2	
NCPAPR	0.07	3.01	8.87	11.4	78.2	
DAP	0.15	4.05	7.96	10.4	76.2	
LSD (p=0.05)	0.05	0.55	0.77	NS	2.5	
0-75 mm soil depth						
Control	0.23	3.31	8.19	10.6	77.2	1.69
SSP-15	0.17	3.76	9.25	11.8	78.4	1.78
SSP-30	0.18	3.92	8.95	11.2	79.8	1.84
SSP-45	0.17	4.07	9.2	11.7	78.9	2.04
SSP-60	0.16	3.39	9.24	11.5	80.4	1.81
JPR	0.11	3.33	8.89	11.2	79.7	1.38
NCPR	0.09	3.28	9.54	12.0	79.8	1.08
JPAPR	0.15	3.54	8.71	11.1	78.8	1.46
NCPAPR	0.12	3.48	9.41	11.8	79.9	1.45
DAP	0.25	4.32	8.49	10.8	78.3	2.64
LSD (p=0.05)	0.06	0.52	0.81	NS	2.0	0.46

[a] Sum of exchangeable bases (Na, K, Ca, Mg) + KCl-Al

[b] (Exchangeable Ca / ECEC)*100

NS - not significant
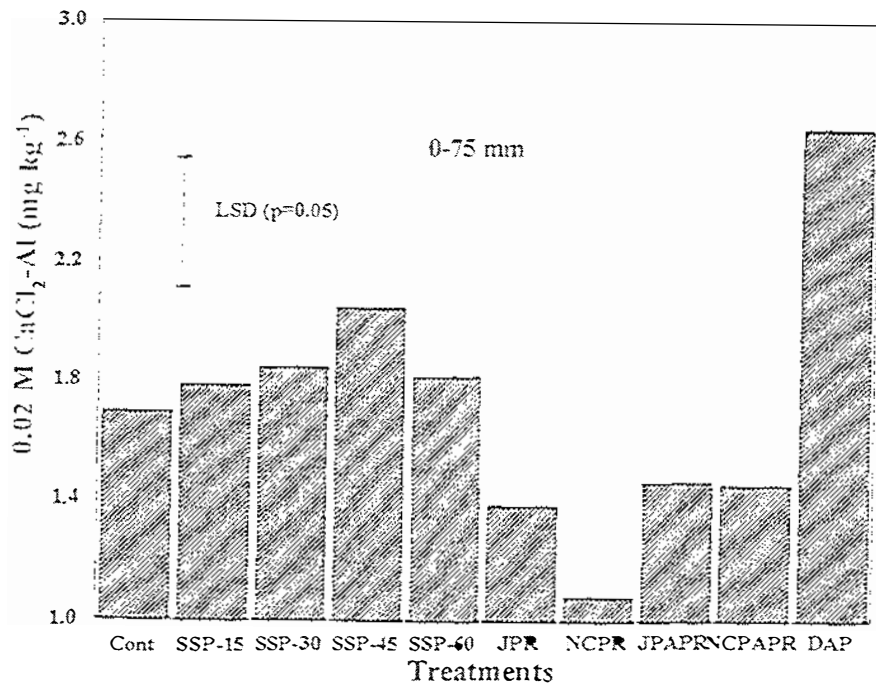
Fig 3.6. Effect of P fertiliser application on 0.02 M CaCl₂-extractable Al at 0-75 mm soil depth.

Both 0.02 M CaCl$_2$-Al and KCl-Al were related to pH (H$_2$O) and pH (KCl) (Figs 3.7 & 3.8). The relationships were similar to those of Edmeades et al. (1983). From these results and those of Edmeades et al. (1983) it could be inferred that in the future, if the pH was to decrease by about 0.2-0.5 units below the current levels, soil Al would be likely to reach toxic levels.

Aluminium extracted by 0.5 M CuCl$_2$ (CuCl$_2$-Al), which is a measure of the organically bound Al + Al in the form of simple hydroxy Al polymers + exchangeable Al + solution Al (Juo and Kamprath, 1979), was 10 to 50 times higher than exchangeable Al values (Table 3.3). It was not affected by either phosphate rock or PAPR treatments. The DAP treatment, however, increased this form of Al. Increasing rates of superphosphate increased CuCl$_2$-Al up to 45 kg P ha^{-1} followed by a sharp decline in CuCl$_2$-Al at 60 kg P ha^{-1}. A possible reason for this could be that at the lower rates of superphosphate, the increased supply of Ca from the fertiliser and Cu in the extractant displaced increased amounts of Al from the organic matter and hydroxy Al polymers, but at the highest rate of superphosphate, the phosphate concentration became high enough to precipitate the displaced Al as aluminium phosphate, thus reducing Al in solution.

3.3.7 Soil Ca

Although the phosphate fertilisers such as NCPAPR and high rates of SSP affected the soil pH only slightly, they had a significant effect on soil exchangeable Ca (Table 3.3). Calcium is the dominant exchangeable cation in the soils of the experimental area and 74 to 80% of the effective cation exchange capacity (ECEC) is exchangeable Ca. Plots receiving SSP at high rates, and plots receiving NCPR and NCPAPR had significantly higher exchangeable Ca and Ca saturation than control plots at both soil depths due to Ca input from the fertilisers. Loganathan et al. (1995) and Wright et al. (1991) also reported significant increases in exchangeable Ca due to NCPR application in laboratory incubation trials. The effects of JPR and JPAPR on exchangeable Ca were not significant.

(a)

$Y = exp(-3.70 * X) * 9.2E+007$

$(R^2 = 0.74)$

KCl-exchangeable Al ($cmol_c kg^{-1}$)

Soil pH (H_2O)

(b)

$Y = exp(-2.34 * X) * 705376$

$(R^2 = 0.76)$

0.02 M $CaCl_2$-extractable Al ($mg kg^{-1}$)
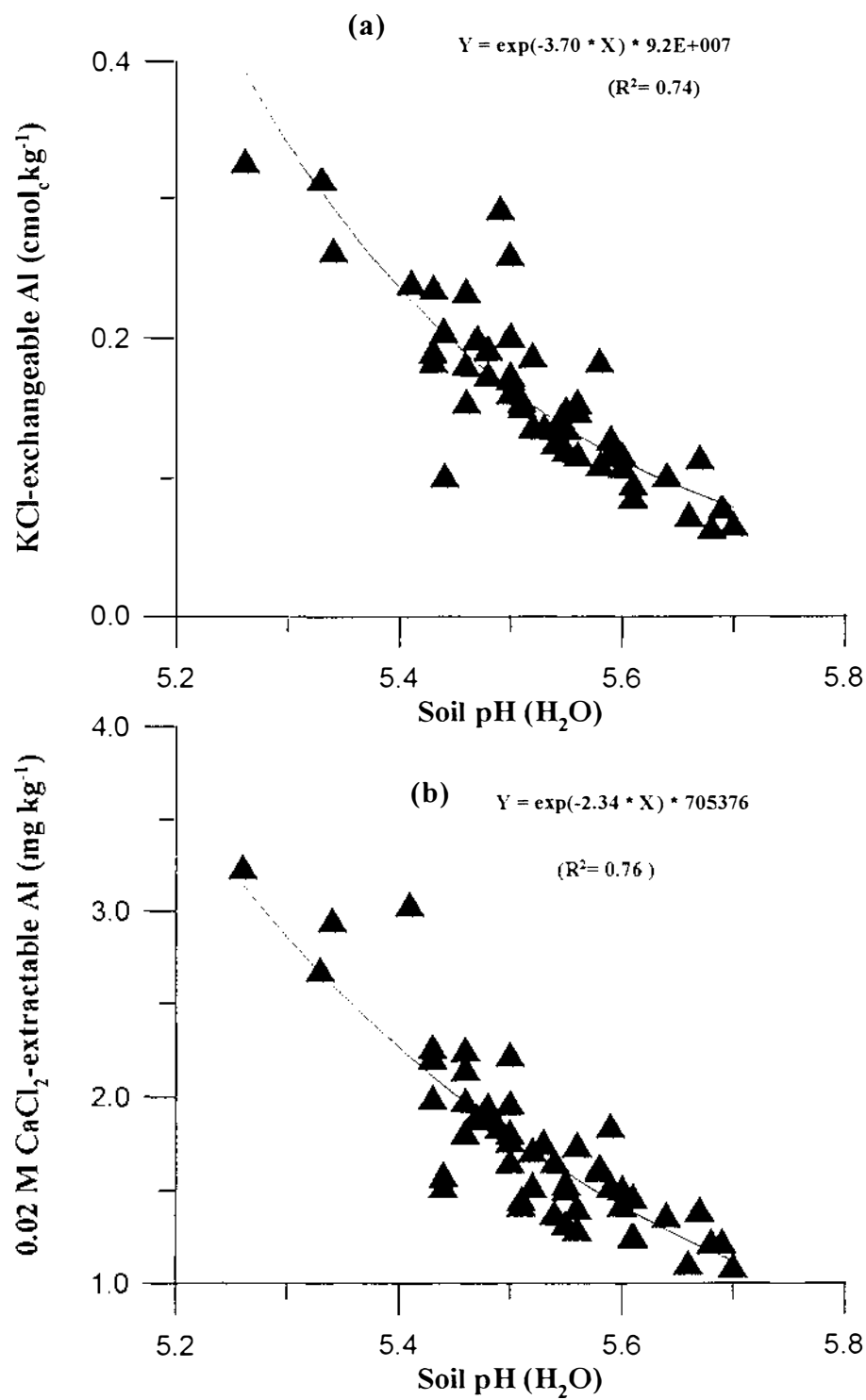
Soil pH (H_2O)

Fig. 3.7. Relationship between pH (H_2O) and (a) KCl-exchangeable Al
(b) $CaCl_2$-extractable Al.
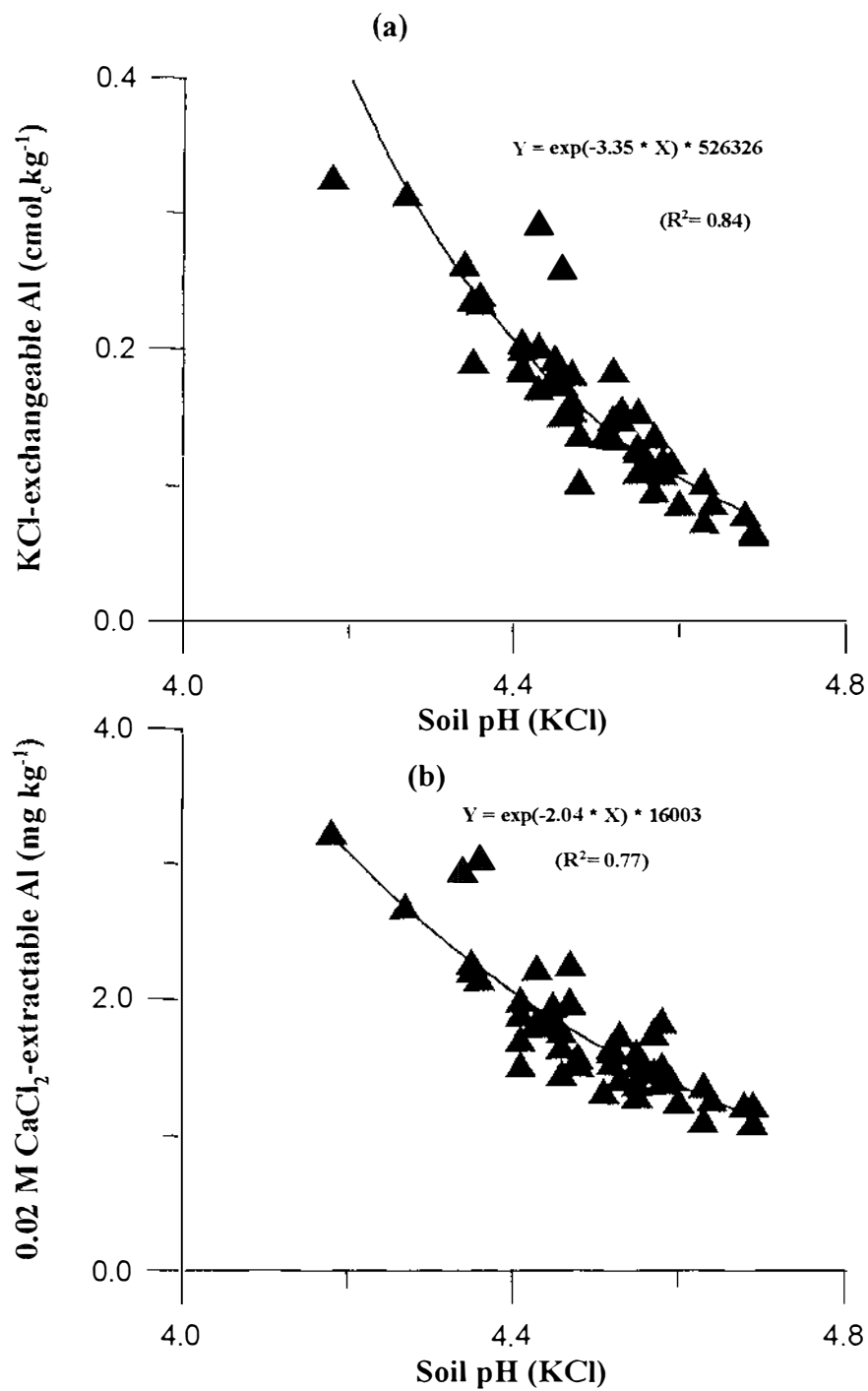
Fig. 3.8. Relationship between soil pH (KCl) and (a) KCl-exchangeable Al (b) CaCl$_2$-extractable Al.

This difference in behaviour of NCPR and JPR is probably due to the higher reactivity and hence greater dissolution of NCPR.

3.3.8 Cost effectiveness of using RPR's compared to SSP

The economic advantage of RPR over SSP depends on price ratios between RPR, SSP, S and lime (including application cost) and on two technical factors: the ratio of S:P required and the rate of RPR dissolution in the soil. For example, allowing for complete dissolution of RPR, the calculated liming value of NCPR is equivalent to 4.1 kg $CaCO_3$ per kg P (Appendix 3). The current cost of lime applied to New Zealand pastures is in the range $ 0.02 to 0.065/kg. Thus the liming value associated with 1 kg P as RPR is $ 0.08-0.27 whereas the cost of 1 kg P in RPR is about $ 1.50. The cost of P in SSP is about $ 2.10 kg/P if no value is attributed to the sulphur content of SSP (Sinclair et al., 1993). Therefore in situations where lime is required, the liming value of RPR would moderately enhance its economic advantage over superphosphate. However, if there is a need for S as well as P, elemental S may have to be applied along with RPR as an alternative to SSP. If the S:P ratio required is the same as that in SSP, the acid produced by oxidation of elemental S in the soil would exactly nullify the liming effect of RPR (Sinclair et al., 1993).

3.4 Conclusions

The present study on a marginally acidic Yellow Grey Earth soil (pH (H_2O) 5.4-5.8) under legume-based pasture indicates that irrespective of the rate or form of phosphate fertiliser used, the soil becomes increasingly acidic with time. However, the rate of acidification varies with the type of fertiliser used. Applications of reactive phosphate rocks such as NCPR increased the soil pH, exchangeable Ca and Ca saturation but significantly lowered exchangeable and soluble Al compared to the control treatment. The JPR and NCPAPR also had similar effects, but the magnitude of the effects was lower than that of NCPR. In contrast to these fertilisers, DAP significantly lowered soil pH,

exchangeable Ca and Ca saturation and increased soluble Al and exchangeable acidity compared to the control treatment. Superphosphate in general had no effect on soil pH and soil Al relative to the control treatment, but increased exchangeable Ca and Ca saturation at higher rates of application.

This study also indicates that of the total NCPR (1591 kg ha^{-1}) applied over the 7 yr study period, 68 % had dissolved, producing a liming effect equivalent to 652 kg of pure lime (CaCO$_3$). The close agreement between (1) the predicted pH values, using field lime trials and observed pH values and (2) the predicted pH values based on NCPR dissolution with observed pH values supports the hypothesis that the liming action of RPR's occurs through the dissolution of both the free CaCO$_3$ and the apatite mineral.

The results suggested that continuous use of certain reactive phosphate rocks can significantly slow down the rate of soil acidification in pastoral soils. However, the economic and agronomic advantage of using RPR depends on price ratios of RPR, SSP, S and lime, application costs, the ratio of S:P required and the rate of RPR dissolution in soils.

Chapter 4

Changes in soil solution composition and aluminium speciation under legume-based pastures in response to long-term phosphate fertiliser application[1]

4.1 Introduction

In New Zealand, most farmland is sown in permanent perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.) based pasture. Pasture production is maintained by the surface application of lime and / or fertiliser, particularly P. Most of these New Zealand grassland soils are responsive to liming up to a soil pH (H_2O) of 5.8-6.0 (Edmeades et al., 1984). However, the reasons for such lime responses on New Zealand soils are not yet fully understood. Some lime-related factors such as Mo availability (Edmeades et al., 1984) and Mn toxicity (Smith and Edmeades, 1983) have been eliminated as potential mechanisms for lime responses in many situations.

In a comprehensive review of data obtained from a national series of field trials on lime, that covered all the major soil types in New Zealand, Edmeades and Wheeler (1985) concluded that Al toxicity could be a factor limiting pasture production on a number of North Island hill country soils and on upland soils in the South Island. Therefore, an understanding of the soil solution Al chemistry of the soils on which these pastures are grown could assist in understanding the responses of pastures to lime or fertiliser.

To date, the major means of improving crop performance on acid soils have been liming and the use of Al-tolerant germplasm, although in some instances organic matter and gypsum have been found to be successful in ameliorating Al toxicity. While use of Al-tolerant germplasm provides an ideal solution to the soil acidity problem, locally adapted, Al-tolerant cultivars for a number of crop species are not yet available. This presents a serious limitation to crop production in regions where application and incorporation of lime is prohibitively expensive. Recent work has suggested other possible means such as

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1 V. Manoharan et al. 1996. Aust. J. Soil Res. 34:985-998.

application of high rates of reactive phosphate rock (Easterwood et al., 1989; Wright et al., 1991) to combat soil acidity and Al toxicity. Recent reports (MacLean et al., 1992; Rengel, 1992) have also indicated that F and Ca may be capable of alleviating the toxic effects of Al.

Diagnosis of soil acidity and Al toxicity problems using pH measurements alone has been imprecise (Edmeades et al., 1984), and consequently there has been a move towards using direct measures of potentially toxic Al in soil solution (Carr et al., 1991). Many investigators have reported that the calculated activity of Al^{3+} in soil solution is the single best indicator of plant toxicity (Pavan and Bingham, 1982), but evidence also exists for the toxicity of the monomeric hydroxyl cations, $Al(OH)^{2+}$ and $Al(OH)_2^{+}$ (Alva et al., 1986b c).

In contrast, studies have shown that some Al species such as $Al(SO_4)^{+}$ (Kinraide and Parker, 1987a), Al-F complexes (Cameron et al., 1986; MacLean et al., 1992) and Al-organo complexes (Hue et al., 1986) are non-toxic to plants. Alva et al. (1988) suggested that the beneficial effects of phosphogypsum could be attributed, at least in part to ion pairing of Al with F and SO_4 thus alleviating Al toxicity. Phosphate fertilisers which contain considerable amounts of F and SO_4 and have varying proton neutralising capacities may cause similar effects after long-term application. Little published data, however, is available on the Al species present in soil solutions under varying P fertiliser management practices although Wright et al. (1991) have shown that in a short-term incubation study the application of NCPR shifted the Al speciation from toxic to non-toxic forms.

In Chapter 3 it was reported that the long-term application of P fertilisers changed exchangeable Al, soluble Al and pH significantly in pasture soils, and that the changes depended on the type of P fertiliser. The objective of this study was to examine the effects of long-term application of six types of phosphate fertilisers on soil solution composition and Al speciation under white clover-based pasture.

4.2 Materials and Methods

4.2.1 Soil sample collection

Soil samples from the field trial described in Chapter 3 were collected in August 1993 by taking a composite of 20 cores per plot using a 25 mm diameter corer. Two sets of samples, at depths 0-30 mm and 30-75 mm were collected from each plot. From each sample about 250 g of moist soil was used for soil solution analysis and the remainder of the sample was air dried. Air dried samples, ground to pass through a 2 mm sieve, were used for chemical analysis. Details of the chemical analyses are described in Chapter 3.

4.2.2 Soil solution analysis

Soil solutions were removed from the field moist soil by centrifugation at 10,000 rpm (12,000 RCF) in a refrigerated centrifuge at 5°C (Elkhatib et al., 1987). Soil solution pH and electrical conductivity (EC) were measured immediately using a portion of the soil solution and the rest of the solution was filtered through syringes fitted with 0.22 μm millipore filters. The ionic strength of the soil solution was calculated from the EC using the equation, ionic strength (mol L^{-1}) = 0.013 * EC (dS m^{-1}) (Lindsay, 1979). Total soil solution concentrations of Na, K, Ca, Mg were measured by atomic absorption-emission spectroscopy. Anions (Cl, SO_4, NO_3) concentrations were measured by ion chromatography and PO_4 concentration was measured by the malachite green method (Motomizu et al., 1983).

The quantities of soil solutions available from the 0-30 mm soil depth were not sufficient for the PO_4 analysis. Therefore only the solutions from the 30-75 mm depth were analysed for PO_4. Except for high rates of SSP (SSP-30, SSP-45, SSP-60) and DAP treatments all other treatments had PO_4 concentrations below the detection limit.

Free and total F concentrations were measured with a F-ion selective electrode. Free F was measured directly in the soil solution while total ionic strength adjustment buffer (TISAB) was used for the measurement of total solution F (Adriano and Doner, 1982).

4.2.3 Soil solution Al analysis

Labile (mainly inorganic) monomeric and non-labile (mainly organic) monomeric Al were determined according to methods outlined by Driscoll (1984). Organic-monomeric Al was separated by passing an aliquot of soil solution through a column of strongly acidic cation exchange resin (Amberlite IR-120). This procedure assumes that inorganic forms of Al are decomplexed and Al^{3+} is retained on the cation-exchange column, while strongly bound organic complexes pass through.

The cation exchange column was prepared using a 60 mm length glass tube having a diameter of 3 mm. The ion-exchange medium was prepared by mixing the Na^+ form of the resin with a small amount of the H^+ form of the resin and adjusting the proportions of the two resins until the resin-solution pH was close to the pH of the solutions being analysed. This adjustment minimised the changes in the pH of the samples when processed through the exchange column. A peristaltic pump was used to maintain the flow rate constant while the solution passed through the cation exchange column.

The concentrations of Al in the soil solution before and after passing through the column were measured by the pyrocatecol violet (PCV) method (Dougan and Wilson, 1974). A four minute reaction time was used for the determination of total monomeric Al (Seip et al., 1984). Total (acid-reactive) Al was measured after acidifying an aliquot of the sample to pH 1 for one hour followed by addition of the reducing reagents, PCV and buffer (Driscoll, 1984). Absorbance was measured after one hour.

Aluminium speciation was calculated using a computer equilibrium programme $MINEQL^+$ (Schecher and McAvoy, 1991) assuming that all the dissolved species are in equilibrium.

Activity coefficients were calculated using the Davies equation, as the ionic strengths were well below 0.1 M (Stumm and Morgan, 1981).

$$\log \gamma_i = -0.509\, Z_i^2 \left(u^{1/2} / (1+u^{1/2}) \right) - 0.3\, u.$$

where γ_i is the activity coefficient, Z_i is the valency of the ion concerned and u is the ionic strength.

4.2.4 Statistical analysis

Statistical Analysis System (SAS) programmes were used for all statistical analyses.

4.3 Results and Discussion

4.3.1 Soil chemical properties

In general the effects of P fertilisers on soil chemical properties were similar to those reported in Chapter 3. Soil pH was significantly increased at 0-30 and 30-75 mm depths by the application of NCPR compared with the control (Fig. 4.1a). In contrast the DAP treatment significantly reduced the soil pH at the 30-75 mm depth. The SSP treatment had no significant effect on soil pH relative to the control at either depth but had a significantly lower pH than the NCPR treatment. In general the effect of fertiliser addition on pH increase was in the order NCPR > NCPAPR >JPR. Soil pH values were lower in the 30-75 mm than in the 0-30 mm depth irrespective of treatments. Reasons for these trends are discussed in Chapter 3.

Exchangeable acidity was lowest for the NCPR and NCPAPR treatments at both depths but the difference between these treatments and control was statistically significant only at the 30-75 mm depth (Table 4.1). The DAP treatment had significantly increased exchangeable acidity in the 30-75 mm depth only. The concentrations of 0.02 M $CaCl_2$-
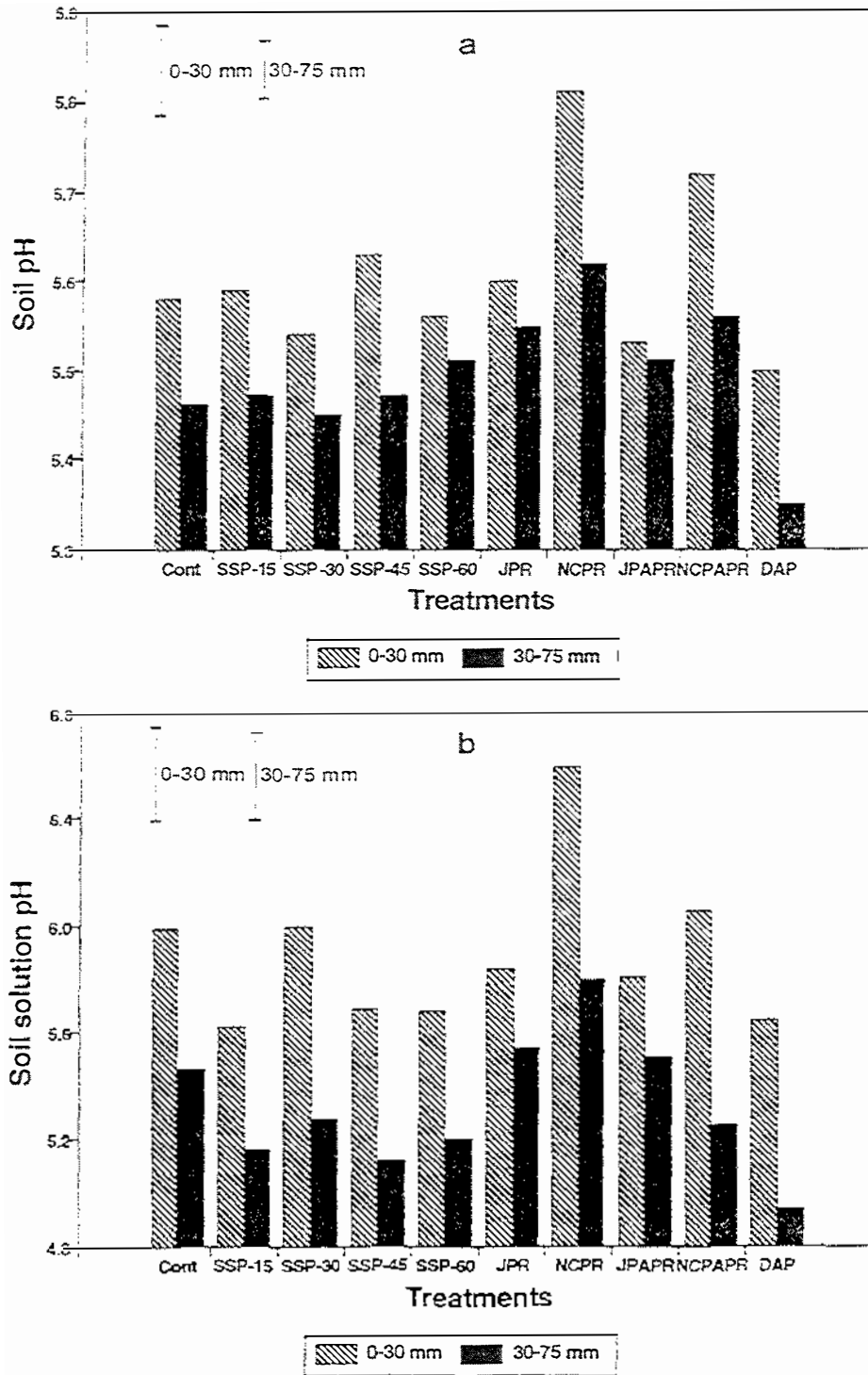
Fig 4.1. Effect of P fertilisers on (a) soil pH (1:2.5 soil to water ratio), and (b) solution pH at 0-30 and 30-75 mm soil depths. Vertical bars represent l.s.d. values at p=0.05.

Table 4.1. Effect of P fertiliser application on soil chemical properties.

Treatment	Exchange-able Ca (cmol$_c$ kg^{-1})	Exchange acidity (cmol$_c$ kg^{-1})	0.02M CaCl$_2$-Al (mg kg^{-1})	Exchange-able Ca (cmol$_c$ kg^{-1})	Exchange acidity (cmol$_c$ kg^{-1})	0.02M CaCl$_2$-Al (mg kg^{-1})
		Soil Depth (0-30 mm)			Soil Depth (30-75 mm)	
Cont	8.2	0.41	0.75	6.6	0.64	1.77
SSP-15	8.6	0.38	0.86	6.7	0.70	1.66
SSP-30	8.6	0.42	0.85	7.0	0.63	1.82
SSP-45	8.8	0.42	0.98	6.8	0.55	1.97
SSP-60	8.9	0.43	1.00	6.9	0.68	2.03
JPR	8.2	0.39	0.81	6.9	0.54	1.79
NCPR	9.3	0.28	0.44	7.4	0.45	1.34
JPAPR	8.5	0.40	0.76	6.6	0.62	1.56
NCPAPR	9.2	0.33	0.83	7.2	0.41	1.63
DAP	7.8	0.45	1.39	6.0	0.81	2.48
LSD (P=0.05)	0.9	0.09	0.29	0.7	0.15	0.38

extractable Al was greater in the subsurface soil than in the surface soil (Table 4.1), as expected from the pH values. The concentration of this form of Al was significantly reduced only by the NCPR treatment. In contrast, the DAP treatment had significantly higher concentrations of Al than the control soil. In all samples 0.02 M $CaCl_2$-Al levels were lower than the critical levels of 3-5 mg kg^{-1} reported for Al toxicity in white clover (Edmeades et al., 1983; Hume et al., 1988).

Plots receiving NCPR, NCPAPR and high rates of SSP had significantly higher concentrations of exchangeable Ca than the control at both depths (Table 4.1), probably because of higher soluble Ca input from these fertilisers. The effects of JPR and JPAPR on exchangeable Ca concentrations were not significant.

4.3.2 Soil solution composition

Soil solution pH varied with treatment in a similar manner to that of soil pH (Fig. 4.1a&b). Like soil pH, solution pH was higher in the surface soil than in the subsurface soil. On average the surface soil solution pH was 0.6 unit higher than the subsurface soil solution pH. At both depths, only the high rates of SSP (SSP-45 and SSP-60) significantly increased the soil solution Ca concentration compared with the control (Table 4.2). The Ca liberated into the soil solution, was balanced largely by SO_4.

Although NCPR significantly increased the exchangeable Ca (Table 4.1), soil solution Ca concentration was not increased significantly compared with the control (Table 4.2). This is presumably due to an increase in cation exchange capacity associated with the increase in pH observed on the NCPR-treated plots. Increased cation exchange capacity may have increased Ca adsorption by soil and therefore reduced soil solution Ca concentration.

Soil solution SO_4 concentration ranged from 302-956 and 400-842 μM in the surface and subsurface soils respectively. Although S in the form of gypsum had been applied annually to all plots to ensure equivalent S addition to the SSP-60 treatment, only the higher rates

Table 4.2. Soil solution composition as affected by P fertiliser application.

Soil Depth (0-30 mm)

Treatment	SO$_4$	[a]F(tot)	NO$_3$	Cl	Na	K	Mg	Ca	[b]Al(tm)	[c]Al(tot)	[d]Al(org)
					μmol L^{-1}						%
Cont	492	2.7	220	2284	762	586	236	1006	1.6	3.3	87.5
SSP-15	662	4.9	292	1588	622	298	222	1296	2.2	3.5	72.7
SSP-30	636	11.9	266	1866	1010	372	260	1194	2.1	2.6	80.0
SSP-45	822	16.6	488	1984	822	614	272	1418	3.5	3.5	60.0
SSP-60	956	23.5	312	1802	818	566	304	1456	4.8	5.1	47.9
JPR	404	6.2	164	1714	684	360	196	962	2.0	2.9	70.0
NCPR	574	17.2	216	1686	780	614	230	1122	1.5	2.1	86.7
JPAPR	466	5.9	132	2084	766	442	220	1050	2.0	2.7	80.0
NCPAPR	302	11.0	156	1536	716	416	176	824	2.0	2.6	85.0
DAP	412	9.9	294	2054	824	586	240	1094	3.7	5.5	64.9
LSD (P=0.05)	256	2.9	ns	ns	ns	ns	ns	358	1.7	1.2	-

Table 4.2. (continued

Soil Depth (30-75 mm)

Treatment	SO$_4$	[a]F(tot)	NO$_3$	Cl	Na	K	Mg	Ca	[b]Al(tm)	[c]Al(tot)	[d]Al(org)
					μmol L^{-1}						%
Cont	410	3.2	386	1550	558	164	198	964	2.4	3.1	50.0
SSP-15	507	6.7	816	1494	590	112	270	1042	4.0	4.9	47.5
SSP-30	528	10.2	382	1414	536	130	204	1104	5.1	6.3	39.2
SSP-45	762	19.3	936	2071	674	202	344	1596	8.9	11.2	33.0
SSP-60	842	25.6	652	1630	638	180	336	1748	12.2	15.9	26.2
JPR	413	7.3	418	1417	552	110	180	1044	2.7	3.2	55.6
NCPR	502	12.3	498	1760	692	176	194	1084	3.4	3.8	52.9
JPAPR	400	5.6	348	1666	584	114	196	1048	2.5	3.1	56.0
NCPAPR	402	9.4	523	1430	468	132	200	1050	4.5	5.8	42.2
DAP	424	11.2	842	2390	580	286	314	1426	11.7	16.4	23.9
LSD (P=0.05)	143	4.7	ns	ns	ns	ns	ns	482	3.4	4.1	-

[a]F (tot) - total soluble F
[b]Al(tm) - total monomeric Al
[c]Al(tot) - total solution Al (acid reactive)
[d]Al(org) - organic monomeric Al as a percentage of total monomeric Al
ns - not significant at P=0.05.

of SSP increased the soil solution SO_4 compared with the control (Table 4.2). The increases in SO_4 concentration with higher rates of SSP application may arise from the specific adsorption of phosphate and consequent desorption of SO_4 from soil surfaces (Bornemisza and Llanos, 1967). Sloan et al. (1995) found a linear relationship between P fertiliser rate and soil solution SO_4 in incubation studies with banded P fertilisers. This linear relationship between soil solution SO_4 concentration and P fertiliser rate may suggest SO_4 desorption from soil by ligand exchange with orthophosphate. Phosphate forms a stronger bond at the sorption surface than does SO_4 (Kamprath et al., 1956; McBride, 1994).

