MAGNESIUM FERTILISER EFFECTS ON FOREST SOILS UNDER *Pinus radiata*

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ABSTRACT

Magnesium deficiency is of concern in a number of forest regions in New Zealand and has been linked in recent years to a condition in *Pinus radiata* called upper mid crown yellowing (UMCY). Magnesium deficiency is also acknowledged as a common nutrient disorder linked to 'new type forest decline' in Europe and the USA. With increases in the number of rotations and increased growth rates through tree breeding, the incidence of Mg deficiency and UMCY is expected to increase. This study investigated the Mg fertility of a range of forest soils, their responses to the application of Mg fertilisers and Mg uptake by *P. radiata*.

New Zealand Forest Research (Institute Ltd) has established a series of Mg fertiliser trials (FR190 series) in a range of forest soils. Five of these trial sites, located in the North Island of New Zealand, where calcined magnesite (calmag) was applied at 150 kg Mg ha^{-1}, were sampled to investigate the effectiveness of calmag in increasing plant available Mg and to determine the fate of the fertiliser. At all of the sites, within two and three years following calmag application, both soil exchangeable Mg and solution Mg concentrations were increased in the top 5 cm. However, the increases were significant only at three of the sites, where the initial soil exchangeable Mg was low. The other two soils had medium to high concentrations of soil exchangeable Mg prior to Mg fertiliser application. Between 70-90% of the applied fertiliser Mg had dissolved and estimated losses due to leaching ranged from 0-20%. Foliar concentrations of Mg were generally improved in the fertilised trees, but the increases were not significant.

Symptoms of Mg deficiency and UMCY are worse in trees that have high foliar K:Mg ratios. High foliar K:Mg ratios reflect changes in the pools of soil exchangeable Mg and K. Therefore, the effects of Mg fertiliser application on soil K:Mg molar ratios at the FR190 series trials were examined. In the trials where Mg fertiliser application significantly increased soil exchangeable Mg the soil K:Mg molar ratio was significantly reduced. This could see a reversal of the trend of the soil K:Mg ratios increasing with time and a reduction in the severity of Mg and UMCY symptoms. In

the trials that had medium to high concentrations of Mg, the K:Mg molar ratio was not affected by increases in exchangeable Mg from Mg fertiliser application.

As there are several Mg fertilisers with varied solubilities available to foresters a study was conducted to determine the rates of dissolution of a range of Mg fertilisers applied at 200 kg Mg ha^{-1} to a pumice soil under *P. radiata* in Kaingaroa Forest near Rotorua. Twenty seven months after fertiliser application the mean percentage of Mg dissolved were 100% for Epsom salts, 92% for calcined magnesite 1-2 mm, 91% for Granmag 20 (granulated product from 20% acidulation of calcined magnesite, 2-4 mm), 83% for calcined magnesite 2-4 mm and 70% for forestry grade dolomite. The specific dissolution rate constants (μg fertiliser cm^{-2} day^{-1}) for the slowly soluble Mg fertilisers were 279 for calcined magnesite 1-2 mm, 220 for calcined magnesite 2-4 mm, 212 for Granmag 20 and 13 for forestry grade dolomite. A computer program based on an elemental sulfur (S^o) oxidation model, where the rate of S^o oxidation depends on surface area of the particles, explained the rate of dissolution of Mg fertilisers within a narrow fertiliser particle size range.

Application of Mg fertiliser has been shown to increase plant-available Mg. However, there has been no significant increase in foliar Mg concentrations in the fertilised trees. It was thought that though the bulk soil had sufficient plant-available Mg, some factors in the rhizosphere might be inhibiting Mg uptake by *P. radiata*. Therefore, trials were conducted to increase the understanding of Mg availability in the soil immediately surrounding the tree roots. Two glasshouse experiments were conducted investigating the tree-induced changes in Mg availability in the rhizosphere of *P. radiata* seedlings. The first used pumice topsoil fertilised with various forms of Mg fertilisers. The second used pumice sub-soil that had lower exchangeable Mg concentrations and pH buffering capacity. The subsoil was fertilised with different rates of Mg and K fertilisers.

There was a significant accumulation of exchangeable Mg in the soil layers near the rhizosplane, compared to the bulk soil for the Epsom salts and granmag fertiliser treatments in the first experiment. A similar accumulation occurred for treatments where Mg fertiliser was applied in the second experiment. Magnesium accumulation at the root surface is probably due to a higher rate of Mg movement by mass-flow

compared to Mg uptake by the seedlings. The higher rate of Mg movement was probably caused by high seedling transpiration rates. Magnesium accumulation in the rhizosphere could have also been influenced by ectomycorrhizal fungi growth.

Soil pH in the rhizosphere soil of the first experiment was generally unaffected by nutrient uptake of the seedling compared to the bulk soil, probably due to the high buffering capacity of this soil. Whereas, in the second experiment the soil pH, because of the low pH buffering capacity of the soil, was significantly reduced in the rhizosphere compared to the bulk in all treatments. Cation-anion balance without considering N uptake, showed that the seedlings took up an excess of cations compared to anions. Because the ionic form of N taken up by the seedlings was not determined, it was not possible to explain the rhizosphere acidification from the cation-anion balance in the seedlings. Magnesium concentrations in the fertilised seedling in the first experiment increased for all fertiliser types used, but only the increases in root Mg concentrations were significant. In the second experiment Mg fertiliser application significantly increased Mg concentrations in both the shoots and roots.

Recently, Forest Research installed a fertiliser trial that manipulated the soil K:Mg ratio through the application of Mg and K fertiliser. This trial was used to study the losses of Mg due to leaching under *P. radiata* after the application of Mg and K fertiliser. Suction cup lysimeters were installed at 2 depths (10 cm and 45 cm) to monitor changes in soil solution Mg concentrations in the top-soil where the active roots are and the leaching losses of Mg down below 45 cm over an 18 month period after fertiliser application. Magnesium and K fertiliser application resulted in significant increases in soil solution Mg and K concentrations in the 0-10 cm soil layer soon after fertiliser application. However, by 90 to 180 days after application concentrations have returned to levels not significantly different from those of the control treatment.

The soil solution K:Mg molar ratio in the 0-10 cm soil layer was significantly increased by both K fertiliser treatments at all sampling times. Magnesium fertiliser application generally decreased the soil solution K:Mg molar ratio, although none of the decreases were significant. Magnesium fertiliser application significantly decreased the soil

exchangeable K:Mg molar ratio and K fertiliser application significantly increased the soil exchangeable K:Mg molar ratio.

Between 180 to 240 days following application, concentrations of Mg and K in the sub soil lysimeters peaked. Concentrations of solution Mg in the sub soil lysimeters of the fertilised and unfertilised plots were generally greater than solution K concentrations. Estimated leaching losses of Mg were 39.4 kg Mg ha^{-1} in the Mg fertilised plots and 11.2 to 26.9 kg Mg ha^{-1} in the K fertilised plots. Estimated leaching losses of K were 8.9 kg K ha^{-1} for the 200 kg K ha^{-1} treated plots and 17.4 kg K ha^{-1} for the 400 kg K ha^{-1} treated plots. Magnesium fertiliser application did not cause any increase in the leaching losses of K.

This thesis has increased the knowledge base of the Mg fertility of a range of forest soils and their response to application of Mg fertiliser. More research is required to determine the reasons for the slow tree response to increases in soil Mg from Mg fertiliser application and the role of ectomycorrhizal in the Mg uptake by *P. radiata*.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Pinus radiata, or Monterey pine, is a native of Pacific north-west of North America occurring in three patches, along the Californian coast and two islands off Mexico. The total area of natural habitat is approximately 7000 ha, the largest area occurring on the Monterey Peninsula (Hegan 1993). By contrast, in New Zealand, *P. radiata* plantations, after first being introduced in 1859 (Hegan 1993), now cover an area of 1.52 million ha, and makes up approximately 90% of New Zealand's total exotic forest estate (Ministry of Agriculture and Forestry 1998). The area of exotic plantation forest continues to grow - for the year ended 31 March 1998 there was 63,700 ha of new planting and more than 80% was on land previously under pasture. Forestry is worth 2.5 billion dollars in export earnings and accounts for about 12% of New Zealand's total produce exports (Ministry of Agriculture and Forestry 1998).

The main area of *P. radiata* forests in New Zealand is located in the central North Island, accounting for one third of New Zealand's total area planted in *P. radiata*. The other main areas of *P. radiata* forest include Northland, Gisborne and Hawkes Bay in the North Island and Nelson, Marlborough, Canterbury, Otago and Southland in the South Island (Ministry of Agriculture and Forestry 1998). A large proportion of New Zealand's *P. radiata* plantation forests occur on soils that are low in plant available (soil exchangeable) magnesium (Mg) (Metson and Gibson 1977).

The extensive *P. radiata* plantations of the central North Island are planted largely on soils derived from pumiceous parent material (Pumice Soils) (Hewit 1993), that are low in a range of nutrients including Mg. Other major forestry soils low in plant available Mg includes Ultic and Brown soils of Nelson, Otago and Southland and Podzols of Westland (Hunter *et al.* 1991; Maclaren 1993; McLaren and Cameron 1990). The low

levels of plant available soil Mg are partially responsible for Mg deficiency symptoms that are observed nationally and this is an issue affecting the sustainable productivity of New Zealand's forest estate (Payn 1991).

Magnesium deficiency was first documented in the 1960's in *P. radiata* seedlings and older trees planted in Kaingaroa (Will 1961; Will 1966). Will (1961) and more recently Hunter *et al.* (1986) reported stunted and malformed growth of severely deficient trees. Will (1961) and Hunter *et al.* (1986), found that severe deficiency symptoms could be corrected, by the application of Mg fertiliser. Further research has shown that *P. radiata* is slow to respond to increased concentrations of soil Mg (Payn 1991; Hunter 1996). Foliar Mg concentrations improve only-several years after fertiliser application. This was thought to be due to the slow fertiliser reaction rates with the soil, restricted movement of Mg to the roots, rapid leaching losses from the soil and an inability of *P. radiata* to assimilate Mg. However, no studies have been reported on the relative contribution of each of these factors to the Mg nutrition of trees on Mg deficient soils.

In recent years Mg deficiency has been linked to a condition in *P. radiata* trees typically more than 12-years-old called upper mid crown yellowing (UMCY) (Beets and Jokela 1994). Symptoms of UMCY include a yellowing of needles in the central portion of the upper crown followed by needle loss and varying degrees of crown die-back (Beets *et al.* 1991). Other factors that may be involved in the occurrence and severity of UMCY include periods of drought, application of K fertiliser and high foliar K:Mg ratios. To date no published information is available on the effects of UMCY on forest productivity. However, predictions of growth losses resulting from UMCY using a leaf-area-based model suggest that a growth reduction of 10% could be attributed to UMCY when half the trees in a stand are affected (Beets *et al.* 1993). The incidence of UMCY is likely to increase in future because faster tree growth rates, increase the Mg demand placed on soil, and number of rotations on the same site is increased. Improved tree breeding and silvicultural practice will increase growth rates. The large number of new plantings on old pasture sites is also a likely factor in the future. Old pasture sites generally have depleted soil Mg reserves and increased K concentrations from fertiliser applications (Beets *et al.* 1993).

To date, most of the Mg research related to forestry has tended to concentrate on the occurrence and causes of Mg deficiency symptoms and UMCY. Emphasis has been on the above ground effects of Mg fertiliser application, for example whether Mg fertiliser application increases foliar Mg concentrations and increases plant biomass (Will 1961; Will 1966; Hunter *et al.* 1986; Beets *et al.* 1993). There are only a limited number of studies in recent years on the effects of Mg fertiliser application on the distribution and fate of applied Mg, and on other soil chemical properties. Both Payn (1991) and Hunter (1996) highlighted the need for further research into the soil parameters that affect Mg supply. Specifically, this research should determine whether soil solution Mg can be correlated with needle Mg concentrations in the tree. It should investigate whether the slow rise in needle Mg concentration can be attributed to either slow rates of release of Mg from different Mg fertilisers, or to differences in Mg chemistry of the rhizosphere soil compared to the bulk soil and consequent influence on the uptake of Mg by the tree. Therefore, there is a need for more in-depth studies of soil chemistry and processes that influence Mg availability in forest soils under *P. radiata.* The plant-availability of Mg from the range of Mg fertilisers also need to be investigated.

1.2 OBJECTIVES OF THE THESIS

The research reported in this thesis attempts to increase knowledge of Mg fertility and fertilisation of forest soils in relation to Mg deficiency and 'upper mid crown yellowing' (UMCY) in *P. radiata.* The specific objectives of the research are:

1. To investigate the effectiveness of calcined magnesite fertiliser applied to forest soils at increasing plant available Mg and foliar Mg concentrations, and reducing UMCY symptoms.
2. To determine the rate of dissolution of a range of Mg fertilisers applied to forest soils under field conditions
3. To determine the plant-induced changes in soil Mg and pH in the rhizosphere of *P. radiata* treated with Mg and K fertilisers.
4. To determine leaching losses of Mg and other cations in forest soils after application of Mg and K fertilisers.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

2.1.1 The Mg cycle in a *Pinus radiata* forest

Soil Mg is derived mainly from the weathering of rocks and minerals. Igneous rocks, such as dunite, peridotite and pyroxenite contain high concentrations of Mg. Magnesium is found mainly in primary minerals such as biotite and serpentine, and in secondary minerals such as dolomite, and aluminosilicate clays. These minerals weather and the Mg ions (Mg^{2+}) released, are then adsorbed on to soil exchange sites or remain in solution as long as the chemical equilibrium between the Mg^{2+} in the exchange complex and that in soil solution is maintained. Magnesium ions are also released from the exchange sites by exchange with other cations in soil solution to maintain the chemical equilibrium mentioned above (Figure 2.1). In Pumice Soils of the central North Island where *P. radiata* is mostly grown, total Mg in soils ranges between 0.7 to 7.0 $cmol_{(+)}kg^{-1}$ and exchangeable Mg between 0.4 to 2.0 $cmol_{(+)}kg^{-1}$ (Metson and Brooks 1975).

From solution, Mg^{2+} is taken up by the tree or leached below the root zone. Magnesium, which is taken up, is partitioned into the various tree components depending on the requirements of those components (Figure 2.1). Webber and Madgwick (1983) reported that, of the 102 kg Mg ha^{-1} contained in the above ground biomass of 29-year-old *P. radiata*, 10% was in the foliage, 16% was in the live branches, 3% was in the cones and 65% was in the stem. A large portion of the Mg taken up by the tree is returned as litterfall or from pruning/thinning or logging operations. Based on the study of Webber and Madgwick (1983), about 35% of the Mg taken up can be expected to be returned to the soil as litter and branches during logging operations. Some Mg is also removed from the cycle in the main stem during

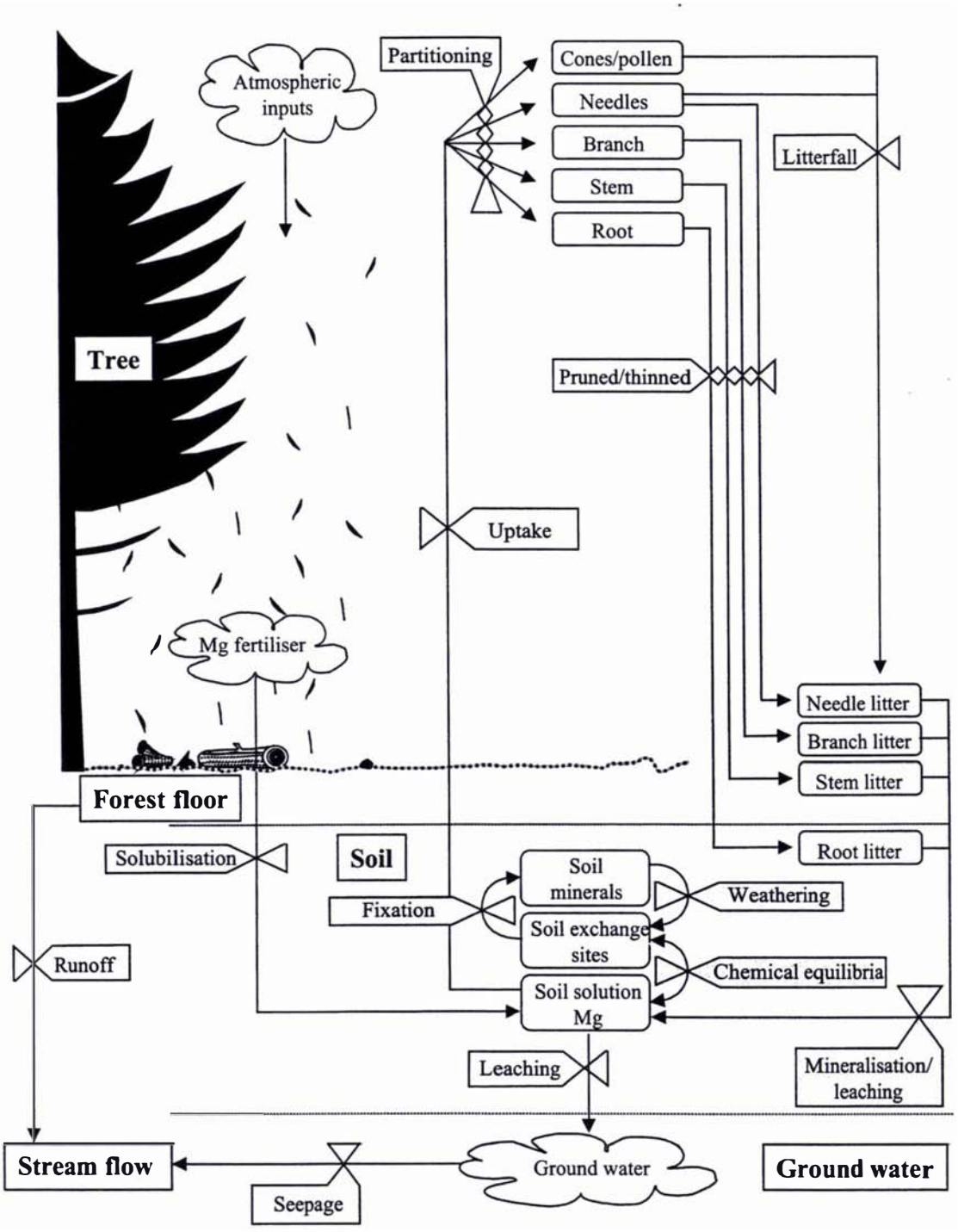

Figure 2.1 The Mg cycle in a *P. radiata* forest system.

production thinning or logging.

Litter decomposes mineralising the Mg contained within it and returning the Mg to soil solution. Magnesium enters the cycle as atmospheric inputs from rain. The amount entering the system depends on how close the forest is to the sea. At Kaingaroa Forest, (in the centre of the North Island) rainfall supplies about 0.8 kg Mg ha^{-1} yr^{-1} as against 4.9 kg Mg ha^{-1} yr^{-1} in a western coastal forest (Hunter *et al.* 1986). Magnesium also enters the cycle through Mg fertiliser application (Figure 2.1).

This literature review covers the following aspects of the Mg cycle: the functions of Mg in forest trees; mechanisms and kinetics of Mg uptake; the effects of fertiliser Mg on forest tree growth; fertiliser Mg reaction in soils; Mg deficiency in forest trees of New Zealand, Europe, America and Australia; and Mg in forest soils of New Zealand and its availability to trees. Depending on the availability of information the discussion, as much as possible, will refer to Mg nutrition of *P. radiata*. A majority of the research on Mg nutrition of *P. radiata* conducted in New Zealand has been on pumice soils of the central North Island and therefore, this research will tend to dominate the discussion in this review.

2.2 MAGNESIUM NUTRITION OF FOREST TREES

2.2.1 Functions of Mg in forest trees

The major role of Mg in trees is as the cation in the centre of the chlorophyll molecule and no other ion can substitute for it (McLaren and Cameron 1990) (Figure 2.2). Therefore, chlorophyll synthesis is strongly dependent on the availability of Mg to the tree. The fraction of total tree Mg associated with chlorophyll however, is relatively small and is in the order of 15 to 20% (Mengel and Kirkby 1987).

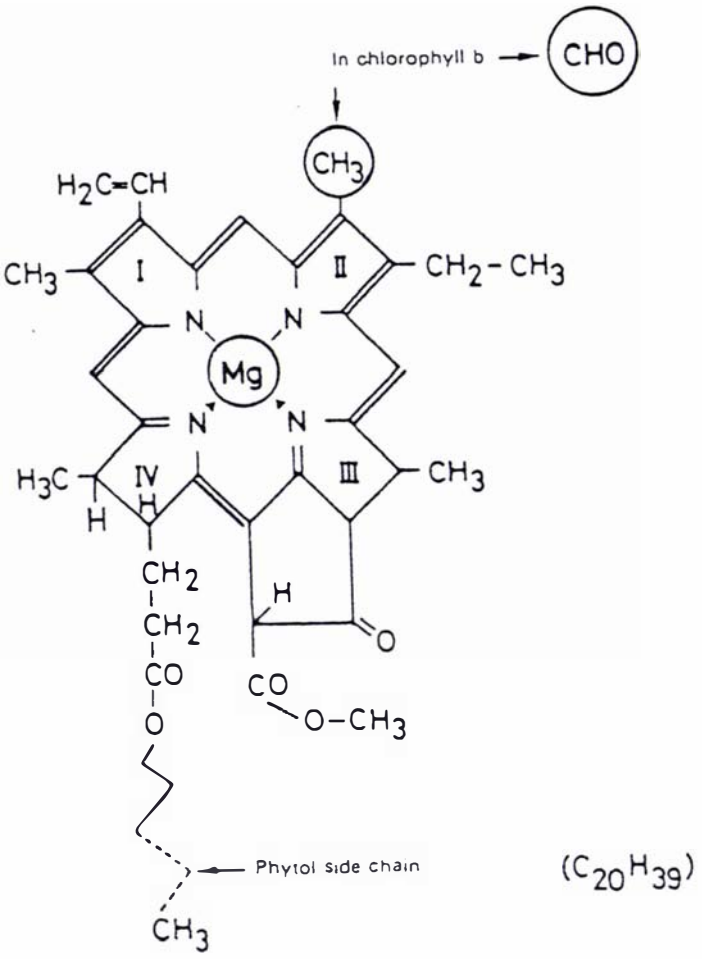

Figure 2.2 Structure of chlorophyll-a molecule showing Mg as the central ion. Absorption of light is due to the ring system of the molecule. In the chlorophyll-b molecule an aldehyde group (CHO) replaces the encircled methyl group (CH_3) (Mengel and Kirkby 1987).

Magnesium is also required for a wide range of physiological processes. Magnesium is required for the synthesis of ribonucleic acid (RNA), the net synthesis of this acid reducing in response to Mg deficiency. Another important role of Mg is as a co-factor in many enzyme reactions, particularly those involving adenosine triphosphate (ATP). ATP is an important molecule in the storage of the energy released during respiration. Respiration is the cellular process by which energy is released from the complex organic molecules formed during photosynthesis and is controlled by specific enzymes. Magnesium forms a bridge between the ATP and the enzyme molecules. The synthesis of ATP also has a requirement for Mg (phosphorolation: ADP + $P_i \rightarrow$ ATP).