4.3.3 Soil solution F

The total solution F concentration ranged from 2.7 to 23.5 and 3.2 to 25.6 μM in the surface and subsurface soils respectively (Table 4.2 and Fig 4.2). There were no marked differences in total solution F concentration between the surface and subsurface soils. Total solution F concentration greatly increased with the application of NCPR and high rates of SSP (SSP-45 and SSP-60). NCPR contains nearly 3 % F compared to 1 % F in SSP. At an application rate of 30 kg P ha^{-1} yr^{-1}, F added from NCPR is 7 kg ha^{-1} yr^{-1} compared with 3 kg ha^{-1} yr^{-1} from SSP, thus soil solution F concentrations in the NCPR plots are expected to be much higher than in SSP plots. The measured solution F concentration in the NCPR plots (17.2 and 12.3 μM in surface and subsurface soils) are however only slightly higher than the SSP-30 plots (11.9 and 10.2 μM in surface and subsurface soils). This could be due to the incomplete dissolution of F in NCPR (Chapter 3) and /or the high solution pH of the NCPR treatment. High pH reduces solution Al concentrations thus limiting the formation of Al-F complexes. Although JPR and NCPR had a similar F/P ratio (0.24), at the same F application rate as NCPR (7 kg F ha^{-1} yr^{-1}), the total solution F concentration was lower for JPR than NCPR. This could be possibly due to the lower dissolution (48 %) of JPR compared to NCPR (68 %).
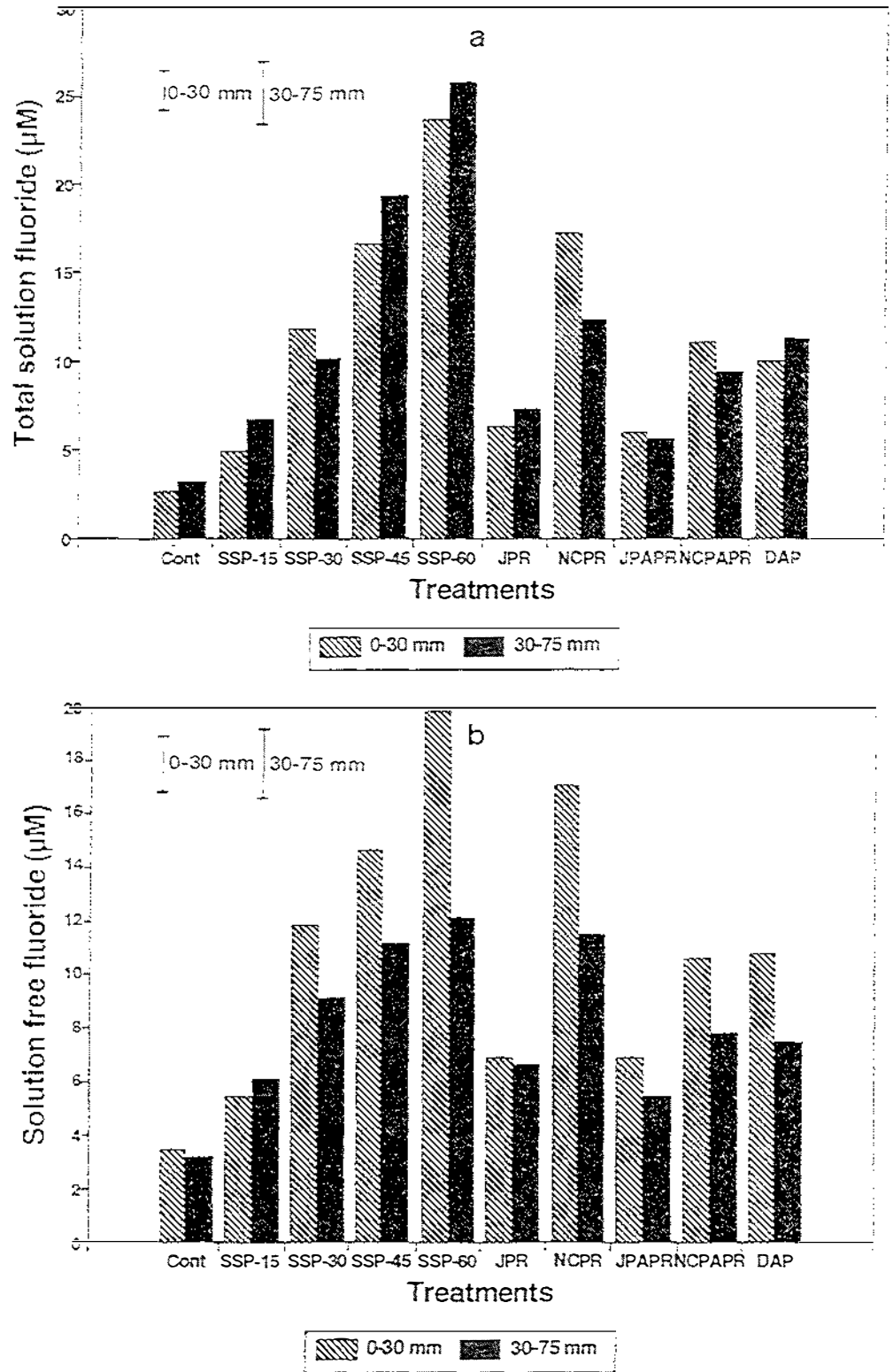
Fig 4.2. Effect of P fertilisers on (a) total solution fluoride, and (b) solution free fluoride concentrations at 0-30 and 30-75 mm soil depths. Vertical bars represent l.s.d. values at P=0.05.

The DAP treated plots had increased total solution F concentrations compared with the control, probably due to both the higher solution Al concentration resulting from low pH and the high F (1.2 %) input from the fertiliser. Barrow and Ellis (1986) as well as Gilpin and Johnson (1980) suggested that the higher solubility of F in acid soils is related to the formation of Al-F complexes. With increasing pH, the stability of Al-F complexes decreases (Lindsay, 1979) and therefore, total F solubility decreases (Barrow and Ellis, 1986).

Free F (F$^-$) concentration in solution ranged from 3.4 to 19.8 μM and 3.2 to 12.1 μM in the surface and subsurface soils respectively (Fig 4.2 b). It was significantly (LSD P$_{(0.05)}$ =1.8 μM) higher in the surface soil (mean of all treatments 10.8 μM) than in the subsurface soil (8.1 μM). The NCPR treatment had the highest percentage of total F as free F, as expected from the high solution pH and low Al concentrations. Barrow and Ellis (1986) reported that the solubility of free F increases with increasing pH, because the negative surface charge on variable charge materials increases, resulting in a repulsion of negatively charged F ions.

4.3.4 Soil Solution Al

Total soluble (acid reactive) Al ranged from 2.1 to 5.5 μM in the surface soils and 3.1 to 16.4 μM in the subsurface soils (Table 4.2), of which total monomeric Al ranged from 1.5 to 4.8 μM and 2.5 to 12.2 μM in the surface and subsurface soils respectively (Table 4.2, Fig 4.3). In general, organic Al complexes (Table 4.2) were more dominant in the surface soils than in the subsurface soils. Irrespective of treatment, about 75 % of the total monomeric Al was complexed with organic anions in surface soils and 40% in the subsurface soils. The organic carbon content in the control plot, for example, is 6.3 % in the surface soil and 4.3 % in the subsurface soil. Thus more organic anions are likely to be present in the surface soil for complexation of Al. The higher solution pH also would have favoured the Al-organic matter complexation in the surface soil (Dahlgren and Ugolini, 1989).
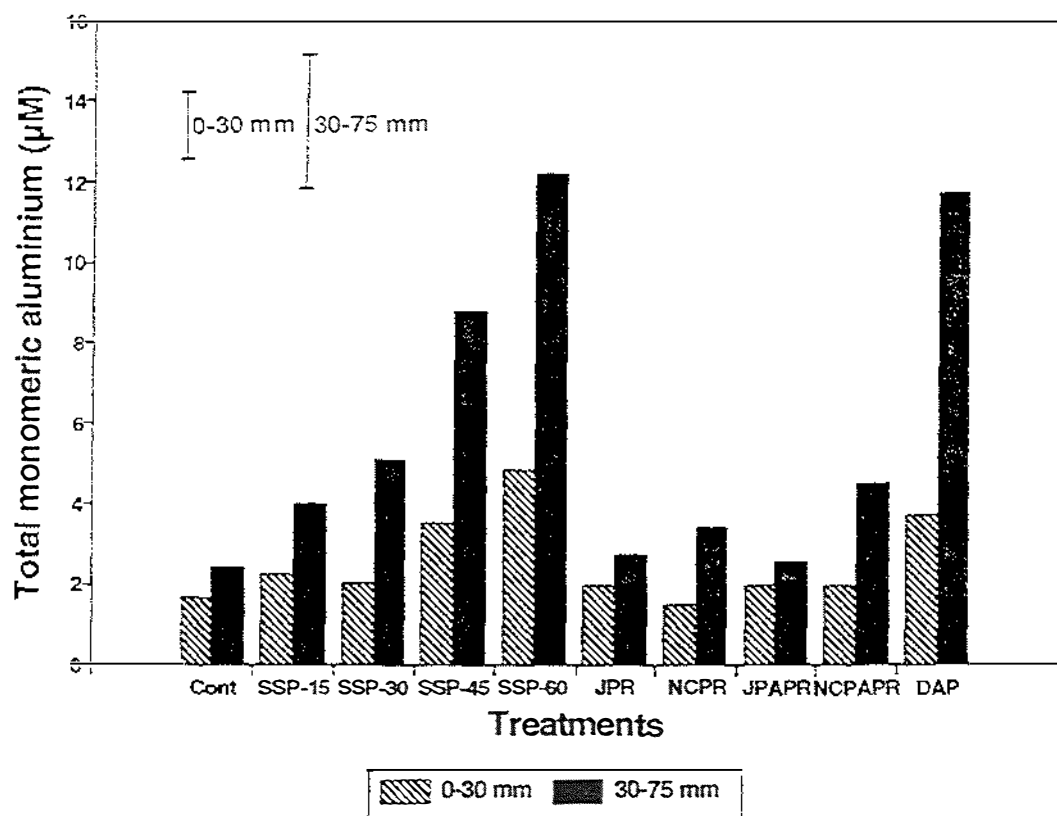
Fig 4.3. Effect of P fertilisers on total monomeric Al concentration in soil solution at 0-30 and 30-75 mm soil depths. Vertical bars represent l.s.d. values at P=0.05.

Applications of DAP and high rates of SSP (SSP-45 and SSP-60) resulted in a large increase in total soluble and total monomeric Al concentrations (Table 4.2, Fig. 4.3) in the soil solution from subsurface soils compared with the control. Treatments with NCPR, NCPAPR, JPR, JPAPR did not have any significant effect on total soluble or total monomeric Al concentrations compared with control. However, these treatments significantly reduced the solution Al concentrations compared with those of the high rates of SSP treatments.

The main reason for the increased Al concentration in the DAP plot was presumably the low solution pH. In the SSP-treated soil, however, the increased Al concentration could not be due to a pH effect alone because the pH decrease was small, while the increase in total solution Al concentration was high (Table 4.2, Fig 4.1). This increase in total solution Al concentration may be due to complexing of Al by F derived from SSP, thus bringing more Al into solution. This is supported by the high positive correlation (r=0.73, N=50) between total solution Al and solution F in the subsurface soil. Moore and Ritchie (1988) have also shown that the addition of F to an acid soil increased total soluble Al.

The effect of F on total solution Al is less pronounced in the surface soil than in the subsurface soil (Table 4.2). In the surface soil, Al is mostly complexed with dissolved organic carbon rather than with F as seen from the higher percentage of organic Al complexes and therefore the F effect is lower. However when the F concentration becomes high as in the SSP-60 treatment (Fig 4.2) it significantly increased total soluble Al in the surface soil (Table 4.2).

4.3.5 Aluminium speciation

An estimate of the inorganic monomeric Al species in the soil solution was obtained using the soil solution composition and the MINEQL$^+$ computer equilibrium programme. Speciation was done only on data from the subsurface soils because of the low inorganic monomeric Al concentration in the surface soils. The predominant forms of inorganic monomeric Al present in soil solution were predicted to be the alumino-fluoride complexes, AlF^{2+} and AlF_2^+ (Fig. 4.4). The dominance of the inorganic monomeric fraction by F-complexes and hydroxy Al species has also been reported for acid soil solutions (Munns et al., 1992). Aluminium sulphate complexes were predicted to be negligible even at the highest rate of SSP application, which produced the highest concentrations of SO_4 in soil solution (Table 4.2). Increased rates of SSP application greatly increased the predicted percentage of the Al-F complexes. SSP at the highest rate (SSP-60) resulted in 98 % of the inorganic monomeric Al being predicted to be complexed with F.

In NCPR-treated soils only 78 % of the inorganic monomeric Al was complexed with F. This may be compared to 95 % for the SSP-30 treatment in which the total solution F concentration was approximately the same. This was due to the higher pH in the NCPR-treated soils along with the lower Al concentration. At high pH, Al-F complexes are not stable, and result in increased levels of free F as indicated in Fig 4.2.

Studies by Pavan and Bingham (1982) and Alva et al. (1986b c) have suggested that the most phytotoxic Al species are Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$. However studies by Bruce et al. (1988) and Menzies et al. (1994) suggested that only Al^{3+} and $Al(OH)^{2+}$ are highly phytotoxic and that $Al(OH)_2^{1+}$ is relatively non-toxic. When considering the phytotoxicity of Al species, activities rather than concentrations are important. In this study the predicted total toxic Al ($Al^{3+} + Al(OH)^{2+} + Al(OH)_2^+$) activity in the DAP-treated plots was 0.96 μM and for all other treatments it was ≤ 0.23 μM (Table 4.3). These values are much lower than the Al^{3+} activity values of 2-3 μM reported in a nutrient solution study by
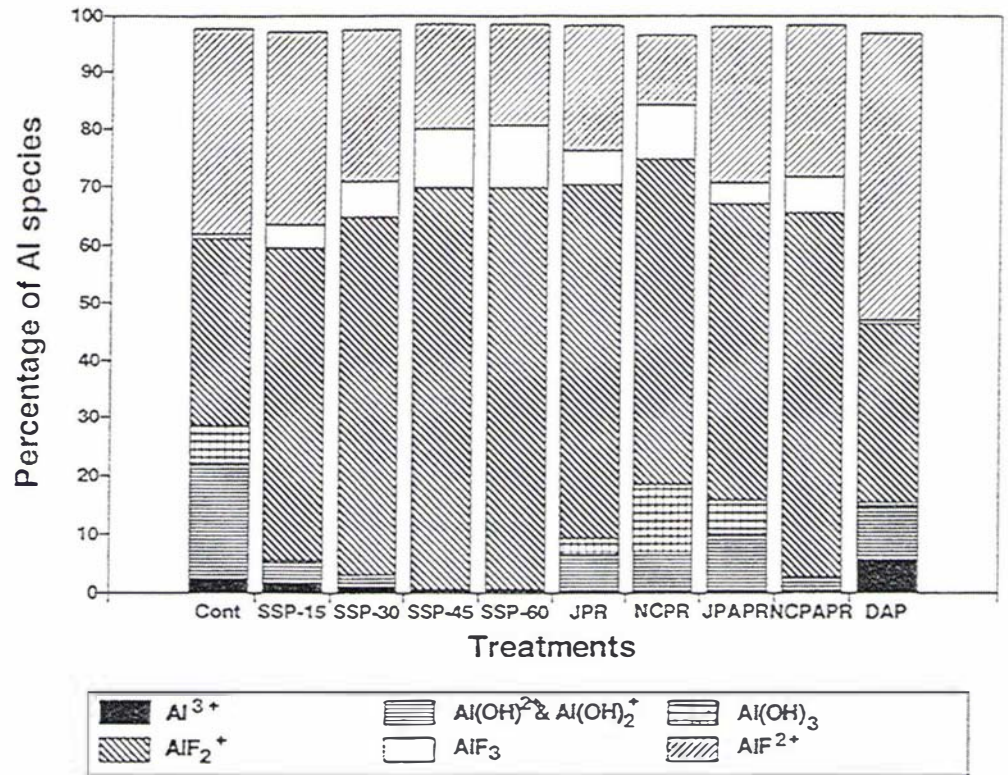
Fig 4.4. Effect of P fertilisers on relative proportions of the concentration of inorganic monomeric Al species at 30-75 mm soil depth.

Table 4.3. Effect of P fertiliser application on the predicted activity of toxic Al species in soil solution.

Treatment	Al^{3+}	$Al(OH)^{2+}$	$Al(OH)_2^{1+}$	Total
		$\mu mol\ L^{-1}$		
Cont	0.02	0.06	0.15	0.23
SSP-15	0.03	0.06	0.08	0.16
SSP-30	0.03	0.05	0.07	0.15
SSP-45	0.01	0.02	0.03	0.06
SSP-60	0.01	0.03	0.04	0.09
JPR	0.00	0.02	0.08	0.10
NCPR	0.00	0.01	0.06	0.07
JPAPR	0.01	0.02	0.08	0.11
NCPAPR	0.02	0.03	0.04	0.08
DAP	0.29	0.34	0.33	0.96

Edmeades et al. (1991b) for a 50% yield reduction in two cultivars of ryegrass (*Lolium perenne*), two red clover (*Trifolium pratense*) cultivars and *Lotus corniculatus* cv Maitland. Nevertheless, Alva et al. (1990) have shown in nutrient solution studies that nodulation was much more sensitive to Al than was host plant (cowpea) growth. The Al^{3+} activities for 10 % reduction in nodule number and nodule dry weight were approximately 0.3 and 0.5 µM respectively. Critical Al activities for plant top and root growth were in the range of 4 to 8 µM.

The increased predicted activity of toxic Al species (Table 4.3) in the DAP-treated plots was probably because of a lower solution pH along with a lower total F/ total Al molar ratio in the soil solution compared with other treatments. The toxic Al as a percentage of the total inorganic monomeric Al concentration for this treatment is however still low (15%) compared with the control treatment (Fig. 4.4), with much of the Al still being complexed with F. All other P fertilisers appear to decrease the toxic aquo- and hydroxy-Al activity, with higher rates of SSP (SSP-45 and SSP-60) having the greatest effect (Table 4.3). Although higher rates of SSP significantly increased the concentration of total inorganic monomeric Al (Table 4.2), unlike the DAP treatment, SSP decreased the activities of toxic uncomplexed forms of Al, probably due to the higher solution F concentrations (Fig. 4.3) and hence a greater proportion of Al-F complexation in the SSP plots (Fig 4.4).

4.4 Conclusions

The present study on a marginally acidic soil demonstrated that long-term application of phosphate fertilisers can markedly affect the concentration and speciation of Al in the soil solution. Application of DAP and high rates of SSP increased total Al concentrations in the soil solution even though SSP had no effect on soil pH. The increased Al concentration in the SSP treatments could be due to high total solution F in these treatments complexing Al, and hence bringing more Al into the soil solution. Application of NCPR decreased total Al concentrations, presumably by increasing soil pH.

Total soil solution Al concentration increased following the application of DAP, as did the predicted concentration of toxic Al species -Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$. Application of high rates of SSP decreased the toxic Al concentration, despite the higher total soil solution Al concentration compared with the control soil. The concentration of toxic Al species in NCPR-treated soils was also lower than in the control soil.

This study suggests that application of fertilisers such as SSP can increase the concentration of monomeric Al in the soil solution. Most of this Al however appears to be in the form of Al-F complexes that are considered to be relatively non-toxic. However, given the very high concentrations of these Al-F complexes in soils receiving high rates of P fertilisers, it is important to assertain just how toxic they may be to plants.

Chapter 5

Assessing aluminium phytotoxicity using barley (*Hordeum vulgare* L.) seedlings in long-term phosphate-fertilised pasture soils[1]

5.1 Introduction

Soil test methods are needed to determine when Al toxicity will limit plant growth, and to estimate the amount of lime or other amendments to be used. Whole-soil measurements such as pH, exchangeable Al and Al saturation have been widely used as diagnostic tools for the prediction of Al toxicity. While critical values for such attributes derived for a given crop on a given soil have generally proved to be a good prediction of plant performance, these predictors have not proven particularly useful when applied to a given species over a range of soils (Menzies et al., 1994).

More recently, attention has shifted to concentrations and chemical activities of Al species in soil solution as predictors of Al toxicity. Aluminium in aqueous systems exists in a variety of mononuclear and polynuclear forms, some of which are toxic to plants. Current evidence suggests that Al^{3+} and/or Al-hydroxy species are the most toxic to plants (Ritchie, 1989). Aluminium complexed with anions such as SO_4, F and organic ligands does not appear to decrease plant growth (Cameron et al., 1986; Hue et al., 1986; MacLean et al., 1992). In addition, cations such as Ca (Rhue and Grogan, 1977; Alva et al., 1986b; Cameron et al., 1986) and to a lesser extent Mg (Rhue and Grogan, 1977; Kinraide et al., 1985; Edmeades et al., 1991b) have been shown to mitigate Al toxicity. Hence, the concentration of total soluble Al may not be suitable as a soil test, because it does not consider the activity and forms of soluble Al. Slattery et al. (1995) reported that the combination of Ca activity and the sum of the activities of Al monomers, together with organic carbon content, may provide a better description of the responsiveness of acid soils to lime applications than the conventional Al toxicity indices.

In Chapter 4 it was shown that long-term application of phosphate fertilisers to pasture soils can change the soil solution composition and Al speciation substantially, mainly by

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[1] V. Manoharan et al. Commun. Soil Sci. Plant Anal. 27:1731-1748.

complexation of Al with F derived from the phosphate fertilisers. This may have a significant effect on the critical Al toxicity threshhold level in these fertilised soils compared with unfertilised soils. This is mainly due to the reduction in free Al^{3+} activity due to F complexation of Al and also due to the ameliorative effect of Ca on Al toxicity.

Recently, short-term bioassay techniques using root development of seedlings in soil have been used to identify soils with Al toxicity problems (Ahlrichs et al., 1990; Ritchey et al., 1988). These bioassay techniques allow the separation of Al effects on root elongation from those on plant nutrition and should be useful in evaluating the applicability of chemical methods to predict the Al toxicity of a soil (Wright et al., 1989).

The present study had two objectives: (i) to investigate the effects of long-term application of phosphate fertiliser and pH on soil solution Al species, soil solution composition and barley root growth; (ii) to compare pH, $CaCl_2$-extractable Al and various soil solution Al indices for their usefulness in predicting barley root growth.

5.2 Materials and Methods

5.2.1 Soil sample collection, analysis and root growth measurement

Soil samples (40-100 mm) were collected from two adjacent pasture sites at the Ballantrae hill country research station. One site had had no phosphate fertiliser applied for over 20 years (low phosphorus, LP) and the other had had a high phosphorus input (375 kg ha^{-1} yr^{-1} single superphosphate (SSP)) for 20 years (high phosphorus, HP). The soils at the sites are classified as Yellow Brown / Yellow Earth integrades (Typic Dystrochrepts).

Soil samples were incubated for 6 weeks (at 80 % of the field capacity) with either $Ca(OH)_2$ or HCl to obtain varying pH levels.

The incubated soil samples were placed into 250 ml plastic cups. Seeds of barley (*Hordeum vulgare* L.) were pregerminated for 3 days and planted at 4 seedlings per cup. The plants were grown for 3 days in a glasshouse. At the end of the growth period seedlings were removed from the soil and the lengths of the longest roots were measured.

About 240 g samples of moist soil were then used for soil solution analysis and the remainder of the samples were air dried, and pH in water (pH(H_2O)) and 0.02 M $CaCl_2$ - extractable Al ($CaCl_2$ - Al) determined as described in Chapter 3.

5.2.2 Soil solution analysis

Soil solution extraction and analysis was carried out as described in Chapter 4.

5.2.3 Relative root length

For each soil, relative root length (RRL) was determined by expressing root length in each treatment as a percentage of the longest root length which was that of the highest rate of Ca(OH)$_2$ treatment.

5.2.4 Statistical Analysis

Statistical Analysis System (SAS) programs were used for all statistical analyses.

5.3 Results and Discussion

5.3.1 Soil solution composition

There were marked differences in soil solution composition in both the HP and the LP soils in response to pH changes arising from additions of HCl or Ca(OH)$_2$. With decreasing pH, soil solution concentrations of cations (Ca, Mg, K and Na) increased in both soils (Table 5.1 and 5.2). However, the increase in soil solution Ca was much greater in the HP soil compared to the LP soil as the solution pH (pHss) changed from 5.7 to 3.9 in the HP soil and from 6.0 to 3.8 in the LP soil. The higher Ca concentrations in the HP soil would be due to increased Ca input from the application of SSP, which contains nearly 20 % Ca. With the HCl addition, proton replacement of Ca from the soil exchange sites and increased dissolution of Ca - phosphate compounds would have increased the soil solution Ca concentration substantially in the HP soil compared to the LP soil.

Table 5.0. Some chemical and physical properties of the experimental soils.

Soil	pH (H_2O)	Olsen P $\mu g\ g^{-1}$	[a]SO_4 $\mu g\ g^{-1}$	K $cmol_c\ kg^{-1}$	Ca $cmol_c\ kg^{-1}$	Mg $cmol_c\ kg^{-1}$	Na $cmol_c\ kg^{-1}$	CEC $cmol_c\ kg^{-1}$	Organic Carbon (%)
Low phosphorus	5.8	10.5	10.0	0.56	2.4	1.0	0.19	14	4.1
High phosphorus	5.9	86.7	42.3	1.41	5.0	1.2	0.17	28	5.4

[a] Phosphate extractable sulphate was measured by the method of Searle (1979)

Table 5.1. Effect of pH on soil solution composition in the high phosphorus soil.

pH (ss)	Na	K	Ca	Mg	Cl	NO$_3$	SO$_4$	F (total)	μ^a
					mM				M
3.87	996	3813	18083	4262	49506	5813	10	251	0.063
3.98	981	4029	17137	4333	43705	7333	10	220	0.058
4.14	808	3705	11141	3126	25583	7490	41	154	0.040
4.25	798	3022	8170	3017	16071	8108	40	105	0.030
4.30	710	2573	6022	2653	9328	8931	69	76	0.023
4.59	545	1561	2857	1222	240	9470	68	32	0.013
4.62	500	1476	2757	1112	220	8642	69	26	0.011
4.90	505	1181	3495	1071	266	10061	111	17	0.013
5.06	503	1012	3924	921	269	10368	180	10	0.014
5.27	416	737	4446	856	249	11071	179	6	0.015
5.68	348	365	4124	423	210	11064	169	5	0.021

[a] ionic strength

Table 5.2. Effect of pH on soil solution composition in the low phosphorus soil.

pH(ss)	Na	K	Ca	Mg	Cl	NO_3	SO_4	F (total)	μ [a]
				◄——— μM ———————►					M
3.83	1545	1688	7380	4218	33768	112	122	56	0.042
3.94	1290	1248	6266	3490	26290	87	105	53	0.034
4.07	1163	956	4938	3608	19078	156	137	42	0.026
4.40	968	559	3070	244	10390	975	106	24	0.014
4.44	885	397	2235	1860	7498	1281	151	17	0.012
4.36	927	495	2489	2367	10018	614	127	23	0.016
4.48	748	386	2134	1836	7212	1186	155	21	0.012
4.68	684	316	946	1444	1689	725	143	13	0.009
4.82	482	220	664	986	1246	656	169	12	0.007
5.18	376	125	534	464	1128	869	170	8	0.004
5.42	276	36	374	48	379	752	177	1	0.002
5.95	308	41	188	52	383	659	99	2	0.002
6.03	367	50	295	53	460	631	123	2	0.002

[a] ionic strength

At low pH values Cl was the dominant anion in both soils (Table 5.1 and 5.2), since HCl was used to acidify the soil samples. The NO_3 concentrations were much higher in the HP soil (5813 to 11,071 μM) than in the LP soil (87 to 1281 μM). Although the HP soil was expected to have higher SO_4 concentrations due to a higher SO_4 input from the SSP applied, on average there was little difference in SO_4 concentration between the LP and the HP soils and at low pH, soil solution SO_4 concentrations were actually lower in the HP soil. Further work is required to explain these observations.

Total F concentrations ranged from 5 to 251 μM, in the HP soil and 1 to 56 μM for the LP soil (Fig 5.1). The reason for the high soluble F in the HP soils is probably the higher annual input of F from SSP which contains nearly 1% F as an impurity. Decreasing pH increased the F concentration in both the HP and the LP soils (Fig 5.1). This could be due to increased dissolution of F compounds with acidification, and desorption of F as a result of increased complexation of F with Al in soil solution (Wenzel and Blum, 1992b).

In general the soil solution ionic strength of the HP soil was higher than that of the LP soil, due to the high concentrations of NO_3 and Ca in the HP soil solution. The ranges of ionic strengths of the soil solutions for the HP were 0.01 to 0.06 and 0.002 to 0.04 mol l^{-1} for the LP soils. These values are in general higher than the values of 0.002 and 0.005 respectively reported in Australia (Gillman and Bell, 1978) and in New Zealand (Edmeades et al., 1985) for field pasture soils. Samples were acidified with HCl which could have increased the ionic strength markedly as shown by the very high levels of Cl in some of the soil solutions. The incubation of samples for 6 weeks may also have increased the rate of mineralisation and subsequently increased the ionic strength.

Decrease in pH increased the solution concentration of total monomeric Al substantially in both soils (Fig 5.2). There was no significant difference in total monomeric Al concentration between the two soils at any pH tested. However, the relative percentages of each species of monomeric Al varied with pH and fertiliser application (Fig 5.3). The proportion of Al-F complexes increased markedly with increasing pH. This corresponded to a reduction in the proportion of Al^{3+} as pH increased in both soils. However, the percentage of AlF complexes was much higher in the HP soil than in the LP soil, as would be expected from the higher solution F concentration in the HP soil at similar pH values
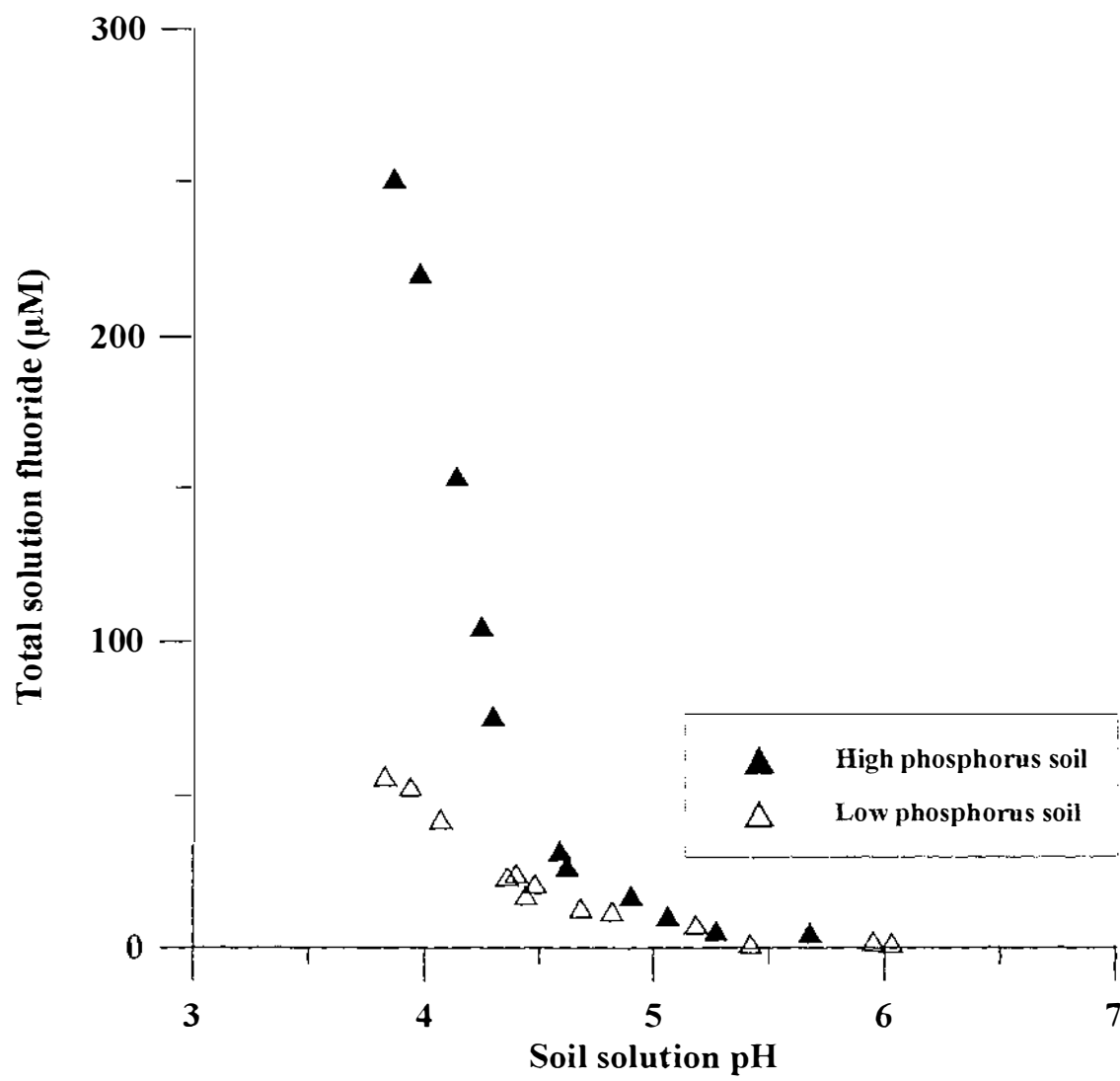
Fig 5.1. Relationship between total solution F and solution pH in high phosphorus and low phosphorus soils.
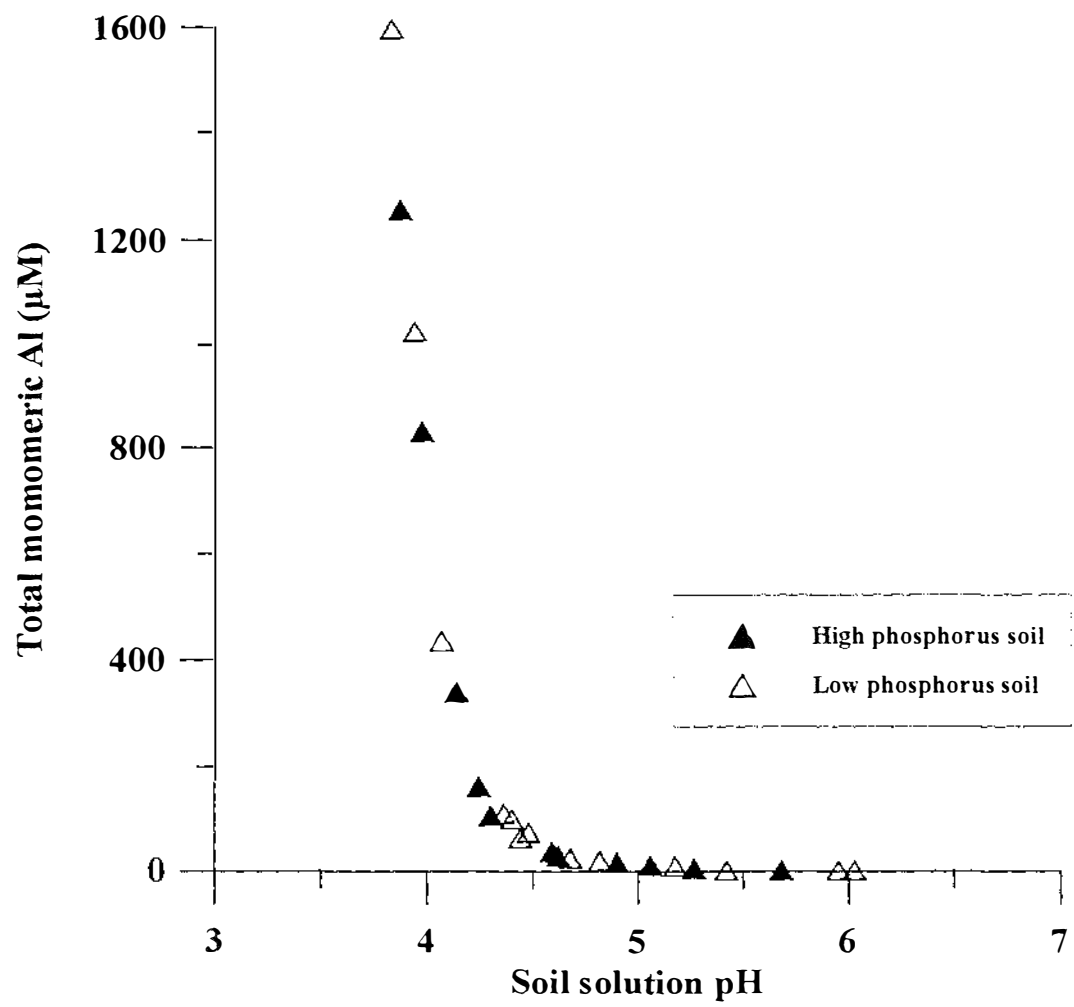
Fig 5.2. Relationship between total monomeric Al concentration and solution pH in high phosphorus and low phosphorus soils.
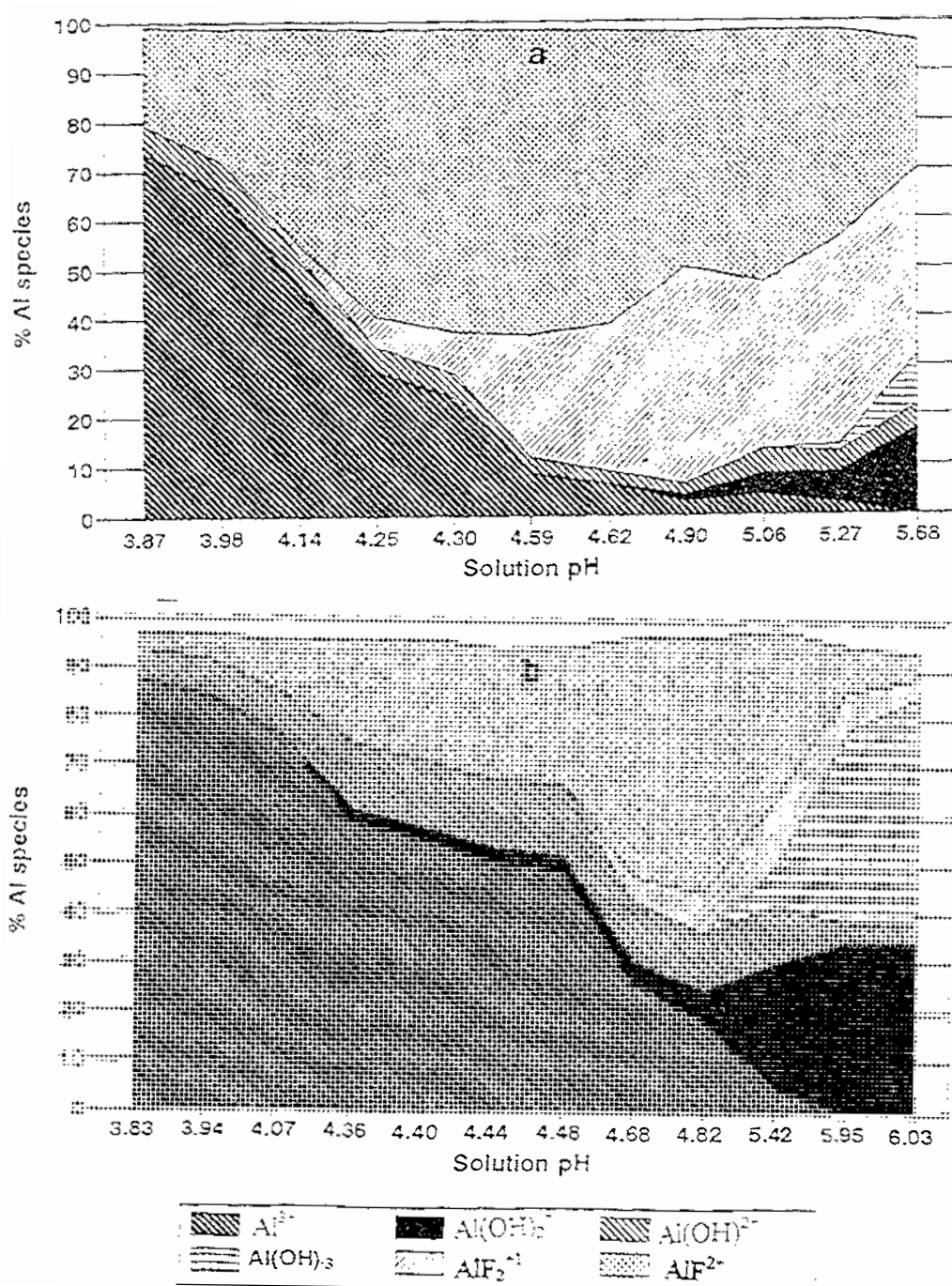
Fig 5.3. Relative percentages of Al species concentration in the (a) High phosphorus and (b) Low phosphorus soils.

(Fig 5.1). The relative proportion of Al^{3+} is greatest at low pH and this may be a consequence of reduced hydrolysis of Al^{3+} coupled with sufficiently high total Al concentrations to swamp the limited amount of total F available for the formation of F complexes. At higher pH values, hydrolysis of Al^{3+} becomes more prevalent.

5.3.2 pH and root growth

Measurements of $pH(H_2O)$ and pH(ss) are commonly used in the study of the soil acidity-plant response relationship. RRL was plotted against soil and soil solution pH (Fig 5.4, 5.5). Rearranged Mitscherlich equations $(y = a - b\,exp(-cx))$ were used for the regressions of RRL on pH measurements. Both $pH(H_2O)$ and pH(ss) gave high R^2 values (Table 5.3). However the pH values corresponding to 90 % RRL were different for the two soils (pH(ss) 5.46 and 5.05 for the LP and the HP soils respectively Table 5.4). Also in the pH (ss) range of 4.5 to 5.0, which is normally the range where soil acidity problems occur in field soils, as much as 20% difference in RRL was observed between the LP and the HP soils at a given pH (Fig 5.4). Bache and Ross (1991) in a field study have also shown that large additions of P fertilisers allowed barley to withstand high concentrations of soluble Al, thus decreasing the critical soil $pH(H_2O)$ from 5.9 to 5.5. Edmeades et al. (1983) also reported that critical values for pH (H_2O) and Al in soil solution were dependent on soil type and P treatments.

5.3.3 CaCl$_2$ - Al and root growth

Soil Al extracted by 0.02 M $CaCl_2$ ($CaCl_2$- Al) was also closely related to RRL (Table 5.3). A plot of RRL as a function of $CaCl_2$-Al is shown in Fig 5.6. However the R^2 values for these relationships described by a rearranged Mitscherlich equation of the form $(y = a + b\,exp(-cx))$ were less than those for other soil solution Al indices. Also the critical $CaCl_2$-Al concentrations for 90% RRL were different for the LP and the HP soils (Table 5.4). The differences in RRL between the soils were even greater for RRL between 30 and 70 %. This indicates that $CaCl_2$- Al may contain non-toxic Al species such as Al-organic matter and Al-F complexes in different proportions in the two soils. Hume et al. (1988) reported that $CaCl_2$-Al had a higher correlation with white clover top weight than pH or exchangeable Al. However, they reported that there were differences between soils
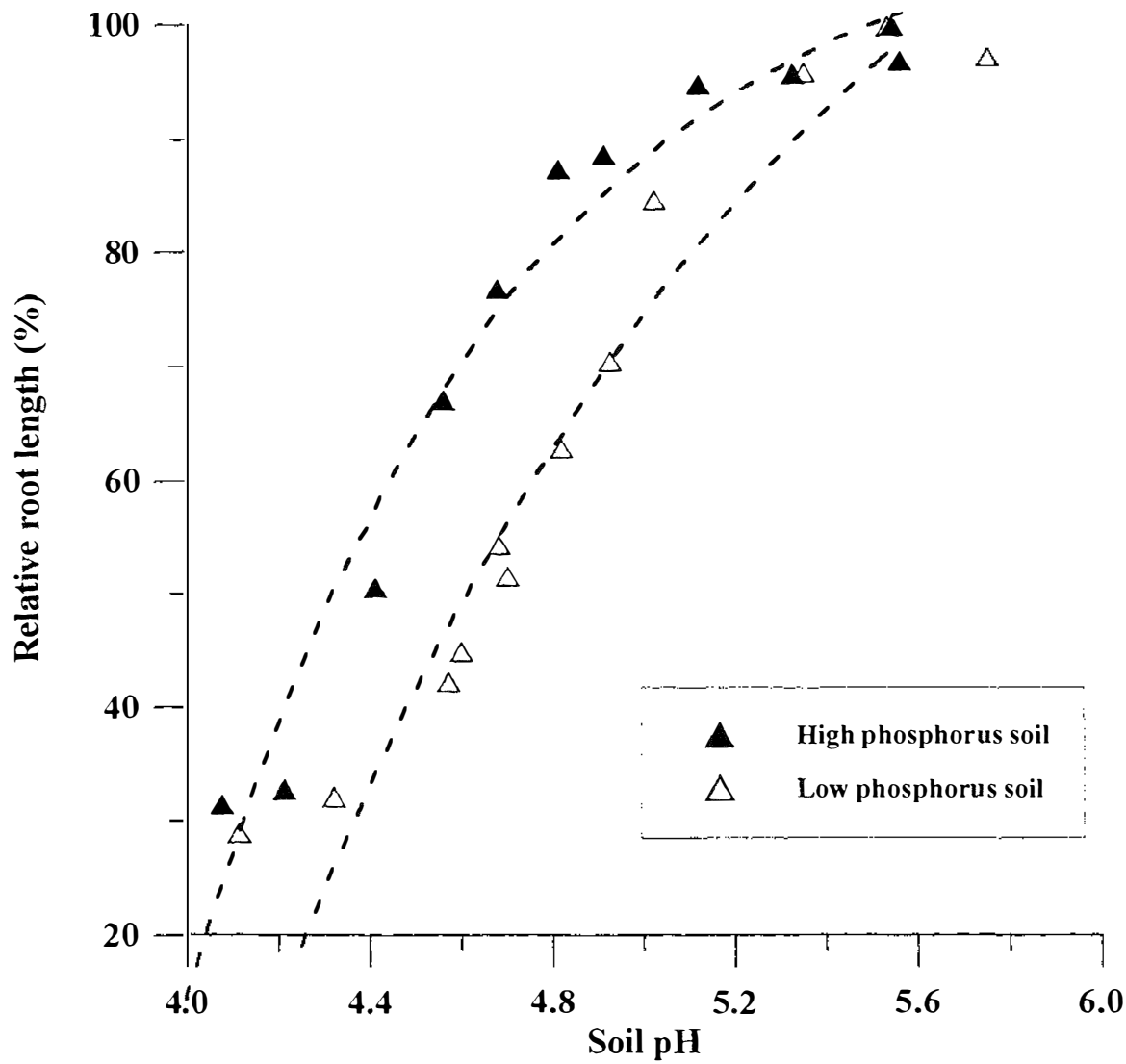
Fig 5.4. Relationship between relative root length and soil pH in high phosphorus and low phosphorus soils.
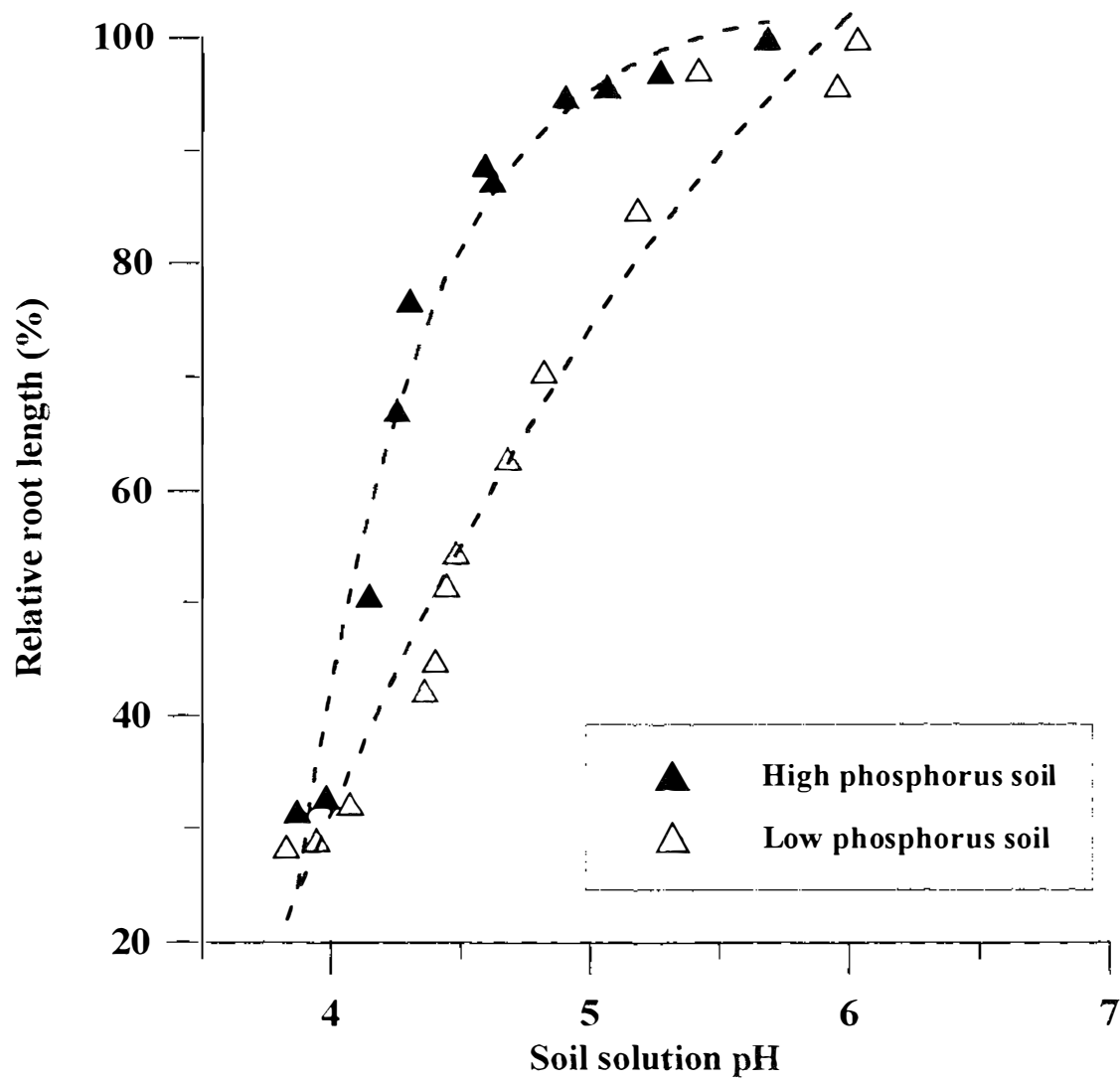
Fig 5.5. Relationship between relative root length and soil solution pH in high phosphorus and low phosphorus soils.

Table 5.3. Coefficient of determination (R^2) of the non-linear equations fitted to the regression of relative root length against various Al toxicity indices in high phosphorus (HP) and low phosphorus (LP) soils.

Al toxicity indices	R^2 (%)		
	HP	LP	HP+LP
Soil pH	95.6	94.3	81.9
Solution pH	95.6	96.4	76.4
Total monomeric Al	99.6	96.5	81.2
Inorganic monomeric Al	99.3	95.9	82.4
Al^{3+} concentration	96.9	89.2	87.9
$[Al^{3+}]$	98.2	90.8	92.2
$[Al(OH)^{2+}]$	98.7	95.3	96.0
$[Al(OH)_2^+]$	96.4	96.4	96.5
$[Al^{3+}] + [AlOH^{2+}] + [AlOH^+]$	98.3	93.5	94.3
$[Al^{3+}]/[Ca^{2+}]$	98.9	96.9	97.3
$[Ca^{2+}]/[Al^{3+}+AlOH^{2+}+Al(OH)_2^+]$	97.5	98.7	94.9
CAB^a	96.9	98.9	96.1
$0.5 \log[Ca^{2+}]-0.33 \log[Al^{3+}]$	95.6	96.3	87.9
0.02 M $CaCl_2 - Al$	92.9	92.1	86.3

[ ] denotes activity

^{a}CAB= $(2\log[Ca^{2+}] -3\log[Al^{3+}] +2\log[Al(OH)^{2+}] +\log[Al(OH)_2^+])$ (Noble et al., 1988)

Table 5.4. Relative root length (90 %) values for selected Al toxicity indices in high phosphorus (HP) and low phosphorus (LP) soils.

Al toxicity indices	HP	LP	HP+LP
Soil pH	5.12	5.35	5.19
Solution pH	5.05	5.46	5.18
Total monomeric Al	34.60	6.50	11.30
Inorganic monomeric Al	28.60	4.30	8.50
$[Al^{3+}]$	1.38	0.02	0.54
$[Al^{3+}]+[AlOH^{2+}]+[Al(OH)_2^+]$	2.40	0.86	1.42
CAB[a]	27.00	22.00	23.50
$[Al^{3+}]/[Ca^{2+}]$ $*10^{-4}$	4.23	4.51	4.43
0.02 M $CaCl_2$ -Al	6.98	5.05	5.20

[ ] denotes activity

[a]CAB= $(2 \log[Ca^{2+}]$ -3 $\log[Al^{3+}]$ +2 $\log[Al(OH)^{2+}]$ +$\log[Al(OH)_2^+])$ (Noble et al., 1988c)
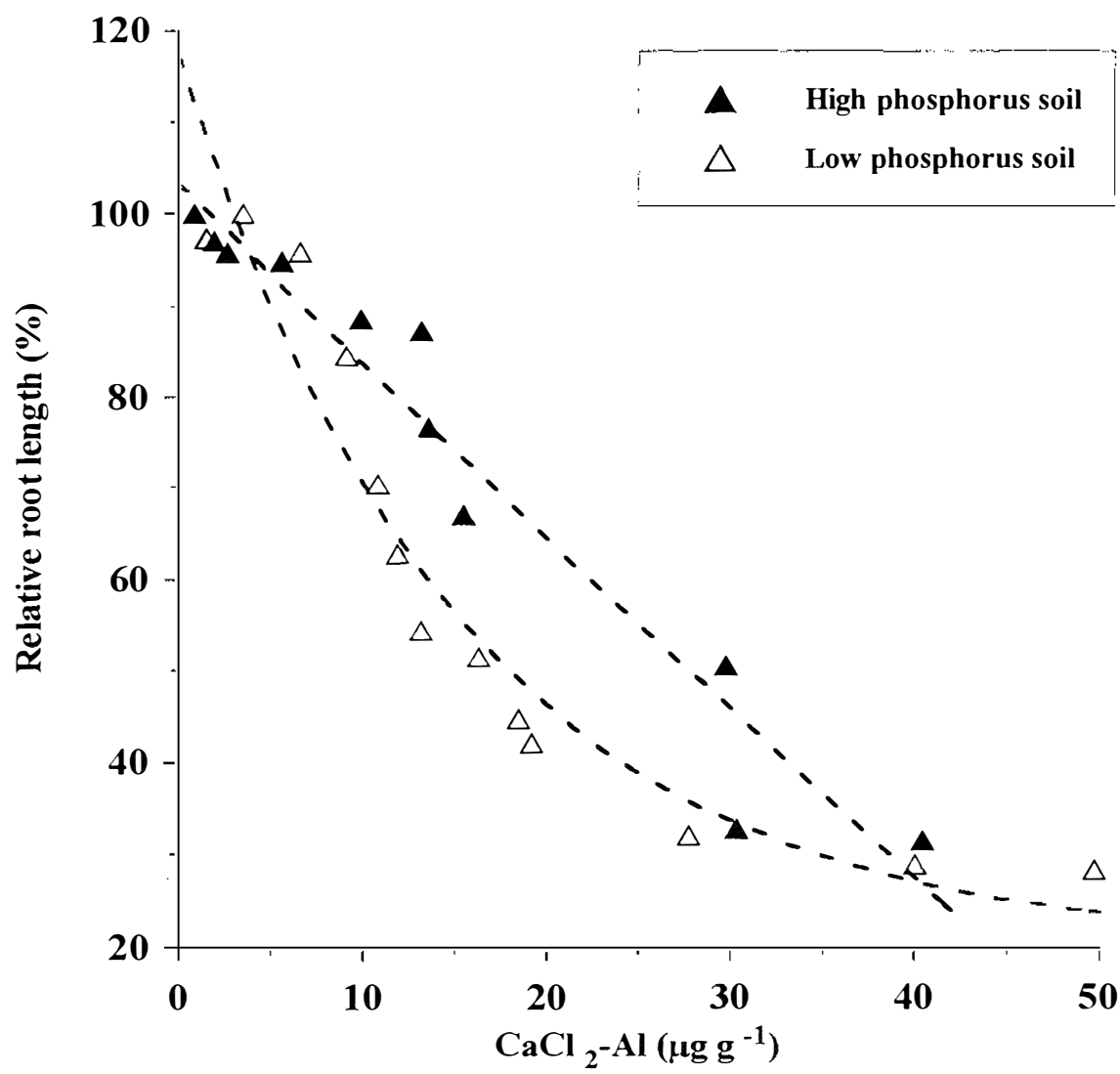
Fig 5.6. Relationship between relative root length and CaCl$_2$-Al.

in apparent plant tolerance to $CaCl_2$-Al, which appeared to be caused by differing organic carbon levels in the $CaCl_2$ extracts. Moore and Ritchie (1988) suggested that soil solution pH, total soluble Al and Al extracted by 0.01 M $CaCl_2$ were not good predictors of the likelihood of Al toxicity in soils containing soluble F, because the extracting solution does not extract Al in proportion to the activity of toxic forms of Al in the soil solution. Another reason is that extracting solutions like 0.02 M $CaCl_2$ are likely to remove Al from exchange sites in addition to soluble Al. But other investigators reported that in acid soils the amount of Al extracted by dilute $CaCl_2$ was related to plant growth (Bromfield et al., 1983; Jarvis, 1987), possibly because the soils used by these researchers had similar properties.

5.3.4 Soil solution Al indices and root growth

Seven soil solution Al indices were related to RRL to assess the suitability of these indices for identifying Al toxicity. Rearranged Mitscherlich equations $(y = a + b\ exp(-cx))$ were fitted to the regressions of RRL on soil solution Al attributes. The fitted lines are plotted (Fig 5.7a - d) and the coefficients of determination (R^2) are presented in Table 5.3 for those regressions which accounted for an appreciable proportion of the sample variability (>80 %).

When the data for the LP and the HP soils were analysed separately, all the soil solution Al indices gave R^2 values > 89% (Table 5.3). However when data from both soils were combined and analysed, R^2 values decreased markedly for total monomeric Al and inorganic monomeric Al as shown in Table 5.3. The reduction in R^2 values for the combined data indicated that relative proportions of the toxic Al species in the total monomeric Al and inorganic monomeric Als. The less toxic Al-F complexes in the HP soil constituted on average 65% of the inorganic monomeric Al in solution compared with 25% in the LP soils. Another factor causing differences in Al toxicity in the two soils may be the higher ionic strength in the HP soil compared to the LP soil. Consideration of ionic strength improved the R^2 values in the combined data through its effect on the activity of Al species.
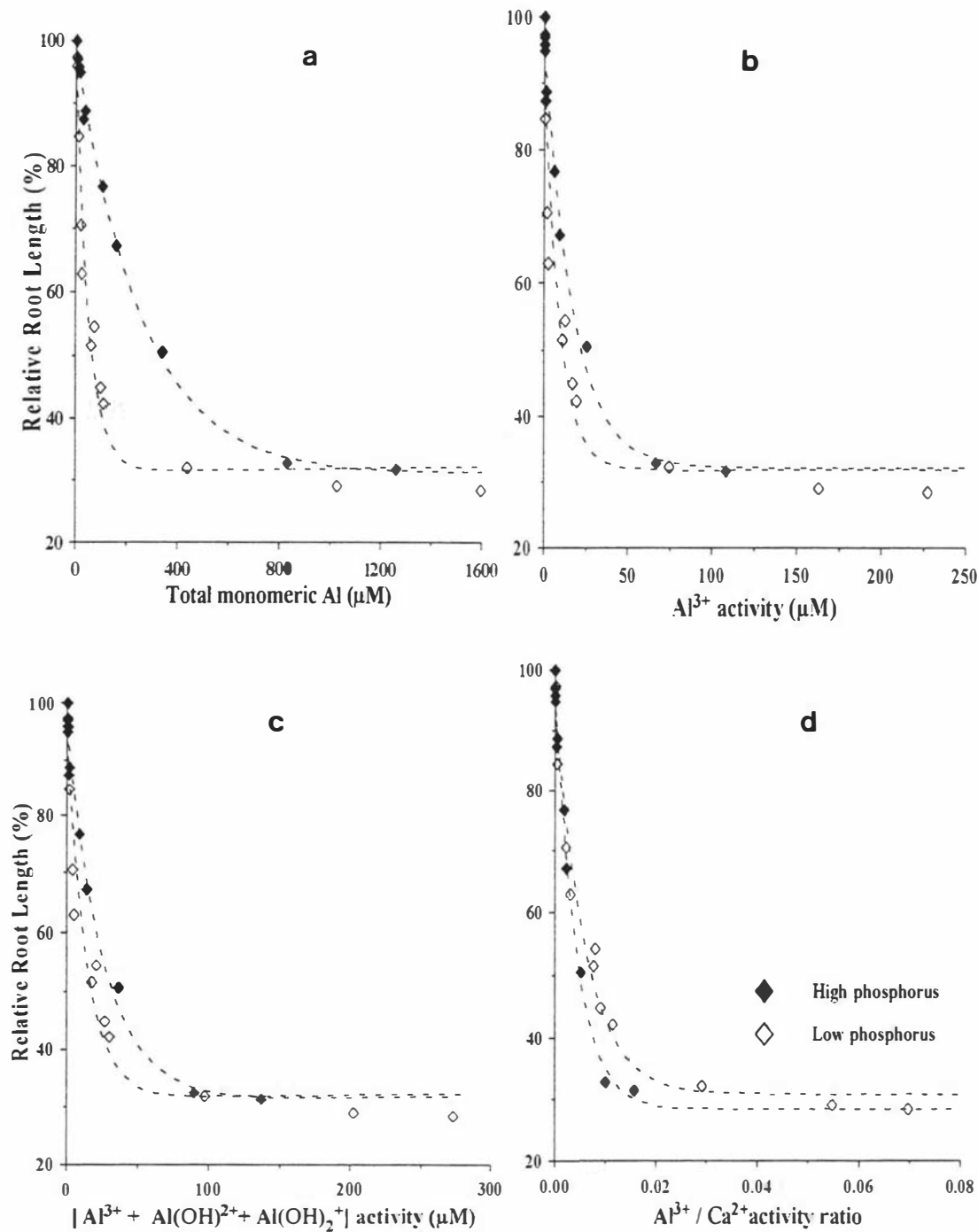
Fig 5.7. Relationship between relative root length and (a) total monomeric Al concentration (b) Al^{3+} activity (c) toxic Al (Al^{3+} + $Al(OH)^{2+}$ + $Al(OH)_2^{1+}$) activity and (d) Al^{3+} / Ca^{2+} activity ratio.

Individually Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ activities gave the highest R^2 values when correlated with RRL. This is consistent with these species being the toxic agents. However, since the Al-hydroxy species are strongly interrelated with Al^{3+} ($R^2 = 0.96$ and 0.73 for $Al(OH)_2^+$ and $Al(OH)^{2+}$ respectively) it is not possible to separate their toxic effects on root growth.

Even though the R^2 values were high for the RRL relationships with all Al toxicity indices the critical Al values associated with 90 % RRL for the HP and LP soils were different for many of the indices. The 90% RRL values for total monomeric Al concentration were 35 μM and 6.5 μM in the HP and the LP soils respectively. But when data from both soils were combined and analysed the 90% RRL value was 11 μM. Similar wide variations in critical levels were observed for the inorganic monomeric Al. The higher critical Al toxicity values for HP soils compared to LP soils is probably due to higher F concentration in HP soils which causes reduction in toxicity.

Critical Al^{3+} activity values associated with 90 % RRL were 0.02 μM and 1.38 μM in the LP and the HP soils respectively and 0.54 μM for the combined data of the two soils. The total toxic Al ($Al^{3+} + Al(OH)^{2+} + Al(OH)_2^+$) activities at 90 % RRL were 2.40 and 0.86 for HP and LP soils respectively and 1.42 μM for the combined data of the two soils. About 30% reduction in root growth occurred at Al^{3+} activities of 8.8 μM and 4.0 μM in the HP and the LP soils respectively. This agrees well with the results of Tanaka et al. (1987) where barley root elongation was strongly inhibited when Al^{3+} activity exceeded 5 μM.

Regressions (using exponential models) of root growth on Al-F complexes produced a low coefficient of determination ($R^2 = 0.56$) when the data for the two soils were combined, supporting the view that these species are less toxic to plant growth (Cameron et al., 1986; Wright et al., 1989b; and MacLean et al., 1992).

The general belief that organically complexed Al is non-toxic to plants, has also been supported by the low R^2 (0.48) values observed in this study between the RRL and organic Al. It has been suggested in nutrient solution studies that the toxicity of Al was ameliorated by the addition of organic acids (Suthipradit et al., 1990). Adams and Moore

(1983) found that Al was toxic at solution concentrations greater than 0.4 μM in the Bt horizon low in organic carbon (0.14-0.30%) but not in horizons higher in organic carbon (0.28-1.22%) with solution Al concentration between 9 and 134 μM.

5.3.5 Calcium -aluminium balance (CAB)

Amelioration of Al toxicity by cations, especially Ca, is well established (Alva et al., 1986a; Wright and Wright, 1987). Therefore, a number of ratios of Al species to Ca were calculated and non-linear equations were fitted to the regression of RRL on these Al : Ca ratios. The coefficients of determination are reported in Table 5.3. The CAB (2 log $[Ca^{2+}]$ - 3 log $[Al^{3+}]$ + 2 log $[AlOH^{2+}]$ + log $[Al(OH)_2^+]$) (Noble et al., 198$\overset{c}{\underset{\wedge}{8}}$) values corresponding to 90% RRL were 27 and 22 for the HP and the LP soils respectively. Menzies et al. (1994) reported that for mungbean the CAB value corresponding to 90% RRL was 31. All the ratios of Al species to Ca were good predictors of root growth, the highest coefficient of determination being obtained for the activity ratio of Al^{3+}/Ca^{2+}. Very similar Al^{3+}/Ca^{2+} activity ratios corresponding to 90 % RRL for the two soils ($4.23*10^{-4}$ and $4.51*10^{-4}$ for the HP and the LP soils respectively, Table 5.4, Fig 5.7d) indicate that this index may be useful in predicting Al toxicity irrespective of fertiliser effects.

5.4 Conclusions

The previous field study (Chapter 4) showed that long-term application of P fertilisers could substantially change Al species and Ca concentrations in the soil solution. Results of this glasshouse experiment showed that the relationships between soil Al indices and barley root growth are different for soils with different phosphate fertiliser history. The inability of total monomeric Al and 0.02 M $CaCl_2$- extractable Al to explain variations in root growth in the combined data for fertilised and unfertilised soils indicated that the relative proportions of the total monomeric or extractable Al that were actually phytotoxic were different for fertilised and unfertilised soils. This is mainly due to the higher percentage of less toxic Al-F complexes in the fertilised soil and the higher Ca concentration. The combination of Al-F complexes and high Ca concentrations cause the "critical Al toxicity levels" to be much higher in the fertilised soils. The ability of the activity ratio of Al^{3+}/Ca^{2+} to predict Al toxicity most consistently across soils with different

phosphate fertiliser histories indicates that soil solution Ca should be taken into account together with toxic Al species in the assessment of Al phytotoxicity.

Chapter 6

Evaluation of soil test procedures for predicting aluminium toxicity in different soil types

6.1 Introduction

In Chapter 5, it was found that long-term application of P fertilisers can influence the critical levels of various Al toxicity indices. Of these, the Al^{3+}/Ca^{2+} activity ratio in the soil solution was shown to be the best predictor of Al toxicity in a single soil type.

It is also important to determine whether these Al toxicity indices are suitable for predicting Al toxicity in contrasting soils. Conventional tests for Al toxicity in soils using bulk soil measurements (pH, exchangeable Al, percent Al saturation of CEC, and salt-extractable Al) often have difficulty in predicting Al toxicity problems across a wide range of soils (Adams and Lund, 1966; Wright et al., 1989a). However, for soils having similar parent materials and clay minerals, these measurements have sometimes been found to be useful in predicting Al toxicity for a given plant (Blamey and Nathanson, 1977; McCormick and Amendale, 1983; Manrique, 1986).