Magnesium forms the bridge between adenosine diphosphate (ADP) and the enzyme phosphoribulo-kinase. The partitioning of carbohydrate in the tree is also affected by the supply of Mg. Magnesium-deficient conifers tend to accumulate non-structural carbohydrates in their leaves probably due to inhibition of phloem loading of sucrose. This can decrease the carbohydrate content of sink sites such as roots. Limitation of the supply of carbohydrate to the roots strongly impairs root growth (Mengel and Kirkby 1987; Marschner 1995; Slovik 1997)

2.2.2 Magnesium uptake by trees

2.2.2.1 Nutrient uptake kinetics

The uptake of Mg by trees is in the ionic form, Mg^{2+}. Plants take up nutrient ions either passively, via the apoplasmic pathway where ions move freely through the free spaces in the cell walls and into the endodermis, or actively via the symplasmic pathway (Barber 1984).

Two types of passive ion-influx kinetics have been recognised. The first includes, passive ion movement of ions into plant roots down chemical gradients (from a higher to lower concentration) and electrochemical potential gradients (cations are attracted to a negative electropotential). Plant cells are negatively charged, so cations may move into the cell by physical, non-metabolic forces (Barber 1984; Mengel and Kirkby 1987). This type of passive ion-influx is not ion specific. Non-specific competition occurs between the cation species for the negative charges of a plant cell. Increasing the supply of one cation in soil solution can depress the uptake of other cations (Mengel and Kirkby 1987).

This was demonstrated in intact corn roots grown in a split-root system. In this system, 50% of the roots were fed with a nutrient solution that contained 1 m*M* Mg and the other 50% of the roots were fed with a solution that contained 1 m*M* Mg and 1 m*M* K (Claassen and Barber 1977). Magnesium uptake by the 50% of roots that were fed with a solution containing both Mg and 1 m*M* K was 1.89 μmoles g FW^{-1} sec^{-1} compared to 3.34 μmoles g FW^{-1} sec^{-1} in the other 50% of roots supplied with Mg and no K. A

similar response has been recorded for banana plants grown in sand culture in 1 m^3 lysimeters (Turner and Barkus 1983). Increasing the application of K from 2.92 g K per lysimeter to 14.60 g K significantly reduced the uptake of Mg from 3.25 to 2.98 $\mu g\ g^{-1}\ d^{-1}$. Therefore, if Mg is taken up passively by *P. radiata*, high concentrations of K in solution may restrict the uptake of Mg. At high concentrations of K in solution, K can also be taken up passively. This is discussed further in the following paragraphs in this section.

The other form of passive ion uptake occurs along electrochemical potential gradients, which is dependent on respiration energy (Barber 1984). The involvement of respiration energy is only to maintain the electrochemical potential gradient. The electrochemical potential gradient is produced by H^+ efflux pump-ATPase involved in the active uptake of anions and located in the plasmamembrane (Mengel and Kirkby 1987; Haynes 1990).

The passive uptake of Mg along electrochemical gradients is believed to be mediated by molecules called ionophores (Mengel and Kirkby 1987). Ionophores are capable of forming complexes with cations and can be found in plant cell membranes. Ionophores act as carriers of cations across plant cell membranes. The tendency of a cation to form a complex with an ionophore increases as its hydration energy decreases. For example, the Mg ion has very high hydration energy compared to K, so ionophores generally have greater selectivity for K than Mg. This could be a reason for selective cation uptake by plants and antagonism between different cations (Mengel and Kirkby 1987).

Active ion uptake is the uptake of ions against electrochemical gradients. It requires respiration energy, and is believed to involve carrier-molecules, possibly ATPase enzyme molecules. These molecules are located in the plasma membrane and when combined with an ion outside the membrane, transport the ion through the plasma membrane and deposit it into the cytoplasm (Nye and Tinker 1977; Barber 1984). The carrier-molecules involved in active ion uptake are ion specific and competition for absorption by the same carrier is related to the valency of the ion. Investigations indicate that H, K, NH_4, Rb, and Cs competes for the same carrier. Among the divalent cations, Ca, Sr and Ba compete for the same carrier (Barber 1984; Mengel and Kirkby

1987). Divalent Mg might also be expected to compete with Ca, Sr and Ba for the same carrier, although this has not been reported. Therefore, under conditions when Mg and K are actively taken up by *P. radiata*, no competition between K and Mg is expected.

Research evidence indicates that anions are actively transported across the plasma membrane into the cytoplasm (Barber 1984). Calcium uptake follows the apoplasmic pathway, so is passively taken-up (Barber 1984; Mengel and Kirkby 1987). Potassium can be taken-up either passively or actively partially dependent on the concentration of K in solution (Barber 1984; Mengel and Kirkby 1987). Studies by Epstein *et al.* (1963), indicated that active uptake of K by excised barley roots occurred at solution concentrations in the range 0 to 1 mmol l^{-1}, and at concentrations between 1 to 10 mmol l^{-1} passive uptake occurred. Similarly, Cheeseman and Hanson (1979), found that active K uptake by corn roots occurred at solution concentrations below 0.5 mmol l^{-1}.

The evidence for Mg uptake is mixed. As found for the uptake of K, Lazarof and Pitman (1966) showed that passive uptake of Mg by intact barley seedlings occurred at high solution concentrations (15 mmol l^{-1}), but at low concentrations of Mg (0.5 mmol l^{-1}) energy-dependent active uptake occurred. Leggett and Gilbert (1969) found evidence for active uptake of Mg at solution concentrations between 0 to 5 mmol l^{-1} by excised soybean roots. In contrast to the above studies, Ferguson and Clarkson (1976), suggested that Mg uptake by corn roots was by passive uptake for solution Mg concentrations of 0.2 mmol l^{-1}.

The above studies suggest the Mg and K compete with each other at high concentrations of these ions when passive uptake operates. At low concentrations, when active uptake mechanisms operate, no competition occurs.

The rate of cation uptake is generally related to concentration in solution. For example, Turner and Barkus (1983) reported an increase in Mg uptake by banana plants grown in sand culture in 1 m^3 lysimeters when Mg concentration increased. They found that plant uptake of Mg increased from 2 $\mu g\ g^{-1}\ d^{-1}$ to 3 $\mu g\ g^{-1}\ d^{-1}$ when the supply of Mg was increased from 0.48 to 2.40 g Mg per lysimeter. However, the rate of ion uptake will reach a maximum at high solution concentration. Michaelis-Menton kinetics

developed to describe enzyme reaction rates, have been used to describe this situation for ions that are actively taken up (Barber 1984). This is related to the enzyme controlled carrier molecules that are thought to be involved in ion movement across the plasma membrane.

2.2.2.2 Magnesium requirements of forest trees

A range of uptake rates for Mg have been reported for *P. radiata* (Table 2.1). Hunter *et al.* (1986) reported uptake values as low as 2 kg Mg ha^{-1} yr^{-1} for a severely deficient six-year-old stand. Uptake rates increased to a maximum of 9 kg Mg ha^{-1} yr^{-1} five years after the application of Mg fertiliser to this stand. Madgwick *et al.* (1977) reported rates of Mg uptake between 5.9 and 13.8 kg Mg ha^{-1} yr^{-1} for healthy stands of two to 22-year-old *P. radiata*. Based on unpublished biomass data, Payn (1991) calculated a maximum Mg uptake rate of approximately 18 kg Mg ha^{-1} yr^{-1} for 17 year old *P. radiata* growing at Puruki experimental catchment, near Rotorua. These rates of uptake are comparable with those recorded for other coniferous trees grown in European and American forests (Table 2.1). These ranged from 2.9 kg Mg ha^{-1} yr^{-1} for 200-500 year-old *Picea engelmannii* growing in Colorado USA to 9.6 kg Mg ha^{-1} yr^{-1} for 51-year-old *Pinus banksiana* growing in Wisconsin, USA.

Evidence has been provided by Madgwick *et al.* (1977) of decreasing Mg uptake by healthy *P. radiata* with increasing age. They reported annual uptake of Mg of 10.5 kg Mg ha^{-1} for two- to four-year-old *P. radiata* and for eight- to 10-year-old trees, annual uptake declined to 5.9 kg Mg ha^{-1}. The rates of Mg uptake are also lower in trees suffering from Mg deficiency or forest decline (Table 2.1) (Hunter et al. 1986; Schulze et al. 1989). This could be linked to the low availability of Mg from the soil and the subsequent disruption of carbohydrate supply to the roots, as reported in Section 2.2.1, and restricted root growth in Mg deficient trees. From the above literature, it appears that plant age and Mg fertiliser application are two major factors influencing Mg uptake by forest trees.

Table 2.1 Rates of Mg uptake for a range of forest trees

Location	Species	Age (years)	Rate of Mg uptake (kg Mg $ha^{-1}.yr^{-1}$)	Reference
Kaingaroa, NZ[B]	*Pinus radiata*	4-10	5.9-13.8	Madgwick *et al* 1977
Southern Kaingaroa, NZ[A]	*Pinus radiata*	11	2.0	Hunter *et al.* 1986
Southern Kaingaroa, NZ[B]	*Pinus radiata*	11	9.0	Hunter *et al.* 1986
Purukohukohu Experimental Basin, NZ	*Pinus radiata*	~17	max. 18	Payn 1991
South USA	*Pinus taeda*	20	6.3	Switz and Nelson 1972
Wisconsin, USA	*Pinus banksiana*	51	9.6	Bockheim and Leide 1991
Colorado, USA	*Picea engelmannii*	200-500	2.9	Arthur and Fahey 1992
North Carolina, USA	Picea rubens	Old growth	3.4	Johnson *et al.* 1991
Bavaria, Germany[A]	*Picea abies*	30	6.3	Schulze *et al.* 1989
Bavaria, Germany[B]	*Picea abies*	30	8.3	Schulze *et al.* 1989
Valday Hills, Russia	*Picea* spp.	Natural	8	Bazilevich and Shitikova 1989

[A] Mg-deficient, declining stands; [B] healthy stands

2.2.2.3 Partitioning of Mg within *P. radiata*

Slow responses to Mg fertiliser application by *P. radiata* have been reported in a number of studies when measured by increases in foliar Mg concentrations (Hunter *et al.* 1986; Payn *et al.* 1995; Hunter 1996). The partitioning of Mg into tree components other than the foliage could be one reason for these observed slow responses (Schaaf 1997). The study of Hunter *et al.* (1986) showed the distribution of Mg in the various components of the tree when Mg supply was not limiting growth (Figure 2.3). Based on their data, there does not appear to be any major build-up of Mg in any one component. The largest portion (39%) of Mg within the tree was in the live branches. This is partly because the live branches are the heaviest component of tree biomass (36% of total biomass). The next largest portion of Mg (22%) was tied-up in the foliage. In severely Mg deficient trees, Hunter *et al.* (1986) reported that the largest portion (25%) of Mg within the tree was also in the live branches. The next largest portion of Mg (19%) was tied up in the stem wood, because of reduced growth rates in the severely Mg deficient trees. Dead branches also account for a considerable portion (16% compared to 3% in the healthy trees) of the Mg within the severely Mg deficient trees. Foliage Mg made-up only 11% of the Mg within the tree. This reflects not only the lower Mg concentrations in the Mg deficient foliage, but also poor needle retention of one year and two plus year-old needles. The biomass of two plus year-old needles in the Mg deficient trees was 173 kg ha^{-1} DW compared to 1732 kg ha^{-1} DW in the healthy trees.

Hunter *et al.* (1986) reported that the highest concentration of Mg in the healthy tree was found in the immature foliage (0.13%). The two plus year-old foliage and branches had a Mg concentration of 0.08% and the lowest concentration of Mg was in the wood and stump (0.03%). In severely Mg deficient trees, Mg concentrations of all components were lower than those in the healthy trees. In the severely Mg deficient trees, concentrations of Mg in the immature foliage was 0.06% and two plus year-old foliage and branches had Mg concentrations of 0.04% and 0.05%, respectively.

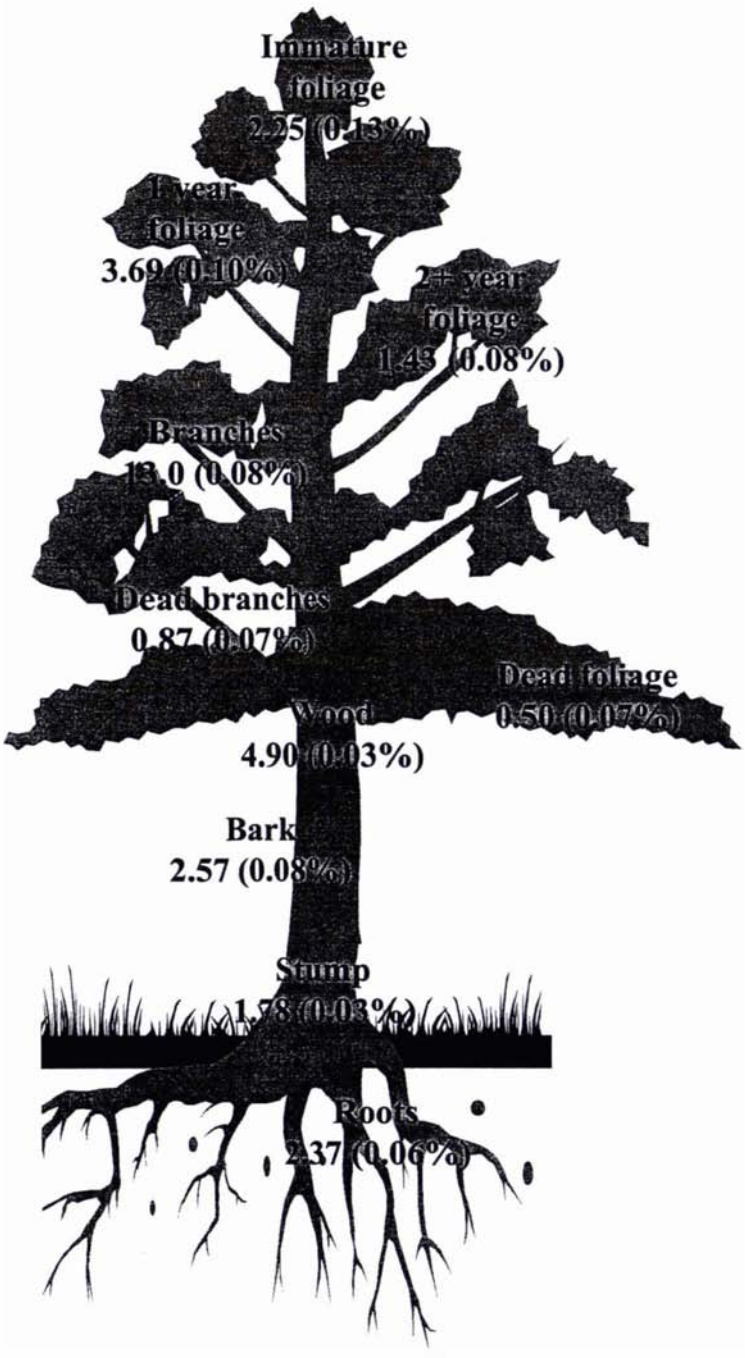

Figure 2.3 Magnesium content (kg Mg ha^{-1}) and concentration (% Mg) on a dry weight basis of fertilised (100 kg Mg ha^{-1}) 11-year-old *P. radiata* trees (Hunter *et al.* 1986).

Therefore, fertiliser Mg when applied to severely Mg deficient trees increases the Mg concentrations of all tree components. A large portion of the extra fertiliser Mg taken up by the trees can be found in the foliage mostly because of better needle retention.

2.2.2.4 Role of ectomycorrhizal fungi in tree uptake of Mg

Pinus radiata roots are colonised by ectomycorrhizal fungi (Foster and Marks 1967; Skinner and Bowen 1974; Comerford and Skinner 1989). The role of ectomycorrhiza on Mg nutrition of *P. radiata* has not been reported in literature. However, many authors have reported that a variety of tree species grew better and accumulated a range of nutrients when infected by ectomycorrhizal fungi (Skinner and Bowen 1974; Bledsoe and Zasoski 1983; Rygiewicz and Bledsoe 1984; George and Marschner 1996). Therefore, as observed for other nutrients, ectomycorrhiza infection of the roots might also improve the uptake of Mg by *P. radiata*, but this needs to be confirmed by research.

2.2.3 Effect of Mg on tree growth and yields

Due to the vital role Mg plays in the nutrition of trees (Section 2.2.1), Mg deficiency could be expected to affect the growth and dry matter yields of *P. radiata.* However, there are only a few reported cases where poor growth and low dry matter yields were attributed to Mg deficiency, most of these involved young trees or seedlings. This may be due to the lack of long-term studies where both Mg deficiency and tree biomass have been routinely monitored.

In 1980, severe Mg deficiency was responsible for stunted and malformed growth of six-year-old *P. radiata* trees (foliar Mg concentrations of 0.03-0.04%) in southern Kaingaroa (Hunter *et al.* 1986; Hunter 1996). When the trees were fertilised with 100 kg Mg ha^{-1} (25% as Epsom salts, 75% as dolomite) they grew 66% more in height and 45% more in root-collar basal area than the trees that received no fertiliser during a five-year monitoring period. Will (1961) also reported decreased growth rates in severely Mg deficient seedlings with necrotic needles on pumice soils at Whakarewarewa nursery.

Payn *et al.* (1995) reported that magnesium deficiency affected the dry matter allocation patterns in *P. radiata*, decreasing the root:shoot dry matter weight ratio. They observed that Mg-deficient seven-year-old trees at Kaingaroa showed much larger improvements in root biomass five years after fertilisation with 400 kg Mg ha^{-1} applied as dolomite compared to the trees which received no fertiliser. However, shoot biomass was not increased by fertiliser application in this study. In another study Payn *et al.* (1995) reported increased growth and biomass in seedlings grown in nutrient solution as the concentration of Mg in solution increased from 0.2 mg l^{-1} to 1.0 mg l^{-1} and 10 mg l^{-1}.

Predictions based on a leaf-area model suggested that a 10 percent loss in growth rate could be ascribed to upper mid crown yellowing (UMCY) (chlorosis associated with Mg deficiency, discussed further in Section 2.3.3.2), if half the trees in a stand were affected by UMCY (Beets *et al.* 1993). But no growth reductions have been reported from field trials of older trees (> 12-years) on pumice soils and suffering from UMCY (Beets and Jokela 1994).

2.3 MAGNESIUM DEFICIENCY IN FOREST TREES

2.3.1 Magnesium deficiency and 'new type forest decline' in Europe and North America

Magnesium deficiency is acknowledged as a common nutrient disorder in forests growing in acidic soils of Europe and the north-eastern part of North America (Evers and Huttl 1991; Liu and Huttl 1991; Huttl and Frielinghaus 1994; Schaaf 1995; Landmann *et al.* 1997). In Europe, Mg deficiency has been linked to 'new type forest decline' or 'crown thinning' in stands dominated by Norway spruce (*Picea abies*), but also including Scots pine (*Pinus sylvestris*), Corsican pine (*Pinus nigra* var. *maritime*), Douglas fir (*Pseudotsuga menziesii*), Beech (*Fagus sylvatica L.*), Oak (*Quercus* species) and Silver fir (*Abies alba*) (Landmann *et al.* 1997). In north-eastern North America, Mg deficiency was reported in declining stands of sugar maple (*Acer saccharum* March.), yellow birch (*Betula alleghensis*), red maple (*Acer rubrum*),

balsam fir (*Abies balsamea*) and mountain maple (*Acer spicatum*) (Landmann *et al.* 1997).

2.3.1.1 Symptoms of Mg deficiency

Magnesium deficiency is revealed by a yellowing of whole leaves and needles or parts of them (chlorosis). In leaves, typical symptoms are a discolouration of the region between the veins, mostly starting in the centre of the leaf. Sometimes the whole leaf appears light-green to yellowish in colour. Needles also turn yellow when Mg deficient, but the symptoms are more variable. In coniferous trees with more than one needle age class, yellow coloration starts in the oldest needles with yellowing of the needle tips. In more severe cases, all needles except for those of the current age class turn yellow. The yellow tones range from brownish-yellow in the oldest needles to light yellow in one to two year old needles (Ende and Evers 1997).

2.3.1.2 Extent of Mg deficiency in Europe and North America

In Europe, historical comparisons of foliar Mg concentrations in forest stands in several areas suggest there has been a long-term deterioration of Mg nutrition (Landmann *et al.* 1997). However, Mg deficiency was not a major concern until the late 1970s, as damage symptoms tended to be confined to small areas of forest. During the 1980s more severe Mg deficiency symptoms were reported over wide areas of mid-elevation mountains of Europe, predominantly on basic-cations-depleted acidic soils (Landmann *et al.* 1997).

Currently vast tracts of forest in central Europe are affected by Mg deficiency and the associated 'new type forest decline'. Surveys of forest health have shown that between 10-25% of Norway spruce are affected by varying degrees of yellowing depending on the regions (Landmann *et al.* 1997). The large mid-elevation mountain forests (600-1200 m) are the main Mg deficient area and this includes the Harz Mountains, the Fichtelgebirge, the Bavarian Forest and the Black Forest of Germany, the Ardennes Mountains of Belgium, and the Vosges Mountains of France (Evers and Huttl 1991; Landmann *et al.* 1997).

Other areas, mostly mid-elevation mountains also have basic-cations-depleted acidic soils, where Mg deficiency is common. These include, the Solling, the Hills, The Eggegebirge, the Thuringian Forest, the Upper Palatinate Forest, the Ore Mountains, the Hunsruck, the Eifel, and the Palatinate Forest of Germany, the Bohemian Forest of Austria, and the Forez (northern-eastern Massif Central), the Artense (central Massf Central), and the Plateau de Millevaches (western Massif Central) of France (Evers and Huttl 1991; Landmann *et al.* 1997). Magnesium deficiency has also been recorded in lowland areas on basic-cations-depleted and acidic sandy soils in north-eastern Germany and parts of The Netherlands (Evers and Huttl 1991; Landmann *et al.* 1997).

In America, Mg deficiency is less wide spread than in Europe and its occurrence is not as well documented. The areas where Mg deficiency has been reported in Canada include the Lower Laurentians north and east of Quebec City and north of Montreal. In eastern United States, Mg deficiency has been documented in high-elevation areas in the northern Appalachians including Camels Hump and the Green Mountains of Vermont, the Adirondacks and the Whiteface Mountains of New York (Landmann *et al.* 1997).

2.3.1.3 Magnesium deficiency in relation to acid deposition

The primary cause of Mg deficiency and the associated condition of 'new type forest decline' is the low Mg status of forest soils developed from parent materials with low Mg content and having a high resistance to weathering (eg, schist, sandstone and gneiss) (Evers and Huttl 1991; Landmann *et al.* 1997). Severe Mg deficiency has been reported in Norway spruce (*Picea abies*) in soils with exchangeable Mg levels of less than 0.17 $cmol_{(+)}kg^{-1}$.

However, in recent years acid deposition has also been recognised as a major factor in the unprecedented development of Mg deficiency symptoms that occurred in central Europe during the 1980s (Evers and Huttl 1991; Huttl and Frielinghaus 1994; Katzensteiner and Glatzel 1997). Acid deposition contributes to Mg deficiency in a number of ways. Deposition of free H^+ contributes directly to the acidification of forest

soils in Europe. The deposition of SO_4^{2-} and NO_3^- from industrial pollution enhances the leaching losses of Mg by providing mobile anions to the soil. High rates of NH_x deposition also have the potential to acidify forest soils.

Increased soil acidity may lead to the mobilisation of ions such as Al^{3+} which are antagonists to the uptake of Mg (Evers and Huttl 1991; Huttl and Frielinghaus 1994; Katzensteiner and Glatzel 1997). In addition, H^+ and Al^{3+} ions displace Mg^{2+} ions from the exchange sites, which can be subsequently leached from the soil (McLaren and Cameron 1990). Acid deposition, particularly acid fog, may cause direct foliar damage resulting in enhanced leaching of Mg from the canopy (Evers and Huttl 1991; Huttl and Frielinghaus 1994).