Soil solution Al appears to have the most potential for use as a diagnostic tool for Al toxicity across a range of soils (Baker, 1988; Bruce et al., 1988). Soil solution however contains non-toxic as well as toxic forms of Al and methods are required to separate these species and to determine only the toxic forms of Al. One such approach involves separating soil solution Al into operationally defined fractions based on the rate of reaction between a complexing agent [e.g. 8-hydroxyquinoline (HQ), ferron, aluminon, pyrocatecol violet (PCV), or chrome azurol S (CAS)] and soluble Al (Blamey et al., 1983; James et al., 1983; Hodges, 1987; Bartlett et al., 1987; Hawke and Powell.,1994). If these reactions are allowed to go to completion, these complexing agents apparently

react with non-toxic as well as toxic forms of Al. At shorter times however these complexing agents may react preferentially with the simpler more toxic forms of Al.

Thus labile Al, as measured by HQ in a short reaction time of 15 s (James et al., 1983), has been shown to be closely correlated with the growth of subterranean clover in acidic topsoils (Whitten and Ritchie, 1991). In another study HQ reacted in 15 s with only a small proportion of the non-toxic Al that was complexed with F, and appeared to provide a good estimate of toxic Al in nutrient solutions (Noble et al., 1988a).

Bartlett et al. (1987) have shown that the amount of coloured complex formed between Al and PCV in a given length of time is indicative of the lability or reactivity of the Al. Hawke and Powell (1994) proposed a CAS colorimetric method combining flow injection analysis with short reaction times (10 s) to assess toxic Al in soil solution. This method was said to measure free Al (Al^{3+}+ monomeric hydroxy Al species+some of the organic Al complexes).

Many of the procedures described above appear to work best when most of the solution Al is present in inorganic forms. Measurement of uncomplexed Al in the presence of subtantial amounts of organic ligands presents more of a problem and the sensitivity and selectivity of such measurements varies among the different complexing agents used in the colorimetric methods. For example HQ reacted in 15 s with a greater proportion of Al complexed with fulvic acid than PCV in 30 s (Kerven et al., 1989 a, b). This indicates that PCV requires a longer time to react with Al-organic complexes compared with HQ. Therefore, the PCV method may be able to exclude some of the high molecular weight, organically complexed Al, which is considered to be non-phytotoxic.

Although there have been many studies investigating the rates of reaction of Al with these complexing agents it is only rarely that these kinetic studies have been combined with complete Al speciation calculations to determine which of the Al species were most likely

to have reacted with the complexing agents during the short-time colorimetric measurements.

Similarly, only a few studies have actually evaluated the usefulness of these complexing agents in predicting Al toxicity in plants. In addition, some of these methods are very time consuming, and require special skills and instruments and therefore may not be useful as a routine chemical test for Al toxicity.

If it could be shown that one or more of these complexing agents react with a defined fraction of solution Al that is toxic to plants then this would provide a more convenient, rapid assay for Al toxicity than the time-consuming, expensive speciation procedure used in the previous chapter.

6.2 Objectives

The objective of this study was to evaluate a range of techniques for predicting the potential toxicity of Al for early root growth in widely different soil types.

6.3 Materials and Methods

Four contrasting soils from the North and South Islands of New Zealand were collected to a depth of approximately 75 mm after clearing the surface of plant debris. The soils were air-dried and passed through a 2 mm sieve. The classification and selected properties of the soils are shown in Table 6.1.

6.3.1 Plant growth conditions

The soils were amended with different rates of either $Ca(OH)_2$ or HCl to obtain varying pH values. The amended soils were incubated at field capacity for 4 weeks at room temperature (20-25°C). Seeds of barley (*Hordeum vulgare* L.) were pregerminated on a

Table 6.1. Some chemical and physical properties of the experimental soils.

Soil	Classification	pH (H₂O)	Organic Carbon %	Total N %	Olsen P $\mu g\ g^{-1}$	[a]SO₄ $\mu g\ g^{-1}$	K $cmol_c\ kg^{-1}$	Ca $cmol_c\ kg^{-1}$	Mg $cmol_c\ kg^{-1}$	Na $cmol_c\ kg^{-1}$	[b]ECEC $cmol_c\ kg^{-1}$
Oruanui	Podzolic Orthic Pumice Soil	4.6	7.8	0.46	92.9	11.8	0.44	2.1	0.39	0.20	3.4
Te Koporu	Humus-pan Densipan Podzol	4.1	12.7	0.26	0.5	9.0	0.07	0.2	1.59	0.56	4.6
Cargill	Acidic Mafic Brown Soil	5.5	5.2	0.39	42.4	14.0	2.11	12.0	2.68	0.50	17.4
Wharekohe	Perch-gleyed Densipan Ultic Soil	4.2	3.4	0.11	2.9	4.0	0.07	0.9	0.52	0.28	3.2

[a] Phosphate extractable sulphate was measured by the method of Searle (1979).

[b] Effective cation exchange capacity (ECEC) = KCl-extractable Al + Σ exchangeable bases (Na + K + Ca + Mg).

moist paper and planted, four per cup, in 300-ml plastic cups containing the moist soils inside a glasshouse maintained at 25°C. Each treatment was replicated four times. The cups were placed on trays and covered with polyethylene sheets, so that watering would not be required during the 3-day growth period. Root growth was measured as described in Chapter 5.

6.3.2 Analytical techniques

Soon after the seedlings were separated from the soil, soil solutions were removed from subsamples of the moist soils by centrifugation (Elkhatib et al., 1987). Soil solution pH and electrical conductivity were measured immediately. Total soil solution concentrations of Ca, Na, K, Mg were determined by atomic absorption/emission spectrophotometry. Ion chromatography was used to analyse for Cl, NO_3 and SO_4. Fluoride was measured with a F-ion selective electrode. Aluminium measurements (Driscoll, 1984) and speciation were carried out as described in Chapter 4.

Aluminium reactivities were determined in subsamples of the soil solutions using the PCV method described in Chapter 4. The PCV method was selected because PCV is thought to take a longer time to react with the non-phytotoxic organic Al complexes than other complexing agents (eg. HQ) and therefore by utilising short-term PCV reactions these non-phytotoxic Al species may be excluded from the Al determination. The method involves adding 1,10 phenonthroline, PCV, followed by hexamethylene (pH-6.2) to the sample solutions. Samples were mixed thoroughly for approximately 8-10 s using a mechanical shaker and the absorbancy changes at 15 s, 20s, 30s, 1 min, 2 min, and 4 min time periods were recorded. The concentrations of the reacted Al were calculated from a calibration curve.

A further subsample of moist soil in which the seedlings had been grown was air-dried and analyzed for soil pH 1:2.5 (H_2O), and 0.02M $CaCl_2$- and 1 M KCl-extractable Al by the methods described in Chapter 3.

6.4 Results and Discussion

6.4.1 Chemical properties of the bulk soils

Chemical properties and the classification of the soils are described in Table 6.1. Initial soil pH of the samples varied from 4.1 to 5.5. Soil Olsen P varied from 0.5 to 92.9 $\mu g\ g^{-1}$. The high P value in the Oruanui soil is mainly due to long-term application of SSP at this site when it was under pasture before the establishment of forest (Beets and Brownlie, 1987) and could also be due to organic matter decomposition and subsequent increase in soil P during incubation. Cargill clay had very high exchangeable K, Ca, and Mg compared with the other soils. There was little variation in exchangeable Na concentration within the soil types studied. The soils also had widely different effective cation exchange capacites.

6.4.2 Soil solution composition

There was a wide range in the concentrations of ions in the soil solutions (Table 6.2). The total monomeric Al concentration of the soil solutions varied from 0.6 to 362 μM while soil solution pH varied from 3.73 to 6.54. The total monomeric Al increased with decreasing pH. The solution Ca varied from 40 to 7022 μM. Increased pH corresponded to increased Ca concentration in the Oruanui, Te Koporu and Wharekohe soils, but not in the Cargill soil, because of the addition of $Ca(OH)_2$ to adjust pH in the first three soils. In the Cargill soil, HCl was added instead of $Ca(OH)_2$ to adjust pH. Magnesium concentration varied from 182 to 1261μM with only two of the fifteen treatments having more than 1000 μM. There was a wide variation in K concentration (91 to 3006 μM), and as for Ca, the Oruanui and Cargill soils had a higher K concentration than the other two soils. This is mainly because of the high exchangeable K in the former soils. Sodium concentrations varied from 622 to 2160 μM. There was no consistent effect of pH on K, Mg and Na concentrations.

Table 6.2. Soil solution composition.[a]

Trt No	Soil	Solution pH	Na	K	Ca	Mg	Cl	NO$_3$	SO$_4$	F	Total monomeric Al	ionic strength
							μM					M
1	Oruanui	3.73	1121	3006	1929	643	760	15497	249	31.5	362.3	0.0197
		(0.01)	(11)	(35)	(25)	(11)	(16)	(102)	(1.5)	(0.55)	(7.5)	(0.00013)
2	Oruanui	3.90	942	1768	4885	851	737	17244	275	19.4	268.0	0.0231
		(0.01)	(32)	(69)	(141)	(5.5)	(4)	(295)	(2)	(0.6)	(13.1)	(0.00017)
3	Oruanui	4.28	766	967	6361	811	672	17612	379	9.3	83.6	0.0234
		(0.02)	(33)	(120)	(296)	(12)	(30)	(434)	(2)	(0.1)	(1.6)	(0.00036)
4	Oruanui	5.03	622	479	7022	705	720	18208	471	2.3	11.4	0.0242
		(0.02)	(7)	(8)	(1120)	(2)	(4)	(99)	(5)	(0.05)	(0.6)	(0.00027)
5	Te Koporu	3.95	1984	140	40	594	2817	5.0	673	0.7	58.0	0.0069
		(0.02)	(20)	(4)	(8)	(7)	(54)	(0.1)	(3)	(0)	(1.5)	(0.00005)
6	Te Koporu	4.15	1975	126	120	474	2937	10	287	0.6	54.0	0.0058
		(0.02)	(54)	(3.5)	(9)	(13)	(45)	(0.5)	(6)	(0)	(1.4)	(0.00005)
7	Te Koporu	4.16	2160	157	222	670	3128	25.8	861	0.7	44.2	(0.0073)
		(0.02)	(68)	(3)	(9)	(3)	(77)	(2.5)	(5.5)	(0)	(1.05)	(0.00005)
8	Te Koporu	4.44	2012	131	347	610	2959	21	850	0.6	34.3	0.0071
		(0.02)	(12)	(2)	(6)	(12)	(36)	(3.3)	(4)	(0)	(0.7)	(0.00018)
9	Cargill	5.63	842	793	1163	665	389	5535	22	0.6	0.6	0.0075
		(0.07)	(25)	(29)	(39)	(16)	(18)	(241)	(2.5)	(0)	(0.1)	(0.00018)
10	Cargill	5.33	1317	1639	4948	1017	11837	8018	10	1.2	3.0	0.0221
		(0.03)	(53)	(95)	(207)	(7)	(413)	(209)	(0.5)	(0.1)	(0.4)	(0.00068)
11	Cargill	5.10	1967	2023	6719	1261	28887	1194	10	2.2	11.8	0.0348
		(0.02)	(60)	(104)	(313)	(2)	(354)	(44)	(1)	(0.05)	(0.6)	(0.00047)
12	Wharekohe	4.48	996	113	82	186	1954	17	25	0.7	30.2	0.0036
		(0.03)	(37)	(2)	(4)	(5)	(64)	(1)	(2)	(0)	(0.3)	(0.00006)
13	Wharekohe	4.87	969	93	171	182	1843	175	46	0.6	19.5	0.0032
		(0.02)	(59)	(2)	(10)	(9)	(82)	(10)	(2.5)	(0)	(0.6)	(0.00005)
14	Wharekohe	5.38	1110	106	347	217	2377	10	34	0.5	9.1	0.0035
		(0.01)	(96)	(5)	(15)	(13)	(86)	(0.5)	(3)	(0)	(1.2)	(0.00013)
15	Wharekohe	6.54	980	91	892	246	2187	10	18	0.5	2.1	0.0043
		(0.05)	(47)	(3)	(34)	(9)	(171)	(1)	(1)	(0)	(0.2)	(0.0001)

[a] Values within paranthesis ( ) are standard errors

A wide range of soil solution anion concentrations was also observed. Sulphate concentrations varied from 10 to 861 μM. The average SO_4 concentration in the Cargill and Wharekohe soils was much lower than those in the other two soils. There were large differences in NO_3 concentration (5 μM to 18 mM) in the soil solution. The NO_3 concentration was highest for the Oruanui soil (possibly due to the higher organic carbon and N content, Table 6.1). The exceptionally high Cl concentration in the Cargill soil is due to the large additions of HCl to this highly buffered soil to reduce the pH. Only the Oruanui soil had high concentrations of total solution F (31.5μM) due to the previous applications of F in SSP and potassic superphosphate when the land was under pasture. However, the F concentration decreased (to 2.3 μM) with the addition of $Ca(OH)_2$. Other soils had F concentrations less than 2 μM. The ionic strengths of the soil solutions were 0.0197-0.0242, 0.0069-0.0071, 0.0075-0.0348, 0.0036-0.0043 in the Oruanui, Te Koporu, Cargill and Wharekohe soils respectively. The ionic strength was well correlated with K, Ca, Mg, NO_3, and Cl concentrations in the soil solutions, but not with the concentrations of SO_4 or Na (Table 6.3). The wide variations in anion, cation and Al concentrations in these soil solutions would have provided a good test of a common Al toxicity index for different soil types.

6.4.3 Root growth

The effects of $Ca(OH)_2$ or HCl addition on soil pH, extractable Al concentrations and root elongation in the different soils are given in Table 6.4. Large differences in root elongation with varying pHs were noted in all soils. The mean root length ranged from 33 to 86 mm. The relative root length (RRL) was calculated as follows:

$$RRL = \frac{\text{Mean longest root length in a treatment}}{\text{Greatest mean root length of all treatments in that soil}} * 100$$

Table 6.3. Correlation matrix of the concentrations of soil solution ions, pH and ionic strength (μ).

	Solution pH	Na	K	Ca	Mg	Cl	NO$_3$	SO$_4$	F	μ
Solution pH	1.00									
Na	-0.31	1.00								
K	-0.25	-0.13	1.00							
Ca	-0.03	-0.32	0.55	1.00						
Mg	-0.23	0.24	0.65**	0.75**	1.00					
Cl	0.15	0.42	0.37	0.43	0.64	1.00				
NO$_3$	-0.30	-0.59	0.59	0.72**	0.43	-0.23	1.00			
SO$_4$	-0.54	0.53	-0.25	-0.14	0.12	-0.27	0.02	1.00		
F	-0.45	-0.26	0.79**	0.25	0.22	-0.18	0.68**	-0.01	1.00	
μ	-0.19	-0.10	0.76**	0.93***	0.87***	0.57	0.66**	-0.08	0.42	1.00

, * Significant at the 0.05 and 0.01 probability levels, respectively.

Table 6.4. Effect of Ca(OH)₂ or HCl addition on root elongation, soil pH and extractable Al.

Treatment No	Soil	Soil pH (H₂O)	Soil pH (0.01 M CaCl₂)	0.02 M CaCl₂-Al (mg kg⁻¹)	1 M KCl-Al (cmolᴄ kg⁻¹)	Root Length* (mm)
1	Oruanui	3.91	3.63	40.9	7.42	48^d
2	Oruanui	4.03	3.79	20.0	5.21	55^c
3	Oruanui	4.30	4.05	6.7	3.12	74^b
4	Oruanui	4.77	4.52	1.6	0.20	86^a
5	Te Koporu	3.96	3.20	26.5	3.00	33^c
6	Te Koporu	4.16	3.38	15.6	2.09	36^c
7	Te Koporu	4.26	3.51	9.7	1.42	49^b
8	Te Koporu	4.50	3.79	3.7	0.46	63^a
9	Cargill	5.48	4.89	0.6	0.15	85^a
10	Cargill	5.07	4.76	1.0	0.20	86^a
11	Cargill	4.99	4.75	1.0	0.20	36^b
12	Wharekohe	4.35	3.42	10.7	1.10	37^c
13	Wharekohe	4.90	4.02	2.2	0.37	49^b
14	Wharekohe	5.47	4.66	0.4	0.01	48^b
15	Wharekohe	6.49	5.81	0.1	0.01	65^a

* Root length followed by same letter are not different at the 0.05 probability level.
(Duncan's new multiple range test was done on each soil separately)

It should be noted that comparison of RRL values between soils requires an estimate of the maximum potential root growth in the absence of any Al toxicity for each soil. Ideally there should be a number of treatments with reasonably high pH (and low Al concentrations) for each soil to provide a good estimate of this maximum potential root length.

In the current study, the highest pH values obtained in some soils were still rather low and there was little evidence of a plateauing of RRL values at maximum pH. This raises the question of whether a good estimate of the maximum root length was obtained for all soils.

Inspection of the solution Al values (see section 6.4.7-Table 6.8) however, suggested that in all soils the solution Al concentrations in the treatments with the highest pH were well below published critical levels. It was therefore assumed that these treatments did indeed provide suitable estimates of maximum root length for the calculation of RRL values.

The RRL for the 15 different treatments are shown in Fig. 6.1. Acidic soil conditions severely restricted root growth (RRL<50%) in most of the treatments.

6.4.4 pH and root growth

Although theoretically one would expect an exponential relationship between root growth and soil or solution pH, inspection of the data points shows a clear linear relationship within the pH range studied. Therefore linear regression equations were used to determine the relationship between soil and soil solution pH with RRL. In all soils except the Cargill soil, the regressions of RRL on soil pH (H_2O) and soil solution pH had high R^2 values (Table 6.5). The RRL was positively related to soil and solution pH (Fig 6.2 a, b). The lower R^2 values for Cargill soil could be attributed to the narrow pH range and fewer data points in this soil. However, when all the soils were combined and analysed, R^2 values were very low.
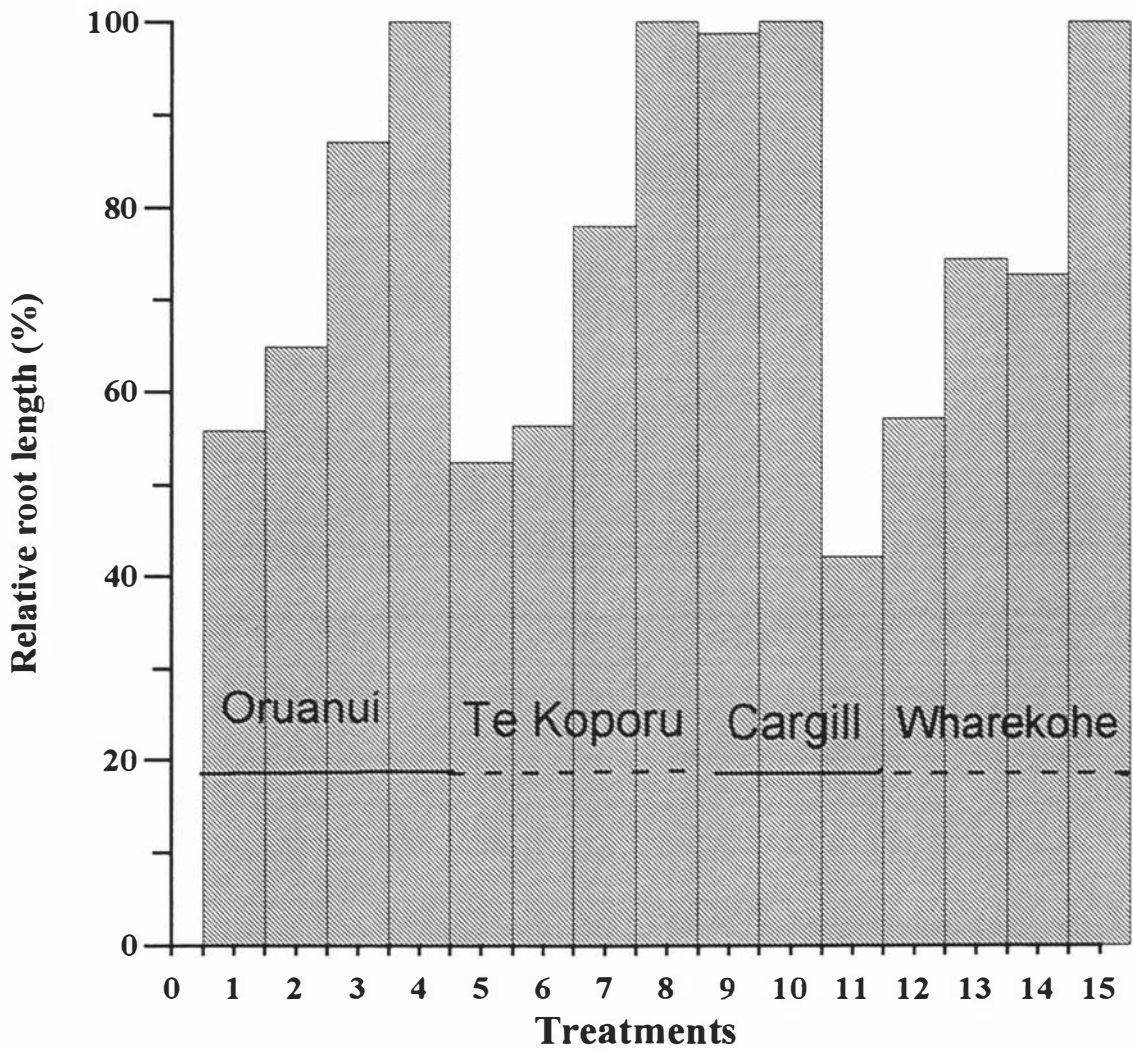
Fig 6.1. Treatment effects on relative root length (RRL).
(Refer Table 6.4 for treatment numbers)

Table 6.5. Coefficient of determination (R^2) of regression equation relating solid and solution acidity parameters and RRL.

Parameter	Model [**]	Oruanui	Te Koporu	Cargill	Wharekohe	All soils
Soil pH	y = bx+c	0.93	0.91	0.37	0.92	0.27
Solution pH	y = bx+c	0.90	0.88	0.72	0.92	0.31
$CaCl_2$-Al	logy = b*log(x)+c	0.97	0.96	0.30	0.87	0.32
KCl-Al	y = bx+c	0.96	0.92	0.23	0.60	0.20
Al (inorg) [*]	y = a+b*exp(c*x)	0.99	0.52	0.96	0.56	0.28
Al^{3+} activity	log(y) = bx+c	0.99	0.80	0.90	0.62	0.31
Al^{3+}/Ca^{2+} activity ratio	y = a+b*exp(c*x)	0.99	0.93	0.98	0.42	0.36

[*] Inorganic monomeric Al
[**] Models giving the highest R^2 values are presented
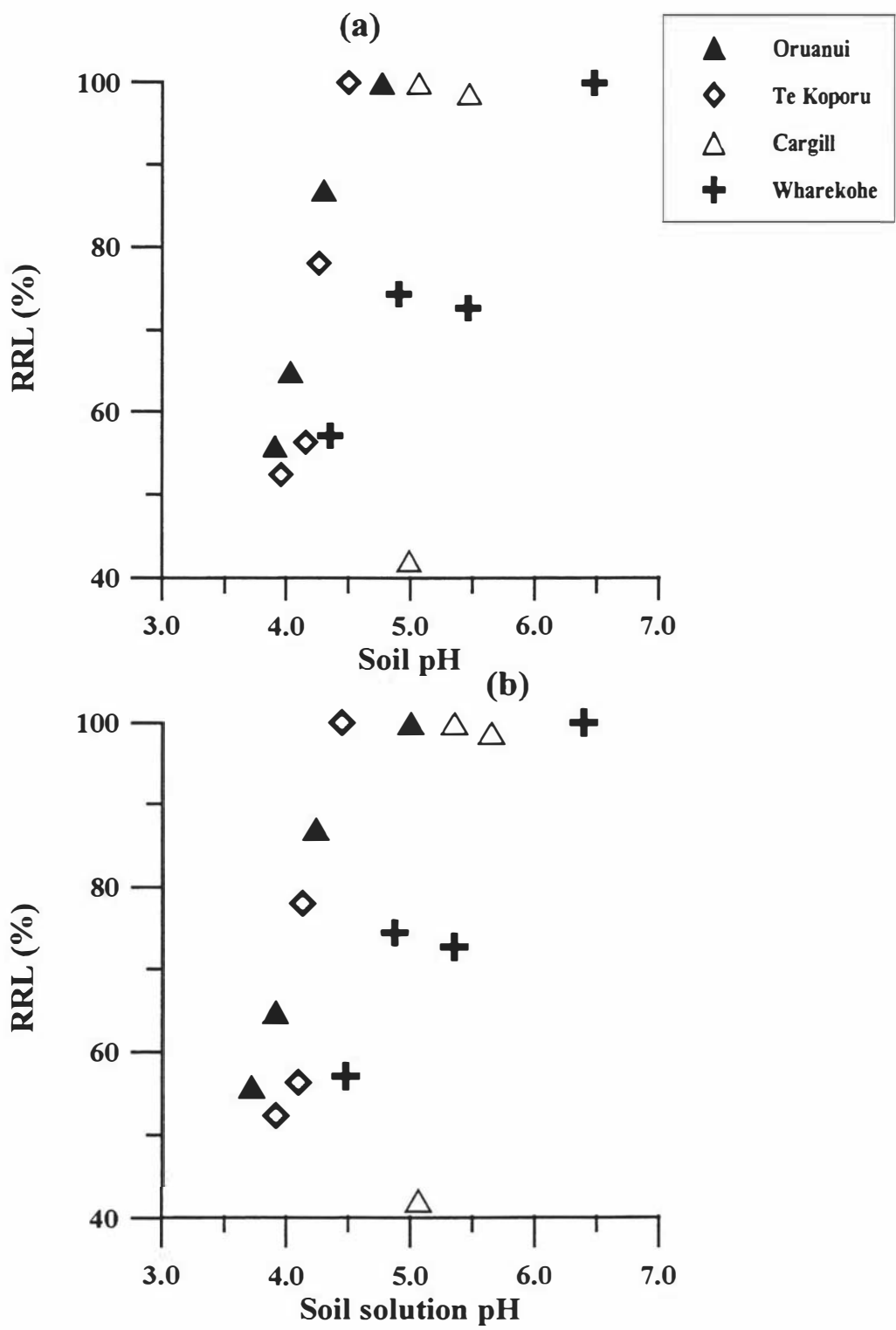
Fig 6.2. Relationship between relative root length (RRL) and (a) soil pH and
(b) soil solution pH.

The poor relationship between pH and RRL across different soils suggests that it is not the acidity per se that is affecting root growth. This is supported by the work of Cameron et al. (1986) which suggests that within the pH range studied, pH is not likely to be a major limitation on root growth. Instead it may be the association of pH and Al that is responsible for the observed depressions in root growth.

The relationship between pH and Al^{3+} may vary between soils depending on the soil mineralogy. For example, if gibbsite controls Al solubility (log K of 8.04; Lindsay, 1979), at pH 4.5 the Al^{3+} concentration would be 3.47 μM. However, if kaolinite controls Al solubility, at a Si concentration of $10^{-3.1}$ M and using a log K value of 5.45 for kaolinite solubility (Lindsay, 1979), the Al^{3+} concentration at pH 4.5 would be 0.02 μM (Shuman, 1995). Therefore, it is possible that the poor relationship between pH and RRL when data for all soils were combined, compared with data for individual soils, is due to mineralogical differences among the soils.

6.4.5 Aluminium extraction methods and root growth

Amounts of soil Al extracted by 0.02 M $CaCl_2$, and 1 M KCl are shown in Table 6.4. 1 M KCl-extractable Al was much higher than 0.02 M $CaCl_2$-extractable Al because 1M KCl removes most of the exchangeable and soluble Al while 0.02 M $CaCl_2$ removes only the soluble and very little exchangeable Al.

Although it was expected that the soluble Al that is extracted by 0.02 M $CaCl_2$ might be a better indicator of Al toxicity, in short-term root growth studies such as this, it did not improve the R^2 values over a high ionic strength extractant such as 1 M KCl in the individual soils (Table 6.5, Fig 6.3). In the combined data from all soils, however, the Al extracted by 0.02 M $CaCl_2$ was slightly better related to RRL than 1M KCl-extractable Al (Table 6.5).
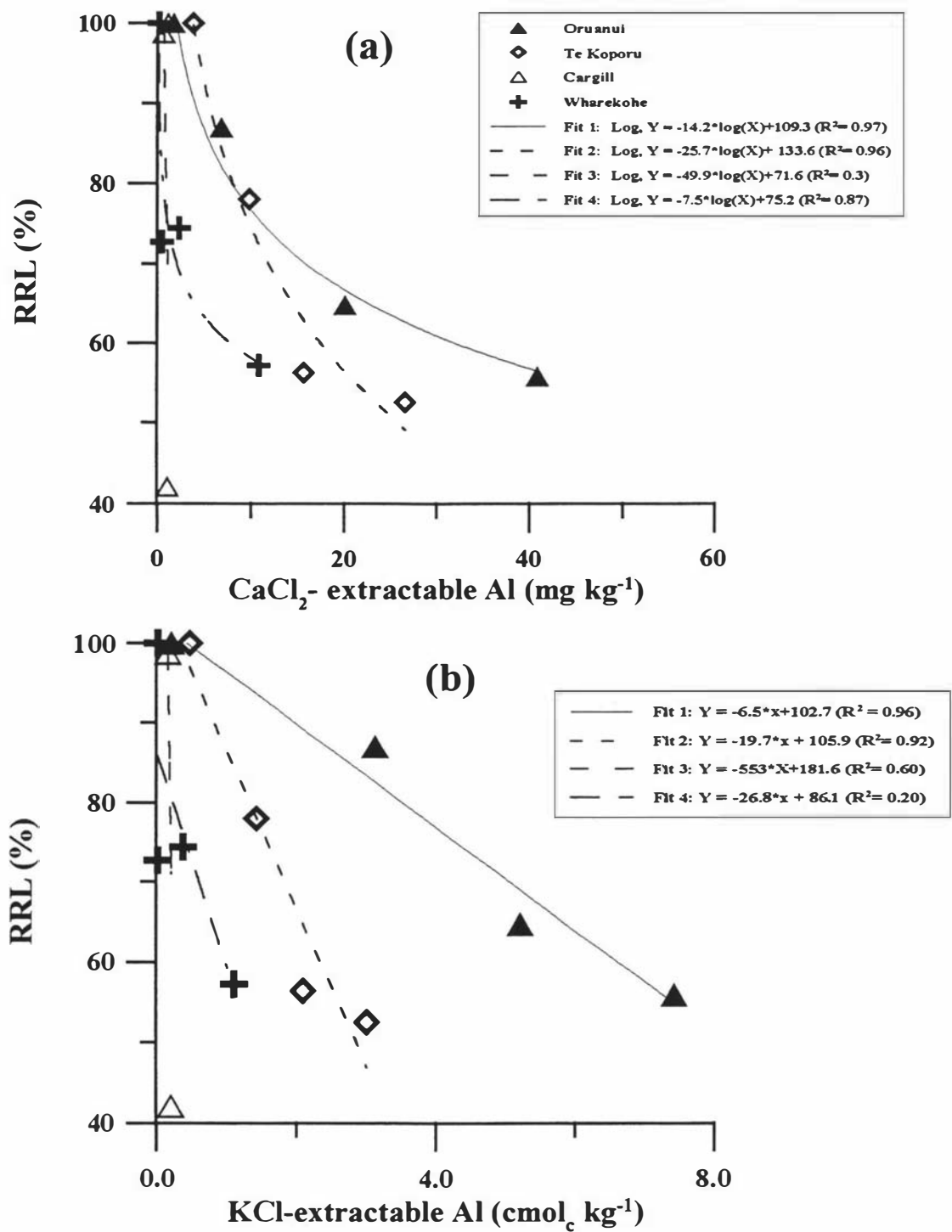
Fig 6.3. Relationship between relative root length (RRL) and (a) $CaCl_2$- extractable Al and (b) KCl-extractable Al.

The amount of Al extracted by dilute $CaCl_2$ has been shown to be related to plant growth in acid soils by other investigators (Hoyt and Nyborg, 1971; Bromfield et al., 1983; Jarvis,1987). Mckenzie and Nyborg (1984) found that Al extracted with 0.02 M $CaCl_2$ was a more accurate indicator of root yield impairment in acid subsoils than soil pH or exchangeable Al. The amount of Al extracted by 0.02 M $CaCl_2$ is expected to be more closely related to soil solution Al than the Al extracted by the high ionic strength 1M KCl. However, the ionic strength of the 0.02 M $CaCl_2$ solution was still much higher than the mean ionic strength found in the soil solutions in this experiment (Table 6.2). Therefore it might have extracted different pools of soil solid phase Al in addition to soil solution Al. Another limitation of dilute $CaCl_2$ as an extractant for Al is that, as discussed in Chapter 5, in soils containing large quantities of F much of the Al extracted by $CaCl_2$ may be in the form of less toxic Al-F complexes.

The RRL was negatively related to the amounts of soil Al extracted by KCl and $CaCl_2$ (Fig 6.3 a b). The R^2 values for the regression equations fitted to these relationships for individual soils (except the Cargill soil) were high, but when the data from all the soils were combined and analysed the R^2 values were very low (Table 6.5). An inspection of the data points in Fig 6.3 suggested that one of the treatments in the Cargill soil could be an outlier. In this treatment, although extractable Al levels were low, root growth was severely restricted. This treatment corresponded to the highest rate of application of HCl and as a result had very high Cl concentrations in the soil solution (Table 6.2). Therefore it is possible that root growth in this treatment was inhibited by Cl toxicity.

The regression analyses were therefore repeated for the combined data of RRL vs $CaCl_2$-Al, and for RRL vs KCl-Al omitting that point. Although the recalculated R^2 values (0.51 for $CaCl_2$-Al and 0.38 for KCl-Al) were slightly higher than the previously calculated R^2 values, they did not improve the predictability greatly.

Thus it would appear that the Al extracted by these reagents might have consisted of differing proportions of non-toxic and toxic Al species in the different soils.

6.4.6 Soil Solution Al and root growth

Total monomeric Al in the soil solutions ranged from 0.6 to 362 μM (Table 6.2). From 17 to 100 % of this total monomeric Al was complexed with organics (Al_{org}) (Table 6.6). In general, the concentration of Al_{org} decreased (Table 6.6) with $Ca(OH)_2$ addition and increased with HCl addition, although when expressed as a percentage of total monomeric Al, Al_{org} % actually increased with increasing pH because inorganic monomeric Al decreased at a faster rate than Al_{org} with increasing pH.

Amounts of soil solution Al reacting with PCV (PCV-Al) in 15 s, 30 s, 1 min, 2 min, 4 min are shown in Table 6.6. When each soil type was considered separately, as in the case of soil pH and extractable Al, the PCV-Al determined after all times of reaction related well with RRL (R^2 =83-99%) (Table 6.7). However, the R^2 values were again very low when data from all soils were combined and analysed. This could be due to the fact that even in the shortest time used in this study (15 s) some of the non-toxic Al species might have reacted with PCV, as shown by Hawke and Powell (1994) in a more recent study. In different soils, PCV appears to be reacting with different amounts of the non-toxic organic Al fractions in the soil solution (Table 6.6). For example treatments 9, 10, 14 and 15 have nearly all the monomeric Al in the form of Al_{org} and yet PCV at 15 s reacted with 50 to 77% of the monomeric Al.

Kerven et al. (1989b) and in a more recent study Hawke and Powell (1994), have shown that PCV may react even in short-time periods with non-toxic Al complexes and therefore overestimate the toxic component. However, Bartlett et al. (1991) found a stronger correlation between Al reacting with PCV in 30 sec and root length of *Medicago sativa* in nutrient solution studies, compared with longer reaction times.

There were no differences between PCV-Al measured over different time periods in explaining the variation in RRL (R^2 values being nearly the same). This is due to the high

Table 6.6. Concentration of solution Al (μM) reacted with PCV at different time periods, Al(org)[a] concentration (μM) and %Al(org)[b].

Treatments	15 s	30 s	1 min	2 min	3 min	4 min[c]	Al(org)	Al(org) %	% Al reacted with PCV[d] (15 s)
1	256.2	284.3	314.4	341.9	354.5	362.3	70.4	20	71
2	162.1	187.1	215.9	244.4	259.7	268.0	45.0	17	61
3	55.4	61.1	68.7	76.5	80.9	83.6	23.7	28	66
4	6.3	6.8	7.5	9.1	10.1	11.4	10.9	95	55
5	25.1	31.5	39.2	48.4	53.9	58.0	52.3	90	43
6	24.1	29.7	36.8	45.5	50.7	54.0	50.9	95	45
7	19.0	23.9	30.1	37.1	41.3	44.2	38.9	88	43
8	14.1	17.8	22.6	28.3	31.8	34.3	32.6	96	41
9	0.4	0.4	0.5	0.5	0.5	0.6	3.9	100	77
10	2.0	2.2	2.4	2.7	2.8	3.0	4.6	99	66
11	8.5	9.3	10.2	11.1	11.6	11.8	5.5	47	72
12	14.0	17.3	21.2	25.7	28.3	30.2	29.2	97	46
13	8.9	10.7	13.2	16.2	18.2	19.5	19.3	98	46
14	4.6	5.3	6.3	7.6	8.4	9.1	10.2	99	50
15	1.6	1.6	1.7	1.8	2.0	2.1	4.6	100	76

a-Organic monomeric aluminium concentration

b- [organic monomeric Al] / [total monomeric Al] *100

c-Total monomeric aluminium (Seip et al., 1984).

d-% Al reacted = [Solution Al reacted in 15 sec with PCV]/ [Total monomeric Al]*100

Table 6.7. Coefficient of determination (R^2) between PCV-Al measured at different time periods and RRL.

Time	Model[a]	Oruanui soil	Te Koporu soil	Cargill soil	Wharekohe soil	All soils
15 s	exponential	0.99[**]	0.99[**]	0.96[**]	0.62[**]	0.26
30 s	exponential	0.99[**]	0.99[**]	0.96[**]	0.62[**]	0.26
1 min	exponential	0.99[**]	0.99[**]	0.96[**]	0.62[**]	0.25
2 min	exponential	0.99[**]	0.99[**]	0.96[**]	0.62[**]	0.22
3 min	exponential	0.99[**]	0.99[**]	0.96[**]	0.61[**]	0.25
4 min	exponential	0.99[**]	0.98[**]	0.95[**]	0.61[**]	0.22

[a]Model y=a+b*exp(c*x), (x=PCV-Al, y=RRL)

correlations between Al reacted with PCV at different time periods (Correlation coefficients (r) between any time periods were identical and highly significant; r=0.99[***]). If the amounts of Al reacting with PCV at different time periods are inter-correlated, then regressions of RRL with PCV at different time periods may give similar R^2 values, but the critical Al level will vary for the different PCV reaction times (Fig 6.4).

6.4.7 Al speciation

An estimate of inorganic monomeric Al speciation in soil solution was obtained using the soil solution composition and the MINEQL[+] program (Schecher and McAvoy, 1991). The calculated concentrations of Al species are shown in Table 6.8. The inorganic monomeric Al as determined by the difference between total monomeric Al and organic monomeric Al was used as the Al input.

The free Al^{3+} concentration varied from 0 to 216 μM (Table 6.8) with Oruanui soil having the highest concentration. However, in most of the soil treatments the Al^{3+} concentration was below 4 μM. Increases in pH decreased Al^{3+} concentration markedly. Even though the Oruanui soil treatment 1 and the Te Koporu soil treatment 5 had similar soil pH values (Table 6.4), the Al^{3+} concentration was much higher in the Oruanui soil. This could be due to the differences in the mineralogy, organic matter content (Table 6.1) and also the differences in anion concentrations (Table 6.2). This supports the earlier observation that Al toxicity can not always be predicted by soil pH alone.

6.4.8 Comparisons between Al measured with PCV and estimated Al species concentrations

Kerven et al. (1989 b) considered that Al measured by a 1 min PCV method was inorganic monomeric Al. In solutions of Te Koporu, Cargill and Wharekohe soils which contain a high percentage of organic Al, the concentration of inorganic monomeric Al measured by 1 min PCV method was higher (Fig 6.5b) than the inorganic monomeric Al
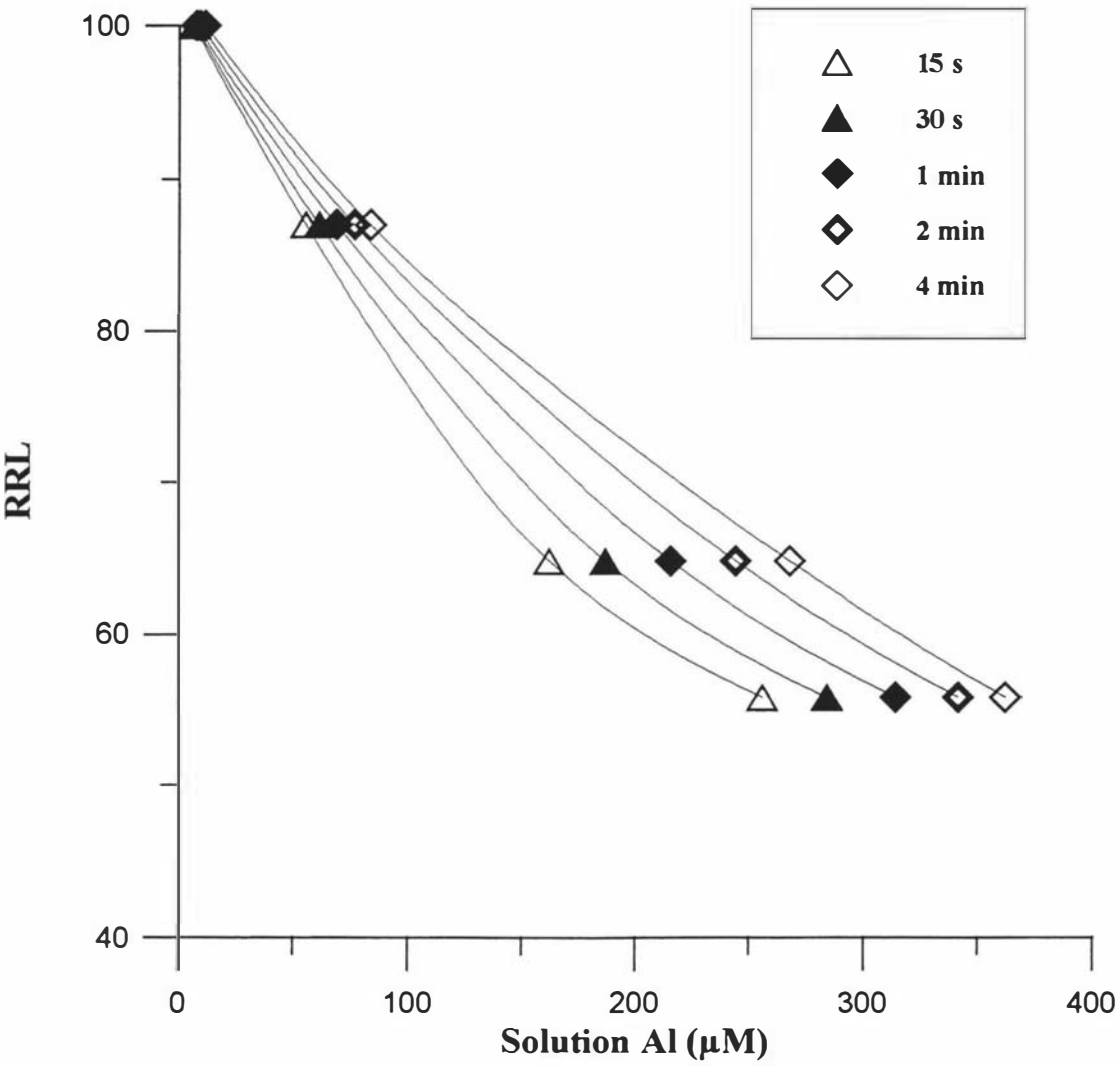
Fig 6.4. Relationship between relative root length (RRL) and Al reacted with PCV in different time periods (Oruanui soil).

Table 6.8. Calculated Al species concentration (μM) in the soil solutions.

Treatment No.	Soil	Al^{3+}	$Al(OH)_2^{1+}$	$Al(OH)^{2+}$	Total toxic Al [a]	AlF_2^{1+}	AlF^{2+}	$AlSO_4^{1+}$
1	Oruanui	216.0	0.50	11.88	228.37	0.24	31.03	31.83
2	Oruanui	168.0	0.86	13.78	182.63	0.12	19.18	20.78
3	Oruanui	36.6	1.05	7.08	44.70	0.12	9.02	5.95
4	Oruanui	0.02	0.02	0.02	0.05	0.19	0.25	0.00
5	Te Koporu	2.92	0.01	0.27	3.20	0.00	0.63	1.81
6	Te Koporu	2.24	0.00	0.31	2.55	0.00	0.58	0.61
7	Te Koporu	2.37	0.00	0.35	2.72	0.00	0.61	1.84
8	Te Koporu	0.56	0.04	0.16	0.76	0.02	0.40	0.43
9	Cargill	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	Cargill	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	Cargill	1.15	1.48	1.50	4.12	0.15	1.73	4.12
12	Wharekohe	0.51	0.05	0.18	0.74	0.02	0.39	0.74
13	Wharekohe	0.02	0.01	0.02	0.05	0.02	0.10	0.05
14	Wharekohe	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	Wharekohe	0.00	0.00	0.00	0.00	0.00	0.00	0.00

[a] $[Al^{3+} + Al(OH)^{2+} + Al(OH)_2^{1+}]$
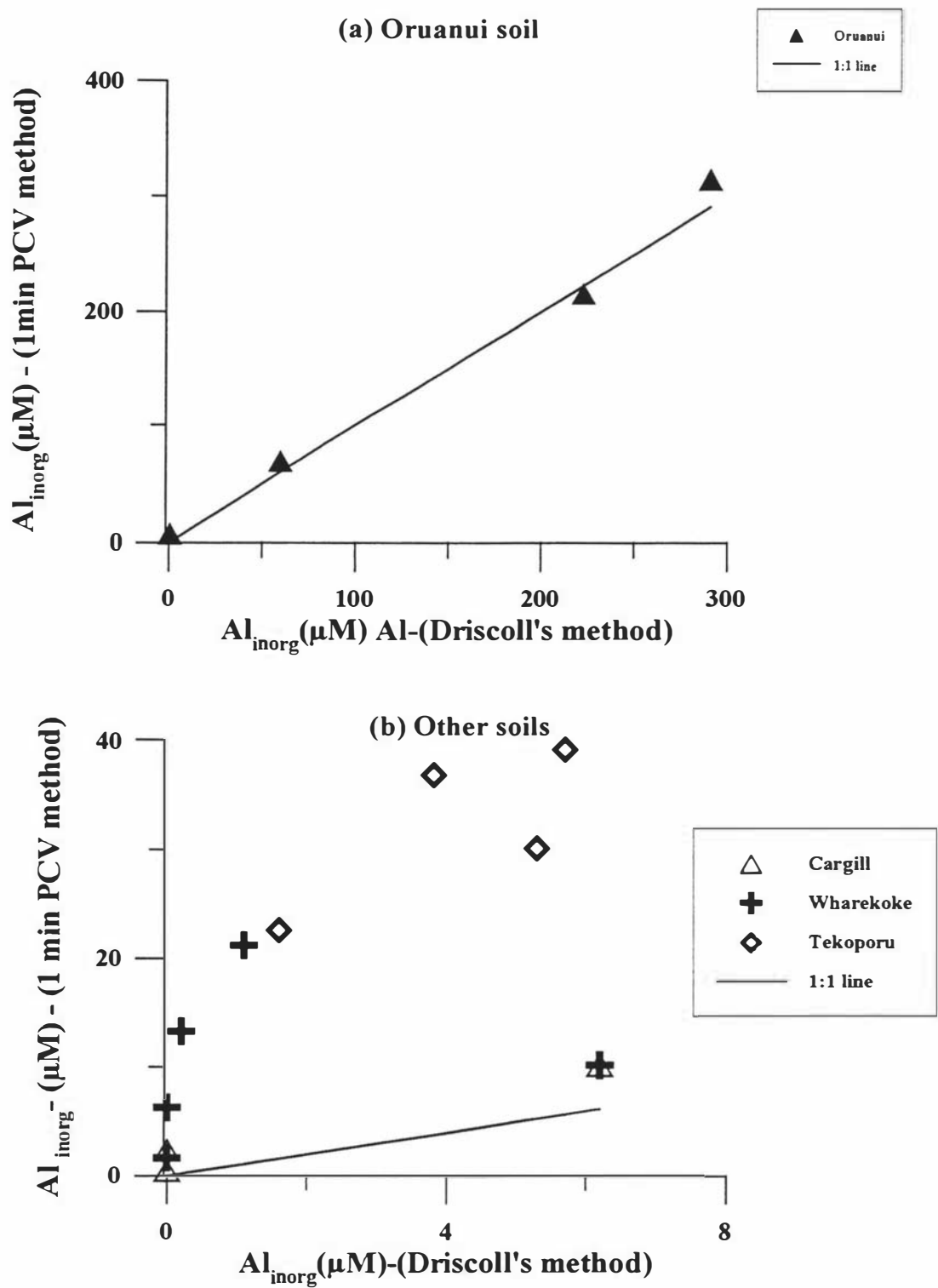
Fig 6.5. Comparison between inorganic monomeric Al (Al_{inorg}) measured by
Driscoll's method and 1 min PCV method (Kerven et al., 1989b).

measured by the cation exchange method of Driscoll (1984). However, in the Oruanui soil which had a lower percentage of organic Al, both methods agreed fairly well (Fig 6.5a). This suggests that in soils with a high percentage of organic Al, PCV in 1 min reacts with organic Al as well as inorganic Al, in contrast to what Kerven et al. (1989b) reported.

The comparison between Al reacted with PCV in 15 s and calculated toxic Al concentrations indicated that even in the shortest possible time (15 s), PCV has reacted with some of the non-toxic organic Al species in Te Koporu, Cargill and Wharekohe soils (Fig 6.6b). However, in the Oruanui soil which had a lower percentage of Al_{org}, the Al concentration measured in 15 s was similar to the total toxic Al concentration predicted from speciation calculations. It is noted that the solutions with the higher percentage of organic Al (Table 6.6a) showed the greatest disparity between the concentration of toxic Al species measured with 15 s PCV and the sum of predicted concentrations of toxic Al species.

6.4.9 Al species and root growth

Many investigators have reported that the activity of Al^{3+} in soil solution is the single best indicator of plant toxicity (Adams and Lund, 1966; Pavan and Bingham, 1982). Cameron et al. (1986) found that barley root growth was severely affected when the Al^{3+} concentration was as low as 4 μM. As reported in Chapter 5, in a single soil type, root elongation was better predicted using soil solution Al activities rather than concentrations. Calculated activities (as described in Chapter 4) of toxic Al species are given in Table 6.9. A plot of RRL vs calculated Al^{3+} activity is shown in Fig 6.7 and the R^2 values are given in Table 6.5. Similar results were obtained when RRL vs calculated total toxic Al $\{Al^{3+} + Al(OH)^{2+} + Al(OH)_2^+\}$ activities were plotted (Fig 6.8). Calculated soil solution Al^{3+}, or toxic Al activity, was not effective in this study in estimating the extent of root elongation. Widely different root growth was found in soil solutions with the same Al^{3+} or toxic Al activity (Fig 6.7, 6.8).
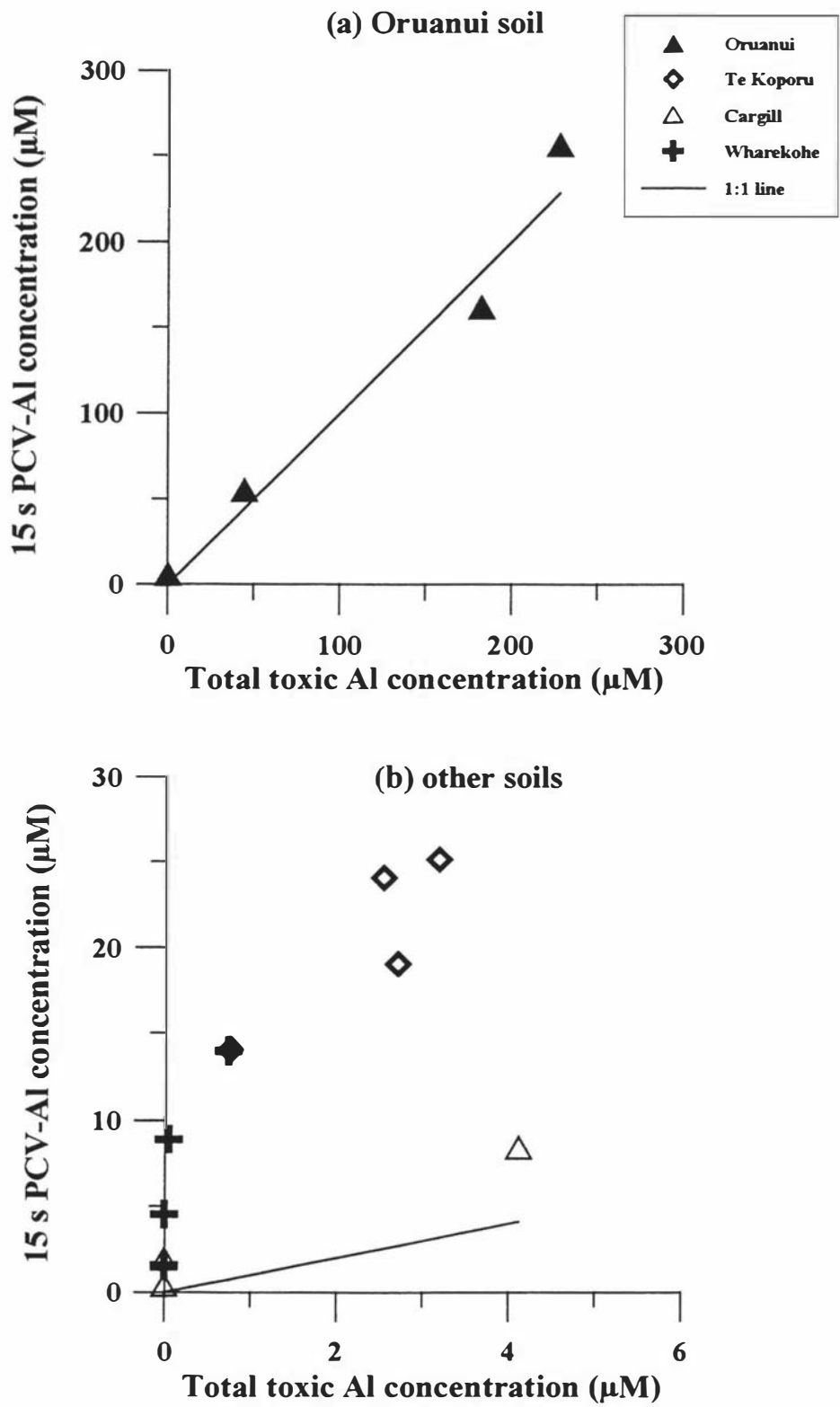
Fig. 6.6. Comparison between 15 s PCV-Al and estimated total toxic Al $(Al^{3+} + Al(OH)^{2+} + Al(OH)_2^{1+})$ concentration.

Table 6.9. Calculated activities (μM) of Al species, and total Ca and Al^{3+}/Ca^{2+} activity ratios.

Treatment	Al^{3+}	$Al(OH)_2^{+1}$	$Al(OH)^{2+}$	Total toxic Al^*	Ca^{2+}	Al^{3+}/Ca^{2+}
1	58.30	0.42	6.59	65.31	1069	0.05455
2	41.23	0.72	7.31	49.27	2592	0.01595
3	8.89	0.88	3.74	13.52	3363	0.00265
4	0.01	0.01	0.01	0.03	3675	0.0000
5	1.30	0.01	0.19	1.49	28	0.05232
6	1.06	0.00	0.22	1.28	86	0.01342
7	1.03	0.00	0.24	1.27	153	0.00677
8	0.25	0.03	0.11	0.39	240	0.00102
9	0.00	0.00	0.00	0.00	797	0.00000
10	0.00	0.00	0.00	0.00	2654	0.00000
11	0.21	1.20	0.70	2.11	3141	0.00010
12	0.29	0.05	0.14	0.47	63	0.00425
13	0.01	0.01	0.02	0.04	133	0.00010
14	0.00	0.00	0.00	0.00	266	0.00000
15	0.00	0.00	0.00	0.00	667	0.00000

*$(Al^{3+} + Al(OH)^{2+} + Al(OH)_2^{1+})$
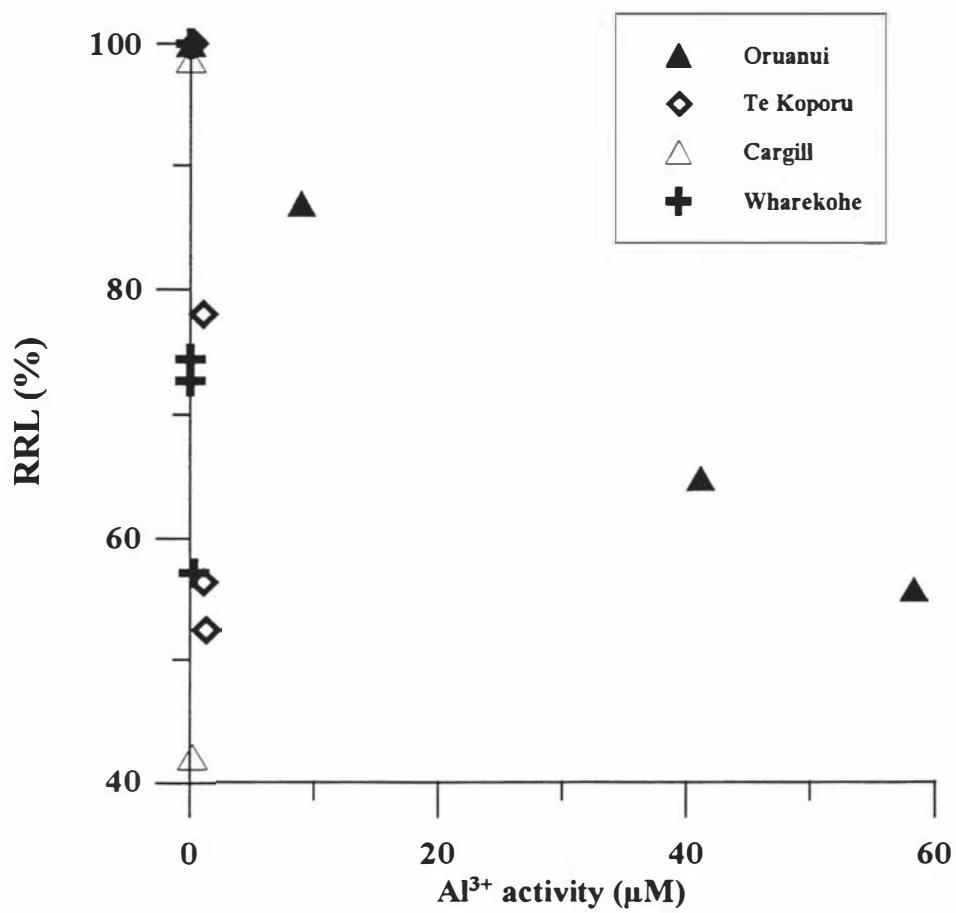
Fig 6.7. Relationship between relative root length (RRL) and calculated Al^{3+} activity.
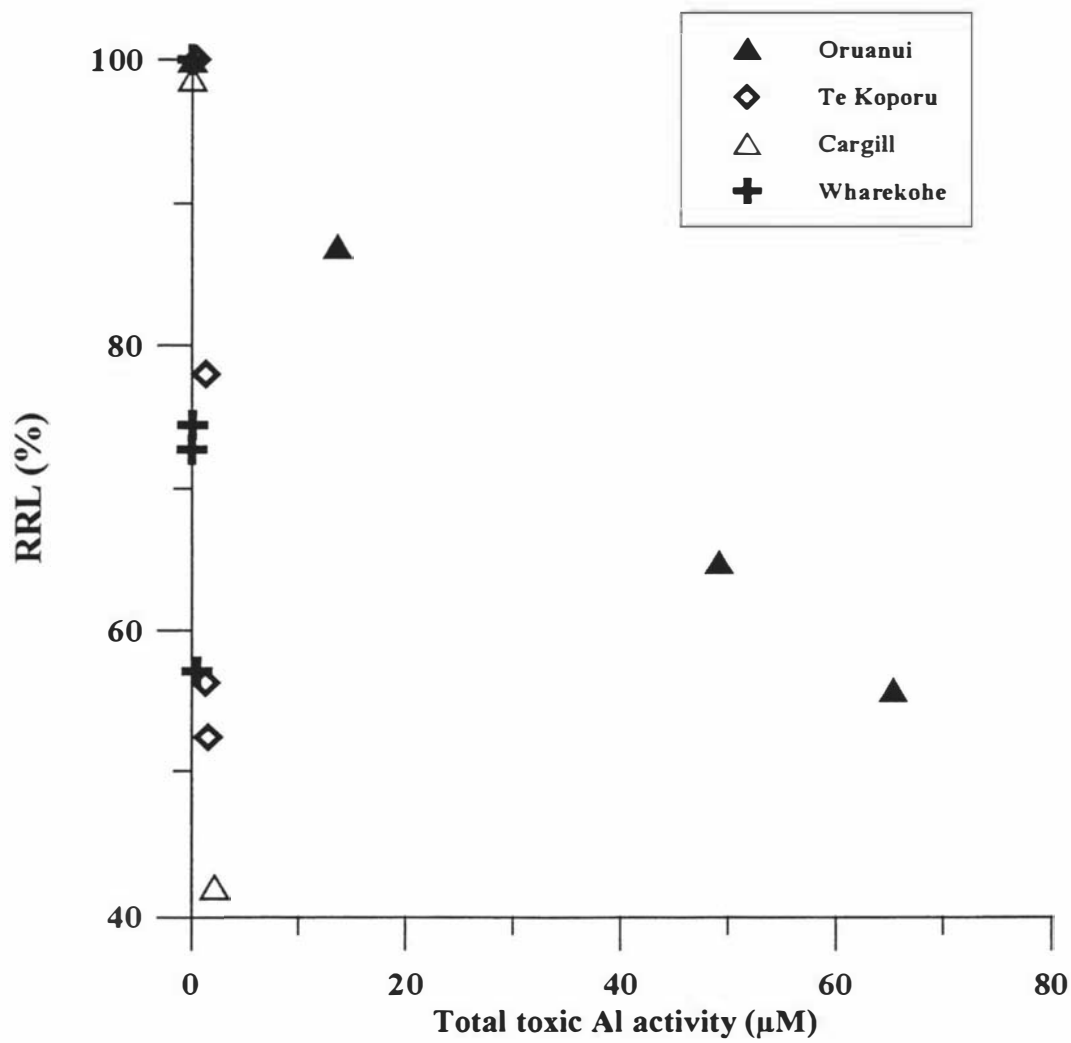
Fig 6.8. Relationship between relative root length (RRL) and calculated total toxic Al $(Al^{3+} + Al(OH)^{2+} + Al(OH)_2^{1+})$ activity.

6.5 Aluminium-calcium interactions and root growth

In Chapter 5, the Al^{3+}/Ca^{2+} activity ratio was found to be the best predictor of Al toxicity in soils from a single soil type with different P fertiliser histories. In order to determine the usefulness of this ratio in widely different soil types, RRL was plotted against Al^{3+}/Ca^{2+} activity ratio using combined data of the four soils (Fig 6.9). Inspection of the data suggested that inclusion of the Ca concentration had improved the relationship with RRL considerably although the R^2 value (0.32) was still low. As in the case of $CaCl_2$-Al the low pH data point (Trt 11) of the Cargill soil was a conspicuous outlier. When this point was omitted from the regression analysis the R^2 value improved to 0.61. This supports the finding in Chapter 5 that the activity of Ca in the soil solution can markedly influence the apparent toxicity of Al. The highest R^2 value for the regressions of RRL vs Al^{3+}/Ca^{2+} activity ratio indicates that this ratio can reasonably predict Al toxicity even in contrasting soil types.

6.6 Conclusions

In soils with similar physical properties, mineralogy and low organic matter content, short-time PCV-Al determination in soil solution can be used as a simple and reliable method to predict Al toxicity. However, the direct use of short-time colorimetric procedures to predict critical Al toxicity levels for different soil types could be limited by the variations in organic Al and other factors such as ionic strength, cation and anion types and concentrations in soil solutions.

The comparison between Al reacted with PCV in 15 s and calculated toxic Al concentrations indicated that even in the shortest possible time (15 s), PCV has reacted with some of the non-toxic Al species in soils which had higher (>90 % of the total monomeric Al) solution organic Al. However in a soil which had lower (<40 % of the total monomeric Al) organic Al in solution the predicted toxic Al species was almost
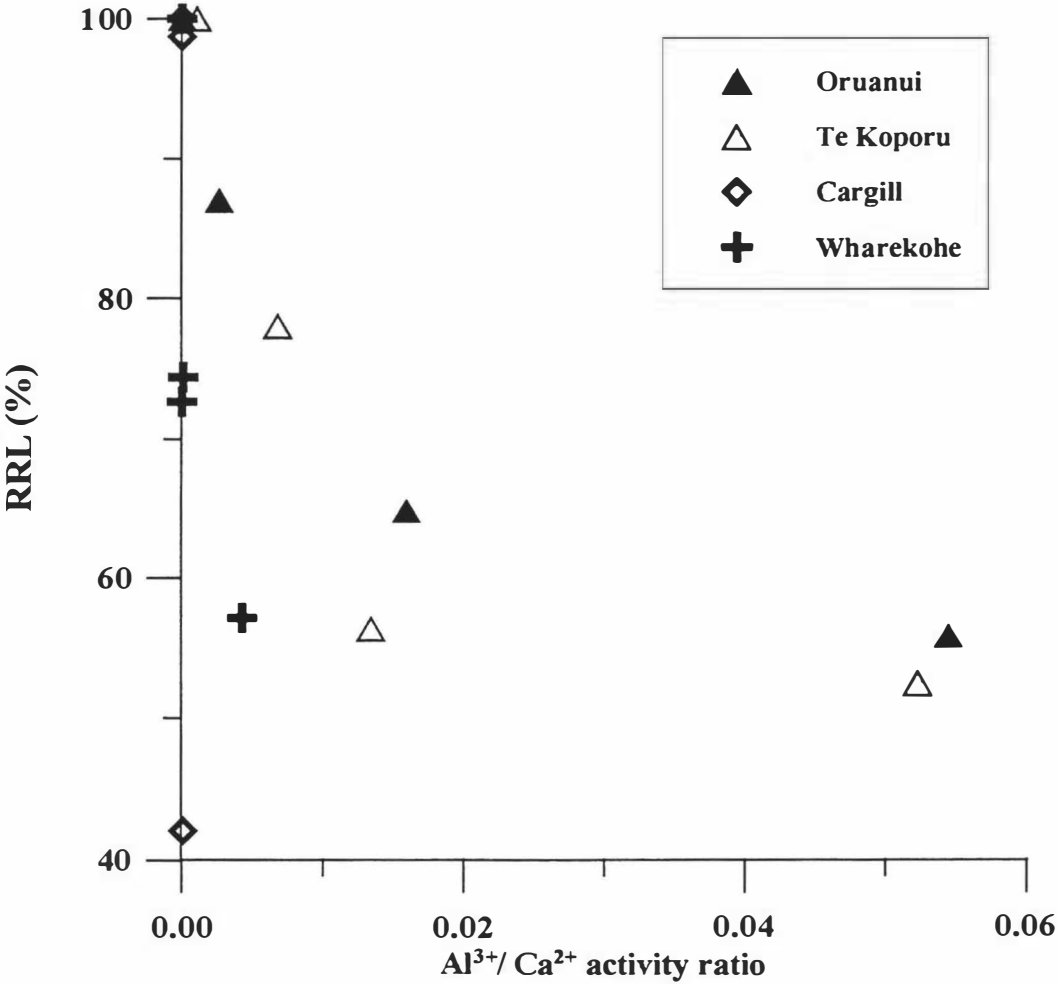
Fig 6.9. Relationship between relative root length (RRL) and Al^{3+}/Ca^{2+} activity ratio.

similar to the measured values using PCV 15 s. This indicates that short-time PCV method can be used as a rapid and routine method to determine toxic Al species in soils with low ratio of organic Al to total Al in soil solution.

Results from this study also indicate that speciation calculations are needed in order to predict Al toxicity more accurately in contrasting soil types. Among the Al toxicity indicies studied, as observed in Chapter 5 on soils of similar parent materials, the activity ratio of Al^{3+}/Ca^{2+} is again the best predictor of Al toxicity but now in widely different soils.

Chapter 7

Interactive effects of soil acidity and fluoride on soil solution chemistry and barley (*Hordeum vulgare* L.) root growth

7.1 Introduction

In Chapter 4 it was demonstrated that, although application of high rates of SSP had little or no effect on soil pH, there was a marked effect on the concentration and speciation of Al in the soil solution. The total monomeric Al concentrations in soil solution increased markedly after high rates of SSP addition. It was suggested that this increase in Al concentrations resulted from the addition of F, as an impurity in the SSP.