2.3.1.4 Correction of 'new type forest decline'

Magnesium fertiliser application is a fairly new strategy adopted to correct the low foliar Mg concentrations observed in forests with 'new type forest decline' in the 1980s (Kaupenjohann 1997). Several Mg fertilisation trials have been conducted in Germany since the 1980s to determine whether Mg fertiliser application can correct this disorder and if so, what rate of application is necessary. The results from these trials indicated that Mg deficiency symptoms can be reduced or completely overcome by the application of soluble Mg fertilisers (Evers and Huttl 1991). The application of $MgSO_4$ to Mg deficient young spruce and beech trees resulted in a very fast regreening response within 12 months (Ende and Zoettl 1991; Liu and Huettl 1991; Schaaf 1997).

In contrast, Schaaf (1995) found only slow tree response to Mg fertiliser application despite the Mg fertiliser having a major effect on the soil Mg. Application of $Mg(OH)_2$ (at 1040 kg Mg ha^{-1}) to a 60-year old Norway spruce stand showing severe Mg deficiency symptoms on a typic Dystrochrept soil (soil pH(water) of 3.7 in the top 20 cm) in Fichtel Mountains, Germany increased Mg concentrations in soil solution at 25 cm soil depth within three months of fertiliser application by more than a factor of 10. Exchangeable Mg concentrations in the top 50 cm of soil in the fertilised plots were 175.2 kg Mg ha^{-1} compared to 52.8 kg Mg ha^{-1} in the no-fertiliser controls. However, it took four and a half years after Mg fertiliser application before foliar concentrations

increased from about 0.067% to adequate levels of about 0.11% Mg. Schaaf (1995) reported that the delay in improvement of the Mg nutrition of the tree was due to the unfavourable chemical status of the soil (low soil pH, Al and H toxicity). Magnesium uptake only increased after the soil pH and the Mg/Al and Ca/H ratios had increased, reducing the incidence of Al and H toxicity.

2.3.2 Magnesium deficiency in Australian forests

Magnesium deficiency is generally uncommon in Australian soils (Williams and Raupach 1983). Khanna *et al.* (1992) estimated leaching of 67 kg Mg ha^{-1} below 40 cm soil depth during the initial year after the application of NPK fertiliser (400 kg N ha^{-1} as ammonium sulfate, 200 kg P ha^{-1} as superphosphate, 100 kg K ha^{-1} as potassium sulfate) to a 10-year-old stand of *P. radiata* growing on a Yellow Podzolic Soil near Canberra. Losses of Mg from the no-fertiliser controls were not reported. The soil used in the study of Khanna *et al.* (1992) had considerable amounts of exchangeable Mg particularly at depth (below 40 cm). The soil from the 40-50 cm depth had exchangeable Mg concentrations of 2.9 $cmol_{(+)}kg^{-1}$ (equivalent to about 590 kg Mg ha^{-1} at a bulk density of 1700 kg m^3) and from the 50-60 cm depth had 4.4 $cmol_{(+)}kg^{-1}$ (equivalent to about 900 kg Mg ha^{-1} at a bulk density of 1700 kg m^3), so Khanna *et al.* (1992) thought it was unlikely that this leaching loss of Mg would affect the Mg nutrition of *P. radiata*.

However, the majority of the roots responsible for a large proportion of the uptake of Mg are likely to be in the upper soil horizons (above 40 cm depth), where the weighted average Mg concentrations reported by Khanna *et al.* (1992) was 0.31 $cmol_{(+)}kg^{-1}$ (equivalent to about 230 kg Mg ha^{-1} at a mean bulk density of 1510 kg m^3). Therefore, Mg deficiency in the trees could be a problem in the future if losses of Mg from the top 40 cm continued at 67 kg Mg ha^{-1} yr^{-1}.

Turner and Lambert (1987) surveyed the nutritional status of 15 plus years-old *P. radiata* stands growing in the Gurang State Forest on the central tablelands of New South Wales. Soils were predominantly derived from Ordovican slate, Silurian slate and greywacke. They reported a decline of between 0.38 to 0.55 $cmol_{(+)}kg^{-1}$ in

concentrations of exchangeable Mg in the top 7.5 cm soil depth, in soil samples collected in 1984, from an average value of 1.06 $cmol_{(+)}kg^{-1}$ for the soils at the same sites obtained in a preliminary nutritional survey conducted in 1974.

Therefore, the potential does exist for Mg deficiency to occur on some Australian soils, particularly where NPK fertiliser has been applied over long periods of time. Ammonia, Ca and K applied to the soil in NPK fertiliser replaces Mg on the exchange sites promoting leaching of Mg. Tree growth is also likely to be increased by NPK fertiliser application increasing the demand on soil Mg. Magnesium deficiency symptoms have recently been reported in N fertilised stands of *P. radiata* and *Eucalyptus* in Tasmania (P. Smethurst pers. com.).

2.3.3 Magnesium deficiency in *P. radiata* in New Zealand

2.3.3.1 History of Mg deficiency

Magnesium deficiency symptoms in *P. radiata* have been observed throughout New Zealand, but are most prevalent in the central North Island, Westland, Nelson, Otago and Southland (Hunter *et al* 1991; Maclaren 1993; McLaren and Cameron 1990). The first properly documented incidence of Mg deficiency symptoms in *P. radiata* were recorded by Will (1961) in seedlings growing on Pumice Soil in Whakarewarewa nursery and Kaingaroa nursery near Rotorua during the summer of 1957-1958. The symptoms were characterised by needle tip chlorosis. The same symptoms were also observed by Will (1961) in Corsican pine (*P. nigra* subsp. laricio) and Lodgepole pine (*P. contorta*). He concluded that the likely cause for the observed deficiency symptoms was low levels of soil exchangeable Mg (0.10 $cmol_{(+)}kg^{-1}$) and foliar Mg (0.06% in 1-year-old foliage). Will (1961) also found that the Mg deficiency symptoms disappeared after the application of $MgSO_4$ (250 kg fertiliser ha^{-1}) and $MgSO_4$ in combination with other fertilisers. Application of Dolomite at 2500 kg and 190 kg fertiliser ha^{-1} also corrected the deficiency.

The first reported incidence of Mg deficiency in older trees was also reported by Will (1966). From the late 1950s until 1961, varying degrees of chlorosis were observed in

three- to 12-year-old stands of *P. radiata* growing in Pumice Soils bordering the Rotorua-Waikaremoana highway. In the spring of 1961, trees in compartment (cpt) 1039 of Kaingaroa Forest showed severe needle-tip chlorosis of two and three-year-old needles, the causes of which were investigated. Analysis of foliage samples showed that Mg tended to be lower in chlorotic needles (0.09%) compared to green foliage (0.11%). In spring of 1963, needle chlorosis in young trees was even more widespread than in 1961. Investigations were begun to establish the cause for the chlorosis.

Foliage analysis of five-year-old trees in cpt 69 showed that severe chlorosis occurred in needles with very low concentrations of foliar Mg (0.022%). Will (1966), concluded that Mg deficiency was responsible for the observed needle-tip chlorosis. In the winter of 1964, Will (1966), established Mg fertiliser trials on Mg deficient stands of *P. radiata* growing in pumice soils of Kaingaroa Forest to determine whether Mg fertiliser application could prevent chlorosis from developing the following spring.

However, little or no chlorosis occurred in the following spring, even in the unfertilised trees. Will (1966) thought this was related to higher rainfall in the spring of 1964, as the spring of 1963 was one of the driest on record. Drought reduces the moisture content in the topsoil layer to near wilting point, reducing the rate of movement of Mg from the bulk soil to the root surface. This may have caused a reduction in tree uptake ofMg, causing chlorosis in the spring of 1963 observed by Will (1966).

Will (1966) also noted that older trees (15 years plus) were not affected by Mg deficiency. He suggested that the roots of the older trees may have penetrated through the rhyolitic soil material in the surface soil into the subsoil containing buried topsoils of older, more weathered tephras, which had higher Mg concentrations than the surface soil.

Chlorosis was also observed to be particularly severe in pruned stands. This is because Mg is highly mobile within the tree (Mengel and Kirkby 1987) and in Mg-stressed trees a portion of the Mg required for new growth is obtained from older foliage. But this older foliage is removed from the tree by pruning, thereby reducing the pool of Mg that is available for translocation to the new growth.

The early incidences of Mg deficiency were confined to the northern part of Kaingaroa where *P. radiata* was the dominant species (Hunter *et al.* 1986). In southern Kaingaroa, failure to establish *P. radiata* because of frost damage meant that other pine species had been planted which were less sensitive to Mg deficiency, probably because of lower requirements for Mg or due to slower growth rates (Hunter *et al.* 1986).

However, improvements in establishment techniques have allowed *P. radiata* to be planted as a second rotation in southern Kaingaroa (Payn 1991). In spite of extremely low concentrations of soil exchangeable Mg (0.1 $cmol_{(+)}kg^{-1}$) and reserve Mg (boiling 1 *M* HCl extractable Mg of 0.38 $cmol_{(+)}kg^{-1}$) in southern Kaingaroa, the new plantings of *P. radiata* grew satisfactorily without any obvious symptoms of Mg deficiency for several years. However, by 1980 patches of severe Mg deficiency were noted in six-year-old stands of *P. radiata.* Symptoms of necrotic-tipped, yellow needles, poor needle retention, dead lower branches and stunted growth were generally more severe than those previously recorded in northern Kaingaroa (Hunter *et al.* 1986).

In 1991, a disorder of *P. radiata* called 'mid crown yellowing' (MCY) was reported by researchers from Forest Research (Institute Ltd) (Beets *et al.* 1991). 'Mid crown yellowing' had been a concern to forest health officers and others since before 1975. It was suggested that Mg deficiency and nutrient imbalance involving Mg were linked to MCY. MCY was later termed 'upper mid crown yellowing' (UMCY) (Beets *et al.* 1993) because the yellowing was confined mostly to the upper part of the mid-crown. Since 1991 UMCY has been the subject of much investigation.

2.3.3.2 'Upper mid crown yellowing'

Low needle Mg concentrations in *P. radiata* have in recent years been linked with a tree condition called 'upper mid crown yellowing' (UMCY), which is found typically in trees more than 12-years old (Beets and Jokela 1994). The severity of UMCY has been shown to increase as concentrations of foliar Mg decreased and those of K and N increased (Beets and Jokela 1994). Beets and Jokela (1994) assessed UMCY severity by scoring trees from 1-8 based on the severity of symptoms displayed, 1 being a

healthy tree and 8 a tree where the UMCY zone contains dead primary branch whorls and sometimes top death. They recorded strong correlations between UMCY scores and K:Mg concentration ratios in the needles with high scores correlated to high needle K:Mg ratios.

The incidence of UMCY is increasing due in part to a greater awareness of this condition by foresters, and also because of faster tree growth rates increasing the demand on soil Mg. Improved tree breeding and silvicultural practices are increasing growth rates. Other reasons are that Mg fertiliser is rarely applied to forest sites, therefore soil Mg removed with the harvested tree has not been replaced; new plantings of *P. radiata* are being made on ex-pasture sites which have been depleted of their natural supplies of Mg; and there are increases in the number of rotations per site. Intensive harvesting (the use of skidders and crawler tractors, windrowing of slash) also affects the Mg supply from the soil by disturbing the topsoil layer (Beets *et al.* 1993).

2.3.3.3 Symptoms of Mg deficiency and UMCY

Symptoms of Mg deficiency in New Zealand are similar to those recorded in Mg deficient conifers in declining forests of Europe and America and described in section 2.3.1.1. The symptoms observed by Will (1961) in seedlings at Whakarewarewa nursery and Kaingaroa nursery were, in mild cases, a yellowing of the tips of needles near the top of the plant (Figure 2.4). In more severe cases, more needles and greater lengths of needles were affected. The yellow colour is more intense giving a golden appearance to seedlings. In the most severely deficient seedlings needle tips became necrotic and little or no growth occurred in the seedlings showing necrosis. Similar symptoms occur in older trees (three to 12-years old), usually affecting previous season's foliage in the upper crown. In more severe cases, the whole crown is affected (Will 1966; Will 1985). In acute deficiency, growth is stunted and new growth also suffers needle tip chlorosis.

Figure 2.4 Magnesium deficiency in a young *P. radiata* tree.

Will (1966) has reported critical needle concentrations for *P. radiata*, at which symptoms start to reveal the deficiency. However, the display of symptoms may indicate an advanced stage of Mg deficiency, because at the initial stages of Mg deficiency, the tree may not show any visual symptoms. The critical foliage concentrations for *P. radiata* reported by Will (1966) were within the range of 0.6 to 0.8 mg g^{-1} DW. This was based on one-year-old needle analysis of trees of differing ages at Kaingaroa Forest displaying varying degrees of chlorosis. This concentration range is similar to the threshold values for one-year-old needle Mg concentrations reported for Norway spruce (*Picea abies*) (0.7 mg g^{-1} DW), below which chlorotic symptoms reveal the deficiency, and those values reported for one-year-old needle Mg concentrations for Scots pine (*Pinus sylvestris*) (0.5 to 0.6 mg g^{-1} DW) (Ende and Evers 1997).

The symptoms of UMCY include a yellowing of needles (as for Mg deficiency in young trees) in the central portion of the upper crown followed by needle tip necrosis and needle loss, and in severe cases, various degrees of crown die-back (Beets *et al.* 1991) (Figure 2.5).

Figure 2.5 Upper mid crown yellowing in *P. radiata* trees.

2.3.3.4 Correction of Mg deficiency and UMCY by the application of Mg fertiliser

Magnesium fertiliser is not routinely applied to forest soils in New Zealand. The majority of the little Mg fertiliser applied has been to nurseries (Ballard and Will 1978) and in trials investigating whether Mg deficiency and UMCY could be corrected by applying Mg fertiliser.

As mentioned in Section 2.3.3.1, the use of Mg fertiliser to correct deficiency symptoms was first documented by Will (1961) where Epsom salts and dolomite fertiliser were found to improve colour and growth of seedlings in Pumice Soil at Whakarewarewa and Kaingaroa nurseries. In another early report, Epsom salts (112 kg Mg ha^{-1}) applied in combination with sulfate of ammonia to six-year-old and 10-year-old *P. radiata* trees, showing some yellowing of needles, in Nelson improved tree growth compared to trees fertilised with nitrogen alone (Appleton and Slow 1966).

In a trial at southern Kaingaroa, Hunter *et al.* (1986), treated an area of six-year-old *P. radiata* growing in Pumice Soil and showing severe Mg deficiency symptoms with 100 kg Mg ha^{-1} as Epsom salts (25% of Mg applied) and dolomite (75% of Mg applied). The symptoms included yellowing of needles with necrotic brown tips, poor needle retention and stunted, malformed growth. Needle Mg concentrations were between 0.03-0.04% at the start of the trial. Magnesium fertiliser application gradually increased Mg concentrations in needles to reach a peak of 0.11% in the fourth year, but it took two years for the Mg concentrations to reach the critical concentrations of 0.08%.

As discussed in Section 2.2.3, in this trial Hunter *et al.* (1986) also reported a response in growth, as measured by increases in height and basal area, to Mg fertiliser application. Similarly for needle concentrations, it was two years before any differences in growth were observed between fertilised and unfertilised trees. In five years after fertiliser application, the Mg fertilised trees grew 45% more in root-collar basal area and 66% more in height compared to the no-fertiliser control trees. The slow response was thought to be due to the low base saturation of the soil (3%) and the time required for a build-up of exchangeable Mg before the Mg was made available to the roots. This may have been due to slow rate of dissolution of Mg from dolomite.

Payn (1991) initiated a Mg fertiliser trial to investigate the effects of applying Epsom salts on tree growth and foliar chemistry in an eight-year-old stand of *P. radiata* in southern Kaingaroa Forest. At the start of the trial foliar concentrations of Mg were 0.059% in the current needles and the trees displayed severe Mg deficiency symptoms

of chlorosis of a large portion of needles in the crown and poor retention of needle classes older than one year.

Epsom salts applied at 400 kg Mg ha^{-1} increased current needle concentrations to 0.108%, above the critical level reported by Will (1966), within six months of application. This indicated a faster response than reported by Hunter *et al.* (1986) to the application of dolomite and Epsom salt and by Schaaf (1995) for Norway spruce (*Picea abies*) fertilised with $Mg(OH)_2$. However, one year old needles remained at deficient levels of 0.061%. Foliar concentrations of Mg in the current needles of the trees which received no-fertiliser had declined further to 0.046% and in one-year-old needles, to 0.033%.

These levels were similar to those reported by Hunter *et al.* (1986) in a severely deficient stand also in southern Kaingaroa. There was no significant improvements in growth due to Mg fertiliser application in the trial of Payn (1991) in spite of the improvements in needle Mg concentrations. However, a response within six months in the trial of Payn (1991) was unlikely given that Hunter *et al.* (1986) only started to record increased growth responses to fertilisation after two years. Had this trial been run over a longer period, growth responses may have been recorded.

Payn *et al.* (1995) investigated whether different levels of Mg supply affected root biomass and dry matter allocation patterns between roots and shoots of *P. radiata*. They sampled an eight-year-old stand of *P. radiata*, which had been fertilised with dolomite fertiliser at the rate of 400 kg Mg ha^{-1}, three years after planting. At the time of fertiliser application, needle concentrations were at a deficient level of 0.069%. Needle Mg concentrations of the fertilised trees had increased to adequate concentrations of 0.150% five years after fertiliser application. However, in spite of the improvements in needle concentrations there were no significant differences in height (4.78 m in control trees and 4.82 m in the fertilised trees) or basal area (51.4 m^2 ha^{-1} in control trees and 52.2 m^2 ha^{-1} in the fertilised trees) between the fertilised trees and no-fertiliser control trees.

2.4 MAGNESIUM IN FOREST SOILS OF NEW ZEALAND

Soils generally contain between 0.1 and 1% Mg, but not all of this Mg is in a plant available form. Magnesium is found in three forms in the soil, very slowly available mineral and organic Mg; readily available soil exchangeable Mg and immediately available solution Mg (Lindsay 1979; Barber 1984; McLaren and Cameron 1990).

The estimated Mg supplying power of a range of New Zealand soils is shown in Table 2.2. From this table it can be seen that the parts of New Zealand where Mg deficiency occur most strongly in *P. radiata* are likely to be those areas where the Mg supplying power of the soil is low to very low.

2.4.1 Non-exchangeable Mg

2.4.1.1 Mineral Mg

Most of the Mg found in soils is in the mineral, non-exchangeable form (> 90%) (McLaren and Cameron 1990). The principal Mg-bearing primary minerals in the parent materials of New Zealand soils belong to the ferromagnesian group of minerals and the micas. The ferromagnesian group includes the primary silicate minerals, olivine, pyroxene, and amphibole. The main Mg bearing minerals in the mica group is muscovite and biotite (Metson 1968; Metson 1974).

Magnesium can also be found in high concentrations in the secondary minerals, carbonates and silicates. The secondary silicate minerals are mainly hydrous derivatives of primary mineral silicates such as olivine and hornblende (part of the amphibole family). These include chlorites, vermiculite and serpentine. The carbonate minerals include dolomite ($CaMg(CO_3)_2$) and magnesite ($MgCO_3$). The importance of carbonates as suppliers of soil Mg is mainly through their use as fertiliser, although they are also soil forming parent material in some places in New Zealand (Metson 1974). Magnesium also occurs as a lattice constituent of 2:1 secondary clay minerals such as vermiculite, montmorillonite and illite (Metson 1968; McLaren and Cameron 1993).

Table 2.2 Distribution of exchangeable magnesium and 'reserve' magnesium (means) for the topsoil (0 to 15-20 cm soil depth) of some major New Zealand Soil Orders (adapted from Metson and Brooks 1975)

Soil Order[A]	Location[A]	Exchangeable Mg[B] (Mg_e)	Reserve Mg[C] (Mg_r)
Brown Soils	Throughout New Zealand	Low-medium Mg	Medium-high Mg
Granular Soils	Northern North Island, South Auckland, Waikato	Medium Mg	Low Mg
Oxidic Soils	Auckland and Northland	Medium Mg	Very low Mg
Pallic Soils	Eastern North and South Islands, Manawatu	Medium Mg	Medium-high Mg
Podzols	Northland, North and South Island high country, West Coast of South Island	Low Mg	Low Mg
Pumice Soils	Central North Island	Low Mg	Very low-low Mg
Semiarid Soils	Otago, South Canterbury	Medium Mg	Medium-high Mg
Ultic soils	Northern North Island, Wellington, Malborough, Nelson	Low-medium Mg	Low Mg

[A] Hewitt (1993); [B] Exchangeable Mg determined by extraction with 1*M* ammonium acetate, pH 7.0; [C] Reserve Mg determined by boiling 1*M* HCl extraction

Rating	Range ($cmol_{(+)}kg^{-1}$)	
	Mg_e	Mg_r
Very high	> 7	> 30
High	3-7	15-30
Medium	1-3	7-15
Low	0.5-1	3-7
Very low	< 0.5	< 3

The Mg concentrations and formulas of selected examples of the main Mg containing soil minerals are presented in Table 2.3. From the values presented in this table it can be seen that the Mg content of a soil is strongly influenced by the amount and type of the minerals in the parent material. For example, some Brown Soils (Mafic Brown Soils) of Southland are formed from parent material containing Mg-rich serpentine so these soils have very high reserves of Mg (Molloy 1988). The Semiarid Soils of central Otago and southern Canterbury contain predominantly mica and illite clay minerals so these soils were also found to have medium to high reserves of Mg. (Metson and Brooks 1975; Hewitt 1993). In addition, the release of exchangeable and solution Mg occurs mainly from these secondary clay minerals of soil (Metson 1974). Therefore, the amounts and species of clay mineral contained within a soil provides a guide as to the potential of a soil, by weathering, to replenish exchangeable or plant available fraction. For example, Pumice Soils formed from rhyolitic ash and pumice parent material, contain very little clay, and this clay fraction contains mainly allophane. Allophane has a very low Mg content. The low Mg content of the rhyolitic ash and pumice parent material is the main reason for the low plant available Mg contents of Pumice Soils and for the wide spread incidence of Mg deficiency in forests of the central North Island.

2.4.1.2 Magnesium in soil organic matter

The amount of organic matter in soils is highly variable. However, most mineral topsoils in New Zealand have organic matter levels ranging from about 3 to 20% (McLaren and Cameron 1990). Due to the variability in organic matter contents in topsoils, the Mg content is also likely to be highly variable. In Pumice Soils under *P. radiata* the organic matter content of topsoils (Ah horizon) could be as much as 34% (McLaren and Cameron 1990). Hunter *et al.* (1986) found 8.38 kg Mg ha^{-1} (0.13% Mg) in the forest floor litter layer (L, F, and H horizons) of a healthy 11-year-old *P. radiata* stand on Pumice Soil at southern Kaingaroa Forest. Will *et al.* (1983), reported the Mg concentration of 14-year-old *P. radiata* needle litter-fall was 0.07%. Therefore, the organic matter pool of Mg could be a significant source of Mg available to the tree.