Speciation studies also suggested that most of the Al in the soil solution was present in the form of Al-F complex ions. Indeed, it appeared that although the concentration of total monomeric Al in the soil solution had increased, the concentration of ions such as Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{1+}$ had decreased as a result of competition from F for Al.

Both Al (Foy, 1992) and F (Weinstein and Alscher-Herman, 1982) individually can be phytotoxic. Interestingly however, there is evidence that Al-F complex ions may be less phytotoxic than Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{1+}$ ions. It is therefore unclear what would be the overall net effect of adding large quantities of F-containing P fertilisers on the phytotoxicity of F and Al in soils.

In nutrient solutions, the formation of Al-F complexes has been shown to alleviate Al toxicity to barley seedlings by decreasing the concentrations of free Al (Cameron et al., 1986; Tanaka et al., 1987). MacLean et al. (1992) in a detailed study with varying levels of Al and F, found that the deleterious effects of Al on wheat grown in nutrient solution (*Triticum aestivum* L.) were prevented or attenuated by the inclusion of F in the growth medium and the more F present relative to the concentration of Al, the greater the alleviation of Al toxicity.

In unpolluted soils the concentrations of F in soil solution tend to be <10 μM (Larsen and Widdowson, 1971; David and Driscoll, 1984). In contrast, in three F-polluted sites near Al smelters in Norway, Arnesen et al. (1995) found that soil solution F concentrations varied from 24 to 64 μM.

Similarly, soils with a history of rock phosphate, SSP or phosphogypsum (PG) additions are likely to contain high F concentrations. For example, Omueti and Jones (1977a) reported that application of rock phosphate (mean F 2.53 %; total F added 198 mg F kg^{-1} soil) to a Flanagan soil (Aquic Argiudoll; montmorillonite, mesic) from 1904 to 1925 increased the soil F concentration by 148 mg F kg^{-1} soil in the 0-15 cm soil depth and much of the F added to the soils was still present in 1955. Unfortunately, they have not reported any soil solution F concentrations which are an important factor determining the phyto-availability of F to plants. In Chapter 4 it was shown that eight annual applications of SSP (30-60 kg P $ha^{-1} yr^{-1}$) and NCPR (30 kg P $ha^{-1} yr^{-1}$) significantly increased the total F in the soil solution.

Although the behaviour of F in soils from a phyto-availability viewpoint has been studied by several authors (Hurd-Karrer, 1950; Hansen et al., 1958; Specht and MacIntire, 1961; Hani, 1978; Weinstein and Alscher-Herman, 1982; Braen and Weinstein, 1985; Keerthisinghe et al., 1991), their results have not been consistent. Hurd-Karrer (1950) showed that applications of HF at the rate of 50 mg F kg^{-1} to an acid soil (pH 4.9) decreased the growth of cabbage plants to about half of their normal size in six weeks. But applications of NaF or CaF_2 at the same rate of F did not have any significant effect on plant growth. However, when the F application rate was increased to 78 mg F kg^{-1} both HF and NaF decreased the dry weight of cabbage plants. Studies by Hani (1978) have also shown that the uptake of Al increased and plant growth decreased in corn grown in a NaF-treated soil.

Sikora et al. (1992) studied the effect of different F sources including reagent-grade NH_4F, NH_4SiF_6 and three P suspension fertilisers containing fluorosilicic acid (H_2SiF_6), on corn growth. They found that F application rates of ≤32 mg F kg^{-1} soil had no effect on corn dry-matter weight. However, at higher soil F application rates (32-170 mg F kg^{-1} soil) corn growth was reduced. At these higher F application rates,

F was not thought to be the phytotoxic agent since F concentrations in corn tops were all well below (<0.4 mg kg^{-1}) toxic level. They hypothesised that corn growth decreased due to Al phytotoxicity because F addition increased the total Al concentration in soil solution. The reduced corn growth may have been due to the increased concentrations of Al-F species and / or free Al but this was not investigated in their study.

Holub and Navara (1966) found that a culture solution containing 100 mg F l^{-1} caused total inhibition of germination of *Pisum sativum* (pea) seeds and Purohit and Sharma (1985) reported germination inhibition of *Brassica campestris* (field cabbage) at F concentrations as low as 2.5 mg F l^{-1}. In a more recent study, Horner and Bell (1995) carried out a factorial experiment with three levels of F (0, 30, 100 mg l^{-1}) and three levels of pH (4.0, 4.6, 5.6) in a simple solution culture. Their studies showed a synergistic interaction between acidity and F in the growth of perennial rye grass (*Lolium perenne* cultivar S23) and wheat (*Triticum aestivum* cultivar perinarth) in culture solutions. At low pH, F addition markedly reduced the plant growth. They concluded that at low pH, F is in a non-ionic form and is hence readily taken up by cell membranes. However, their pot trials (2*2 factorial experiment. pH-3.3, 5.6; F-19.5 and 455 mg F kg^{-1} soil) with artificial soil mixtures (mixed with peat), did not show any interaction effect. This could be possibly due to the pH buffering and F fixation capacities of the soils used.

Most studies on F reactions in soils have concentrated on adsorption reactions (Barrow and Shaw, 1977; Slavek et al., 1984). The amount of F sorbed by soils has been shown to vary with soil pH, soil type and concentration of F in the solution. Of these, soil pH is the major variable controlling F sorption and therefore F availability to plants. Barrow and Ellis (1986) as well as Gilpin and Johnson (1980) found a minimum F solubility at about pH 5.5. According to them, the higher F solubility in acid soils is related to the formation of Al-F complexes. With increasing pH, the stability of Al-F complexes decreases (Lindsay, 1979), and therefore total F solubility decreases (Barrow and Ellis, 1986). In a recent study Wenzel and Blum (1992a) investigated F solubility in Luvisols and Regosols contaminated for 50 years by F

from an Al smelter. In their soils F solubility was at a minimum at pH 6.0-6.5 and increased at pH < 6 as well as at pH > 6.5.

This pH dependency of F adsorption may also be influenced by the soil mineralogy. Adsorption of F by montmorillonite is highest near pH 6, whereas adsorption by kaolinite decreases linearly from pH 3 to 7 (Omueti and Jones, 1977 b). In general, kaolinite tends to adsorb more F than montmorillonite (Bar-Yosef et al., 1988). Calcium carbonate and Al and Fe hydroxides have also been shown to adsorb F (Pickering, 1985).

Soil pH not only governs the sorption of F in the soil but is also the major variable controlling the species of F present in soil solution. A number of soluble Al-F complexes are formed below pH 5. At pH below 4.0, F also complexes with Si and H (Parker et al., 1987; Sikora et al., 1992).

There appear to be no detailed studies investigating the combined effects of F and acidity on plant growth in soils. In a recent review McLaughlin et al. (1996) reported that there were limited and inconclusive data on the species of F taken up by plants and whether these species are phytotoxic or not.

The objectives of the study reported in this chapter were (1) to investigate the interactive effects of pH and F on soil solution composition and Al speciation and (2) to determine which Al-F complexes, if any, are phytotoxic to plants.

7.2. Materials and Method

7.2.1 Soil sample collection and incubation

A bulk soil sample (4-10 cm) was collected from the same unfertilised pasture site at Ballantrae where samples had been taken for the experiment reported in Chapter 5. This site had had no P fertiliser applied for over 20 years. Subsamples of the moist soil were incubated with different amounts of HCl for 2 weeks to obtain a range of

pH levels. After 2 weeks, F was added in the form of NaF solution and the samples were again incubated at field capacity at 25 C for nearly 4 weeks. Samples were mixed thoroughly at frequent intervals.

7.2.2 Experimental design and methods of analysis

A randomised factorial design was used with 4 levels of F (0, 40, 80, 160 mg kg^{-1} soil) applied as NaF and 5 levels of soil pH (H$_2$O) (4.25, 4.61, 4.96, 5.24, 5.48) . Each treatment was replicated 3 times. Short-term root growth bioassays were conducted using barley seedlings. In each pot, 4 seedlings were planted. Details of the bioasaay technique are described in Chapter 5. Details of the soil and solution analyses are described in Chapter 4.

7.3. Results and Discussion

7.3.1 Effects of pH and F additions on soil solution pH

Soil solution pH increased slightly or remained constant with increasing rates of F addition for all soil pH treatments (Fig 7.1). Addition of F to soils has also been shown by other workers to increase the soil and solution pH (Perrott et al., 1976; Moore and Ritchie, 1988). This is primarily due to the reaction of F with Al oxides and Al-bearing clay minerals which involves release of OH to the solution (Huang and Jackson, 1965; Perrott et al., 1976; Omueti and Jones, 1977 b). The amount of OH released through F adsorption has been positively correlated with the release of Al from various phyllosilicates and amorphous aluminium hydroxides suggesting degradation of the mineral structure (Huang and Jackson, 1965; Perrott et al., 1976).

7.3.2 Effects of soil pH and F additions on soil solution cation concentrations

Concentrations of Na, K, Ca, and Mg in the soil solution were greater at lower soil pH compared with those at higher soil pH at each level of F added to the soil (Table 7.1). This could be due to the release of exchangeable Na, K, Mg, and Ca into the
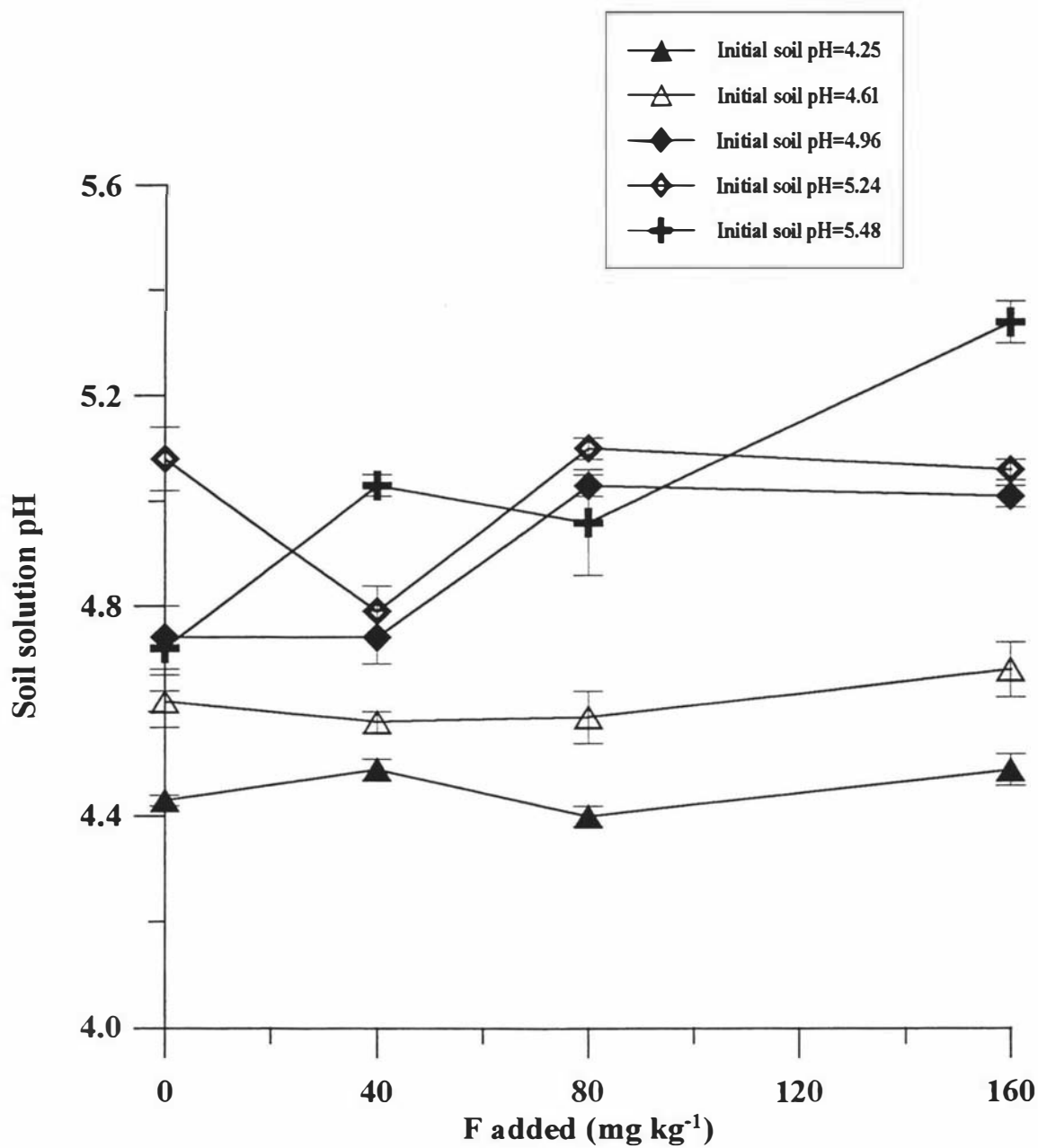
Fig 7.1. Effects of soil pH prior to incubation with F (initial soil pH) and
rate of F addition on soil solution pH after incubation
(vertical bar = standard error of mean).

Table 7.1. Effect of initial soil pH and rate of F addition on soil solution pH and cation concentrations (µM) after incubation.

Initial soil pH	F added (mg kg^{-1})	Solution pH	Na	K	Ca	Mg	[a]Al(inorg)
4.25	0	4.43	1725	496	6698	3270	71
		(0.01)	(20)	(12)	(465)	(89)	(1)
4.25	40	4.49	3481	515	5911	3231	89
		(0.02)	(36)	(13)	(128)	(80)	(11)
4.25	80	4.40	5440	506	5802	3063	133
		(0.02)	(28)	(56)	(206)	(81)	(9)
4.25	160	4.49	7711	459	4740	2538	257
		(0.04)	(74)	(17)	(749)	(87)	(36)
4.61	0	4.63	1410	338	3963	2312	32
		(0.05)	(32)	(11)	(559)	(95)	(1)
4.61	40	4.58	2735	363	3500	2303	51
		(0.02)	(53)	(6.6)	(216)	(22)	(4)
4.61	80	4.59	3168	400	4000	2035	69
		(0.05)	(45)	(67)	(39)	(79)	(6)
4.61	160	4.68	6549	359	2937	1763	165
		(0.05)	(41)	(7)	(172)	(29)	(12)
4.96	0	4.74	1342	330	2582	1696	18
		(0.05)	(22)	(16)	(439)	(45)	(3)
4.96	40	4.74	2361	312	2269	1528	46
		(0.05)	(40)	(5)	(336)	(34)	(4)
4.96	80	5.03	3657	282	3369	1408	48
		(0.02)	(48)	(28)	(749)	(118)	(8)
4.96	160	5.01	5412	268	984	923	98
		(0.02)	(34)	(13)	(115)	(30)	(12)
5.24	0	5.08	1175	279	2160	1313	11
		(0.09)	(34)	(24)	(168)	(92)	(0)
5.24	40	4.79	2100	252	1850	1155	29
		(0.02)	(15)	(4)	(493)	(35)	(4)
5.24	80	5.10	3222	253	1336	988	37
		(0.10)	(47)	(14)	(163)	(41)	(11)
5.24	160	5.06	5514	212	746	638	77
		(0.11)	(77)	(2)	(163)	(33)	(10)
5.48	0	4.72	1205	286	1760	1330	11
		(0.08)	(27)	(17)	(292)	(18)	(0)
5.48	40	5.03	2040	220	865	1066	23
		(0.02)	(34)	(3)	(36)	(28)	(2)
5.48	80	4.96	2993	263	694	938	31
		(0.10)	(68)	(9)	(198)	(61)	(5)
5.48	160	5.34	5497	223	402	605	70
		(0.04)	(115)	(5)	(71)	(37)	(13)

Note: Numbers within brackets are standard error.

[a]Al(inorg) = inorganic monomeric Al

solution by displacement of these cations from exchange sites by protons and Al. The increases in Ca and Mg concentration at low pH were much higher than those of the monovalent cations. Solution Na concentration substantially increased with increasing rates of F, since F was added to the soils in the form of NaF (Table 7.1). Fluoride addition did not have a consistent effect on K concentration in the soil solution. In general, solution Ca concentration decreased with increasing rates of F addition. Solution Mg concentrations also decreased with increased F additions, however the effect was not as prominent as in the case of solution Ca. The decrease of Ca and Mg concentrations was possibly due to the removal of Al coatings and exchangeable Al from clay surfaces by F as indicated by the increase in the concentration of inorganic monomeric Al in soil solution (Fig 7.2). This could expose additional adsorption sites on the clay and increase adsorption of Ca and Mg, thus decreasing Ca and Mg concentrations in soil solution. However, other reaction mechanisms may also be involved because the solution Al concentration did not increase as much as the reduction in Ca or Mg concentrations. A more likely explanation could be that increased surface negative charge caused by strong adsorption of F by the soils increased Ca and Mg adsorption and hence reduced Ca and Mg concentrations in solution.

The formation of CaF_2 has also been cited as a possible reason for decreased solution Ca levels found in F-treated soils (Morshina, 1980; Polomski et al., 1982). However, in the present study, soils in which a decrease in Ca and Mg concentrations in soil solution was observed were all under-saturated with respect to CaF_2 and MgF_2 (Fig 7.3). Therefore, the decrease in Ca and Mg concentration is unlikely to be due to CaF_2 and MgF_2 precipitation.

7.3.3 Effects of soil pH and F additions on soil solution anion concentrations

Low pH soils had higher concentrations of Cl in solution than high pH soils (Table 7.2). This was mainly due to the addition of Cl to the soils in the form of HCl to obtain the differing pH values. Fluoride addition did not have any significant effect on Cl concentration in the soil solution. Nitrate concentration in the solution was substantially increased with increasing pH. Compared with the initial soil pH of 4.25,

Fig 7.2. Effect of initial soil pH and rate of F addition on inorganic monomeric Al concentration (vertical bar = standard error of mean).
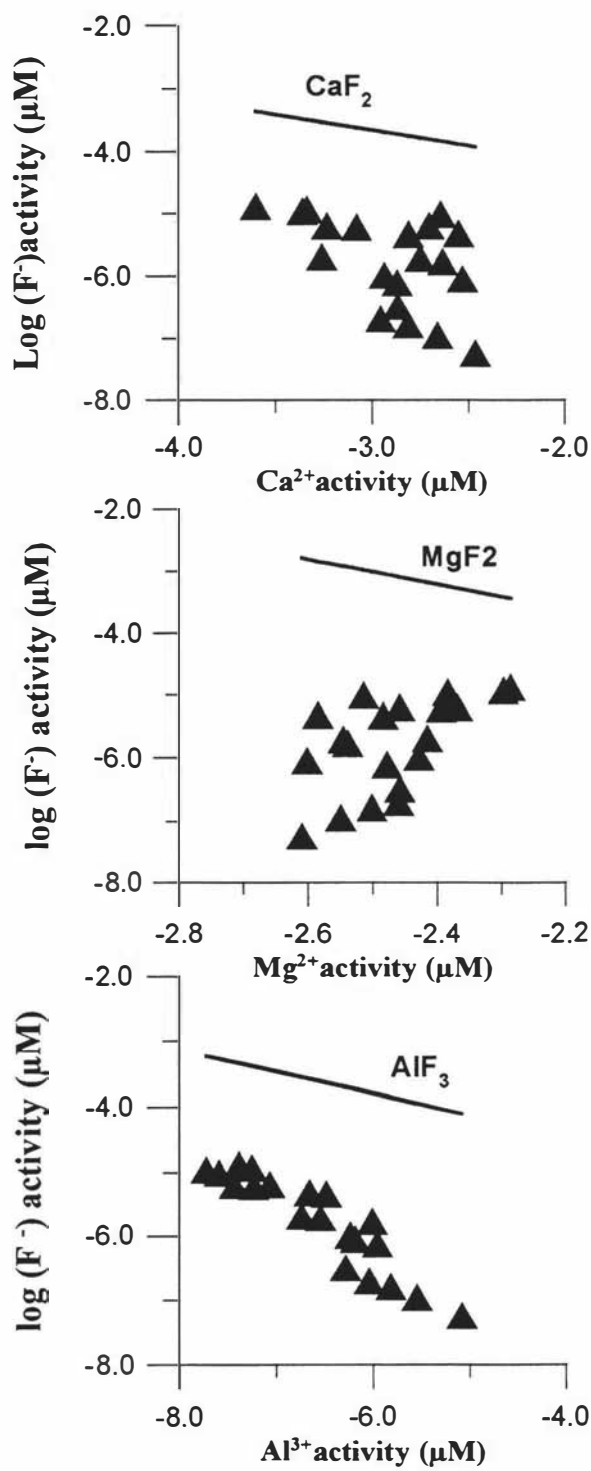
Fig 7.3. Solubility diagrams for CaF$_2$, MgF$_2$ and AlF$_3$(Lindsay, 1979) and F, Ca, Mg and Al activities in soil solution.

Table 7.2. Effect of initial soil pH and rate of F addition on soil solution anion concentrations (μM) and ionic strength (M) after incubation.

Initial soil pH	F added (mg kg⁻¹)	Cl	NO₃	SO₄	ᵃF	ᵇFree F (F⁻)	Ionic strength
4.25	0	23920	1167	0.0	23	0	0.0278
		(808)	(57)	(0.0)	(1)	(0)	(0.0008)
4.25	40	24349	1336	0.0	113	1	0.0304
		(759)	(20)	(0.0)	(2)	(0)	(0.0002)
4.25	80	24084	1601	0.0	234	5	0.0326
		(742)	(73)	(0.0)	(8)	(1)	(0.0011)
4.25	160	25136	1688	0.0	377	2	0.0318
		(873)	(47)	(0.0)	(12)	(0)	(0.0006)
4.61	0	10831	2853	0.0	15	0	0.0215
		(359)	(30)	(0.0)	(1)	(0)	(0.0004)
4.61	40	11197	6505	0.0	79	2	0.0227
		(259)	(105)	(0.0)	(3)	(0)	(0.0003)
4.61	80	11915	6446	0.0	149	10	0.0250
		(69)	(182)	(0.0)	(7)	(2)	(0.0017)
4.61	160	12234	7099	40	295	5	0.0245
		(380)	(197)	(8)	(5)	(0)	(0.0004)
4.96	0	4540	7617	0.0	10	0	0.0157
		(113)	(268)	(0.0)	(1)	(0)	(0.0003)
4.96	40	4541	7738	19	53	1	0.0158
		(162)	(215)	(14)	(1)	(0)	(0.0003)
4.96	80	4961	8355	20	97	7	0.0166
		(476)	(570)	(14)	(2)	(2)	(0.0008)
4.96	160	4736	8127	44	186	6	0.0159
		(289)	(265)	(12)	(6)	(1)	(0.0003)
5.24	0	2077	7621	21	7	0	0.0122
		(77)	(255)	(2)	(1)	(0)	(0.0004)
5.24	40	2182	8077	21	37	1	0.0126
		(16)	(154)	(2)	(1)	(0)	(0.0001)
5.24	80	2225	8469	38	75	6	0.0128
		(68)	(344)	(4)	(5)	(2)	(0.0002)
5.24	160	2286	8419	45	166	12	0.0132
		(73)	(404)	(5)	(5)	(3)	(0.0001)
5.48	0	1678	8079	23	7	0	0.0122
		(96)	(101)	(1)	(0.3)	(0)	(0.0001)
5.48	40	1562	7746	27	36	2	0.0114
		(98)	(215)	(11)	(2)	(0)	(0.0001)
5.48	80	1654	8395	29	75	11	0.0123
		(44)	(374)	(1)	(1)	(0)	(0.0003)
5.48	160	1891	8562	43	159	13	0.0129
		(34)	(182)	(3)	(5)	(3)	(0.0002)

Note: ᵃ Total solution F ᵇ Calculated free F; Numbers within brackets are standard error.

NO_3 concentrations increased by seven fold at the highest initial soil pH of 5.48. Low soil pH values have been shown to reduce mineralisation and nitrification due to reduced microbial activity. Nitrification in soils is markedly reduced below pH 6 and is negligible below pH 4.5 (Alexander, 1980). Fluoride addition slightly increased NO_3 concentration in some of the treatments but the increases were not statistically significant.

Sulphate was not detected in the soils with pH <4.8, with or without F addition (Table 7.2). However, at pH values above 5, solution SO_4 concentration increased with increasing rates of F addition, possibly as a result of ligand exchange of F with SO_4. Lower soil pH increases the electrostatic potential of the adsorption plane (Harward and Reisenauer, 1966; Marsh et al., 1983) thereby increasing the SO_4 adsorption and decreasing SO_4 concentration in solution. In addition, increased pH would have also increased mineralisation of organic sulphur thereby increasing SO_4 concentrations.

7.3.4 Effects of soil pH and F addition on soil solution F concentration

Addition of F substantially increased the total F in the soil solution, this effect being more noticeable at low soil pH than at high soil pH (Fig 7.4). The addition of 160 mg F kg^{-1} soil increased the total F in the soil solution from 23 μM to 377 μM at the lowest soil pH (4.25) compared with 7 μM to 159 μM at the highest soil pH (5.48) (Table 7.2). Other investigators have also reported increases in F solubility as pH is decreased from 5.5 (Barrow and Ellis, 1986; Gilpin and Johnson, 1980).

Under the experimental conditions in this study the soil solutions were quite under-saturated relative to CaF_2, MgF_2 and AlF_3 (Fig 7.3) and therefore the F concentration was not controlled by any of these minerals.
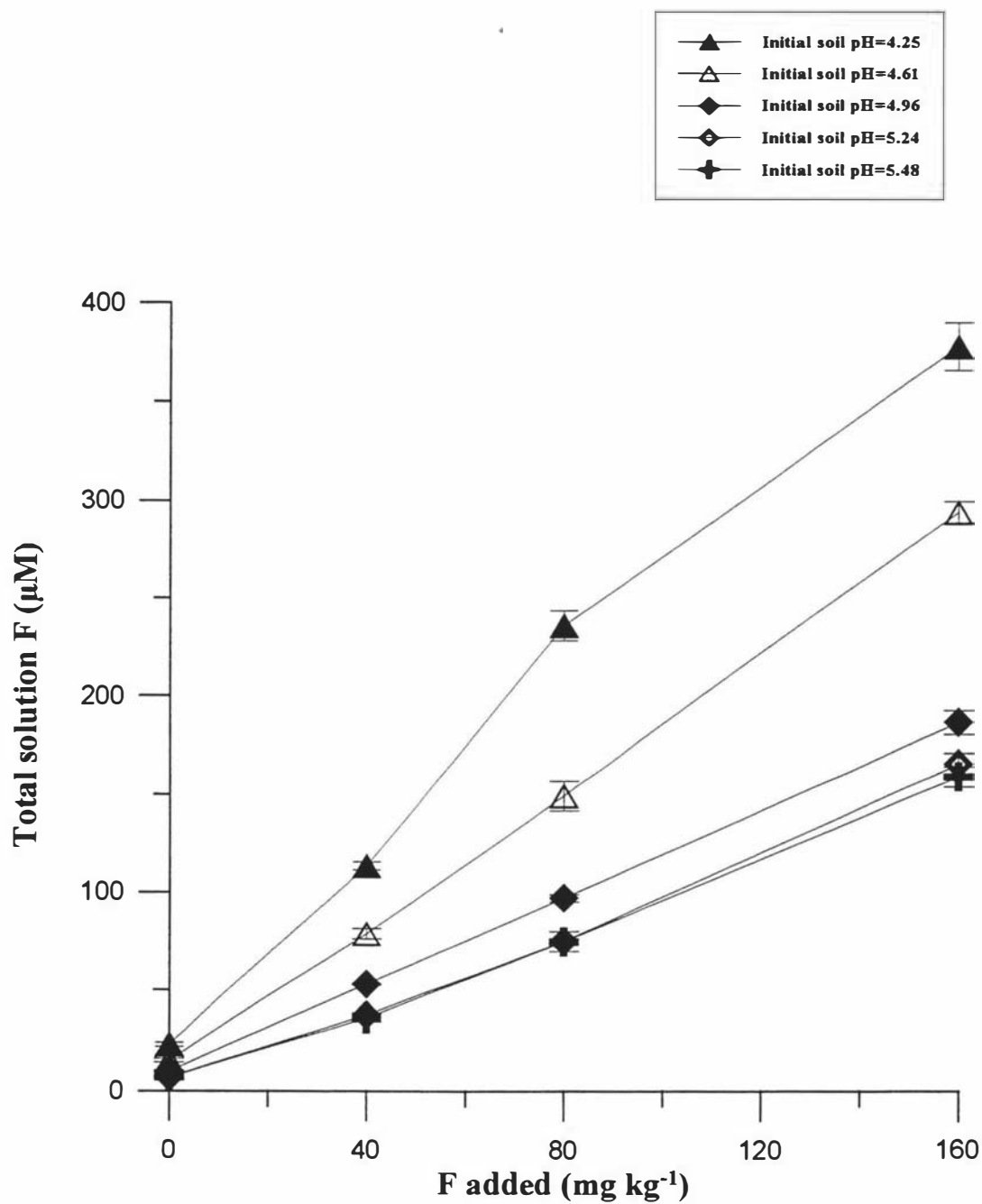
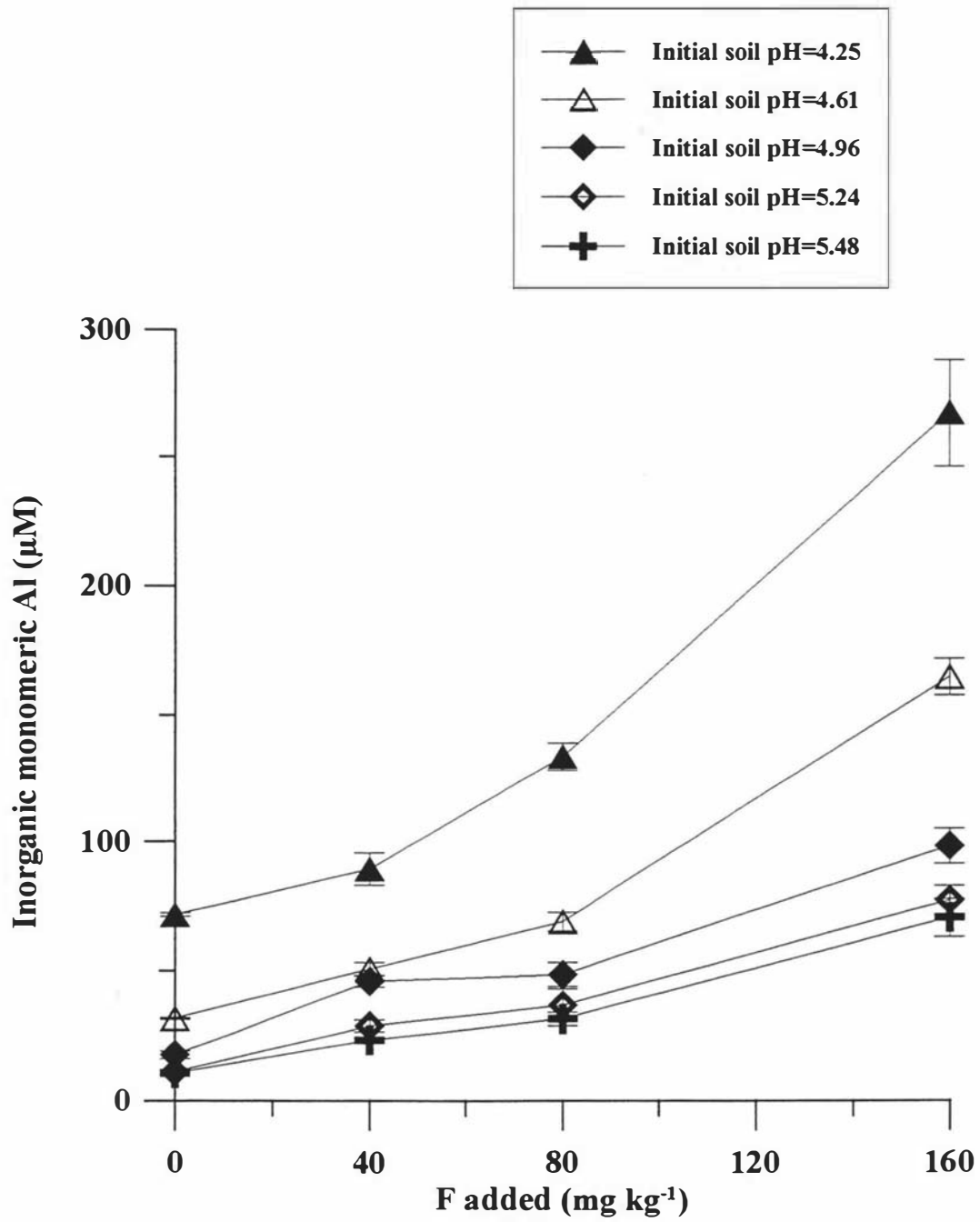**Fig 7.4. Effect of initial soil pH and rate of F addition on total solution F concentration (vertical bar = standard error of mean).**

## 7.3.5 Effects of soil pH and F addition on Al concentration in soil solution

Inorganic monomeric Al concentrations in soil solution increased with decreasing soil pH at all rates of F addition (Fig 7.2). Within a given rate of F addition there was a highly significant non-linear relationship (R^2=0.96 - 0.98) between soil pH and inorganic monomeric Al (Fig 7.5). However, when the data from all the treatments (irrespective of the rate of F addition) were combined and analysed, the relationship between soil pH and inorganic monomeric Al was not significant (R^2=0.12). This is mainly due to the strong interaction of F with Al that results in more Al being brought into the solution irrespective of the soil pH (Fig 7.2). Fluoride can increase the solution Al concentration by (a) complexation of exchangeable Al and bringing into soil solution (Elrashidi and Lindsay, 1986) and/or (b) substitution of OH by F at the surface of amorphous aluminium oxides by ligand exchange (Huang and Jackson, 1965; Perrott et al., 1976) subsequently causing a breakdown of the octahedral Al-O-bonds, due to the high electronegativity of F (Huang and Jackson, 1965). In consequence, Al in the soil solution increases.