Table 2.3 Selected examples of the main magnesium-containing soil minerals

Mineral	Formula	Mg concentration (%)
Amphibole[A]	$Ca_2Al_2Mg_2Fe_3Si_6O_{22}(OH)_2$	3-25
Biotite[A]	$K_2Al_2Si_6(Mg,Fe)_6O_{20}(OH)_4$	0.3-28
Chlorite[B]	$Al_2Mg_5Si_3O_{10}(OH)_8$	up to 23
Dolomite[C]	$CaCO_3.MgCO_3$	10
Illite[B]	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	2
Montmorillonite[B]	$Al_5MgSi_{12}O_{30}(OH)_6$	up to 6
Olivine[C]	$Mg_{1.6}Fe_{0.4}SiO_4$	28
Serpentine[C]	$Mg_6Si_4O_{10}(OH)_8$	21
Vermiculite[B]	$Mg_3Si_4O_{10}(OH)_2.2H_20$	12-17

[A] Katzensteiner and Glatzel 1997; [B] Barber 1984; [C] Metson 1974

2.4.2 Exchangeable Mg

Exchangeable Mg is usually regarded as the fraction that is available for uptake by trees and represents about 5% of the total Mg in New Zealand soils (McLaren and Cameron 1990). In fact tree roots absorb Mg from the immediately available solution Mg fraction, but as this is replenished rapidly from Mg on the exchange complex, so ultimately exchangeable Mg will become plant available (Barber 1984).

Magnesium deficiency in *P. radiata* occurs most strongly where exchangeable Mg concentrations are low. This has been demonstrated by Will (1966), Hunter *et al.* (1986), Payn (1991) and Hunter (1996). The main area where Mg deficiency in *P. radiata* occurs most strongly and is most widely studied, is in the Pumice Soils of the central North Island which have low to very low levels of soil exchangeable Mg (Table 2.2). The other areas where Mg deficiency symptoms in *P. radiata* have been widely reported i.e. the Podzols of Westland and the Brown, and the Ultic soils of Otago, Southland and Nelson (Hunter *et al.* 1991; Maclaren 1993; McLaren and Cameron

1990) are also areas where exchangeable Mg concentrations are low (Table 2.2) (Metson and Gibson 1977).

Given that Mg deficiency in *P. radiata* seems to occur most strongly where soil exchangeable Mg concentrations are low, a strong correlation between soil exchangeable Mg concentrations and foliage Mg concentrations might be expected. However, in several studies no correlation was found between the severity of Mg deficiency symptoms in *P. radiata* and soil exchangeable Mg concentrations (Adams 1973; Ballard *et al.* 1971; Hunter *et al.* 1991). The reason for the absence of any correlation are that soil exchangeable Mg may not be a good measure of tree available Mg or the soil and foliar Mg concentrations in the studies might not have been widely different or other reasons related to soils and foliage sampling.

2.4.3 Measurement of exchangeable and non-exchangeable Mg

2.4.3.1 Non-exchangeable Mg

Measurement of non-exchangeable Mg usually involves extraction of the soil with boiling 1 *M* HCl (Metson 1968). Termed acid-extractable or 'reserve' Mg, this measure of soil Mg has been used as a means of estimating non-exchangeable, or long-term, potentially available Mg (Metson 1974; Metson and Gibson 1977). It should be noted that this method extracts part of the mineral fraction and the entire exchangeable (and solution) fraction. Metson and Brooks (1975) showed that after extraction with boiling 1*M* HCl, little additional Mg was released from the soil during repeated extractions using the same reagent. Therefore, they considered that the Mg not extracted by this method would be unlikely to contribute significantly to the pool of potentially plant available Mg. To determine reserve Mg the amount of exchangeable Mg in the soil should be subtracted from the Mg extracted by the acid.

Acid-extractable soil Mg concentrations were reported in three studies involving soils under *P. radiata.* Adams (1973) reported a significant correlation between needle concentrations of Mg in a stand of four-year-old *P. radiata*, which showed Mg deficiency symptoms of varying severity, and boiling 1*M* HCl-extractable Mg

concentrations in 0-15 cm soil layers of Ahaura stony fine sandy loam from the Inangahua Depression, South Island. The value for acid-extractable Mg corresponding to the critical needle concentration of 0.06-0.08% (Will 1966) was between 4.2 and 5.0 $cmol_{(+)}kg^{-1}$ (Adams 1973).

Hunter *et al.* (1986) measured the boiling 1*M* HCl-extractable Mg concentration of a Pumice Soil (0-60 cm depth) from an 11-year-old stand of *P. radiata* showing severe Mg deficiency symptoms, to determine the quantity of the potentially plant available pool of Mg in the soil. Based on estimated annual Mg requirements of the trees of 2 kg Mg ha^{-1}, Hunter *et al.* (1986) concluded that the 199 kg Mg ha^{-1} acid-extractable Mg in the top 60 cm soil depth over predicted the Mg available to the trees. Hunter (1996), also reported boiling 1 M HCl-extractable Mg for two Pumice Soils (0-10 cm soil depth) from 10-year-old stands of *P. radiata* at southern Kaingaroa Forest and Tauhara Forest (north-east of Taupo). Acid soluble Mg in the southern Kaingaroa soil was 0.52 $cmol_{(+)}kg^{-1}$ and 0.36 $cmol_{(+)}kg^{-1}$ in the Tauhara soil. The lower value in the Tauhara stand was because the Tauhara stand is an ex-pasture site. Ex-pasture sites generally have depleted reserves of soil Mg (Beets *et al.* 1993).

The values reported by Hunter (1996) are considerably lower than those reported by Adams (1973). This is due to differences in the soil groups in the respective study areas. The soil in the study area of Adams is a member of the Brown order of soils which have medium to high (7-30 $cmol_{(+)}kg^{-1}$) levels of 'reserve' Mg, whereas Pumice Soils have very low to low (< 3-7 $cmol_{(+)}kg^{-1}$) 'reserve' Mg levels (Table 2.2) (Metson and Brooks 1975).

2.4.3.2 Exchangeable Mg

Exchangeable Mg, as for other cations, is the soil fraction extracted by treating the soil with salt solutions. This extraction also includes any Mg present in a water-soluble form, although the concentration of this form of Mg is much lower than that of exchangeable Mg. Probably the most common and widely reported method used in New Zealand for the determination of exchangeable Mg is leaching soils with neutral 1 *M* ammonium acetate (NH_4OAc, pH 7) (Metson 1974).

Metson and Brooks (1975) reported exchangeable Mg concentrations determined by the neutral 1 *M* NH_4OAc method in their survey of different New Zealand soil groups. Their results showed that Pumice Soils are generally low in exchangeable Mg compared to other soils. Values for soil exchangeable Mg concentrations determined by the neutral 1 *M* NH_4OAc method for unfertilised Pumice Soil under *P. radiata* have also been widely reported (Table 2.4). The values for exchangeable Mg reported in Table 2.4 fall in the very low to low rating (< 0.5 to 0.5-1.0 $cmol_{(+)}kg^{-1}$) of Metson and Brooks (1975).

Therefore, it is not surprising that Mg deficiency is a major problem in many of the forests on Pumice Soils in the central North Island.

2.4.4 Fertiliser Mg

There is a range of Mg fertilisers currently available for use by foresters. The major ones are presented in Table 2.5, along with their Mg contents and chemical formulae. Magnesium fertiliser, although not routinely applied to New Zealand's plantation forests, has been used in a number of trials to investigate its effectiveness in correcting Mg deficiency in *P. radiata*. The primary objectives of most of these trials were to test the effectiveness of dolomite and Epsom salts at improving the Mg nutrition of the trees and this was discussed in Section 2.3.3.4 (Will 1961; Hunter et al. 1986; Payn 1995; Hunter 1996).

However, in most of these trials the effect of Mg fertiliser application on soil Mg concentration has been reported. Will (1961) reported that dolomite application at rates equivalent to 190 kg Mg ha^{-1} and 2500 kg Mg ha^{-1} to a Pumice Soil at Kaingaroa nursery resulted in considerable increases in soil exchangeable Mg concentrations within nine months of application. Dolomite application at 190 kg Mg ha^{-1} increased exchangeable Mg to 0.35 $cmol_{(+)}kg^{-1}$ and at 2500 kg Mg ha^{-1} to 1.50 $cmol_{(+)}kg^{-1}$, whereas the untreated soils had exchangeable Mg concentrations of 0.1 $cmol_{(+)}kg^{-1}$. Hunter *et al.* (1986) studied the effect on Bray-2 (acidified ammonium fluoride) extractable Mg in the top 60 cm of soil, five years after the application of a mixture of

Table 2.4 Exchangeable Mg concentrations in unfertilised Pumice Soils under *P. radiata*

Site	Soil depth (cm)	Tree age (years)	Exch. Mg ($cmol_{(+)}kg^{-1}$)	Reference
Northern Kaingaroa Forest	0-5	7	0.32	Ballard 1978
Northern Kaingaroa Forest	0-30	25	0.32	Hunter *et al.* 1992
Southern Kaingaroa Forest				
Dry Fly	0-10	11	0.10	Hunter 1996
Waimihia	0-10	10	0.43	Hunter 1996
Tauhara Forest	0-10	10	0.28	Hunter 1996
Mangakino	0-20	4	0.70	Jurgensen *et al.* 1986
Mangakino	0-20	8	0.80	Jurgensen *et al.* 1986
Mangakino	0-20	17	0.40	Jurgensen *et al.* 1986
Tauhara Forest	0-5	12	0.61	Payn 1991
Kaingaroa Nursery	-	1-2	0.10	Will 1961

dolomite and Epsom salts at a rate equivalent to 100 kg Mg ha^{-1}. They found that the fertilised plots had 33 kg Mg ha^{-1} more than the Mg extracted in the unfertilised control soils (62 kg Mg ha^{-1}).

In a trial where dolomite, Epsom salts, fine calcined magnesite (calmag) and serpentine were applied to 10-year-old *P. radiata* on a Pumice Soil at 55 kg Mg ha^{-1} Hunter (1996),

Table 2.5 Selected magnesium fertilisers

Fertiliser	Chemical formula	Total Mg (%)	Solubility[A,C] (% of total Mg)			
			Water	2% Citric acid	1 *M* NH_4NO_3	0.5 *M* $BaCl_2$-TEA pH 8.2
Calcined magnesite (calmag)[A]	MgO	51	0.3	52.5	26.8	15.7
Magnesium hydroxide[B]	$Mg(OH)_2$	33	n.a.	n.a.	n.a.	n.a.
Granulated calmag 20% acidulation[A] (granmag,)	$MgSO_4.MgO$	34	4.5	54.4	32.9	7.9
Fused magnesium phosphate (FMP)[A]	[D]	10	0.1	75	2.0	0.2
Dolomite[A]	$CaCO_3.MgCO_3$	11	1.0	13.6	0.9	0.9
Kieserite[B]	$MgSO_4.H_2O$	16	n.a.	n.a.	27	n.a.
Epsom salts[A]	$MgSO_4.7H_2O$	10	100	100	99	100

[A] Loganathan *et al.* (1999); [B] Hagstrom (1992); [C] Heming and Hollis (1995) [D] Various Mg minerals can be used in the manufacturing process to give a mixture of many minerals with differing formulae (Ando 1987); n.a. not available

found that five years after application, only dolomite and calmag had resulted in significant increases in exchangeable Mg in the 0-10 cm soil layer. The lack of any significant increases in soil exchangeable Mg due to the Epsom salts was probably because of greater uptake of Mg, as needle Mg concentrations in the trees tended to be higher for the Epsom salts treatment in the first two years following application. Greater leaching losses of Mg for the Epsom salts treatment were also possible due to the high solubility of the fertiliser and application of the mobile SO_4^{2-} ion. The lack of any increase in exchangeable Mg in the serpentine treatment reflects the low solubility of the serpentine (Lindsay 1979).

The above studies show that soil exchangeable Mg concentrations can generally be improved by the application of Mg fertilisers, but raise some doubts about the long-term effectiveness of some Mg fertilisers like Epsom salts and serpentine.

2.4.4.1 Dissolution of Mg fertilisers

The effectiveness of slowly soluble Mg fertilisers in supplying Mg to trees depends largely on their rate of dissolution in soils. Heming and Hollis (1995) studied the rate of dissolution of Mg from kieserite (1-3 mm granules), calcined magnesite (1-3 mm granules), fine calcined magnesite (< 1 mm) and dolomitic limestone powder (< 1.5 mm) in five soils of differing soil pH from the south of England. The kieserite and calcined magnesite were applied to the soil at 33 mg Mg kg^{-1} soil and the dolomite at 294 mg Mg kg^{-1} soil and the soil/fertiliser mixes were incubated in the dark at ambient seasonal temperatures (0-25° C.) for up to 25 months. The order of the rate of dissolution after 25 months was kieserite granules > calcined magnesite powder > calcined magnesite granules > dolomite powder. In a similar study, Loganathan *et al.* (1999) determined the dissolution of a range of Mg fertilisers in two Pumice Soils of New Zealand. The fertilisers, calcined magnesite of four particle size fractions, (< 0.25, 0.25-0.50, 0.50-1.00, 1.00-2.00 mm), partially acidulated (20%) granulated calcined magnesite (1-2 mm), partially acidulated (40%) granulated calcined magnesite (1-2 mm), dolomite (< 0.25 mm), Epsom salts (< 0.25 mm) and fused magnesium phosphate (0.25-0.50 mm) were mixed with the soils at 2000 μg Mg g^{-1} of soil and incubated at

60% (w/w) moisture content at 20±2° C for 83 days. At the end of 83 days the rate of dissolution in the two soils was in the order Epsom salts = fine calcined magnesite > coarse calcined magnesite, coarse partially acidulated calcined magnesite, fine dolomite > fused magnesium phosphate.

The studies conducted to determine the rate of Mg fertiliser dissolution prior to 1999 were all based on measuring the increases in exchangeable Mg caused by the application of Mg fertiliser (Heming and Hollis 1995). This method would lead to errors when used under field conditions because part of the dissolved Mg would normally be lost from the site of application by plant uptake and leaching. This would then underestimate the rates of dissolution.

A more accurate method of estimating the rate of dissolution of a fertiliser is to determine the amount of undissolved Mg in the fertiliser and subtract it from the amount applied. Loganathan *et al.* (1999) developed a method for determining undissolved fertiliser Mg in soils by a sequential extraction procedure. This method gave nearly a 100% recovery of fertiliser Mg after incubation of fertilisers with two Pumice Soils in closed polythene bags. The details of the incubation study of Loganathan *et al.* (1999) were described earlier in this section. This method needs to be tested under field conditions.

2.5 PLANT AVAILABILITY OF MAGNESIUM

2.5.1 Soil factors affecting Mg availability

2.5.1.1 Supply of Mg to the roots

The rate of absorption of Mg by tree roots depends on the Mg concentration in soil solution and the movement of Mg from the bulk soil to the root surface. Magnesium moves to the root surface by root interception, mass flow and diffusion (Barber 1984). Mass flow is probably the major supply mechanism for Mg to tree roots. However, mass flow and diffusion to the root surface usually occur simultaneously and it is not possible to strictly separate the two processes (Nye and Tinker 1977). The contribution

of mass flow to the supply of Mg to the tree roots depends on factors such as plant age, plant transpiration rate, soil moisture content and concentration of Mg in solution (Barber 1984; Marschner 1995; Jungk 1996). Diffusion occurs as the result of the concentration gradient of Mg between bulk soil and root surface (Barber 1984; Marschner 1995). Soil water content also plays an important part by affecting effective path lengths and cross sectional area available for diffusion (Marschner 1995). Diffusion in non-mycorrhizal roots is also affected by root hair length. The distance of the extent of maximum nutrient depletion in the rhizosphere is similar to the average root hair length (Marschner 1995).

When soil water content is high (at field capacity), plant transpiration rates are high, and there are high concentrations of Mg in solution, mass flow is unrestricted and becomes the major supply mechanism of Mg to the tree roots. As the water content of the soil falls, the rate of nutrient uptake may exceed the supply by mass flow and concentration gradients develop between the root surface and the surrounding soil. Diffusion then becomes the main Mg supply mechanism (Nye and Tinker 1977; Marschner 1995).

Root interception also contributes to Mg supply to the tree. As roots proliferate through the soil they come in contact with available nutrients such as those adsorbed to soil surfaces. Root surfaces may thus intercept nutrients and take them up, rather than the nutrients moving to the root for absorption (Barber 1984; Marschner 1995). The relative contributions of mass flow, diffusion and root interception to the supply of Mg and K to plant roots have been reported for crops such as maize (Barber 1984). However, no values could be found for *P. radiata* or other forest trees.

2.5.1.2 Effect of soil pH on Mg availability

Soil pH can affect the availability of Mg from soils in a number of ways. In acidic soils, basic cations are usually found only in low concentrations because they have been displaced from the exchange sites by H^+ and Al^{3+} ions and subsequently leached from the soil. The rate of loss of the basic cations by leaching and plant uptake usually exceeds the rate of release from weathering of minerals, so deficiencies often occur in

acid soils (McLaren and Cameron 1990). Most forest soils in New Zealand especially the Pumice Soils of the central North Island tend to be acidic in nature (soil pH(water) in the range of pH4.8 to pH6.0) (Hunter 1996), so this may be a factor affecting the supply of Mg to *P. radiata.*

The Pumice Soils of the central North Island have a significant concentration of variable charge colloids (Leamy *et al.* 1980). Increases in soil pH caused by the application of alkaline fertilisers increase the negative charges on these soil colloids, increasing the effective cation exchange capacity. The application of alkaline Mg fertiliser can increase the soil pH and exchangeable Mg concentration and therefore the availability of Mg in these soils.

Increases in soil pH to pH7 or higher, for example by over-liming, can decrease Mg availability because of $Mg(OH)_2$ precipitation (Tucker 1983).

2.5.1.3 Antagonisms with K, Ca and Al

Potassium, Ca and Al in soils have all been reported to reduce Mg uptake by plants (Metson 1974; Barber 1984; Mengel and Kirkby 1987; Slovik 1997).

Potassium fertiliser application is known to affect the Mg supply to plants in two ways. Potassium competes with Mg for cation exchange sites in the exchange complex, reducing the reserves of exchangeable Mg. There is also competition of Mg uptake with K, as mentioned in Section 2.2.2.1 (Slovik 1997). Sun and Payn (1999) reported that K interfered with Mg nutrition of 26-week old clonal *P. radiata* trees growing in silica sand supplied with nutrient solution containing four Mg concentrations (0.008, 0.04, 0.02 and 0.4 mM) and three concentrations of K (0.25, 0.5 and 2.5 mM) in a factorial designed experiment. At low concentrations of Mg the severity of needle chlorosis and necrosis was enhanced by increasing the K supply, but plant growth and Mg uptake increased. Sun and Payn (1999) did not report the reason for this response, but it might be because increasing the supply of K in solution was overcoming a K deficiency. With increasing rate of Mg supply, increasing K supply markedly increased root Mg concentration, but decreased shoot Mg concentration and decreased Mg uptake.

Sun and Payn (1999), concluded that an excess of K can inhibit the mobilisation and translocation of Mg from roots to shoots at high Mg concentrations. They could not explain how K restricted the mobilisation and translocation of Mg from the roots to the shoot but cited a study by Schell (1997) that suggests that malic acid might be involved in influencing the mobilisation of Mg in the sapwood of *Fagus sylvatica* L. by forming a malate-Mg complex. These complexes are then translocated to the shoots. Potassium might play a role either in disrupting the chemical bonding of Mg with malic acid, or limiting the production of the cation-binding chemical compound.

Calcium is usually the dominant ion in the exchange complex of New Zealand soils. An excess of Ca in the exchange complex may also be expected to interfere with the tree uptake of Mg similar to K antagonism. However, reports of Ca/Mg antagonisms have not been as numerous as for K (Metson 1974). There have been concerns expressed in Europe that the uptake of Mg by coniferous trees may be reduced by increased concentrations of Ca in solution resulting from the application of lime to acidic forest soils (Landmann *et al.* 1997). High concentrations of Ca in solution have been reported to restrict the uptake of Mg in other plants like barley (Barber 1984).

Aluminium also reduces the uptake of Mg (Mengel and Kirkby 1987), particularly in acidic soils where Al concentrations in solution are high. High concentrations of Al can be phytotoxic to trees, usually resulting in decreased fine root growth (Mengel and Kirkby 1987). This has obvious implications for the trees' ability to take-up Mg and other nutrients. Aluminium taken up by tree roots is a strong competitor for polyvalent cation (Ca, Mg, Zn and Mn) binding sites in the apoplasm. Cation uptake rates into the symplasm are strongly enhanced by the apoplasmic loading of polyvalent cations. A reduction in the polyvalent cations loading of the apoplast reduces their uptake by the symplasm and cytoplasm (Marschner 1995; Raspe 1997).

Aluminium may also inhibit the uptake of Mg by blocking or competing for binding sites of transport molecules (ionophores, discussed in 2.2.21) located in tree membranes (Marschner 1995).

Aluminium antagonisms with Mg is a concern in declining forests on acidic soils of Europe (Huttl and Frielinghaus 1994). Schaaf (1995) illustrated the effects of Al on Mg uptake. Schaaf, reported that fertilisation of Norway spruce (*Picea abies*) with $Mg(OH)_2$ at 1040 kg Mg ha^{-1} improved needle Mg concentrations (increasing from a deficient 0.05% to adequate 0.11%) only after increasing the exchangeable Mg/Al ratio. The increase in Mg/Al ratio by Mg fertiliser application reduced the potential risk of Al toxicity and created more favourable conditions for fine root growth.

2.5.2 Chemistry of the soil-root interface (rhizosphere)

The rhizosphere has been defined as 'the zone of soil surrounding the root which is affected by it' (Darrah 1993). The chemistry of this zone is usually considerably different from that of the bulk soil and has a greater influence on plant growth (Kuchenbuch and Jungk 1982; Youssef and Chino 1988; Youssef and Chino 1989; Gijsman 1990a; Gijsman 1990b; Hedley *et al.* 1994; Jungk 1996; Zoysa *et al.* 1997; Zoysa *et al.* 1998). The width of the rhizosphere has been shown to extend from a few mm to several cm from the root surface depending on the plant species (Darrah 1993; Bolan *et al* 1997).

As mentioned in section 2.2.2.4, *P. radiata* forms associations with ectomycorrhiza. The ectomycorrhizal hyphae are considered as part of the root system of a tree and therefore they influence the chemical, physical and biological properties of the rhizosphere. However, the limits of the rhizosphere become difficult to define with mycorrhiza (Foster and Marks 1967). Mycorrhiza which form mycelial strands can penetrate the soil for distances up to 3.5 cm from the roots (Skinner and Bowen 1974), effectively extending the distance of soil that could be regarded as rhizosphere.

2.5.2.1 Cation availability in the rhizosphere

The concentration of a particular cation in the rhizosphere soil can be higher, lower or similar to that in the bulk soil. Factors that affect the plant-availability of cations in the rhizosphere include the concentration in the bulk soil solution, and the difference between the rate of movement of the ion to the root surface and the rate of uptake by the

root itself (Marschner 1995). Therefore, if the solution concentration of a cation that moves to the root surface by mass flow is high and transpiration rate is high, but the rate of cation uptake is low then the cation will accumulate in the rhizosphere soil. However, if the rate of cation uptake is higher than the rate of supply to the roots, there will be a depletion of the cation in the rhizosphere soil.

The difference in pH between the bulk and rhizosphere soils can also influence the cation availability in these two zones. For example, if pH is low in the rhizosphere, Al concentrations can be high (Gijsman 1990c). Also roots of *P. radiata* excrete organic acids, which can increase the plant-availability of certain cations from soil organic matter and minerals (Smith 1969; Marschner 1995).