A highly significant correlation between solution Al(inorg) and F(total) (r=0.94[***], n=20) (Table 7.3) suggests that F may be bringing Al into solution. This is supported by the observation that the molar ratio between solution Al(inorg) and F(total), which was above 1 in the treatments without F addition, decreased to 0.44-0.72 at the lowest rate of F addition but then remained relatively constant despite increasing additions of F (Fig 7.6). This indicates that with increases in F addition correspondingly similar amounts of Al were released into the solution. The results of this study confirm the observations of Moore and Ritchie (1988) and Gibson et al. (1992) who also concluded that addition of F resulted in higher concentrations of total Al in soil solution.
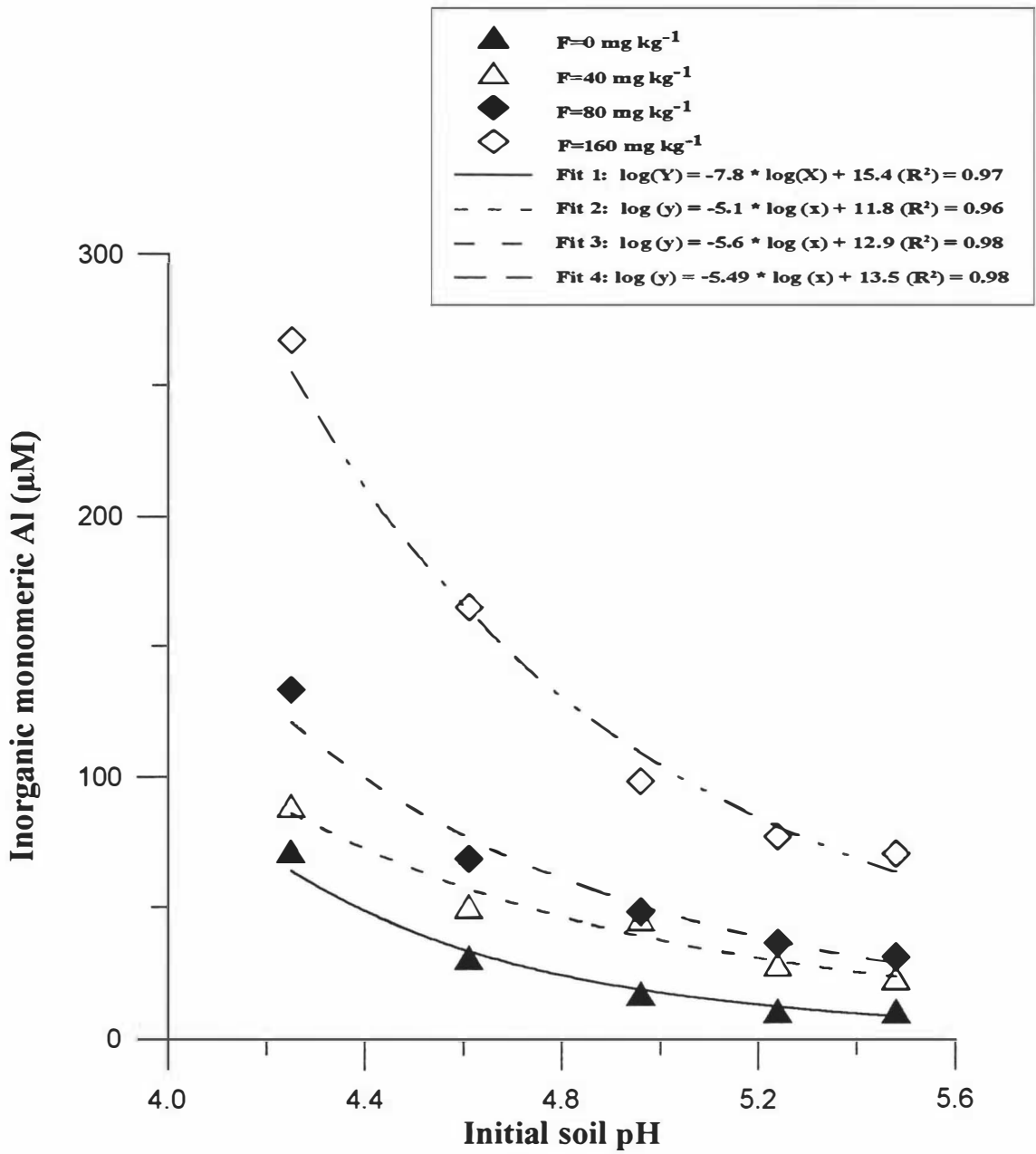
Fig 7.5. Effect of initial soil pH on inorganic monomeric Al concentration in soil solution at different rates of F addition.

Table 7.3. Correlation matrix of the soil solution composition.

	Na	K	Ca	Mg	Cl	NO$_3$	SO$_4$	pH (ss)[a]	[b]F	[c]Al (inorg)
Na	1.00									
K	0.17	1.00								
Ca	0.03	0.95***	1.00							
Mg	0.00	0.97***	0.98***	1.00						
Cl	0.34	0.96***	0.92***	0.93***	1.00					
NO$_3$	-0.15	-0.90***	-0.90***	-0.93***	-0.94***	1.00				
SO$_4$	0.29	-0.76**	-0.81***	-0.84***	-0.67**	0.72**	1.00			
pH (ss)	0.01	-0.89***	-0.86**	-0.90***	-0.82***	0.80***	0.81***	1.00		
F	0.96***	0.33	0.19	0.17	0.48	-0.28	0.11	-0.19	1.00	
Al (inorg)	0.87***	0.53	0.41	0.39	0.68**	-0.51	-0.10	-0.40	0.94***	1.00

[a] pH(ss)-Soil solution pH

[b]Total solution F

[c]Al (inorg)- Inorganic monomeric Al

, * Significant at the 0.05 and 0.01 probability levels, respectively.

Fig 7.6. Effect of soil pH and rate of F addition on Al(inorg)/F molar ratio in soil solution.

7.3.6 Effects of soil pH and F additions on Al speciation

Increasing pH greatly reduced the calculated Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ concentrations in the soil solution (Table 7.4). At the initial soil pH of 4.25, the Al^{3+} concentration was 36.7 μM compared with 2.6 μM at the initial soil pH of 5.48 when F was not added to the 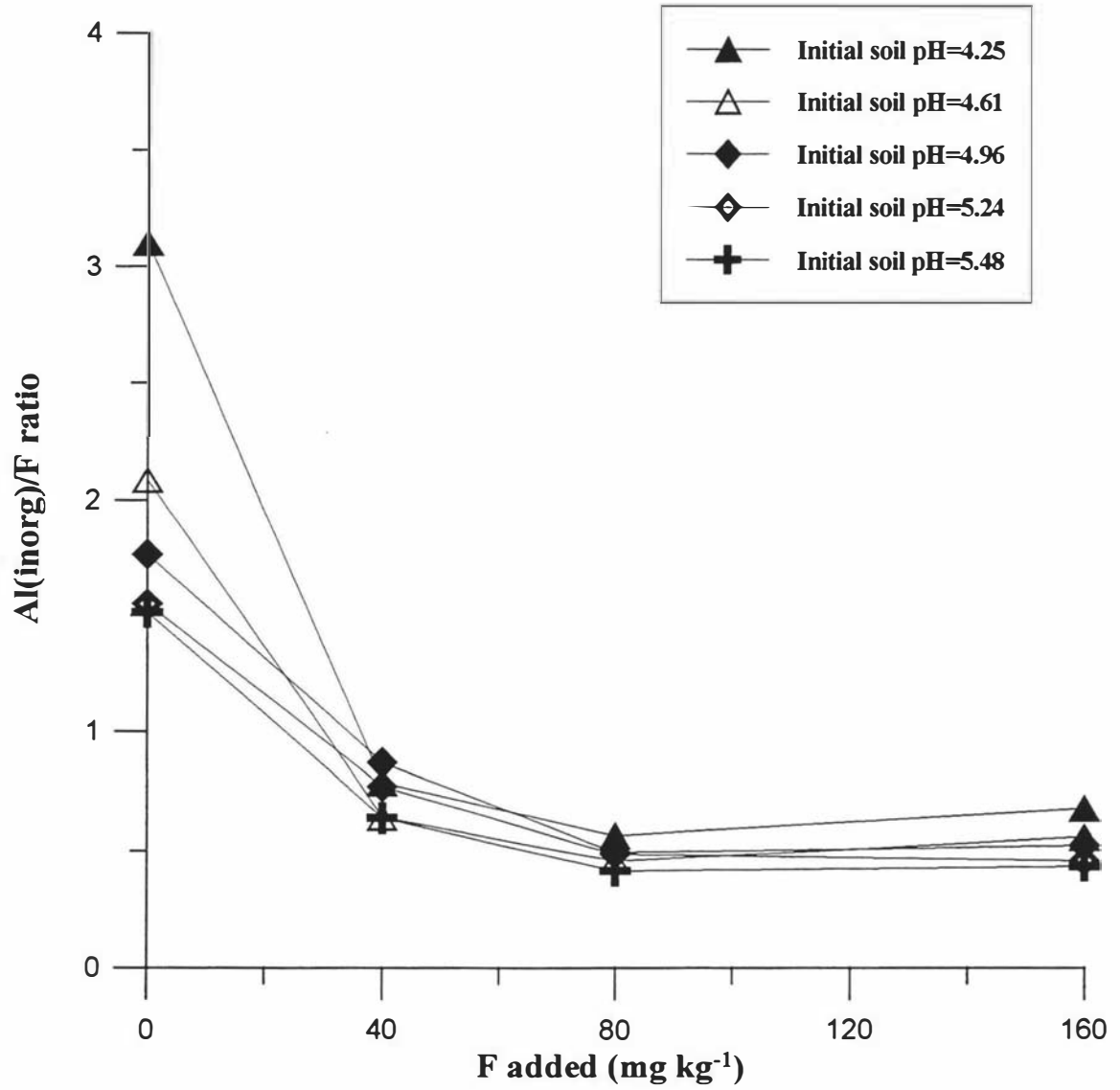soil. Fluoride addition substantially reduced the calculated concentrations of free Al ions (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$) in the soil solution (Table 7.4), although it increased the concentration of inorganic monomeric Al in the soil solution (Fig 7.2). For any F addition, 90-99 % of the inorganic monomeric Al in the soil solution was predicted to be complexed with F (Table 7.5).

However, it is interesting to note the difference between this study conducted on soil and earlier results obtained in nutrient solutions. In nutrient solution, where initial concentrations of Al are fixed, high rates of F have been shown to complex all the Al in the solution (MacLean et al., 1992). In contrast in this study on soil, soil solution Al was not 100 % complexed with F even at the highest rates of F addition. This was particularly the case at very low pHs. In fact there was a slight increase in calculated Al^{3+} concentration at the highest rate of F addition in the very low pH treatments (Table 7.4).

This observation reinforces the difficulty of transfering conclusions on the effect of F on the phytotoxicity of Al from nutrient solution studies, where the total solution Al concentration is fixed, to soils where addition of F not only changes the speciation of Al, but also increases the total concentration of Al in the soil solution.

7.3.7 Effects of soil pH and F addition on barley root growth

There was a significant interaction between initial soil pH and the rate of F addition on barley root growth (P<0.001). Applications of F significantly reduced (p<0.001) root growth in low pH soils (initial soil pHs 4.25 , 4.61) but there was little effect of F additions on root growth at higher pH (Fig 7.7). Statistical tests showed that there were no significant differences in root growth between different rates of F addition

Table 7.4. Effect of pH and rate of F addition on calculated concentrations of Al species (µM) in soil solution.

Initial soil pH	F added (mg kg^{-1})	Al^{3+}	Al(OH)$^{2+}$	Al(OH)$_2$$^{1+}$	Al(OH)$_3$	AlF^{2+}	AlF$_2$$^{1+}$	AlF$_3$
4.25	0	36.7	6.9	2.2	0.1	21.6	0.7	2.0
4.25	40	3.1	0.1	0.2	0.0	43.0	32.9	0.0
4.25	80	1.1	0.3	0.1	0.0	41.3	86.5	0.0
4.25	160	4.7	1.6	0.4	0.0	103.2	127.3	5.7
4.61	0	10.8	4.8	1.7	0.1	13.3	0.9	0.0
4.61	40	1.1	0.5	0.2	0.0	22.2	25.3	1.1
4.61	80	0.1	0.0	0.1	0.1	9.5	49.6	9.3
4.61	160	1.3	0.7	0.3	0.0	46.3	106.3	9.9
4.96	0	4.9	2.8	1.1	0.1	8.2	0.8	0.0
4.96	40	3.5	1.9	0.8	0.1	27.3	12.1	0.2
4.96	80	0.3	0.3	0.3	0.0	11.3	31.8	4.3
4.96	160	0.1	0.1	0.1	0.0	11.8	64.0	11.8
5.24	0	1.5	1.7	1.8	0.3	4.9	0.9	0.0
5.24	40	1.6	1.0	0.5	0.1	15.6	9.7	0.3
5.24	80	0.2	0.2	0.2	0.0	6.6	21.9	4.2
5.24	160	0.2	0.2	0.2	0.0	11.7	53.3	11.2
5.48	0	2.6	1.4	0.6	0.1	5.5	0.7	0.0
5.48	40	0.5	0.5	0.5	0.1	10.2	11.2	0.4
5.48	80	0.1	0.1	0.1	0.0	4.5	22.2	4.4
5.48	160	0.1	0.2	0.3	0.1	8.9	47.7	12.7

Table 7.5. Calculated concentrations of soil solution Al species as a % of inorganic monomeric Al.

| Initial soil pH	F added (mg kg^{-1})	Al^{3+}	Al(OH)$^{2+}$	Al(OH)$_2$$^{1+}$	AlF^{2+}	AlF$_2$$^{1+}$	AlF$_3$
4.25	0	51.4	14.3	3.0	30.2	0.7	0.0
4.25	40	3.8	0.9	0.0	53.0	40.6	0.8
4.25	80	0.0	0.0	0.0	30.1	64.0	4.9
4.25	160	1.6	0.0	0.0	41.9	52.9	2.4
4.61	0	34.3	15.3	5.4	41.9	2.8	0.0
4.61	40	2.2	0.4	0.0	43.5	51.0	2.2
4.61	80	0.0	0.0	0.0	13.7	72.2	13.8
4.61	160	0.5	0.0	0.0	27.4	64.9	6.2
4.96	0	26.9	14.6	6.4	46.9	4.7	0.0
4.96	40	8.6	3.8	1.6	60.5	25.2	0.0
4.96	80	0.4	0.4	0.4	21.7	66.5	10.0
4.96	160	0.0	0.0	0.0	13.4	72.7	13.4
5.24	0	13.1	11.1	15.8	44.3	10.1	2.7
5.24	40	5.3	3.0	1.4	53.2	35.4	0.8
5.24	80	0.4	0.5	0.5	17.6	66.8	13.9
5.24	160	0.0	0.0	0.0	14.4	69.0	15.8
5.48	0	23.6	12.6	5.6	51.6	6.1	0.0
5.48	40	2.1	2.3	1.9	43.6	47.9	1.8
5.48	80	0.0	0.0	0.0	13.6	70.9	14.9
5.48	160	0.0	0.0	0.0	11.3	67.9	19.7
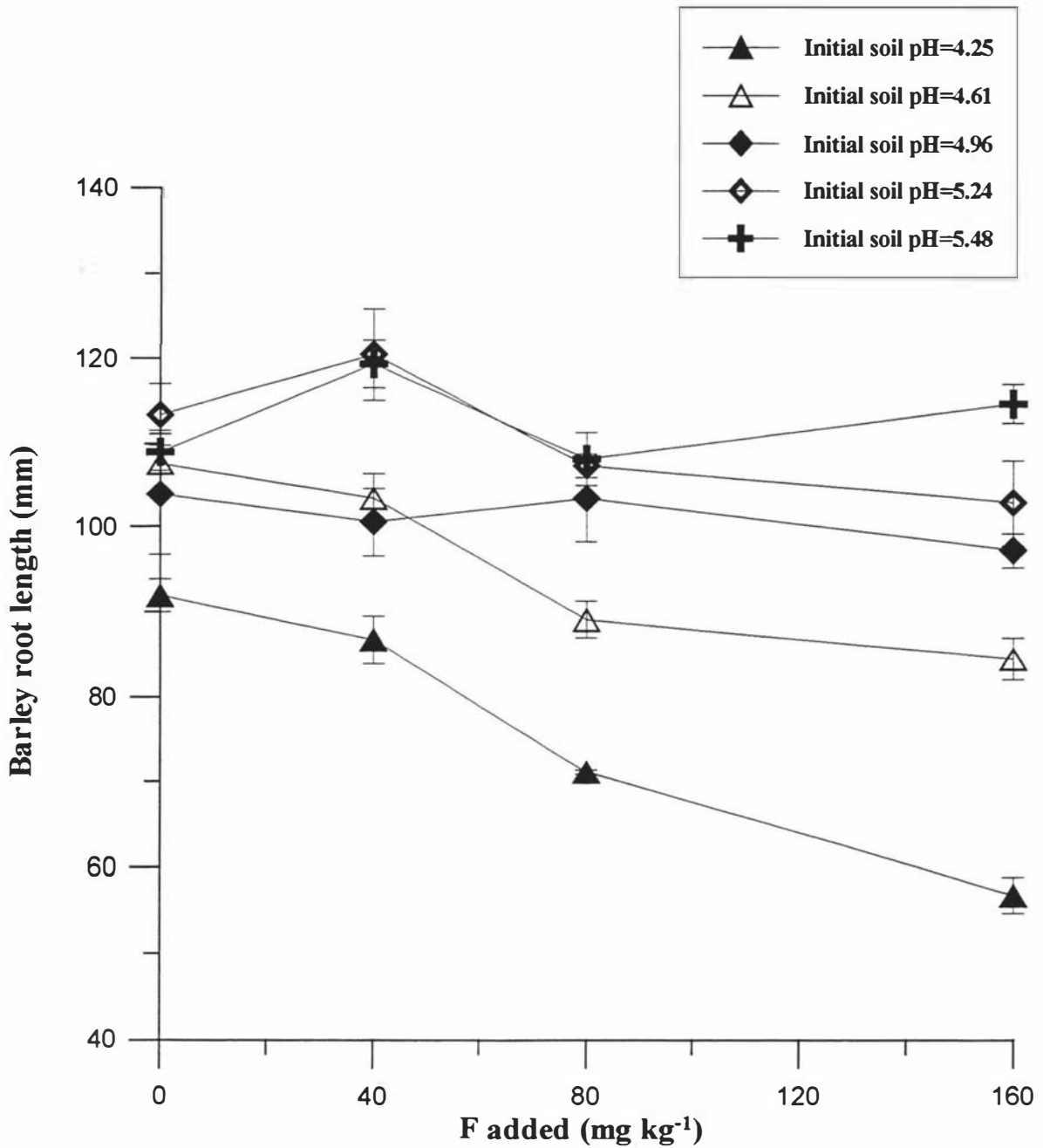
Fig 7.7. Effect of rate of F addition and initial soil pH on barley root growth.
(vertical bar = standard error of mean)

when the initial soil pH was 5.48, but there were significant differences in root growth with increases in F addition at the most acidic soil pH (pH 4.25). At this pH, root growth was reduced by nearly 40% at the F addition rate of 160 mg kg^{-1} compared with the no - F treatment.

The reduction in root growth observed at high rates of F addition could possibly be due to:

(a) increased Al^{3+} concentration in the soil solution with increasing rates of F addition, especially in the strongly acidic soils and /or

(b) F-induced nutrient deficiency and /or

(c) direct effects of F injury to the plants and / or

(d) toxicity of Al-F complexes to plant roots at high concentrations.

These possibilities are considered below.

The increased Al^{3+} concentration is unlikely to be the primary reason for the reduction in root growth because soils which did not receive F, had higher concentrations of Al^{3+} compared with soils which received F irrespective of the soil pH (Table 7.3). This does not match the pattern of root growth which was severely decreased at the highest F application rate compared with the no-F treatment. In addition, Fig 7.8 shows that at Al^{3+} activities of <2 μM there was widely varying root growth; it varied from 57 mm to 120 mm and there was no significant relationship between activities of Al^{3+} and root growth. Similarly there were no significant relationships between activities of Al(OH)$_2^{1+}$ (Fig 7.9), Al(OH)$^{2+}$ (Fig 7.10), or "toxic" Al (Fig 7.11) and root growth, again indicating that factors other than these may be more important in inhibiting root growth in this study.

The second possible explanation is F-induced Ca deficiency, which can directly affect short-term root growth or indirectly aggravate Al toxicity. Although increased rates of F addition decreased the Ca concentration in the soil solution (Table 7.1), it was not below the requirement for plant growth in normal soil conditions (Loneragan et al., 1968; Loneragan and Snowball, 1969). But high Ca concentrations in the soil solution (higher than those needed to avoid Ca deficiency) have been shown to be beneficial in:
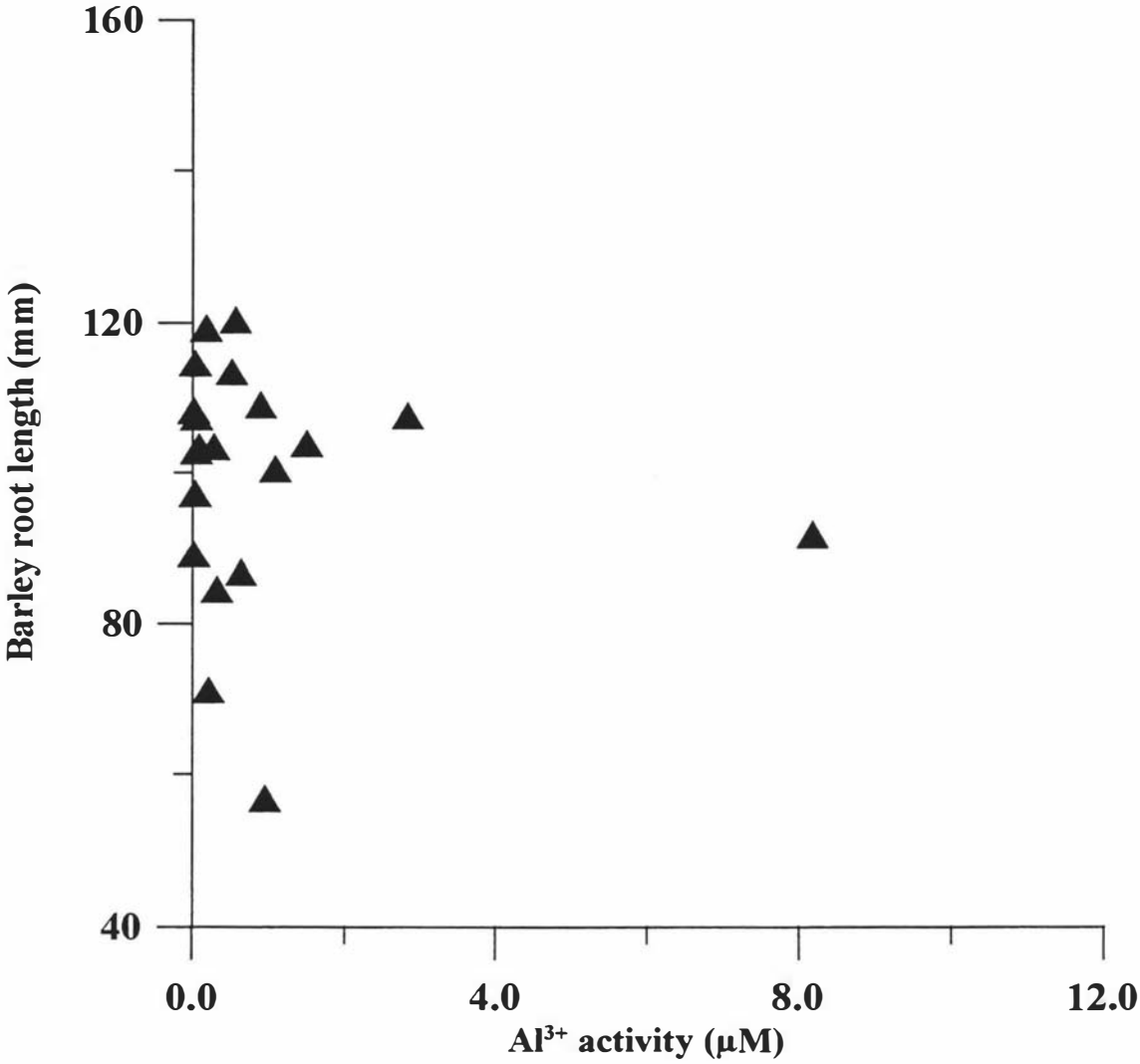
Fig 7.8. Effect of Al^{3+} activity on barley root growth.

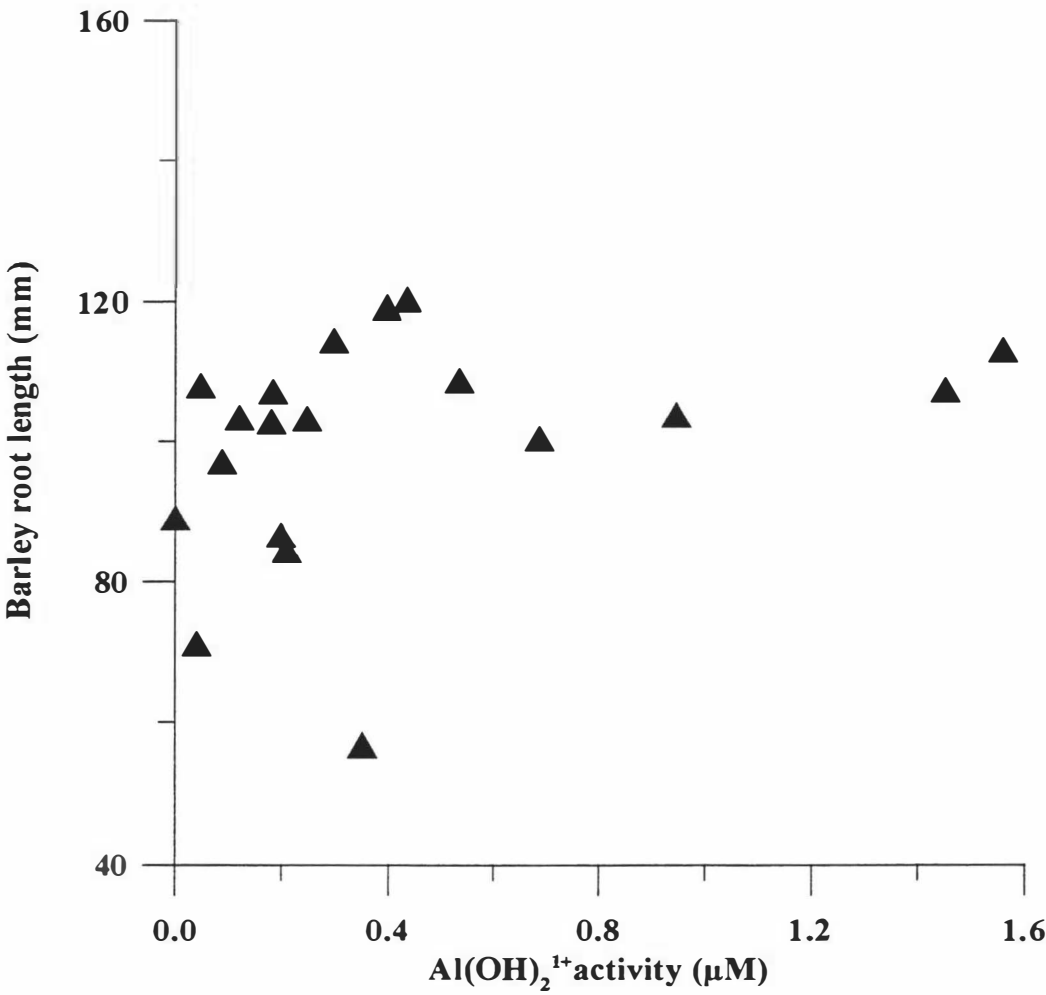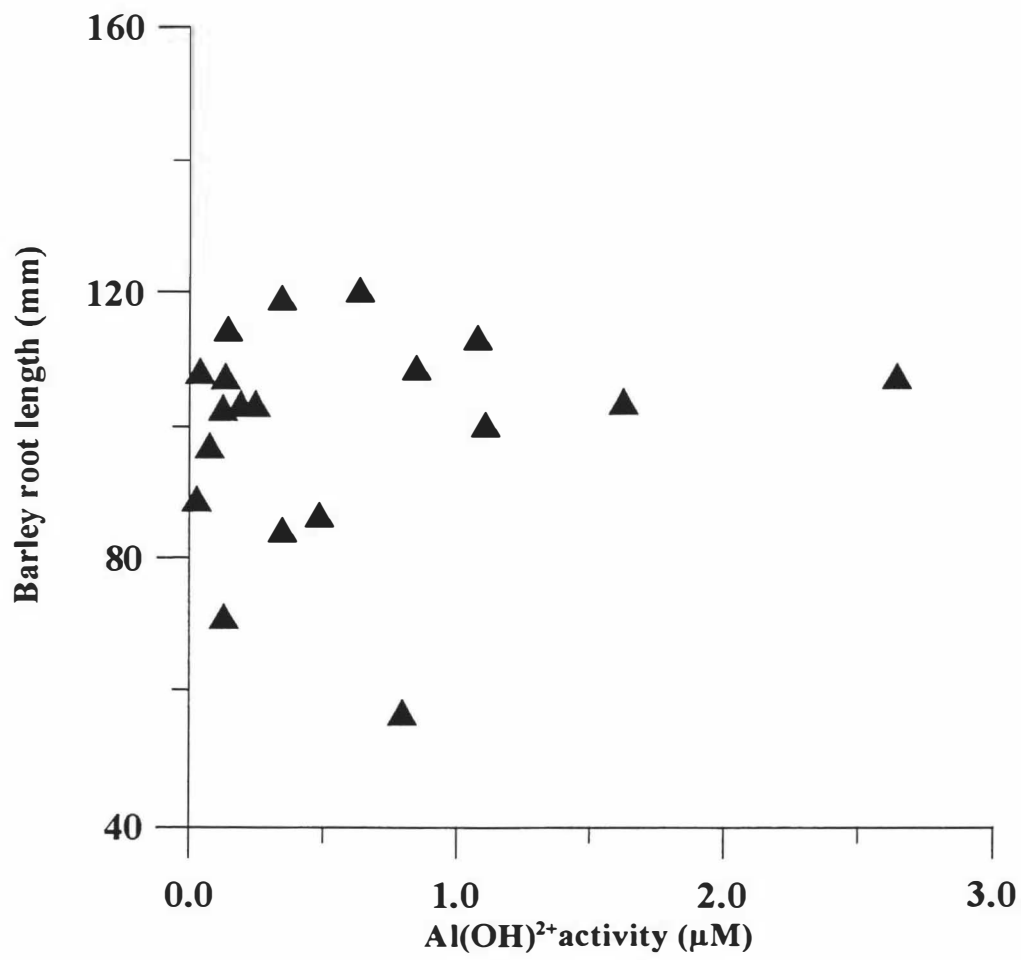**Fig 7.9. Effect of Al(OH)$_2^{1+}$activity on barley root growth.**

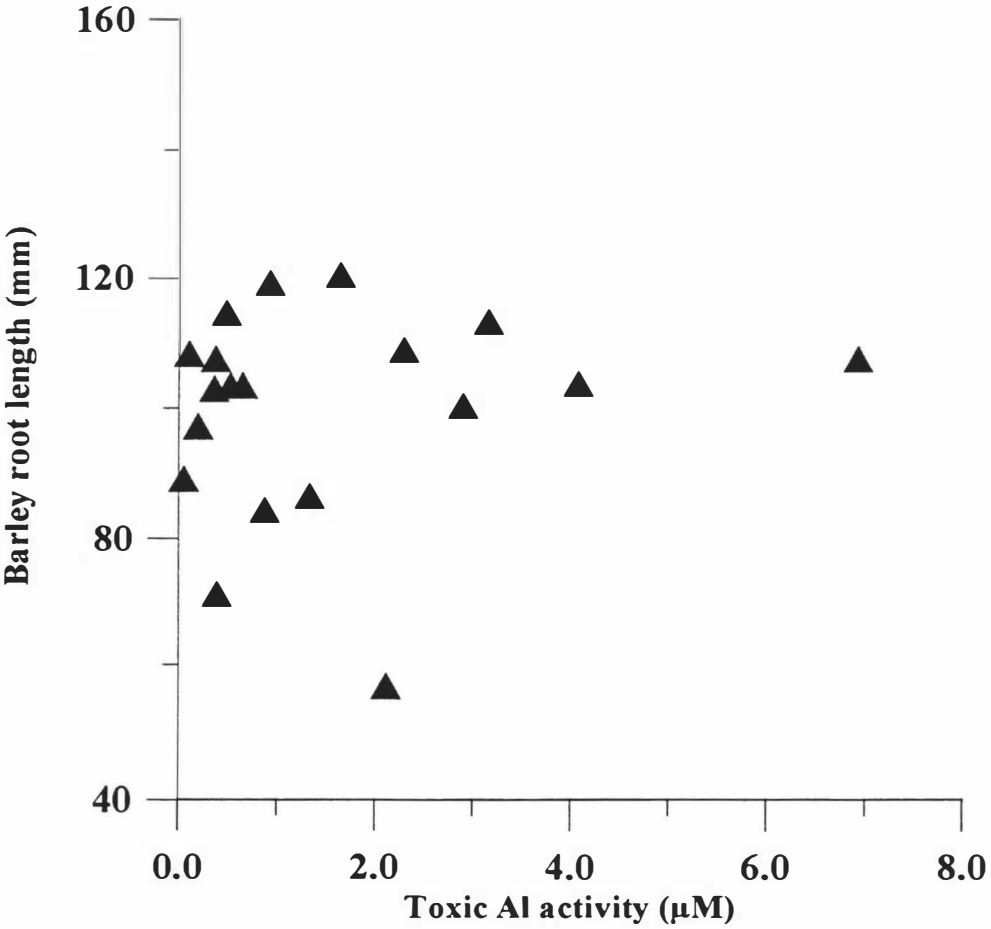Fig 7.10. Effect of Al(OH)²⁺activity on barley root growth.

Fig 7.11. Relationship between "toxic" Al (Al^{3+} + $Al(OH)^{2+}$ + $Al(OH)_2^{1+}$) activity and barley root growth.

-combating Al toxicity (Rengel, 1992) and

-combating F toxicity (Pack, 1966; Ramagopal et al. 1969; Garrec et al. 1974; 1978).

However, in this study at low pHs where the root growth was severely reduced with the high F additions, the solution Ca concentrations were much higher (3000-7000 μM) compared with the high pHs (400-2000 μM) where the root growth was not significantly reduced. At low soil pH (4.25) additions of 80 and 160 mg F kg^{-1} decreased Ca concentrations by about 20 and 30 % respectively but the corresponding Al^{3+} concentration decreases were about 3000 % and 700 %. This causes an enormous decrease in Al^{3+} / Ca^{2+} ratio with F additions but the root growth instead of increasing as expected from Chapter 5 has in fact decreased. Therefore it is unlikely that Ca is having any significant role in the root growth phenomenon observed in this study.