No literature on the rhizosphere cation (Mg, K and Ca) chemistry of *P. radiata* could be found, although a number of studies on the cation chemistry of rhizosphere soils of other plants have been reported. Kuchenbuch and Jungk (1982) reported a general depletion of exchangeable K concentration in the rhizosphere of four-day-old rape (*Brassica napus*) plants growing in Herrenhausen sandy soil. The depletion of K was attributed to the rate of supply of K to the roots by diffusion being lower than the rate of K up-take by the rape. However, in the two soil slices closest to the rhizoplane (up to 0.4 mm from the rhizoplane) there was an increase in exchangeable K. This was attributed to the contribution of K from the root hairs. Root hairs had grown through the 30 μm mesh used to separate the roots from the soil and were included in the chemical analysis of the soil slices. Rygiewicz and Bledsoe (1984) have shown that ectomycorrhiza of Douglas fir (*Pseudotsuga menziesii*), western hemlock (*Tsuga heterophylla*) and Sitka spruce (*Picea sitchensis*) took-up Rubidium-86 (^{86}Rb) (a tracer used for K) and a portion of the ^{86}Rb was concentrated in the hyphae, presumably in the fungal vacuole. Ectomycorrhizal hyphae might produce similar results in the rhizosphere of *P. radiata*.

In a study of acid soluble Mg and Ca concentrations in the rhizosphere of barley (var. dorirumugi), Youssef and Chino (1988) reported an accumulation of both Mg and Ca. The soil used was a clay loam and the experiment was run for five weeks after planting.

The reason for the accumulation of Mg and Ca was not discussed but was probably due to the rate of supply of these cations to the root surface exceeding the rate of uptake.

Supporting the results reported by Kuchenbuch and Jungk (1982) and Youssef and Chino (1988), two studies (Rengel and Robinson 1990; Kelly *et al.* 1992) which modelled the plant uptake of Mg, K and Ca have reported that Mg and Ca accumulated in rhizosphere soils, whereas K was depleted. Rengel and Robinson (1990) modelled the Mg uptake by two annual ryegrass cultivars (Wilo and Gulf) from an acid Fragiaquic Paleudult soil. The soil was limed at three rates (0, 1 and 3 g kg^{-1}) and fertilised with triple superphosphate, muriate of potash and K_2SO_4 at rates corresponding to 40, 170 and 10 mg kg^{-1} of P, K and S, respectively. Rengel and Robinson (1990) reported that due to relatively large mass flow of Mg and Ca compared to plant uptake, accumulations of these cations in solution occurred at the rhizoplane for all the lime and fertiliser treatments. In contrast K was depleted in the rhizosphere because plant uptake exceeded the rate of supply from diffusion. Kelly *et al.* (1992), also predicted that K would be depleted and Mg would accumulate in the rhizosphere of one-year-old loblolly pine (*Pinus taeda* L.) seedlings using the Barber-Cushman (Barber 1984) approach. The reasons for this was similar to that reported by Rengel and Robinson (1990).

A contrast to the above studies that suggest that K will tend to be depleted in the rhizosphere was provided by Wang and Zabowski (1998). They studied the nutrient composition of rhizosphere solutions of one-year-old Douglas fir (*Pseudotsuga menziesii*) in two unfertilised soils. Whether the seedlings were infected with ectomycorrhiza was not reported. One soil was a mesiac Pachic Xerumbrept soil and the other a frigid Typic Haplorth soil. Rhizosphere solution concentrations of Mg, K and Ca in both soils were higher than those in the bulk soil solutions. This was thought to be due to increased weathering of soil minerals in the rhizosphere due to decreases in soil pH, exudation of organic acids by tree roots and greater population of microorganisms in the rhizosphere.

Hylander *et al.* (1999), also recorded increases in exchangeable K in the soil layers close to the rhizoplane of cotton and soybean. Whereas, Wang and Zabowski (1998)

attributed the increase in rhizosphere solution K to increased weathering of minerals in the rhizosphere of Douglas fir, Hylander *et al.* (1999) attributed the accumulation of exchangeable K to the excess supply of K by mass flow compared to plant uptake. This was confirmed by calculation of plant uptake and the mass flux of K across a unit area normal to the direction of flow using the equation of Jury *et al.* (1991). Calculated rates of supply of K by diffusion alone, could not account for the accumulation of K in the rhizosphere soil of cotton and soybean. They explained this as due to cotton and soybean plants not being able to take-up all the K supplied to the roots, because of their poor growth. However, the poor growth of the cotton and soybean plants is likely to reduce mass flow because it is linked with transpiration (which would be low in poorly growing plants). It is possible that evaporation from the rhizobox compartment that contained the plants is also contributing to mass flow of K, but the authors did not consider this in their discussion. Hylander *et al.* (1999) also studied exchangeable K concentrations in the rhizosphere of rice and maize. In contrast to their findings for cotton and soybean, exchangeable K was depleted in the rhizosphere of rice and maize. They explained this as due to faster rates of growth of rice and maize, than cotton and soybean.

Based on the above studies it appears that cation concentrations in the rhizosphere vary according to the type of plant, rate of movement to the root (whether supply is by diffusion or mass flow) and soil type. In Pumice Soils where the Mg levels are low, depletion of Mg could occur in the rhizosphere of *P. radiata* when the rate of supply of Mg to the roots is restricted by low soil water content during the drier summer months. This could help to explain why Mg deficiency symptoms are more severe during drought periods and re-greening occurs when the soil moisture content increases after rain. However, in areas where soil Mg levels, soil moisture and transpiration rates are high, Mg may accumulate in the rhizosphere. The behaviour of cations in the rhizosphere of *P. radiata* however, is yet to be determined. The ectomycorrhiza associated with *P. radiata* may also influence this behaviour.

2.5.2.2 Rhizosphere acidification

The rhizosphere pH may differ from the bulk soil pH by as much as two units, depending on plant and soil factors (Marschner 1995). One of the main factors involved in root-induced changes in rhizosphere pH is an imbalance in the ratio of cations to anions taken up by the tree (Marschner 1995). If the trees take up an excess of cations over anions, roots generally excrete H^+ ions causing a decrease in rhizosphere pH. If the trees take up an excess of anions over cations, roots generally excrete OH^- or HCO_3^- causing an increase in rhizosphere pH. The excretion of H^+ or OH^- is stoichiometrically equal to the respective excess cation or anion uptake (Nye 1981; Troelstra 1983; Haynes 1990; Gijsman 1990a, b).

As N is the main nutrient taken-up by plants, the ionic form of N that is taken up largely determines the cation-anion balance and hence rhizosphere pH (Bledsoe and Zasoski 1983; Youseff and Chino 1989; Gijsman 1990 b, c; Zoysa *et al.* 1998). Nitrogen is taken up by trees in three forms - as a cation (NH_4^+), as an anion (NO_3^-) and in leguminous trees a neutral form (N_2 fixation). Ammonium uptake is correlated with a higher rate of H^+ net release and NO_3^- uptake with a higher rate of OH^- or HCO_3^- excretion (Marschner 1995).

Bledsoe and Zasoski (1983) grew ectomycorrhizal-infected Douglas fir (*Pseudotsuga menziesii*) seedlings in peat-vermiculite mix fertilised with either NO_3^- or NH_4^+ and found that the N source significantly affected the rhizosphere pH compared to the bulk soil. When NH_4^+ was used, the rhizosphere pH decreased and when NO_3^- was used the rhizosphere pH increased. Similarly, Gijsman (1990 b, c) grew three-year-old Douglas-fir (*Pseudotsuga menziesii*) trees in a strongly acid (pH(water) 3.87) soil fertilised with NO_3^-, NH_4^+ or a combination of both. As Bledsoe and Zasoski (1983) found, changes in rhizosphere pH were strongly related to the form of N applied to the soil - NH_4^+ application decreased rhizosphere pH and NO_3^- application increased rhizosphere pH. In addition, when NO_3^- and NH_4^+ were applied in equal proportions, rhizosphere pH increased. The reason for the increase to rhizosphere pH when both NO_3^- and NH_4^+ were applied was not explained by Gijsman (1990 b, c) but it could have been due to a greater proportion of N being taken-up as NO_3^- than NH_4^+. Total N concentration in the

trees, as affected by the different sources of N, suggested that Douglas-fir preferentially took-up a greater proportion of N as NO_3^- than NH_4^+ (Gijsman 1990a), resulting in a net efflux of OH^- (or HCO_3^-) into the rhizosphere.

Studies by Adams and Attiwell (1982) and Olykan and Adams (1995) have shown that when *P. radiata* seedlings were grown in solution with either NO_3^- or NH_4^+ as a N source, the seedlings supplied with NH_4^+ had greater concentrations of N in shoots and roots compared to seedlings fertilised with NO_3^-. Olykan and Adams (1995) also reported that the seedlings growing in NH_4^+-fertilised solution were taller and had heavier roots and shoots than NO_3^--fed seedlings. However, Adams and Attiwell (1982) reported no significant differences in seedling growth between NO_3^- and NH_4^+ fed seedlings despite the differences in plant N concentrations. These results indicate that *P. radiata* preferentially absorbs NH_4^+ compared to NO_3^-.

The excretion of organic acids by roots is also a major contributor to root-induced changes in the rhizosphere soil pH (Marschner 1995). *Pinus radiata* seedlings have been shown to excrete considerable amounts of acetic acid and oxalic acid (Smith 1969). This should cause a decrease in rhizosphere pH.

2.5.3 Losses of plant available Mg

Magnesium can be lost from the soil by leaching in soil water moving below the root zone and by crop removal. Magnesium can also be lost by surface runoff removing litter and topsoil. For example, Parfitt *et al.* (1996) measured 0.42 mmol l^{-1} of Mg in the surface runoff during a rainfall event in October 1995 from an unfertilised 20-year-old stand of *P. radiata* growing in the Manawatu.

2.5.3.1 Leaching of Mg from forest soils

Average leaching losses of Mg from New Zealand pasture soils range between 5 to 17 kg Mg ha^{-1} yr^{-1} depending on rainfall, soil properties such as texture and structure, fertiliser application and soil pH (During 1984; McLaren and Cameron 1990). Parfitt *et*

al. (1997) measured the leaching losses of Mg below 20 cm under an unfertilised 20-year-old stand of *P. radiata* on a Typic Orthic Brown Soil in the Manawatu. Mean annual rainfall at the site was 1291 mm. They estimated losses of Mg were 14.7 kg Mg ha^{-1} yr^{-1} based on concentrations of Mg in soil solution collected by lysimeters and an estimate of the amount of water draining through the soil profile. Payn (1991) reported greater losses of 17.3 kg Mg ha^{-1} below 20 cm over a one year period from an unfertilised stand of three-year-old *P. radiata* in a Pumice Soil near Taupo, with an annual rainfall of about 1290 mm. Greater losses of Mg could be expected from a young stand, as there would be greater through fall of rain in a young stand. A closed canopy of P. radiata can retain about 15% of annual rainfall, which is evaporated directly from the canopy and therefore does not contribute to soil water (Whitehead and Kelliher 1991 a, b).

Fertiliser application can dramatically increase the amount of Mg lost due to leaching. Payn (1991) reported that estimated losses below 20 cm increased to 336.6 kg Mg ha^{-1} during the year following the application of highly soluble Epsom salts fertiliser at 400 kg Mg ha^{-1} to the same stand described in the preceding paragraph. Other studies have also reported increased leaching losses of Mg after the application of Mg fertilisers. Derome and Saarsalmi (1999) reported much smaller leaching losses below 20 cm soil depth of 11.9 and 4.0 kg Mg ha^{-1} over a four year period after application of dolomite fertiliser at 100 kg Mg ha^{-1} to two stands Scots pine (Pinus sylvestris), with an average annual rainfall of 439 mm, growing in an Orthic Podzol Soil at Harjavalta, SW Finland. The corresponding losses for the unfertilised control stands were 2.9 and 0.8 kg Mg ha^{-1}. The large differences in the effect of Mg fertiliser on Mg leaching between the studies of Derome and Saarsalmi (1999) and Payn (1991) reflect differences in the fertilisers used, the amount applied, soil type, and rainfall. There were also differences in the way leaching losses were estimated by Payn (1991) and Derome and Saarsalmi (1999). This is discussed in the next section.

2.5.3.2 Estimating leaching losses of Mg

Losses of Mg from a forest soil can be estimated in a number of ways. Two methods of estimation used in the studies described in the last section are presented here. Payn

(1991) used a basic nutrient balance to estimate losses of Mg from a Pumice Soil. In this method he determined the difference in the amount of exchangeable Mg in soil samples taken one year apart (in March 1990 and March 1991) and adjusted the values to account for uptake of Mg by the trees he assumed the balance to be the amount of Mg lost by leaching. This method at best only provides a very broad estimation of leaching loss as factors other than tree uptake, and leaching losses, for example release of H^+ and other cations into solution by decomposing organic matter, can influence changes in exchangeable Mg between two years of sampling.

The studies of Parfitt *et al.* (1997), and Derome and Saarsalmi (1999) estimated the leaching losses of Mg by measuring the concentration of Mg in solution moving below the depth of interest and multiplying it by the estimated amount of soil water draining through the profile. Parfitt *et al.* (1997) estimated the drainage using a water budget for the depth of soil of interest based on daily rainfall inputs, allowing for 26% interception by the canopy and potential evapotranspiration calculated from meteorological data. Derome and Saarsalmi (1999) did not explain how the drainage was estimated in their study. To estimate the amount of water draining through a profile more accurately requires values for rainfall, transpiration from the dry tree canopy, evaporation of rainfall retained by the canopy, evapotranspiration from the understorey and the plant available soil water holding capacity (Whitehead and Kelliher 1991a and b). This can involve some complex measurements and calculations. In addition drainage should be calculated on a daily basis so the above-mentioned parameters used in the calculations should, ideally, be measured or determined daily.

Concentrations of Mg in solution are determined from solutions periodically sampled usually by soil solution samplers, commonly called lysimeters. Lysimeters can take on many different forms and a number of papers have been published which reviewed the different types available (Barbarick et al. 1979; Silkworth and Grigal 1981; Rasmussen *et al.* 1986; Debyle *et al.* 1988; Grossmann and Udluft 1991). As with drainage, to increase the accuracy of leaching loss estimations, Mg concentrations in solution should also be measured daily, but this is not usually possible or practical.

2.5.3.3 Magnesium removal in harvested crop

Logging of a mature stand of *P. radiata* growing in a Pumice Soil was found to remove approximately 65 kg Mg ha^{-1} in stemwood and bark (Webber and Madgwick 1983). Therefore, logging of *P. radiata* from Pumice Soils already low in Mg further depletes soil reserves. Parts of Kaingaroa Forest are currently into their third rotation of *P. radiata*, so Mg deficiency is likely to be an ongoing concern for foresters. By way of a contrast, Feger (1997) calculated the Mg removed in harvesting a crop of 130-year-old Norway spruce (*Picea abies*) from the Black Forest, Germany at 52 kg Mg ha^{-1} (for stemwood and bark), which is similar to the value reported for *P. radiata*. However, the potential for depletion of soil Mg reserves, due to crop removal, is greater in New Zealand compared to Europe because of the shorter rotation times. There could be as many as four rotations in New Zealand (30-year rotation for *P. radiata*) compared to one rotation in Europe inferred from the report of a 130-year rotation for Norway spruce (Feger 1997).

2.6 SUMMARY AND RESEARCH NEEDS

Previous studies on the Mg nutrition of *P. radiata* were largely carried out to test whether Mg fertiliser application can correct Mg deficiency and whether growth (increased biomass and height) rates could be increased. Most trials showed that needle Mg concentrations in young *P. radiata* (less than 12-years-old) could be increased. However, it took several years before significant increases in Mg concentrations were recorded, in spite of soluble Mg fertiliser being applied. In these studies the soil Mg status was generally increased by fertiliser application but the changes in the overall soil chemistry were only briefly described. Therefore, it was not possible to determine whether the slow response to Mg fertiliser by the trees was due to changes in soil chemistry. In recent years, Forest Research (Institute Ltd), have initiated a series of trials testing whether calcined magnesite application, a fertiliser not generally used in the past, could reduce or prevent the incidence of Mg deficiency and UMCY. These studies to date, have only provided limited information on the degree to which the plant available soil Mg pool has been increased by fertiliser application.

To date, most of the trials testing the Mg fertiliser responses of *P. radiata* have tended to concentrate on the performance of dolomite and Epsom salts fertilisers. These trials have generally reported only slow responses to fertiliser application. In the case of dolomite it was suggested that a slow rate of dissolution could be limiting the uptake of Mg by the trees. However, there were no reports of the rates of dissolution of Mg from dolomite in field soils or any of the other Mg fertilisers currently available and whether this could be limiting the Mg uptake by *P. radiata*. More research is required to determine whether the rate of Mg fertiliser dissolution is rapid enough to supply the Mg needs of *P. radiata*. Fertiliser dissolution studies in the past have used laboratory based incubation methods to determine the rate of fertiliser dissolution. The rate of dissolution in these studies were determined by measuring increases in exchangeable Mg in soils treated with fertiliser, over exchangeable Mg in no-fertiliser control soils. The results from these studies cannot be used to obtain information on the rate of dissolution in field soils because plant uptake and leaching losses of Mg would result in an underestimation of the rate of dissolution. A method that can accurately determine the rate of Mg fertiliser dissolution based on the amounts of fertiliser remaining in soils instead of dissolved Mg was recently developed. The use of this method should allow the rates of dissolution of Mg fertilisers to be accurately determined under field conditions.

In most studies the Mg status of bulk soils has been used to assess the availability of Mg to trees, and to explain the tree response to fertiliser application-but with little success. The literature shows that generally, the chemistry of the rhizosphere can vary greatly from that of the bulk soil and one needs to consider the chemistry of the rhizosphere soil to explain plant responses to Mg fertiliser. The reported slow response of *P. radiata* to fertiliser application could be due to changes occurring in the rhizosphere which could be adversely affecting the uptake of Mg by the tree. There have been a limited number of studies on the rhizosphere of coniferous trees, but no reported studies on the chemistry of Mg or other cations in the rhizosphere of *P. radiata* could be found. Research is required to determine if changes in the chemistry of the rhizosphere of *P. radiata* could be limiting the uptake of Mg by the trees. *Pinus radiata* roots are known to form associations with ectomycorrhiza, which may affect the availability and uptake

of Mg by the trees. There is however, no information available on the role of ectomycorrhiza in the Mg nutrition of *P. radiata*.

The quickest responses of *P. radiata* to Mg fertiliser application have been from soluble fertilisers. However, concerns have been raised in the literature that the application of soluble Mg fertilisers do not result in long-term improvements to soil Mg pools and could result in large losses of Mg by leaching. A few reported studies have attempted to estimate the losses of Mg due to Mg fertiliser application, but these have tended to estimate the losses based on changes in the pools of soil Mg and the uptake of Mg *by P. radiata*. This may not accurately reflect the actual losses. A better method is to monitor the losses of Mg by collecting the leachate in lysimeters and determining their Mg concentrations. The leachate Mg concentrations along with measurements or estimations of water draining through the soil profile could give a better estimate of the actual losses of Mg. Research is required in this area, particularly in relation to determining the losses of Mg after Mg fertiliser application.

CHAPTER 3

EFFECT OF CALCINED MAGNESITE ON SOIL AND *Pinus radiata* FOLIAGE MAGNESIUM IN TWO PUMICE SOILS OF KAINGAROA FOREST[1]

3.1 INTRODUCTION

The review of literature presented in Chapter 2 shows that magnesium (Mg) deficiency occurs in many of New Zealand's plantation forests and is an issue affecting sustainable productivity of New Zealand's forest estate (Payn 1991). Deficiency symptoms have been observed nationally, but occur most strongly in forests on the Pumice Soils of the central North Island. Pumice Soils cover an area of around 1.5 million ha (Molloy 1988). Approximately 25% of total *P. radiata* plantings are on Pumice Soils (Ministry of Agriculture and Forestry 1998).

The application of magnesium sulfate (Epsom salts) and dolomite Mg fertilisers has been shown to correct severe Mg deficiency symptoms in *P. radiata* with time (Will 1961; Hunter *et al.* 1986). However, Hunter *et al.* 1986 and Hunter (1996) highlighted the slow response of *P. radiata* to fertilisation with magnesium sulphate and dolomite fertilisers. This was attributed to losses of Mg due to leaching and/or a slow rate of release of fertiliser Mg. In recent years other Mg fertilisers such as calcined magnesite have become more readily available and may be more suitable for forestry applications.

Calcined magnesite (calmag, MgO, 52% Mg) is made by calcining magnesite ($MgCO_3$) for the purpose of increasing the Mg content and to produce a hard coarser material more suitable for aerial application with minimum drift (Loganathan *et al.* 1999).

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[1]**Mitchell, A. D., Loganathan, P., Payn, T. W., and Tillman, R. W. 1999. Effect of calcined magnesite on soil and *Pinus radiata* foliage magnesium in pumice soils of New Zealand. *Australian Journal of Soil Research*, 37, 545-560.**

However, there is very little information in the literature on the effectiveness of calmag fertiliser in increasing plant available soil Mg in forestry soils and increasing foliar Mg concentrations. No recently published information is available on the effect of these or other Mg fertilisers on soil properties and fate of the fertilisers in soils.

Currently, research is being conducted by the New Zealand Forest Research Institute (Forest Research) into the effectiveness of different rates of Mg fertiliser applied to forest stands of differing ages. In September 1994, Forest Research installed two field trials (FR190/4 and 190/5) on Pumice Soils in Kaingaroa Forest, the former in compartment 1206 (cpt1206) and the latter in compartment 1079 (cpt1079). The objective of trial FR190/4 was to assess the effectiveness of different rates of calcined magnesite (calmag) fertiliser, added to a *P. radiata* stand while still young, in reducing both the incidence and severity of UMCY in the stand by mid-rotation. The objective of trial FR190/5 was to investigate the effectiveness of different rates of calmag fertiliser, added to a mid-rotation *P. radiata* stand with UMCY, in reducing the incidence and severity of the condition. These two trials form the basis of the study reported in this chapter.

3.2 OBJECTIVES

The objectives of the study reported in this chapter were:

1. To determine the fate of the calmag fertiliser in Pumice Soils.
2. To investigate how effective calmag fertiliser was in increasing Mg concentrations in the pine needles.
3. To investigate how effective calmag fertiliser applied at a rate of 150 kg Mg ha^{-1}, was in increasing extractable soil Mg (exchangeable, solution and reserve Mg) concentrations in Pumice Soils and to determine the best soil Mg index, if any, that could be used to predict foliage Mg concentration.

3.3 MATERIALS AND METHODS

3.3.1 Field trial description

Site and soil details of both trials are presented in Table 3.1 and Figures 3.1a and b. Profile descriptions are presented in appendix 1. Site selection for both experiments was based on UMCY distribution and severity information provided by aerial mapping and site visits of Kaingaroa Forest. The stand at FR190/4 was adjacent to a stand of 19-year-old trees in which 71 % had UMCY symptoms, with a mean UMCY value of 3 (based on a scale of one to eight, where eight is the most severe UMCY). The stand at FR190/5 was adjacent to a 16-year-old stand, which had an UMCY value of 3, with 89 % of the scored trees having UMCY symptoms.