The third possible reason for the reduction in root growth at high rates of F addition could be direct injury to the roots by high concentrations of free F. In this study, NaF was added to the soil and incubated for nearly a month. At the end of the incubation period nearly 98% of the added F was calculated to be adsorbed by the soil and the free F (F$^-$) concentration was very low in the soil solutions in the low pH soils (Table 7.2). High pH soils had higher free F concentrations, but in these soils there was no significant reduction in root growth. Therefore a simple direct effect of F on root growth seems unlikely. MacLean et al. (1992) have shown in a nutrient solution study that even free F concentrations as high as 200 μM did not inhibit root growth of wheat at a solution pH of 4.2.

It is possible however, that although the amount of free F in soil solution was low at low pH, the chemical form of the F may have been more toxic at low pH. At high pH, F is in an ionic form (F$^-$), which is less readily taken up by cell membranes than the non-ionic HF form which occurs only at pH values below approximately 4.0 (Horner and Bell, 1995). Fluoride is more readily taken up from soil solution into roots in the HF form because diffusion of F$^-$ is prevented by lipid membranes (Kronberger, 1988). It is unlikely however, that significant quantities of HF would have formed at the pH's observed in this study. Speciation calculations did not predict significant

concentrations of HF species in any of the treatments. Even if HF was formed it is likely to have reacted with the soil components rapidly due its high reactivity. Therefore, HF induced reduction in root growth in this study is unlikely.

Finally, the most probable reason for the reduction in root length at high rates of F addition would appear to be the effect of high activities of Al-F complexes on root growth. In the presence of high activities of Al-F complexes in solution, root growth reductions were observed (Fig 7.12, 7.13) at activities of Al^{3+} less than 1 μM which would normally be considered non-phytotoxic (Cameron et al., 1986) for barley root growth. This suggests that Al-F complexes rather than Al^{3+} may be the cause for the reduction in root growth at high activities of Al-F complexes.

Inspection of Figs 7.12 and 7.13 suggests that the concentrations of both AlF^{2+} and AlF_2^{1+} are related to root length. This is confirmed in the correlation matrix (Table 7.6). However, the very close correlation that also exists between the concentrations of these two Al-F complex ions (Table 7.6) makes it difficult to determine which of the two is the more toxic Al-F species.

Table 7.6. Correlations between different forms of Al species and root length.

	Al^{3+}	$Al(OH)_2^{1+}$	$Al(OH)^{2+}$	toxic Al	AlF_2^{1+}	AlF^{2+}	root length
Al^{3+}	1.00						
$Al(OH)_2^{1+}$	0.76 **	1.00					
$Al(OH)^{2+}$	0.98 **	0.86 **	1.00				
toxic Al	0.99 **	0.85 **	1.00	1.00			
AlF_2^{1+}	-0.32	-0.54	-0.41	-0.40	1.00		
AlF^{2+}	0.04	-0.15	0.00	0.00	0.72 *	1.00	
root length	-0.11	0.20	-0.03	-0.04	-0.76 **	-0.83 **	1.00

*, ** Significant at the 0.1 and 0.05 probability levels, respectively.

To shed a little more light into the complex study of relative toxicity of Al-F complexes, a stepwise regression analysis was conducted with root length as the dependent variable and the activities of Al^{3+}, AlF^{2+}, AlF_2^+, $Al(OH)_2^+$, $Al(OH)^{2+}$ as independent variables. The model that best explained root growth included Al^{3+}, AlF^{2+}, AlF_2^+ leaving out $Al(OH)_2^{+1}$, $Al(OH)^{2+}$. Selected regression equations from the
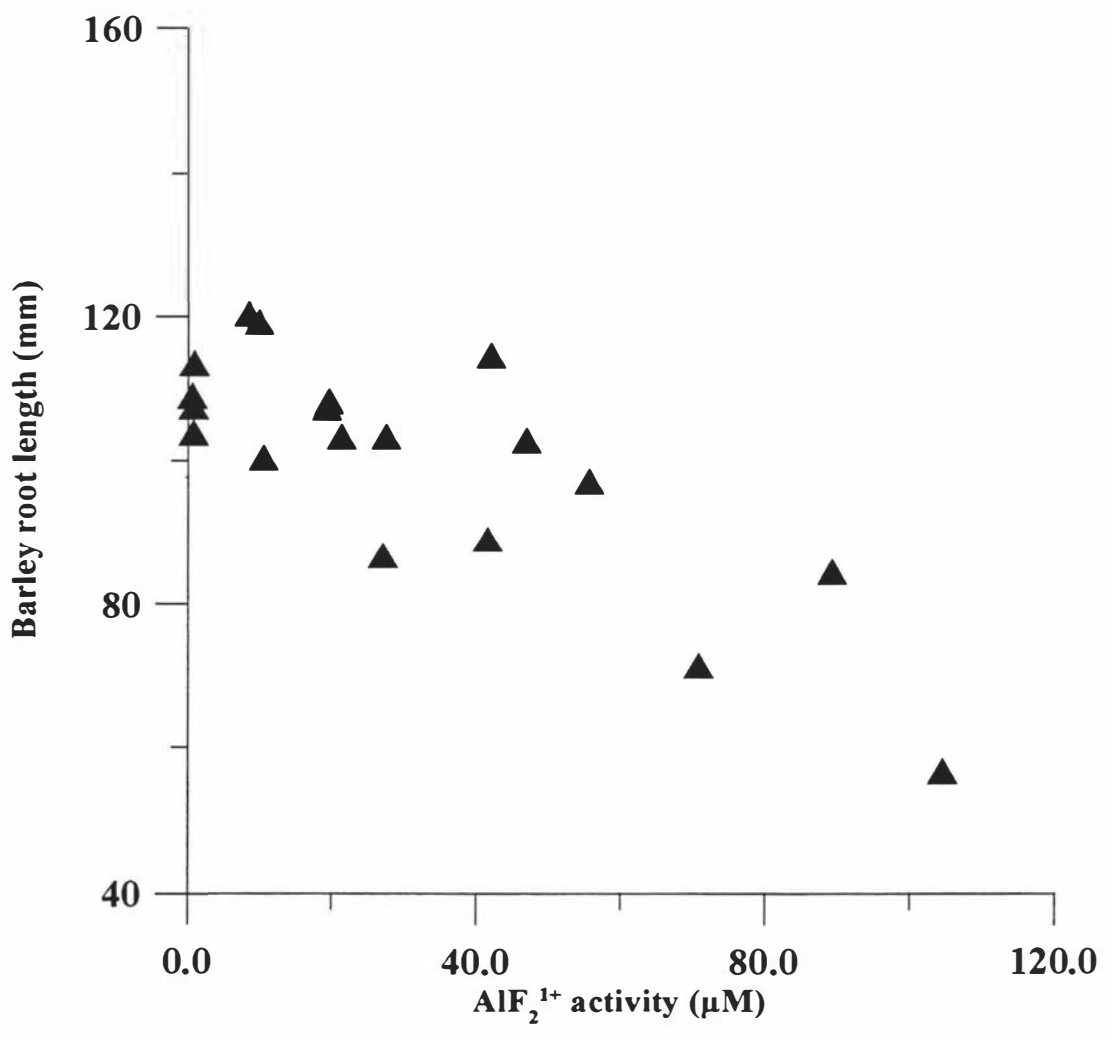
Fig 7.12. Effect of AlF$_2$$^{1+}$ activity on barley root growth.
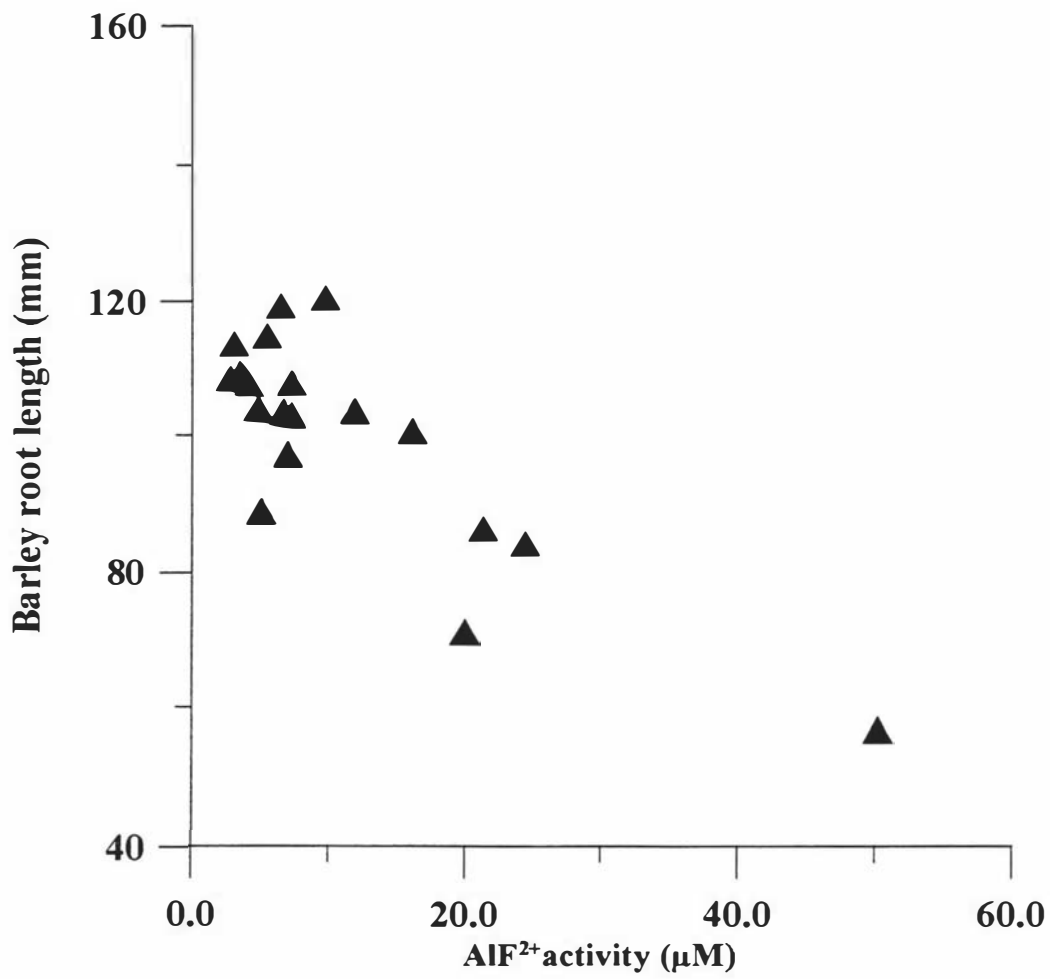
Fig 7.13. Effect of AlF^{2+}activity on barley root growth.

stepwise regression analysis, in which all partial regression coefficients are significant at least at the 5 % level, are shown in Table 7.7.

Table 7.7. Stepwise regression equations relating root length to different forms of Al species.

Stepwise regression equations	Coefficient of determination (R^2)	Equation No
[a]$RL = 113.02 - 1.18(AlF^{2+})$	0.68	[1]
$RL = 114.31 - 0.18(AlF_2^{1+}) - 0.82(AlF^{2+})$	0.74	[2]
$RL = 117.03 - 2.31Al^{3+} - 0.28AlF_2^{1+} - 0.60AlF^{2+}$	0.80	[3]

[a] root length

The stepwise regression analysis showed that AlF^{2+} was the single most important variable, and by itself explained 68 % of the variation in root length. The second most important parameter, when combined with AlF^{2+}, was AlF_2^{1+}, and these two together explained 74 % of the variation. Inclusion of Al^{3+} increased the variation accounted for to 80 %. Surprisingly, Al^{3+} which has been shown to be most phytotoxic to plants explained only a small percentage of variability of root length compared to the Al-F species. This could be possibly due to the much lower concentrations of Al^{3+} in the F added soil solutions compared with the concentrations of Al-F species. Inclusion of any further variables did not result in any significant improvement in R^2. It is note worthy to mention that because of the close relationships between many of the Al forms, non-inclusion of certain Al forms as a significant component (eg. $Al(OH)^{2+}$, $Al(OH)_2^{1+}$) can not be taken to indicate nonparticipation in root growth reductions.

However, comparison of the partial regression coefficients in Eq 3 (Table 7.7) relating root length to different forms of Al suggests that Al^{3+} is more active per unit of concentration in reducing root length than AlF^{2+} or AlF_2^{1+}. The order of activity of Al forms in reducing root growth, as indicated by the size of the partial regression coefficients is $Al^{3+} > AlF^{2+} > AlF_2^{1+}$. Parker et al. (1989) also hypothesed, that F complexed Al is much less toxic than Al^{3+}, but not totally innocuous.

The results of this study contrast with the studies of other workers (Konishi and Miyamoto, 1983; Kinraide et al., 1985; Cameron et al., 1986) that were carried out in nutrient solutions with low levels of Al and F (in all these studies total solution Al concentrations were less than 16 μM). These studies reported that addition of F ameliorated Al toxicity. As was pointed out in section 7.3.6 however, conducting the present study on soils means that it was not possible to keep the total solution Al concentration at the initial (with no F additions) low and constant level because addition of F released larger quantities of Al from the soil solid phase.

The work of MacLean et al. (1992), also in nutrient solution, seems to be the only study conducted on the effect of high levels of Al and F on plant root growth. They showed that F concentrations up to 200 μM alone (without Al) did not affect wheat root growth but Al concentration as low as 25 μM (without F) drastically reduced root growth. The deleterious effects of Al on root growth were ameliorated when Al and F were supplied together, and the degree of attenuation was a function of the relative concentrations of F and Al. At 100 μM Al in nutrient solution, addition of 50 μM F had no effect, 100 μM F partially prevented Al toxicity and the highest F treatment of 200μM completely reversed the inhibitory effects of 100 μM Al. They did not carry out Al speciation calculations to find out which Al-F complexes were predominant in their test solution. Since this observation appears to be contradictory to the present results which showed reduction in barley root growth at high F additions to soil, speciation calculations were carried out on the data published by MacLean et al. (1992) to compare the activities of Al-F complexes formed under their experimental conditions with the approximate toxic threshold levels of Al-F complexes proposed in this study.

Speciation calculations were carried out only for the highest level of Al and different rates of F (100μM Al and 0, 50, 100 and 200μM F; pH 4.2) and assuming that complexation of Al with HEDTA was negligible because of its lower stability constant value for Al compared to F.(note: MacLean et al., 1992 applied Fe to solution as FeHEDTA). The calculated concentrations and activities of various Al species are reported in Table 7.8. The speciation calculation predicted that at the highest rate of

Table 7.8. Effect of F additions on Al species concentrations and activities calculated using the data of MacLean et al (1992). Total Al concentration = 100μM.

F concentration (μM)	Al^{3+}	$Al(OH)^{2+}$	AlF^{2+}	AlF_2^{1+}	AlF_3	$AlSO_4^+$	Al^{3+}	$Al(OH)^{2+}$	AlF^{2+}	AlF_2^{1+}	AlF_3	$AlSO_4^+$
	concentrations (μM)						activities (μM)					
0	33.2	5.4	0.0	0.0	0.0	54.0	11.5	3.4	0.0	0.0	0.0	48.1
50	17.8	2.9	40.0	4.8	0.0	30.2	6.2	1.8	25.4	4.3	0.0	26.9
100	7.4	1.2	54.8	21.8	0.0	12.7	2.6	0.8	34.7	19.4	0.0	8.1
200	0.2	0.0	17.3	71.9	10.1	0.0	0.1	0.0	10.9	63.9	10.1	0.0

F addition (200µM F), 72 %, 17 %, 10 %, 0.2 % of the Al was present in the forms of AlF_2^{1+}, AlF^{2+}, AlF_3 and Al^{3+} respectively, which corresponded to activities of 63.9, 10.9, 10.1 and 0.1 µM respectively. The results of the current study showed that at these activities of the Al species root growth was not significantly reduced (Fig 7.8, 7.12 and 7.13). Therefore, the amelioration of Al toxicity by F addition in the trial of MacLean et al. (1992) was possibly due to the removal of the highly toxic Al^{3+} by complexation with F while at the same time keeping the activities of AlF_2^{1+} and AlF^{2+} below toxic levels.

The results of MacLean et al. (1992) study are therefore not in any way contradictary to the results of the current study. Had they however increased their rates of additions of F further, according to the results of the current study, the activities of Al-F complexes might have increased beyond the threshold values and root growth might have decreased, although there may be some differences in the critical levels for Al-F toxicity between plant species (wheat vs barley).

Comparison of root growth in Fig 7.7 and the Al-F concentrations in Table 7.3 suggests that the approximate threshold toxic levels for the AlF^{2+} (30 µM) and AlF_2^{1+} (60 µM) species observed in this experiment are much higher than the soil solution concentrations of Al-F species observed in the long-term P fertiliser field trial discussed in Chapter 4. Thus, although it was demonstrated in Chapter 4 that application of high rates of SSP can increase the total monomeric Al concentration, the findings of this chapter suggest that this additional Al, most of which is complexed with F, is unlikely to pose a hazard to plant growth. Rather, application of F containing P fertilisers may have beneficial effects due to the complexation of toxic Al (Al^{3+} + $Al(OH)^{2+}$ + $Al(OH)_2^{1+}$) species by F.

7.4 Conclusions

Results of this study indicate that there was a significant interaction between acidity and F on soil solution pH, Al and soluble F. Addition of F to a strongly acidic soil increased the soil solution Al substantially compared with addition of F to a slightly acidic soil. This may have been due to F-accelerated dissolution of clay minerals in

addition to the complexation of exchangeable Al from soil solid phase. Significant correlations between soil solution Al and F indicate complexation of solid phase Al by F thereby bringing more Al into solution.

There was a significant interaction between acidity and F addition on root growth of barley. Addition of high rates of F to strongly acidic soils severely reduced the root growth. Speciation calculations suggested that increasing rates of F addition increased the concentrations of Al-F complexes in the solution. Therefore the reduction in root growth appeared to be related to the presence of high concentrations of Al-F complexes in soil solution. Compared with AlF_2^{1+}, the AlF^{2+} complexes appear to be more toxic to barley root growth.

At the normal rates of application of P fertilisers it is unlikely that the concentrations of Al-F complexes in field soils will be sufficiently high to cause phytotoxicity. Instead, fertilisation is expected to have beneficial effects due to the complexation of toxic Al species by F. However, more information is needed to assess the ubiquity of Al-F complexes in soil solution, and their potential role in acid soil infertility.

Chapter 8

Summary and Conclusions

A review of literature revealed that in legume-based pastures quantitative information on the long-term effect of different types of P fertilisers on the rate of soil acidification is scarce. Further, the interactive effects of components of P fertilisers such as PO_4, SO_4, and F on Al speciation have not been studied in detail under field conditions, either in New Zealand or overseas. The long-term effects of P fertilisers on soil solution chemistry and its impact on Al speciation and Al phytotoxicity are poorly understood.

It is also apparent from the literature that soil solution Al measurements may better predict Al phytotoxicity in contrasting soil types than conventional measures such as soil pH or $CaCl_2$-extractable Al. However, the concentration of total soil solution Al may not be the most suitable test for Al phytotoxicity, because it does not consider the activity and forms of soluble Al. The phytotoxic effects of Al may sometimes be better expressed in terms of the ratio of soil solution Al^{3+} activity to the activities of some other cations especially Ca than Al^{3+} activity alone. There are however, no detailed studies available to indicate whether these ratios can be used successfully to predict Al phytotoxicity in widely contrasting soil types.

Nutrient solution studies have shown that application of F can ameliorate Al toxicity in plants and this is mainly because of the reduction in Al^{3+} activity due to the formation of Al-F complexes. In contrast, application of F to acid soils has been shown to decrease plant growth in some instances. However, there are no detailed studies available on the interactive effects of soil acidity and F on soil solution Al species and their effects on Al phytotoxicity. The difficulty of keeping Al concentrations constant in soil solution at different levels of F addition as opposed to in nutrient solution, may be the reason for the

scanty information available on this subject in soils. There is a need for further research on the interactions of soil acidity and F and their effects on plant growth.

The study reported in this thesis was conducted with the general objectives of identifying and quantifying the effects of different types of P fertilisers on soil acidity and Al speciation in legume-based pastures. As part of the overall study a field trial investigated the effects of seven years of annual applications of different types of P fertilisers on soil acidity, soil solution composition and Al speciation.

This was followed by a series of glasshouse studies. These included a study to assess Al phytotoxicity in long-term P fertilised pasture soils using short-term bioassay methods. This was followed by a study on the development of a chemical test to predict Al toxicity in widely different soil types. Finally, a study on interactive effects of soil acidity and F and its effects on plant growth was carried out.

A field study (Chapter 3) was carried out to investigate the effects of seven annual applications of six types of P fertilisers on soil acidity under legume-based pasture. This study on a marginally acidic soil (soil pH (H_2O) 5.4 - 5.8) indicated that, irrespective of the rate or form of P fertiliser used, the soil becomes increasingly acidic with time. However, the rate of acidification varies with the type of fertiliser used. The rate of acidification was calculated to be 0.32, 1.27, 1.50, and 2.00 k mol H^+ ha^{-1} yr^{-1} in the NCPR-30, control, SSP-30 and DAP-30 treatments respectively. At these rates of acidification the approximate times for the control, NCPR, SSP and DAP plots to reach a pH (H_2O) of 5.0 in the 0-75 mm soil depth would be 15, 91, 18, and 9 years respectively. These predictions clearly show that application of NCPR may not necessarily stop soil acidification in these soils under lequme-based pastures but it can reduce the rate of soil acidification substantially.

In addition to increasing the soil pH, the NCPR treatment also increased exchangeable Ca and Ca saturation but significantly lowered exchangeable and soluble Al compared to the

control treatment. Jordan PR and NCPAPR also had similar effects, but the magnitude of the effects were lower than that of NCPR. In contrast to these fertilisers, DAP significantly lowered soil pH, exchangeable Ca and Ca saturation and increased soluble Al and exchangeable acidity compared to the control treatment. Superphosphate in general had no effect on soil pH and soil Al relative to the control treatment, but increased exchangeable Ca and Ca saturation at higher rates of application. This study also indicated that of the total NCPR (1591 kg ha^{-1}) applied over the 7 yr, 68 % had dissolved, producing a liming effect equivalent to 651.5 kg of pure lime ($CaCO_3$).

In Chapter 4 the effects of long-term P fertiliser application on changes in soil solution composition and Al speciation were studied in detail using the same field trial. The results from this study demonstrated that long-term application of P fertilisers can markedly affect the soil solution composition and thereby the speciation of Al in the soil solution. The most affected ions in solution were Ca, Al, SO_4 and F. High rates of SSP (45 and 60 kg P ha^{-1} yr^{-1}) substantially increased the Ca and SO_4 concentrations. Total solution F ranged from 2.7 to 23.5 μM and 3.2 to 25.6 μM in the subsurface soil. The SSP-60 and control treatments had the highest and lowest concentrations of total solution F respectively in both depths. Total monomeric Al concentration, measured by the PCV (4 min) method, ranged from 1.5 to 4.8 μM in the surface soil and 2.5 to 12.2 μM in the subsurface soil. Application of DAP and high rates of SSP increased total Al concentrations in the soil solution compared with the control treatment even though SSP had no significant effect on soil pH. The increased Al concentration in the SSP treatments was probably due to the complexation of Al by the high total solution F in these treatments, and hence bringing more Al into the soil solution. Application of NCPR decreased total Al concentrations compared with SSP treatments, presumably by increasing soil pH.

Soil solution Al concentration increased following the application of DAP, as did the predicted concentration of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ which are thought to be phytotoxic. Application of high rates of SSP decreased the toxic Al concentration, despite higher total and

inorganic monomeric Al compared with the control soil. The concentration of toxic Al species in NCPR-treated soils was also lower than in the control soil.

This study suggests that application of fertilisers such as SSP can increase the concentration of monomeric Al in the soil solution. Most of this Al however appears to be in the form of Al-F complexes that are considered to be relatively non-toxic compared to Al^{3+} and Al hydroxy species. However, given the high concentrations of Al-F complexes present in soils that have received high rates of P fertilisers, it is important to investigate further whether Al-F complexes are phytotoxic and at what concentrations. This aspect was studied and reported in Chapter 7.

A short-term bioassay was carried out to study the effect of continuous inputs of Ca, F, and SO_4 from P fertilisers, together with changes in soil pH, on Al phytotoxicity (Chapter 5). Soil samples were collected from two adjacent pasture sites, one of which had received no phosphate fertiliser for over 20 years (low phosphorus, LP) and the other which had had high P fertiliser input (375 kg ha^{-1} yr^{-1} SSP) for 20 years (high phosphorus, HP). Soil samples were incubated at 80 % field capacity for 6 weeks with either $Ca(OH)_2$ or HCl to obtain varying pH levels. Incubated soil samples were filled into 250 ml plastic cups. Short term root growth of barley (Hordeum vulgare L.) was then assessed in these soils.

Decreasing soil pH markedly increased the soil solution Ca, total monomeric Al and total solution F in the HP soil compared with LP soil. The inability of total monomeric Al and 0.02 M $CaCl_2$-extractable Al to explain variations in root growth in the combined data for fertilised and unfertilised soils indicated that the relative proportions of phytotoxic Al in the total monomeric or extractable Al were different for fertilised and unfertilised soils. This is mainly due to the higher percentage of less toxic Al-F complexes and the higher Ca concentration in the fertilised soil. Activity ratios of Al^{3+}/Ca^{2+} gave the best prediction of Al phytotoxicity. This ability of the activity ratio of Al^{3+}/Ca^{2+} to predict Al toxicity most consistently across soils with different phosphate fertiliser histories confirmed that soil solution Ca should be taken into account together with toxic Al species in the assessment of Al phytotoxicity.

Another glasshouse study (Chapter 6) was conducted to develop a chemical test to predict the potential toxicity of Al for early root growth in widely contrasting soil types. The results of this study showed that, in soils with similar physical properties, mineralogy and low organic matter content, short time PCV-Al determination in soil solution can be used as a simple and reliable method to predict Al toxicity. However, the direct use of short-time colorimetric procedures to predict critical Al toxicity levels for contrasting soil types could be limited by variations in organic Al and other factors such as ionic strength and cation and anion types and concentrations.

Results from the field trial reported in Chapter 4 indicated that the F component in the P fertiliser can have a significant effect on the Al speciation by forming stable Al-F complexes in soil solutions. However it was not clear whether the Al-F species are toxic and at what concentrations. In order to obtain information on this aspect a study was conducted to (i) investigate the interactive effects of pH and F on soil solution composition and Al speciation and (ii) to determine which species of Al-F complexes, if any, are phytotoxic to plants. Results of this study indicated that there was a significant interaction between acidity and F on soil solution pH, and the concentrations of Al and F. Increasing rates of F addition to soil significantly increased the soil solution Al concentration irrespective of the soil pH. However, the increase in soil solution Al concentration with F addition was substantially greater in strongly acid soils than in slightly acidic soils. This may have been due to F-accelerated dissolution of clay minerals in addition to the exchange reaction of F with OH in the soil colloids in the strongly acidic conditions.

There was a significant interaction between pH and rate of F addition on root growth of barley (Chapter 7). Addition of high rates of F to strongly acidic soil severely reduced the root growth. This is in contrast to results obtained in nutrient solution studies where at a fixed Al level, increasing rates of F ameliorated the Al toxicity. The possible reason for the reduction in root growth in the soil could be the substantial increase in Al

concentration in the soil solution resulting from F addition. Speciation calculations predicted that increasing rates of F addition increased concentrations of Al-F complexes in the solution. Results also indicated that Al-F complexes are not toxic at low concentrations but they are toxic at higher concentrations. This study indicates that due to the confounding and complex nature of soil acidity, extrapolation of results beyond the conditions imposed by specific experiments, such as results from the nutrient solution studies, to soil is difficult and some times dangerous.

The approximate threshold toxic levels of Al-F species found in this experiment were much higher than the Al-F species concentrations observed in the field trial on a marginally acid soil studied in Chapter 4. Therefore, it is unlikely that in marginally acidic soils long-term F inputs via P fertilisers can have any detrimental effects on plant growth. Rather, F addition will reduce the free Al concentrations while keeping the concentrations of Al-F species below the toxic threshold level in the soil solution, thereby reducing the occurrence of Al toxicity. Further studies should be carried out using legumes and ryegrass species to find out the exact threshold toxic levels of Al-F species because the threshold toxic level may vary with the plant species. Compared with AlF_2^{+1}, the AlF^{2+} complexes appeared to be more toxic to barley root growth. Although this is a speculative conclusion, if substantiated, will have serious implications to the measurement of Al toxicity in acid soils fertilised with P fertilisers. More data are thus needed to assess the ubiquity of Al-F complexes in soil solution, and their potential role in acid soil infertility.

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Appendix 1

Rate of acidification

pH (H_2O) (0-75 mm soil depth)				
Year	Control	SSP (30)	NCPR (30)	DAP (30)
1981	5.85			
1985	5.70			
1992	5.48	5.50	5.65	5.39

Rate of acidification in control plots (buffering capacity = 44.5 k mole H^+ ha^{-1} pH^{-1} for the soil depth 0-75 mm)
(a) 1981 to 1985 (4 years)
Δ pH = -0.15
$\therefore$ Rate of acidification $\quad = \quad$ 44.5 * 0.15 k mol H^+ ha^{-1} (4 years)$^{-1}$
$\qquad = \quad \dfrac{44.5 * 0.15}{4}$ k mol H^+ ha^{-1} yr^{-1}
$\qquad = \quad$ 1.67 k mol H^+ ha^{-1} yr^{-1}

(b) 1985-1992 (7 years)
Δ pH = -0.22
$\therefore$ Rate of acidification $\quad = \quad \dfrac{44.5*0.22}{7}$ = 1.40 k mol H^+ ha^{-1} yr^{-1}

Mean rate of acidification $\quad = \quad \dfrac{1.67+1.40}{2}$ = 1.54 k mol H^+ ha^{-1} yr^{-1}

2.   Rate of acidification (NCPR treatment)
1985-1992 (7 years)

Δ pH = -0.05
Rate of acidification $\qquad = \quad \dfrac{44.5 * 0.05}{7}$ = 0.32 k mol H^+ ha^{-1} yr^{-1}

3.   Rate of acidification (DAP treatment)

Δ pH = -0.31

Rate of acidification $\qquad = \quad \dfrac{44.5 * 0.31}{7}$ = 1.97 k mol H^+ ha^{-1} yr^{-1}

4.   Rate of acidification (SSP(30) treatment)
Δ pH = -0.20
Rate of acidification $\qquad = \quad \dfrac{44.5*0.20}{7}$ = 1.27 k mol H^+ ha^{-1} yr^{-1}

Appendix 2

Prediction of number of years to reach pH (H_2O) 5.00

Assumption: Rate of acidification same as present

1. Control plots

Initial pH = 5.48   Final pH = 5.00
Δ pH = -0.48
Rate of acidification   = 0.22 pH/7 yr
$\therefore$ No of years to reach pH 5.0 $= \dfrac{7*0.48}{0.22}$
                                      = 15 years

2. NCPR plots

Initial pH = -5.65   Final pH = 5.00
Δ pH = -0.65
Rate of acidification   = 0.05 pH/7 yr
$\therefore$ No of years to reach pH 5.0 $= \dfrac{7*0.65}{0.05}$
                                      = 91 years

3. DAP plots

Initial pH = 5.39   Final pH = 5.00

Δ pH = -0.39
Rate of acidification   = 0.31 pH/ 7 yr
$\therefore$ No of years to reach pH 5.0 $= \dfrac{7*0.39}{0.31}$
                                      = 9 years

4. SSP (30) plots

Initial pH = 5.50   Final pH = 5.00

Δ pH = 0.50
Rate of acidification   = 0.2 pH/7 yr
$\therefore$ No of years to reach pH 5.0 $= \dfrac{7*0.5}{0.2}$
                                      = 18 years

Appendix 3

Theoretical liming value of North Carolina phosphate rock (NCPR) assuming 100 % dissolution:

Total P content NCPR	$= 13.2\,\%$
Carbonate content of NCPR expressed as % $CaCO_3$	$= 12.0\,\%$ (Syers et al., 1986)
Moles of P in 100 g NCPR	$= \dfrac{13.2}{31}$
Moles of H^+ required for complete dissolution of this P	$= \dfrac{13.2*2}{31}$
$CaCO_3$ equivalent to the above moles of H^+	$= \dfrac{13.2*100}{31}$
	$= 42.6\ g$

$\therefore$ 100g NCPR has a liming value equivalent to $\quad= (42.6+12)$ or 54.6 g $CaCO_3$

i.e. NCPR has 54.6 % $CaCO_3$ equivalent

1 kg NCPR has the potential of neutralizing $\quad= \dfrac{54.6*2*10}{100\ *1000}$ k mol H^+

$= 0.0109$ k mol H^+

$\therefore$ Liming value associated with 1 kg P $\quad= \dfrac{1000*546}{132}\ g$

$= 4.135$kg $CaCO_3$

Total NCPR applied in 7 years	$= 227.3 * 7$
	$= 1591$ kg ha^{-1}
Amount of NCPR dissolved in 7 years period	$= 1591*0.68$
	$= 1081.9$ kg ha^{-1}
Amount of H^+ consumed by NCPR	$= 1081.9*0.0109$
	$= 11.8$ k mol H^+ ha^{-1}

Appendix 4

Prediction of pH increase in NCPR-treated plots based on the results of national series of lime trials.

Total NCPR applied in one year
$$= \frac{30*100}{13.2}$$
$$= 227.3 \text{ kg}$$

$\therefore$ Total NCPR applied in 7 years
$$= 227.3*7$$
$$= 1591.1 \text{ kg}$$

Total free $CaCO_3$ content applied over 7 years
$$= 1591 * 0.12$$
$$= 190.9 \text{ kg}$$

$\therefore$ Weight of apatite fraction
$$= (1591.1-190.9)$$
$$= 1400 \text{ kg}$$

Only 68 % was dissolved
$\therefore$ Total phosphate rock dissolved
$$= 1400*0.68$$
$$= 952 \text{ kg}$$

Assuming complete dissolution of free $CaCO_3$, the percentage increase in P in apatite would be
$$= \frac{13.2*100}{88}$$
$$= 15\%$$
$\therefore$ 952 kg apatite contains
$$= 4.61 \text{ kmol P}$$

Dissolution of 1 kmol P or 1 kmol $CaCO_3$ requires the same number of k mol of H^-

$\therefore$ Total $CaCO_3$ equivalent
$$= (461+190.9)$$
$$= 651.9 \text{ kg}$$

In Edmeades et al. (1984) field study application of
2500 kg lime increased the pH by 0.42 pH units. Assuming 90 % liming value

Total $CaCO_3$ applied
$$= \frac{2500*90}{100}$$
$$= 2250$$

$\therefore$ 651.9 kg $CaCO_3$ will increase the pH by
$$= \frac{651.9*0.42}{2250}$$
$$= 0.12 \text{ pH unit}$$