Treatment details of both trials are presented in Table 3.2. Treatment were broadcast applied in September 1994. The Nitrophoska Blue TE treatment was included in both trials to test whether N and P (plus trace elements) were limiting tree growth at these sites. The weed control treatment was included in FR190/4 to determine the effect of weed control on Mg uptake and included chemicals that would kill the majority of vegetative weeds on site. The weed spray mix consisted of Gallant NF (100 g/l haloxyfop[(R) - isomer]; DowElanco) at 9.7 l/ha, Versatil (300 g/l clopyralidamine salt; DowElanco) at 0.6 l/ha and Gardoprim (500 g/l terbuthylazine; Novartis AG) at 30 l/ha.

3.3.2 Soil sampling and analysis

Soil samples were collected in April 1996 at FR190/4 and in June 1996 at FR190/5 at four depths (0-5, 5-10, 10-15 and 15-20 cm) from the plots treated with zero and the highest rate of Mg (150 kg Mg ha^{-1}) applied only as calmag (nitrophoska-treated plots not included in the study) by randomly taking 26, 2 cm-diameter soil cores and combining them to make a bulk sample for each depth and each plot. Any fresh litter (L horizon) was not included in the sampling. However, the 0-5 cm soil samples included the F and H horizons. In FR190/4, samples were collected only from the weed free plots as uptake of Mg by weeds would affect the correlations between soil Mg and tree

Table 3.1 Site and soil descriptions of the field trials

Trial number	FR190/4 Young trees	FR190/5 Mid-rotation trees
Site and soil pedology details		
Location	Cpt1206 Kaingaroa Forest	Cpt1079 Kaingaroa Forest
NZ Soil Classification[A]	Pumice Soil	Pumice Soil
Soil type[B]	Pekepeke sand	Kaingaroa loamy sand
Soil parent material	Kaharoa ash (660 years BP) over Taupo pumice	Rhyolitic flow-tephra from the latter stages of the Taupo eruption (1800 years BP)
US Soil Taxonomy	Typic Udivitrand	Typic Udivitrand
Selected soil chemical properties		
Soil depth	0-10 cm	0-10 cm
pH(water)	4.7	5.6
pH buffering capacity (mmol H^+ kg^{-1} pH^{-1})	42	36
Exch. Mg ($cmol_{(+)}$ kg^{-1})	0.7	0.6
Exch. K ($cmol_{(+)}$ kg^{-1})	0.3	0.5
Exch. Ca ($cmol_{(+)}$ kg^{-1})	3.2	3.4
ECEC[C] ($cmol_{(+)}$ kg^{-1})	6.8	6.0
Forestry details		
Rotation number	3	2
Year of planting	winter 1993	winter 1976
Current stocking rate	834 stem ha^{-1}	260 stem ha^{-1}
Mean annual rainfall (mm)	1562	1562

[A] Hewitt (1993), [B] Rijkse (1988), [C] Exchangeable bases plus exchangeable aluminium, Blakemore *et al.* (1987)

(a)

(b)

Figure 3.1 Kaingaroa Forest sites for (a) FR190/4 trial and (b) FR190/5 trial.

Table 3.2 Details for the field trials

Trial number	FR190/4 Young trees	FR190/5 Mid-rotation trees
Trial commencement	September 1994	September 1994
Treatments	Calmag (2-5 mm chips) at 0, 75 and 150 kg Mg ha^{-1} with and without weed control. Nitrophoska Blue TE (BASF) at 150 kg Mg ha^{-1} (12 kg ha^{-1} supplied by Nitrophoska and 138 kg ha^{-1} supplied by calmag), 120kg N ha^{-1}, and 50 kg P ha^{-1} with weed control	Calmag (2-5 mm chips) at 75 and 150 kg Mg ha^{-1}. Nitrophoska Blue TE (BASF) at 150 kg Mg ha^{-1} (12 kg ha^{-1} supplied by Nitrophoska and 138 kg ha^{-1} supplied by calmag), 120kg N ha^{-1}, and 50 kg P ha^{-1}, and a no-fertiliser control
Number of replicates	3	5
Plot size	30m x 30 m	30m x 30 m
Measurement trees per plot	75	20

Mg concentrations. In FR190/5, four of the five replicates were sampled. A second set of soil samples was collected in June 1997 at FR190/5 and in August 1997 at FR190/4 at three depths (0-5, 5-10 and 10-15 cm) from the same plots sampled in the previous year.

Soil solutions were extracted from a portion (about 300 g) of the field moist soils by centrifugation at 12,000 rpm (17,200 RCF) in a refrigerated centrifuge at 4° C within two days of sample collection. Centrifugation of the field moist soils yielded approximately 20 ml of solution. The pH of the solutions were measured immediately after centrifugation. Concentrations of Mg, K and Ca in the solution were measured by atomic absorption spectrometry (AAS).

The remaining portion of the field-moist soil was air dried and ground to pass through a 2 mm sieve. Soil samples were analysed for pH, exchangeable Mg, K and Ca (extraction with 1*M* NH_4OAc buffered at pH7.0, Blakemore *et al.* 1987), exchange acidity and exchangeable Al (Yuan 1959), and 1*M* HCl extractable Mg (Metson 1968). Concentrations of Mg, K, Ca and Al in the extracts were measured by AAS and exchange acidity by NaOH titration using phenolpthalein indicator. The pH buffering capacity of the control soils was determined by amending 20 g subsamples of soil with a range of 0.2 *M* NaOH and 0.2 *M* HCl plus distilled water and incubating the soil - solute mix for 25 minutes. A further volume of distilled water was then added to give a total solution volume of 50 ml (1:2.5 soil:solution ratio) and the pH of the soil suspension measured. The pH buffering capacity of the soil was calculated from a tangent to the curve generated by plotting pH against the amount of H^+ or OH^- added to the soil. The amount of fertiliser Mg dissolved was determined using the sequential extraction method of Loganathan *et al.* (1999). In this method, soil samples were extracted with 0.25 *M* $BaCl_2$ - 0.2 *M* Triethanolamine (TEA) at pH8.2, to determine dissolved Mg, followed by extraction with 0.5 *M* HCl to determine partially dissolved Mg, and finally with 2 *M* HCl to determine undissolved Mg.

3.3.3 Foliar sampling and analysis

Foliage samples were taken from both trial sites in March of 1996 and 1997. The current season's fully extended needles from secondary branches in the upper third of the crown were randomly sampled from 12 trees per plot and bulked together to give one sample per plot. Samples were oven dried at 70°C and analysed for Mg and K by AAS after digesting in H_2SO_4/H_2O_2 mix (Nicholson 1984).

3.3.4 UMCY scoring FR190/5

UMCY scoring in FR190/5 was carried out in December 1996. The upper third of the crown of measurement trees were visually assessed for UMCY severity from the ground (Beets and Jokela 1994). Description of the UMCY scores and their corresponding numeric values are presented in appendix 2.

3.4 RESULTS AND DISCUSSION

3.4.1 Effect of Mg fertiliser on soil pH and exchangeable cations

Magnesium fertiliser application significantly ($P < 0.05$) increased soil pH at shallow depths in both 1996 and 1997 sampling in the FR190/5 trial. Soil pH was slightly higher on the Mg fertilised plots in 1997 in the FR190/4 trial (Figure 3.2), but there was no change in 1996. The increase in soil pH for the FR190/5 trial reflects the lower pH buffering capacity of this soil compared to the FR190/4 soils (Table 3.1). The increase in soil pH is due to the liming effect of the calmag fertiliser.

$$MgO + H_2O \Rightarrow Mg(OH)_2 \Leftrightarrow MgOH^- + OH^- \Leftrightarrow Mg^{2+} + 2OH^-$$

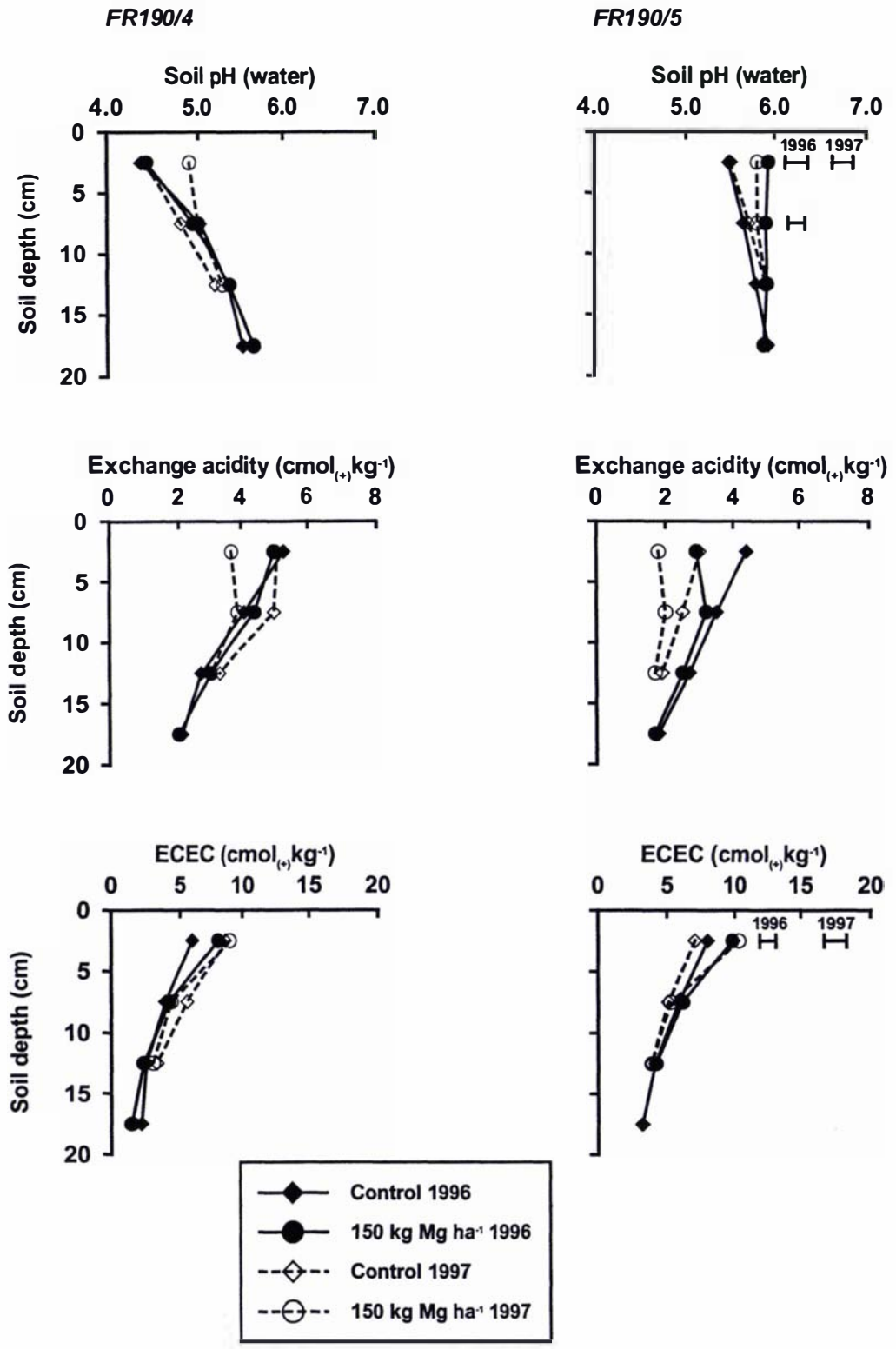

Figure 3.2 Effect of Mg fertiliser application on soil pH, exchange acidity and ECEC for FR190/4 and FR190/5 trials. Horizontal bars represent l.s.d. for treatment means which are significantly different at $P = 0.05$.

As the soil pH increased, the exchange acidity reduced after the application of Mg fertiliser, though this reduction was not statistically significant (Figure 3.2). These soils have significant quantities of variable charge colloids (Leamy *et al.* 1980), and the higher soil pH increased the negative charge on the soil colloids as shown by the increased effective cation exchange capacity (ECEC) (exchangeable bases plus exchangeable aluminium, Blakemore *et al.* 1987). ECEC of the 0-5 cm soil samples increased from 5.9 to 8.0 $cmol_{(+)}kg^{-1}$ with the application of Mg fertiliser at FR190/4 and increased from 8.0 to 9.8 $cmol_{(+)}kg^{-1}$ in the 1996 sampling at FR190/5. Similar increases were recorded in the 1997 sampling (Figure 3.2).

Magnesium fertiliser application significantly ($P < 0.05$) increased exchangeable Mg in the 0-5 cm depth in both trials (about 1.7 $cmol_{(+)}kg^{-1}$ and 3.1 $cmol_{(+)}kg^{-1}$ increase over the control in FR190/4 and FR190/5, respectively) in both years (Figures 3.3 and 3.4). The lower percentage increase in exchangeable Mg in FR190/4 was probably due to the presence of higher exchangeable Al concentrations in this lower pH soil where added Mg displaced lower amounts of exchangeable Al from the exchange sites compared to soils at FR190/5 (Figures 3.3 and 3.4).

Exchangeable Mg is not regarded as a good predictor of foliar Mg concentrations in *P. radiata* (Adams 1973) and critical exchangeable Mg level for optimum growth of *P. radiata* have not been reported in literature, except for Will's (1961) suggestion that the critical level is approximately 0.2 $cmol_{(+)}kg^{-1}$. Exchangeable Mg levels in the control plots of both trials (0-5 cm depth) were well above the critical level suggested by Will (1961). However, the trees in FR190/5 displayed minor UMCY symptoms with scores in the range of 1.9 to 2.5 (relating to yellow needle tips sub-apically). This suggests that either the critical level is higher than Will (1961) suggests, or other factors, such as nutrient antagonisms (e.g. with K and Al), (Metson 1974) and periods of low rainfall are causing UMCY (Mg deficiency) symptoms (Will 1966). Exchangeable Mg values in the surface soils of the Mg-treated plots of both trials would be classed as high, whereas the values in the control plots fall into the low Mg rating based on criteria for a range of New Zealand soils (Metson and Gibson 1977).

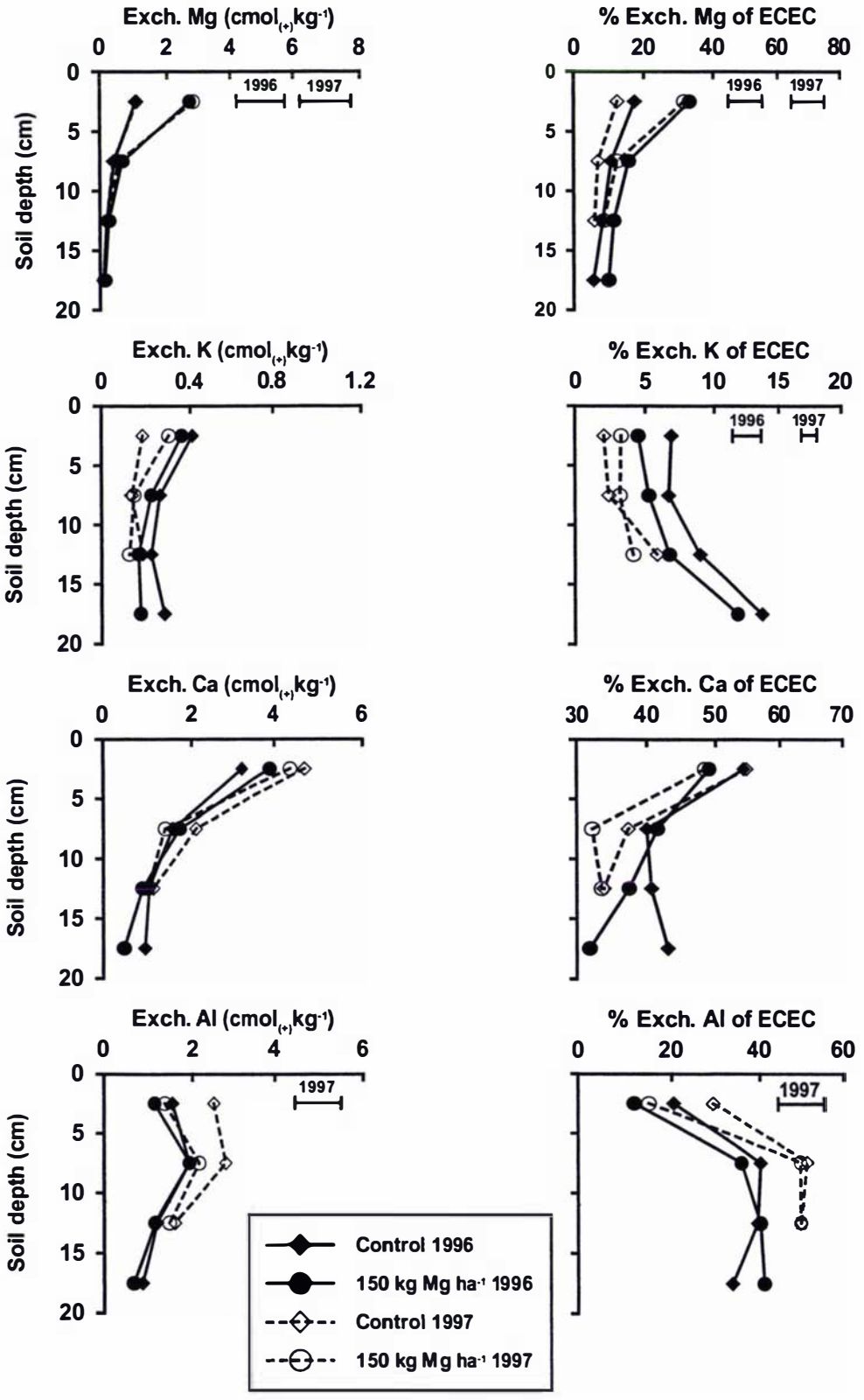

Figure 3.3 Effect of Mg fertiliser application on soil exchangeable cations and cation saturation of ECEC at FR190/4 trial. Horizontal bars represent l.s.d. for treatment means which are significantly different at $P = 0.05$.

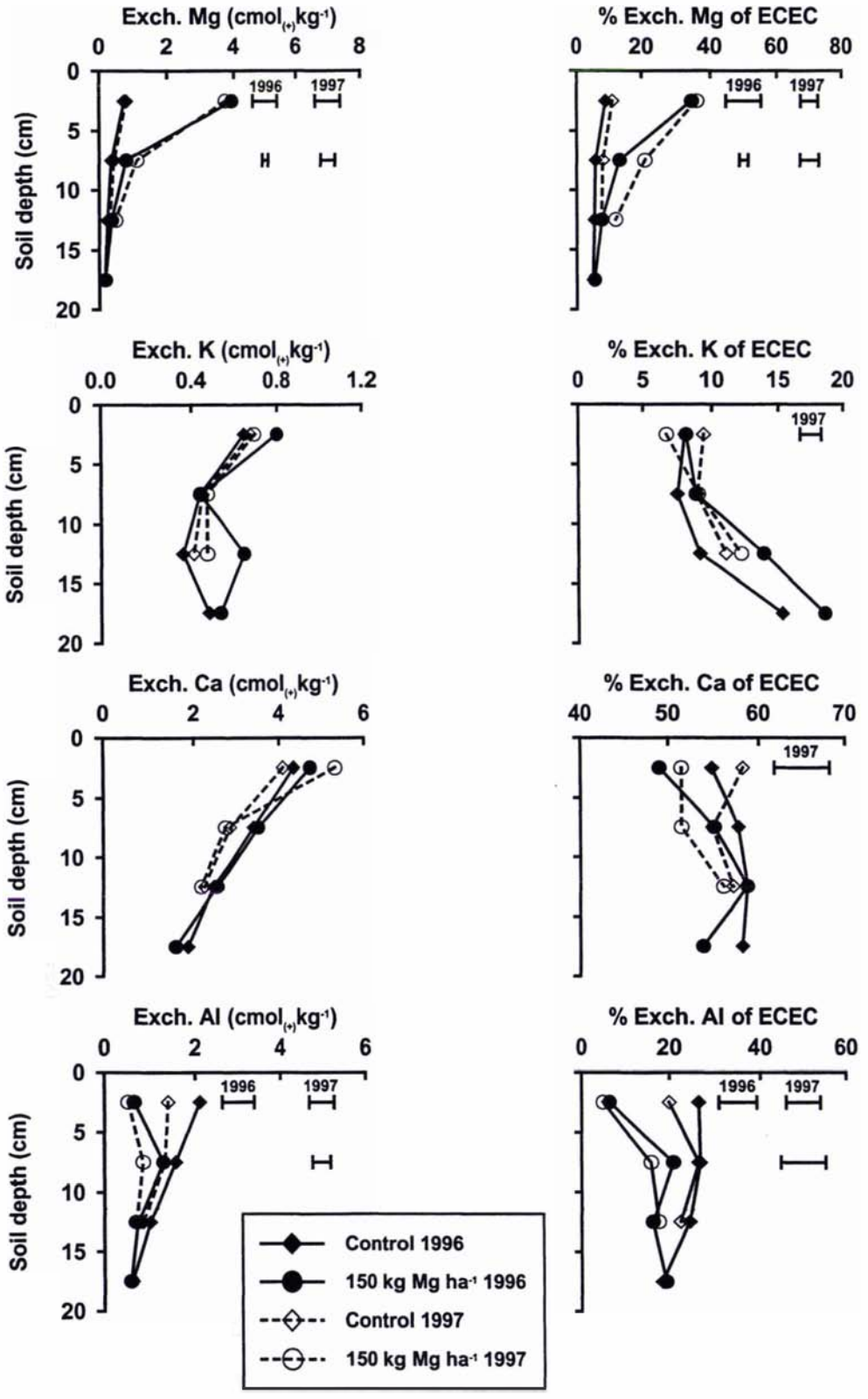

Figure 3.4 Effect of Mg fertiliser application on soil exchangeable cations and cation saturation of ECEC at FR190/5 trial. Horizontal bars represent l.s.d. for treatment means which are significantly different at $P = 0.05$.

The application of Mg fertiliser significantly ($P < 0.05$) reduced exchangeable Al in the 0-5 cm layer of FR190/4 in 1997 and in FR190/5 in 1996 and 1997. The levels of exchangeable K and Ca were not effected (Figure 3.3 and 3.4). Based on simple exchange theory it would have been expected that the addition of divalent Mg would have replaced the monovalent K and divalent Ca more easily than the trivalent Al. In this case the apparent decline in exchangeable Al is probably because the calmag fertiliser increased soil pH (Figure 3.2) which is known to decrease Al solubility and hence exchangeable Al (Edmeades *et al.* 1983; Manoharan *et al.* 1996).

The increase in negative charges on soil colloids as a result of increased soil pH has increased the total exchangeable cation concentrations. Therefore, the effect of Mg fertiliser application on the exchangeable cation concentrations as a percentage of ECEC was examined. The effect of Mg fertiliser on exchangeable Mg and Al was similar, whether results were expressed either as absolute quantities of exchangeable Al and Mg or as a percentage of ECEC (Figure 3.3 and 3.4). However, the effect of Mg fertiliser application on exchangeable K and Ca was different when exchangeable K and Ca were expressed as a percentage of ECEC. In FR190/5 Mg fertiliser produced a marginal increase in exchangeable K and Ca, but significantly ($P < 0.05$) decreased exchangeable K and Ca when expressed as a percentage of ECEC. This suggests that Mg might have exchanged with K and Ca in the exchange complex (Figure 3.4).

Similar results were recorded for exchangeable Ca in FR190/4, whereas for exchangeable K the results were varied between the two years. For 1996, exchangeable K as a percentage of ECEC was significantly ($P < 0.05$) reduced as a result of Mg fertiliser application, but the situation was reversed in 1977 (Figure 3.3).

3.4.2 Effect of Mg fertiliser on exchangeable K to Mg molar ratio

High foliar K:Mg concentration ratios have been linked to more severe UMCY (Beets *et al.* 1993). The foliar K:Mg concentration ratio reflects changes in soil exchangeable K and Mg concentrations (Beets and Jokela 1994). Therefore, the effect of Mg fertiliser application on the exchangeable K:Mg molar ratio was examined. Exchangeable K:Mg molar ratios were significantly lower in the Mg treated plots than in the controls in the

top two soil depths (0-5 and 5-10 cm) in the FR190/5 and in the top soil depth (0-5 cm) in the FR190/4 trial for both sampling times (Figure 3.5). These results show that it is possible to amend the K:Mg ratio in pumice soils by applying Mg fertiliser. Over a period of years this could reverse the trend of soil K:Mg ratios increasing with additional tree rotations (Will 1961; Ballard 1978), thereby reducing the incidence of UMCY.

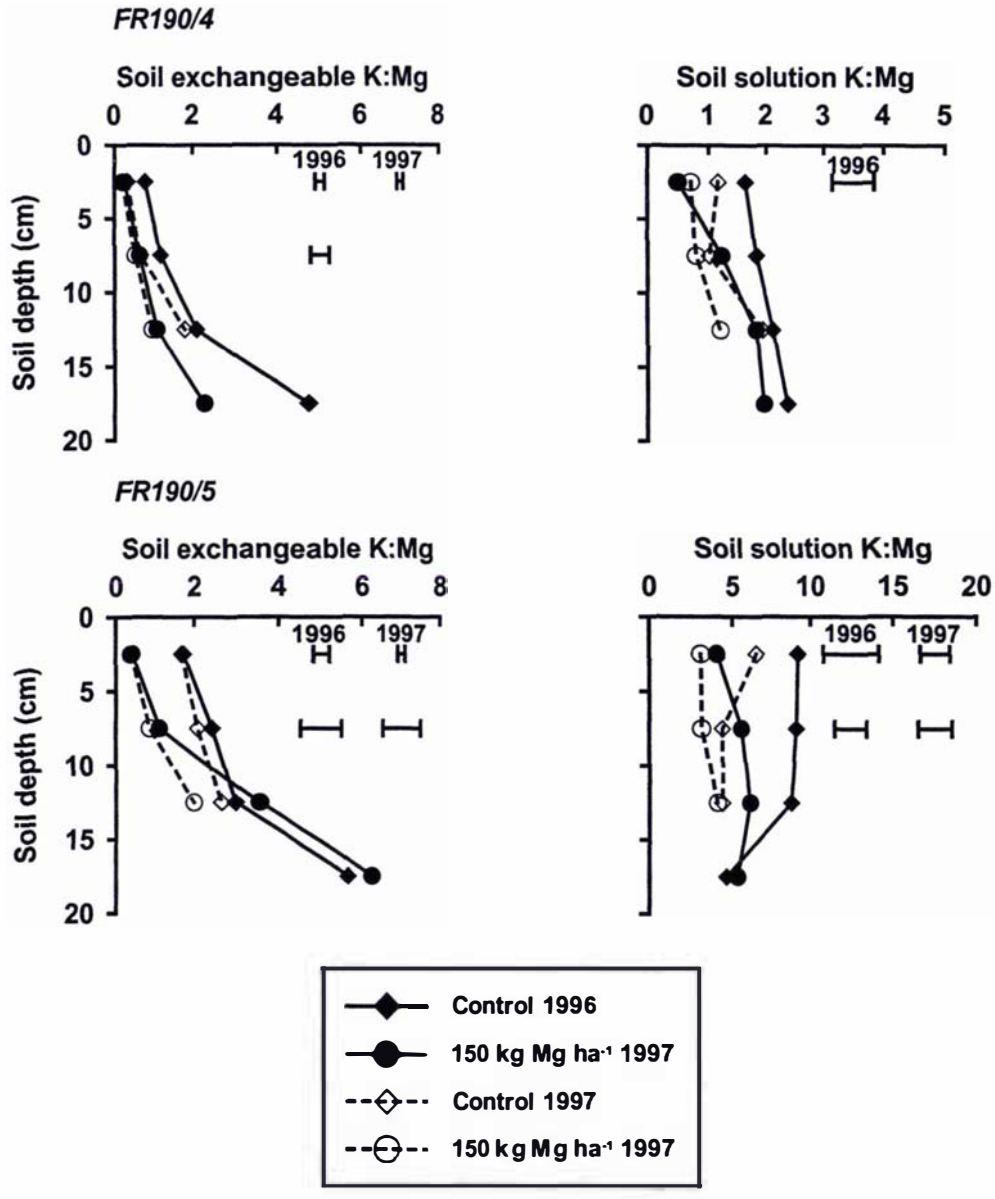

Figure 3.5 Effect of Mg fertiliser application on soil and soil solution K:Mg molar ratios at FR190/4 and FR190/5 trials. Horizontal bars represent l.s.d. for treatment means which are significantly different at $P = 0.05$.

3.4.3 Effect of Mg fertiliser on soil solution concentrations of cations and pH

In both trials, the application of Mg fertiliser significantly ($P < 0.05$) increased solution Mg concentration in the upper soil layers (Figure 3.6), but in general it had no effect on solution K and Ca. These results are similar to those for the exchangeable Mg, K and Ca. Soil solution concentrations of cations in 1996 were generally higher in FR190/4 than in FR190/5 (Figure 3.6). This may be partly due to the time difference in sampling the soils. Soil samples in FR190/4 were collected in early autumn after a long dry period and in FR190/5, samples were collected in winter when significant amounts of solution cations may have been leached. In 1997 both trials were sampled during the winter. FR190/4 had higher levels of solution Mg and Ca than FR190/5, but lower levels of K (Figure 3.6). This was probably due to differences in soil type.

At both sites and both sampling times, Mg fertiliser application slightly increased solution pH for most soil depths but the effects were not significant (Figure 3.6). The slightly higher solution pH in the fertilised plots is due to the liming effect of the calmag fertiliser.

Soil solution K:Mg ratio was significantly ($P < 0.05$) reduced by applying calmag in FR190/5 (for both years) and in FR190/4 for the 1996, but the reduction for 1997 was not statistically significant (Figure 3.5). The results are similar to those for the exchangeable K:Mg ratio.

3.4.4 Calmag fertiliser dissolution in Pumice Soils

Sequential extraction of soil samples collected in 1996 indicate that 19 and 21 months after the of Mg fertiliser was applied to FR190/4 and FR190/5, respectively, only about 8 % of the fertiliser Mg remained in an undissolved form within the 0-10 cm soil layer (Table 3.3). Application of Mg fertiliser has increased soil exchangeable Mg ($BaCl_2$-TEA, pH 8.2 extraction) levels in the topsoil layer (0-5 cm) by 95 kg Mg ha^{-1} in FR190/4 and 104 kg Mg ha^{-1} in FR190/5, over the control plots. These values represent

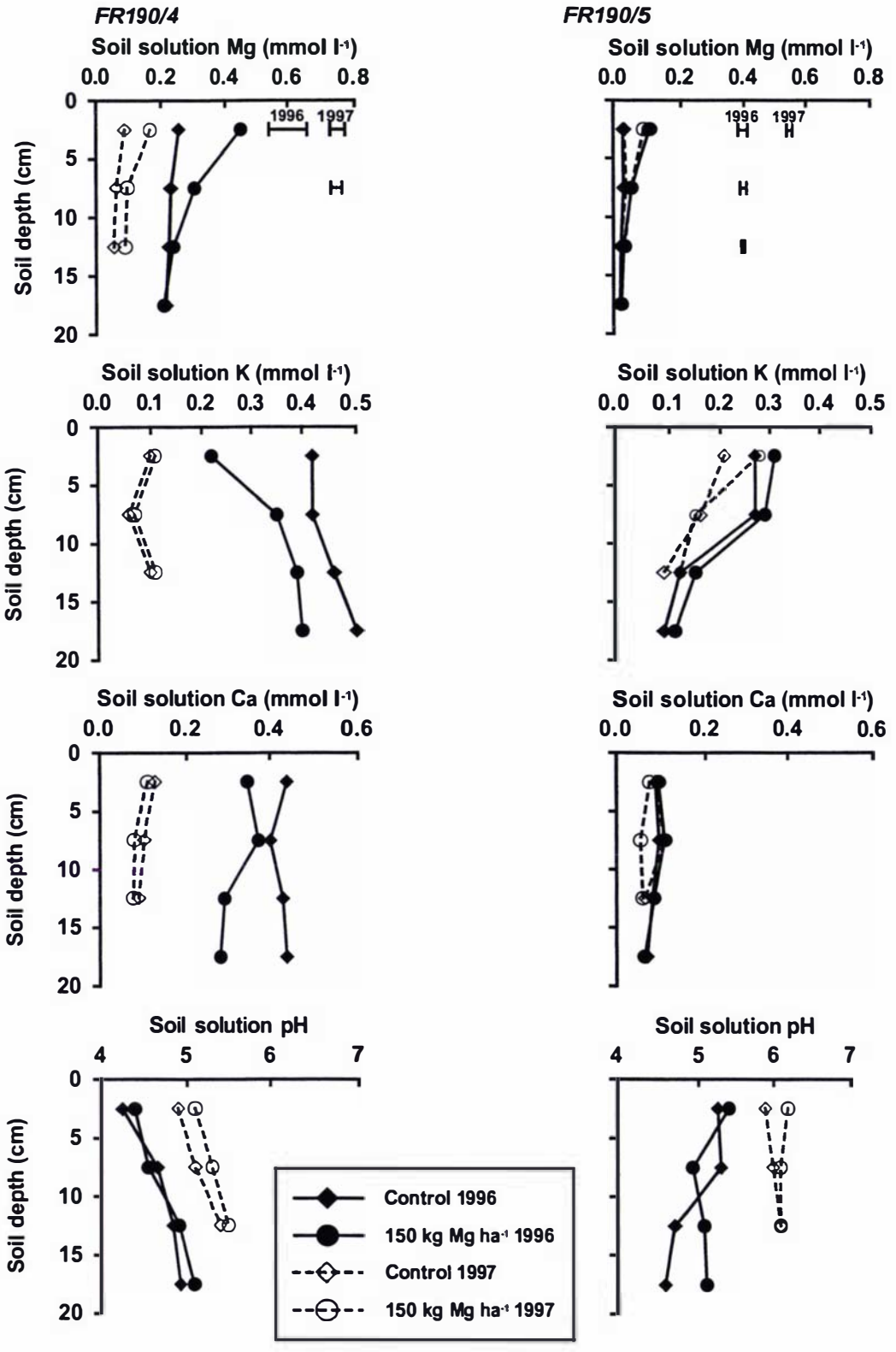

Figure 3.6 Effect of Mg fertiliser application on soil solution cation concentrations and soil solution pH at FR190/4 and FR190/5 trials. Horizontal bars represent l.s.d. for treatment means which are significantly different at $P = 0.05$.

Table 3.3 Dissolved and undissolved fertiliser Mg in 1996 soil samples at FR190/4 and FR190/5 trials

Soil depth (cm)	Dissolved Mg ($BaCl_2$-TEA extraction)		Undissolved Mg (HCl extractions)	
	(kg Mg ha^{-1})	(%)	(kg Mg ha^{-1})	(%)
		FR190/4		
0 - 5	95	63	9	6
5 - 10	13	9	3	2
		FR190/5		
0 - 5	104	69	10	7
5 - 10	15	10	1	<1

approximately 63% and 69% of Mg applied, respectively. The increase in soil exchangeable Mg as determined by NH_4OAc at pH 7.0 was 84 kg Mg ha^{-1} and 102 kg Mg ha^{-1} in FR190/4 and FR190/5 (Figure 3.3 and 3.4), respectively. These were similar to the values determined using the $BaCl_2$-TEA extraction (Table 3.3).

Total recovery (dissolved plus undissolved) of Mg fertiliser in the 0-10 cm soil layer equated to 80% of that applied in FR190/4 and 87% in FR190/5 (Table 3.3). These results indicated that some leaching losses below 10 cm soil depth and/or plant uptake may have occurred. Hunter *et al.* (1986) reported that within 5 years of application about 30-40 % of fertiliser Mg (Epsom salts and dolomite) can be lost due to leaching below the root zone in pumice soils under *P. radiata* in the Central North Island. In the current study, leaching losses from the top 10 cm soil layer are estimated to be approximately 11% and 3% of the Mg fertiliser applied at FR190/4 and FR190/5, respectively. These losses occurred, during the 19 and 21 months after calmag application. The calculation of leaching losses allowed for an estimated increase in total Mg uptake by fertilised 11-year-old *P. radiata* of 9 kg Mg ha^{-1} year (Hunter *et al.* 1986; P. Beets pers. com.). Greater leaching losses are likely in FR190/4 because complete canopy closure has not yet occurred, resulting in less interception of rainfall and transpiration by the trees and greater drainage through the soil profile. These results

are similar to the findings of Schaaf (1997) who determined that only 4% of the Mg fertiliser ($Mg(OH)_2$) applied to Norway spruce growing in Dystrochrepts soils in a German forest was lost due to leaching 18 months after application. Assuming that the leaching losses and tree uptake remains relatively constant, and that the increased soil Mg due to fertiliser is available to the tree, the fertiliser will continue the supply Mg to the trees for 6 years in FR190/4 and 12 years in FR190/5. It is unlikely that the trees will take up all the fertiliser Mg available in the soil. At some point the increased Mg demand by the fertilised trees will exceed the supply of soil Mg derived from the fertiliser.

3.4.5 Effect of Mg fertiliser on foliar Mg

The application of Mg fertiliser has generally increased foliar Mg concentrations in the treated plots over the control treatment at both sites and for both years. However, none of the increases were statistically significant at $P = 0.05$ (Figure 3.7). At FR190/4, in 1997, foliar Mg concentrations increased from marginally deficient levels of 0.08% in the unfertilised trees to adequate levels of 0.093% in the fertilised trees. At FR190/5, in 1997, foliar Mg concentrations increased from 0.101% in the unfertilised trees to 0.109%. Both the fertilised and unfertilised trees at FR190/5 have adequate foliar Mg concentrations. The small increases in foliar Mg concentrations strongly contrasts with the marked increases in soil exchangeable Mg and soil solution Mg (Figure 3.3, 3.4 and 3.6). These results raise the question of how efficient radiata pine is at taking up Mg and about its ability to respond to elevated soil Mg levels. However, a large increase in foliar Mg concentration might not be expected at FR190/5, where the unfertilised trees had adequate foliar Mg concentrations.

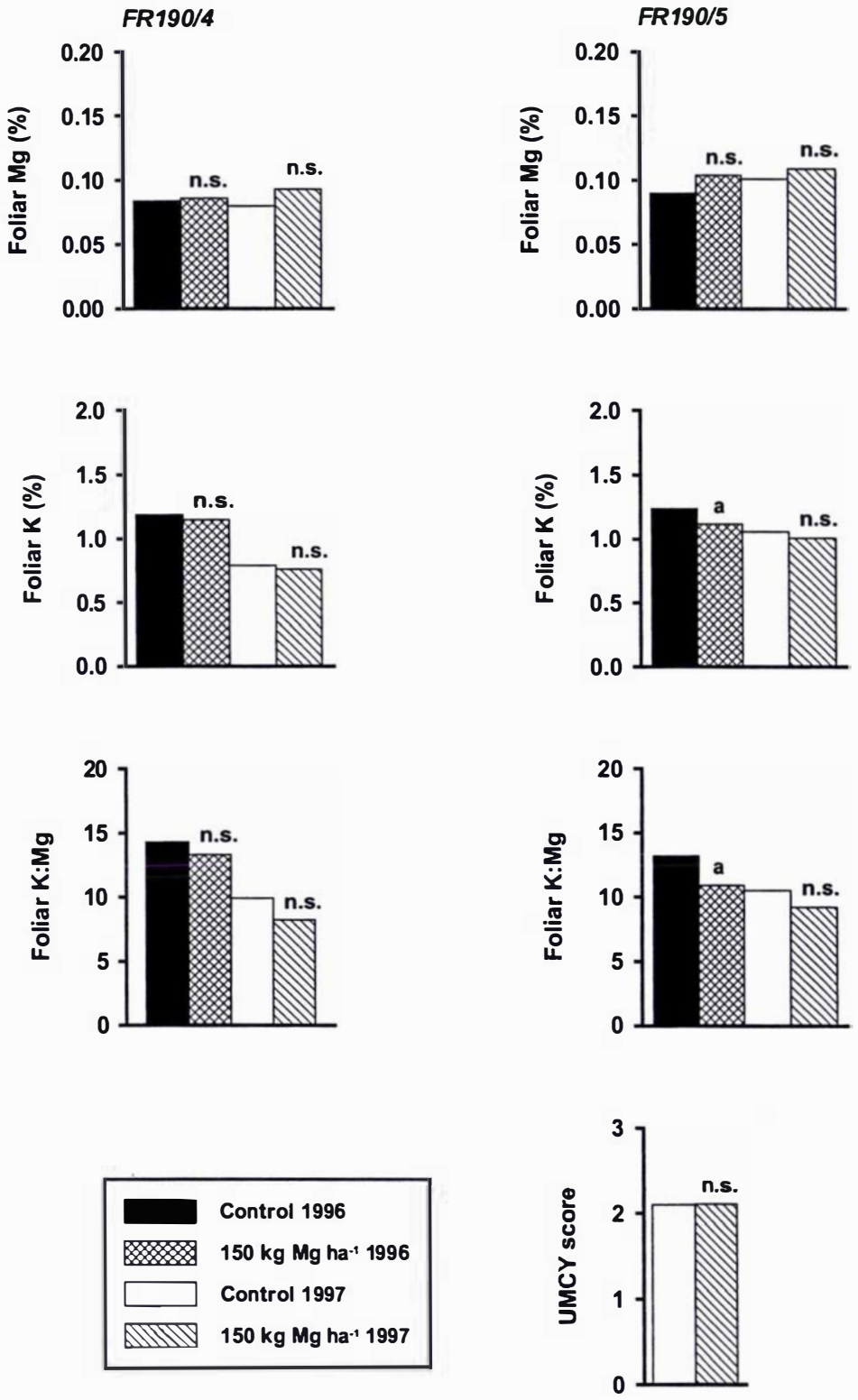

Figure 3.7 Foliage Mg, K and K:Mg, and UMCY score in FR190/4 and FR190/5 trials for 1996 and 1997. a - Difference significant at $P = 0.05$, n.s. - differences not significant.

Other studies reported by Hunter *et al.* (1986), Payn *et al.* (1995) and Hunter (1996) also highlight a slow and poor response by *P. radiata* to elevated soil Mg concentrations. A review of the aforementioned literature showed that foliage Mg concentrations generally peaked 3-4 years after fertiliser application, with foliage levels increasing from deficient concentrations of between 0.05-0.07% Mg to adequate levels of 0.1-0.12 % Mg. Even 5 years after Mg fertiliser application, foliage Mg levels in the studies of Hunter *et al.* (1986), Payn *et al.* (1995) and Hunter (1996) were still only within the adequate range of 0.1-0.13 %.

Similar slow responses have also been recorded by Schaaf (1995) in Germany for a severely Mg deficient stand of Norway Spruce on typic Dystrochrept soils where $Mg(OH)_2$ was applied at a rate equivalent to 1040 kg Mg ha^{-1}. Magnesium fertiliser resulted in a ten-fold increase in soil solution Mg three months after application and a significant increase in soil pH. However, for the first two years foliar Mg concentrations showed no response to fertilisation. Only after four and a half years had foliar Mg concentrations increased to adequate levels of 0.11% Mg compared to 0.07% in the no-fertiliser control trees.

Therefore, it might be expected that the difference in foliar Mg concentrations between the control and fertilised plots will continue to increase with time, but remain at concentrations where slight UMCY may still occur - based on correlations by Beets and Jokela (1994) between UMCY score and foliar Mg concentrations. It is also possible that the slow response to Mg fertilisation may be due to a problem with translocation of Mg from the roots to the foliage (Sun and Payn 1999) or a build-up of Mg in other tree organs.

3.4.6 Effect of Mg fertiliser on foliar K and K to Mg ratio

Foliar K and the K:Mg concentration ratio were affected by application of Mg fertiliser (Figure 3.7). Application of Mg fertiliser reduced foliar K concentrations and foliar K:Mg concentration ratios in both trials at both times of sampling. This decrease was significant ($P < 0.05$) for the 1996 sampling in FR190/5. High foliar K:Mg ratios have

been linked to UMCY (Beets *et al.* 1993), so a decrease in this ratio may reduce the severity of UMCY.

3.4.7 Effect of Mg fertiliser on UMCY in FR190/5

Magnesium fertiliser application slightly increased foliar Mg concentrations (Figure 3.7) but this increase had no effect on UMCY scores (Figure 3.7). Scores ranged from 1.9 to 2.5, indicating only very minor UMCY symptoms were present. This is due to the influence of other factors on the development of UMCY symptoms. Will (1966) found that Mg (UMCY) symptoms were less severe during periods of higher rainfall. Systematic Mg and water deficiency experiments with cloned spruces conducted in Europe demonstrated that yellow needles turned green if the spruces experienced good water supply after a dry period (Ende and Evers 1997). The summer of 1996 at Kaingaroa was wetter than average, which may have reduced the severity of symptoms for that year. Also in the experiment of Ende and Evers (1997), needle yellowing appeared at different foliar Mg concentrations dependent on the genetic composition of the spruces. Similarly, in New Zealand, clonal variations have been reported in the foliar Mg concentrations of radiata pine trees exhibiting UMCY symptoms (Beets and Jokela 1994). The trees used in this current study were planted as seedlings and would, probably have a greater range of genetic variation than clonal trees.

3.4.8 Correlations between foliage and soil Mg and K concentrations

In FR190/4 and FR190/5 some significant correlations were found between foliar Mg concentrations and many of the soil Mg fractions tested (Table 3.4 and 3.5), but no one test could be significantly correlated with foliar Mg for both trials and both times of sampling.

Table 3.4 Correlation coefficients for linear relationships between various soil (0 - 5 cm depth) and foliar Mg and K concentrations at FR190/4 trial

1996	Soil exch. Mg	Soil exch. K	Soil exch. K:Mg	Acid extract. Mg	Solution Mg	Solution K	Solution K:Mg	Foliar Mg	Foliar K:Mg
Soil exch. Mg	1								
Soil exch. K	-0.33	1							
Soil K:Mg	-0.07	-0.77	1						
Acid extract. Mg	0.62	-0.04	-0.27	1					
Solution Mg	0.99**	-0.20	-0.19	0.66	1				
Solution K	0.15	-0.63	0.87**	-0.13	0.02	1			
Solution K:Mg	-0.89**	0.52	-0.12	-0.69	-0.88**	-0.13	1		
Foliar Mg	-0.01	-0.10	-0.06	0.57	0.05	-0.38	-0.39	1	
Foliar K:Mg	-0.45	0.43	-0.55	-0.44	-0.44	-0.49	0.68	-0.40	1
1997									
Soil exch. Mg	1								
Soil exch. K	0.87**	1							
Soil K:Mg	-0.87**	-0.59	1						
Acid extract. Mg	0.48	0.61	-0.50	1					
Solution Mg	0.69	0.61	-0.62	0.79*	1				
Solution K	0.52	0.55	-0.41	0.11	-0.02	1			
Solution K:Mg	-0.53	-0.54	0.36	-0.63	-0.90**	0.31	1		
Foliar Mg	0.52	0.46	-0.37	0.51	0.81*	0.19	-0.67	1	
Foliar K:Mg	-0.47	-0.39	0.40	-0.60	-0.80*	-0.22	0.59	-0.97**	1

Note: * and ** denotes correlation coefficients statistically significant at $P = 0.1$ and $P = 0.05$ respectively

Table 3.5 Correlation coefficients for linear relationships between various soil (0-5 cm depth) and foliar Mg and K concentrations at FR190/5 trial

1996	Soil exch. Mg	Soil exch. K	Soil exch. K:Mg	Acid extract. Mg	Solution Mg	Solution K	Solution K:Mg	Foliar Mg	Foliar K:Mg
Soil exch. Mg	1								
Soil exch. K	0.32	1							
Soil K:Mg	-0.95**	-0.33	1						
Acid extract. Mg	0.96**	0.23	-0.95**	1					
Solution Mg	0.95**	0.31	-0.88**	0.97**	1				
Solution K	0.66*	0.42	-0.76**	0.79**	0.75**	1			
Solution K:Mg	-0.95**	-0.39	0.90**	-0.91**	-0.96**	-0.65*	1		
Foliar Mg	0.58	0.61	-0.63*	0.62*	0.65*	0.85**	-0.61	1	
Foliar K:Mg	-0.67*	-0.62*	0.78**	-0.64*	-0.61	-0.70*	0.70*	-0.85	1
1997									
Soil exch. Mg	1								
Soil exch. K	0.11	1							
Soil K:Mg	-0.98**	-0.14	1						
Acid extract. Mg	0.98**	0.03	-0.95**	1					
Solution Mg	0.95**	0.20	-0.95**	0.93**	1				
Solution K	0.79**	0.49	-0.75**	0.73*	0.84**	1			
Solution K:Mg	-0.87**	-0.13	0.87*	-0.87**	- 0.92**	-0.66*	1		
Foliar Mg	0.65*	0.40	-0.64*	0.64*	0.67*	0.62*	-0.75**	1	
Foliar K:Mg	-0.18	-0.21	0.22	-0.20	-0.40	-0.12	0.52	-0.13	1

Note: * and ** denotes correlation coefficients statistically significant at $P = 0.1$ and $P = 0.05$ respectively

The correlations between the various soil Mg fractions tested in the 0-5 cm layer and foliage Mg for FR190/4 were poor compared to those recorded for FR190/5, although the correlations were considerably better in the second year of sampling (Table 3.4). This could be due to the younger age of the trees and the lesser tree response to elevated soil Mg levels at FR190/4. In addition, the low number of replicates in this trial could be another reason for the poor correlations recorded at FR190/4. A statistically significant ($P < 0.1$) correlation was however, recorded between soil solution Mg concentration and both foliar Mg concentration and foliar K:Mg concentration ratio.

In FR190/5 some good correlations were found between foliar Mg concentrations and many of the soil Mg fractions tested for both times of sampling. Statistically significant ($P < 0.01$ or $P < 0.05$) correlations were recorded between foliar Mg concentrations and acid extractable Mg, soil exchangeable K:Mg molar ratio and soil solution Mg and K concentrations for the 1996 sampling (Table 3.5). The statistically significant correlations in 1996 were repeated in 1997 but the correlations between foliar Mg concentration and soil exchangeable Mg, and soil solution K:Mg molar ratio also were statistically significant ($P < 0.1$ or $P < 0.05$). Good correlations were also found between foliar K:Mg concentration ratio and various other soil Mg fractions in the 0-5 cm layer in the first year of sampling but these were not repeated in 1997 (Table 3.5). The significant positive correlation between solution K and foliar Mg does not necessarily mean that increases in solution K would increase foliar Mg. These two parameters were highly correlated because soil solution K and solution Mg were highly correlated (Table 3.5), and it is reasonable to assume that it was the soil solution Mg which increased foliar Mg not solution K.

Correlations between soil Mg concentrations for the 0-10 cm depth and foliar Mg concentrations were also considered. These resulted in similar trends to those recorded for the 0-5 cm soil depth, but the correlation coefficients were superior for the 0-5 cm depth. Combining the data sets from both trials also did not improve the correlations.

Hunter *et al.* (1991) also attempted to correlate foliar Mg concentrations with a range of measures of soil Mg. He found that the correlation coefficients were very low and non-significant. This suggests that current measures of soil Mg maybe of little value in

predicting foliar Mg levels for a perennial crop like *P. radiata*. In addition, it has been reported that large within-stand differences in the concentrations of foliar Mg and other nutrients exists in *P. radiata* (Beets *et al.* 1993), which would make significant correlations between foliar Mg and soil Mg concentrations difficult to obtain.

The findings reported earlier in this Chapter, that Mg fertiliser application significantly ($P < 0.05$) increased plant available Mg (soil exchangeable and solution Mg) but only slightly increased needle Mg concentrations, explains why there was no consistent relationships between soil Mg and needle Mg concentrations.

3.5 CONCLUSIONS

Calmag fertiliser applied to Pumice Soils at the rate of 150 kg Mg ha^{-1} was very effective in increasing plant-available Mg (soil exchangeable and solution Mg) in these soils within two years after application. Soil exchangeable Mg in the top soil (0-5 cm) was increased from a low rating to a high rating (Metson and Gibson 1977) and the exchangeable K:Mg molar ratio in the top soil was reduced in both trials for each year of sampling.

Approximately 90 percent of the applied fertiliser had dissolved and about three-quarters of the Mg applied remained in an exchangeable form in the top 10 cm of soil within two years after application. Calculations based on a conservative tree uptake of 9 kg Mg ha^{-1} yr^{-1} indicate that only 3-10 % of the fertiliser Mg was unaccounted for - possibly lost below 10 cm soil layer.

The improved Mg fertility of the soil has resulted in small increases in foliar Mg concentrations in the fertilised trees. These results highlight the poor and slow response of *P. radiata* to increased soil Mg concentrations.

Elevated soil Mg levels have been maintained over the two times of sampling, but *P. radiata* is a long-term crop (25-30 year rotation) and the long-term nature of this improvement is unknown. Calculations suggest that Mg fertiliser applied at 150 kg Mg ha^{-1} to 20-year-old *P. radiata* may supply Mg to the trees for another 12 years.

However, a point of time will be reached when the supply will become inadequate for the trees. Further monitoring of both trials will provide information on how long an application of Mg fertiliser can prevent UMCY from developing.

Several measures of soil Mg produced good correlations with foliar Mg, but no one test was consistently superior to the others over both years at both trial sites. None of the soil tests can be recommended for use by forest managers.

CHAPTER 4

INFLUENCE OF SOIL PROPERTIES AND RAINFALL ON THE RATE OF DISSOLUTION OF CALCINED MAGNESITE FERTILISER APPLIED TO A SERIES OF FOREST SOILS OF THE NORTH ISLAND UNDER *Pinus radiata*

4.1 INTRODUCTION

The study of two Pumice Soils from Kaingaroa Forest reported in Chapter 3, indicated that calcined magnesite (calmag) fertiliser had a relatively fast rate of dissolution. Approximately 90% of the applied fertiliser had dissolved in less than two years following application. Calmag was found to be very effective at improving the soil exchangeable Mg status of these soils. However, despite the relatively quick rate of dissolution of calmag and improved Mg fertility of these two soils, the application of Mg fertiliser only resulted in small increases in foliar Mg concentrations. It is not known whether the results obtained from the Kaingaroa studies are applicable to other forest soil types in different locations in the North Island.

Therefore, other trials in the well established FR190 series of Mg fertiliser trials at sites, other than those already studied in Kaingaroa Forest (Chapter 3), be used as the basis of the new study. This study planned to investigate whether differences in the Mg status of the soil, soil pH and rainfall affected the rate of dissolution and Mg availability from fertilisers, and consequently the overall effectiveness of the fertiliser at increasing plant-available Mg. The forestry companies had routinely undertaken foliage analysis from these trials, but had little current information on the Mg fertility of the soils and the fate of Mg fertilisers applied in these trials.

Therefore, three other Forest Research Mg fertiliser trial sites were chosen with a range of soil Mg concentrations and soil pH, and are subject to different rainfall patterns. The three sites included:

FR190/1 Carter Holt Harvey Forests, just south of Tokoroa in Kinleith Forest
FR190/6 Rayonier NZ Ltd, north-west of Gisborne in Mangatu Forest
FR190/7 Rayonier NZ Ltd, north-west of Gisborne in Waipaoa Forest

The Kinleith Forest trial has a Pumice Soil developed in Taupo ignimbrite overlying Taupo lapilli and differs from the Pumice Soils of the Kaingaroa trials described in Chapter 3. The Mangatu Forest trial is a Pumice Soil developed from Waiohau ash and the Waipaoa Forest trial is on a soil developed from tertiary mudstone and shattered argillite. One of the objectives of all these trials was to determine the effect of calmag fertiliser application on Mg uptake by the trees and reducing the incidence of UMCY. These three trials along with the two trials reported in Chapter 3 form the basis for the investigation reported in this chapter.

4.2 OBJECTIVES

The objectives of the study reported in this chapter are:

1. To determine the effects of the soil Mg status, soil pH and rainfall on the rate of dissolution of calmag fertiliser applied at a rate of 150 kg Mg ha^{-1} to five different forest soils.
2. To determine the fate of calmag fertiliser in a range of different forest soils, and to investigate its effectiveness at increasing plant-available Mg in soils and foliage Mg concentrations.

4.3 MATERIALS AND METHODS

4.3.1 Field trial design

Site and soil descriptions for FR190/1, FR190/6 and FR190/7 appear in Table 4.1 and trial descriptions in Table 4.2.

4.3.2 Soil sampling and analysis

Soil samples were collected in March 1998 at three depths (0-5, 5-10, and 10-15 cm) from the plots treated with zero and the highest rate of Mg (150 kg ha^{-1}) applied only as calmag (Nitrophoska and granmag-treated plots not included in the study). The 26 2 cm-diameter soil cores were collected at random and combined to make a bulk sample for each depth and each plot as described in Chapter 3. In FR190/1 samples were collected only from the weed control and no-urea plots. In FR190/6, samples were collected only from the weed control plots. The weed control plots at FR190/1 and FR190/6 were sampled as uptake of Mg by weeds would interfere with uptake by trees and make it difficult to find any relationship between soil Mg concentrations and tree Mg concentrations. In FR190/7 three of the four replicates were sampled.

Soil solutions were extracted from one portion of the field-moist soils from FR190/1 by centrifugation at 12,000 rpm (17200 RCF) in a refrigerated centrifuge at 4°C within two days of sample collection. Soils from FR190/6 and FR190/7 were deemed too dry to obtain any significant quantities of soil solution. Therefore, 30 and 40 ml of deionised water were added to a 150 g sub-sample of the field moist soil from FR190/6 and FR190/7 respectively. This procedure simulated a rainfall event. The original soil samples had gravimetric water contents of about 17 percent at FR190/6 and 16 percent at FR190/7. After wetting, the soils had gravimetric water contents increased to about 37 and 36 percent at FR190/6 and FR190/7, respectively. The wetted soil was left to equilibrate for about 1 hour and the soil solution was extracted as described for FR190/1 (P. Smethurst pers. com.). The pH of the resulting solutions was measured immediately

Table 4.1 Site and soil descriptions of the field trials

	FR190/1	FR190/6	FR190/7
Site and pedology details			
Location	Kinleith farms, Kinleith Forest, Tokoroa	Cpt44, Mangatu Forest, Gisborne	Cpt106, Waipaoa Forest, Gisborne
NZ Soil Classification[A]	Pumice Soil	Brown Soil	Recent Soil
Soil type/soil group	Taupo deep sand	Orthic Brown Soil[A]	Orthic Recent Soil[A]
Soil parent material	Taupo ignimbrite overlying Taupo lapilli[B] (1800 BP)	Waiohau ash deposits[B, C] (11300 BP)	Mudstone and shattered argillite[A]
Selected soil chemical properties			
Soil depth	0 - 10 cm	0 - 10 cm	0 - 10 cm
pH(water)	4.82	4.88	4.73
pH buff. cap. ($mmol\ H^+\ kg^{-1}\ pH^{-1}$)	51	41	42
Exch. Mg ($cmol_{(+)}kg^{-1}$)	0.3	1.3	3.0
Exch. K ($cmol_{(+)}kg^{-1}$)	0.3	0.3	0.7
Exch. Ca ($cmol_{(+)}kg^{-1}$)	3.1	5.7	15.2
ECEC[D] ($cmol_{(+)}kg^{-1}$)	6.0	9.5	29.5
Forestry details			
Rotation number	1	2	1
Time of planting	Winter 1990	Winter 1994	Winter 1983
Stocking rate	667 stems ha^{-1}	100 stems ha^{-1}	350 stems ha^{-1}
Mean annual rainfall[E]	1597 mm	1190 mm	1190 mm

[A] Jessen *et al.* (1999), [B] Molloy (1988), [C] Gage and Black (1979), [D] Σ exchangeable bases plus aluminium, [E] NIWA

Table 4.2 Details for the field trials

	FR190/1	FR190/6	FR190/7
Trial commencement	September 1990	July/August 1994	September 1994
Treatments	Calmag (2-5 mm chips) at 0, 75 and 150 kg Mg ha^{-1} with and without weed control, with and without Urea at 200 kg N ha^{-1}	Calmag (2-5 mm chips) at 0, 75 and 150 kg Mg ha^{-1} with and without weed control. Nitrophoska Blue TE (BASF) at 150 kg Mg ha^{-1} (12 kg ha^{-1} supplied by Nitrophoska and 138 kg ha^{-1} supplied by calmag), 120 kg N ha^{-1} and 50 kg P ha^{-1} with weed control	Calmag (2-5 mm chips) at 75 and 150 kg Mg ha^{-1}. Granmag at 75 and 150 kg Mg ha^{-1}. Nitrophoska Blue TE (BASF) at 150 kg Mg ha^{-1} (12 kg ha^{-1} supplied by Nitrophoska and 138 kg ha^{-1} supplied by calmag), 120kg N ha^{-1} and 50 kg P ha^{-1}. Two no-fertiliser controls per replicate
Replicates	3	3	4
Plot size	20m x 20 m	25m x 25 m	25m x 25 m
Measurement trees per plot	27	6	22

after centrifugation. Concentrations of Mg, K and Ca in solution were measured by atomic absorption spectrometry (AAS).

The remaining portion of the field-moist soil was air-dried and ground to pass through a 2 mm sieve. Soil samples were analysed for pH, exchangeable Mg, K and Ca (extraction with 1*M* NH_4OAc buffered at pH 7.0, Blakemore *et al.* 1987), exchange acidity and exchangeable Al (Yuan 1959), and undissolved fertiliser Mg using the methods as described in Chapter 3 (Loganathan *et al.* 1999). Concentrations of Mg, K, Ca and Al in the extracts were measured by AAS and exchange acidity by NaOH titration using phenolphthalein indicator.

4.3.3 Foliar sampling and analysis

Foliage samples were taken from FR190/1 in March 1998. FR190/7 was sampled in March of 1996. Trials FR190/6 and FR190/7 were not sampled in 1998. Fully extended needles from the current season's growth were randomly sampled from secondary branches in the upper third of the crown on the measurement trees of each plot and bulked to give one sample per plot. Samples were oven dried at 70°C and analysed for Mg and K by AAS after digesting in H_2SO_4/H_2O_2 mix (Nicholson 1984).

4.4 RESULTS AND DISCUSSION

4.4.1 Calmag fertiliser dissolution in soils

Results from the sequential extraction of soil samples from FR190/1 trial indicated that about 13% of the fertiliser remained in an undissolved form in the 0-10 cm soil layer 90 months after Mg fertiliser application (Table 4.3). In the pumice soils from FR190/4 and FR190/5 trials (reported in Chapter 3), with approximately the same soil pH and initial concentrations of exchangeable Mg, and subject to similar rainfall as FR190/1, only about 8% of Mg applied as calmag remained undissolved, but after about 20 months.

Table 4.3 Dissolved and undissolved fertiliser Mg in soil samples taken from the field trials 90 months (FR190/1) and 42 months (FR190/6 and FR190/7) after fertiliser application

Soil depth (cm)	Dissolved Mg recovery ($BaCl_2$-TEA extraction)		Undissolved Mg recovery (HCl extraction)	
	(kg Mg ha^{-1})	(%)	(kg Mg ha^{-1})	(%)
		FR190/1		
0 - 5	61	41	13	9
5 - 10	15	10	6	4
		FR190/6		
0 - 5	43	29	6	4
5 - 10	5	3	28	19
		FR190/7		
0 - 5	50	33	41	27
5 - 10	16	11	16	10

The percent of fertiliser remaining undissolved was slightly higher than at FR190/1 after a period three times longer than at FR190/4 and FR190/5. The greater concentrations of Mg in the fertilised plots at FR190/1 (compared to the no fertiliser controls) as determined by the 0.5*M* and 2*M* HCl extractions of the sequential method, may be due to increases in Mg concentrations in the litter layer and soil organic matter (from litter fall) due to fertiliser application, and not from undissolved Mg fertiliser as the method specifies. This Mg concentration could be measured by analysing the litter layers of the fertilised and control plots, but such measurements were not made in this study.

An estimate of the increase in Mg concentrations in the fertilised plots due to increased Mg additions to soil organic matter from litter fall was calculated as follows. The mean litter fall measured by Hunter *et al.* (1986) over a 1 year period from a Mg fertilised and unfertilised 10-year-old *P. radiata* trees was 3120 kg litter ha^{-1}. Assuming that the Mg

concentrations in the litter reflected the concentrations in the live foliage, and that foliar Mg concentrations have increased in a linear fashion during the 90 months after fertiliser application, an estimate of Mg concentration increase in litter on the fertilised plots would be 0.007% ({0.104%[mean needle Mg concentrations in the fertilised plots]} - {0.09% [mean needle Mg concentrations in the control plots]}/2). Therefore, an estimate of the Mg returned to the forest floor from litter fall since fertiliser application would be 1.6 kg Mg ha^{-1} ({3120 kg litter ha^{-1} yr^{-1} * 0.007/100 * 90 months/12 months yr^{-1}}) which is considerably less than the differences between the amounts of undissolved fertiliser Mg at the FR190/1 and FR190/4 and FR190/5 sites. This calculation illustrates that only a small fraction of the undissolved Mg recovered in FR190/1 can be attributed to an increase in Mg concentration of soil organic matter that originates from litter fall from the fertilised trees.

Another explanation could be that the particle size distribution of the calmag fertiliser may have differed among the various trials. The calmag fertiliser applied in these trials was reported to have had a particle size distribution within the range of 2-5 mm, [FR190/1, FR190/6 and FR190/7, and FR190/4 and FR190/5, refer Chapter 3]. There may have been a higher proportion of the larger particle size fractions in the calmag applied to the FR190/1 trial and particle sizes close to 5 mm may have remained undissolved even after 90 months. Payn (1991) also reported that a large percentage of the 2-5 mm chips of calmag fertiliser applied in September 1989 to a Pumice Soil at Tauhara Forest, near Taupo remained undissolved and highly visible on the soil surface, even 18 months after application. Both the trial reported by Payn (1991) and at the FR190/1 trial was installed several years earlier than the other trials and this difference in particle size distribution is highly possible. It is also possible that the calmag fertiliser used in the late 1980's, early 1990's may have had different physical properties, such as hardness, and therefore would have had a slower rate of dissolution to the calmag fertiliser used in later years at FR190/6 and FR190/7, and FR190/4 and FR190/5 (Chapter 3).

At FR190/6 and FR190/7 approximately 23% and 37%, respectively, of the fertiliser Mg remained in an undissolved form in the top 10 cm soil layer after 42 months (Table 4.3). These results indicate slower overall rates of dissolution at these two sites

compared to the two sites at Kaingaroa Forest described in Chapter 3. At the two Kaingaroa trials about 90% of the fertiliser Mg had dissolved in less than 24 months after application.

4.4.2 Factors influencing fertiliser Mg dissolution

The chemical reaction for the dissolution of calmag fertiliser is given by the following equation.

$$MgO + 2H^{+} \Rightarrow Mg^{2+} + H_2O \qquad (4.1)$$

According to equation 4.1 the rate of dissolution of calmag increases with increased supply of protons (decreases in pH) and increases in sinks for Mg^{2+}. This implies that the rate of dissolution is faster at low soil pH and in soils (sink) with low exchangeable Mg. In addition, moisture is required for the dissolution as well as for the removal of dissolved Mg^{2+}away from the site of the fertiliser particle to promote further dissolution. The soil pH, exchangeable Mg and soil moisture conditions (due to differences in annual rainfall) vary among the five field trial sites. Therefore, the difference in rate of Mg dissolution observed at these sites could be due to differences in the above environmental factors. For example the rate of Mg dissolution was lowest at FR190/7 a site with the lowest mean annual rainfall and the highest soil exchangeable Mg.

Therefore, the effect of mean annual rainfall, soil pH, soil exchangeable Mg and percent Mg saturation of exchange sites $\left(\frac{\text{exch. } Mg^{2+}}{\Sigma\text{exch. bases} + \text{exch. } Al^{3+} \text{ and } H^{+}} * \frac{100}{1}\right)$ on the amount of fertiliser dissolved during the 42 months since application was investigated using data from four of the five trials. This was achieved by plotting dissolved Mg (% of fertiliser Mg added) against mean annual rainfall obtained from the nearest weather station to each trial (NIWA), weighted average soil pH, exchangeable Mg concentration and percent Mg saturation of exchange sites for the 0-10 cm soil layer of the control plots of each trial. The percentage fertiliser Mg dissolved after 42 months at FR190/6 and FR190/7 was determined from the results of the sequential extraction (Table 4.3). The percent Mg dissolution from the FR190/4 and FR190/5 trials was also included in

the analysis, assuming 100% dissolution after 42 months (because approximately 90% Mg dissolution had occurred after 20 months - see Chapter 3). The data from FR190/1 was not used in the analysis because of the different year of establishment of the trial, and the possibility that the physical properties, as well as the particle size distribution of the calmag fertiliser applied in 1990, differed from that applied in 1994 at the other trials.

The graphs of dissolved Mg against each site characteristic tested are shown in Figure 4.1. There are strong linear and quadratic relationships between dissolved Mg and mean annual rainfall (R^2 = 0.902), initial soil exchangeable Mg (R^2 = 0.981) and percent Mg saturation of exchange capacity (R^2 = 0.998). However, there was no relationship between soil pH and dissolved Mg, but the soil pHs all lay within a narrow range of pH4.6 to pH5.5 (Figure 4.1). Had the soil pHs for these trials included some soils with more neutral or very low pHs, there may have been a relationship. Multiple regression analysis of percent dissolution as a function of the three variables: viz. soil pH, initial soil exchangeable Mg concentration or percent Mg saturation of exchange capacity, and rainfall; was not possible because there were only four data sets (four trials). However, the variables of annual rainfall, exchange Mg, and percent Mg saturation of exchange complex, each showed strong individual relationships with percent dissolution. Multiple regression analysis showed that there are strong relationships between percent Mg dissolution and any two pairs of variables according to the following equations.

$$Y = -8.22 * A + 0.052 * B + 26.3; (R^2 = 0.999) \quad (4.2)$$

$$Y = -3.15 * C - 0.011 * B + 125; (R^2 = 0.999) \quad (4.3)$$

where: Y = percent Mg dissolution (0-10 cm soil layer)

A = initial Mg ($cmol_{(+)}kg^{-1}$)

B = mean annual rainfall (mm)

C = percent Mg saturation of exchange complex

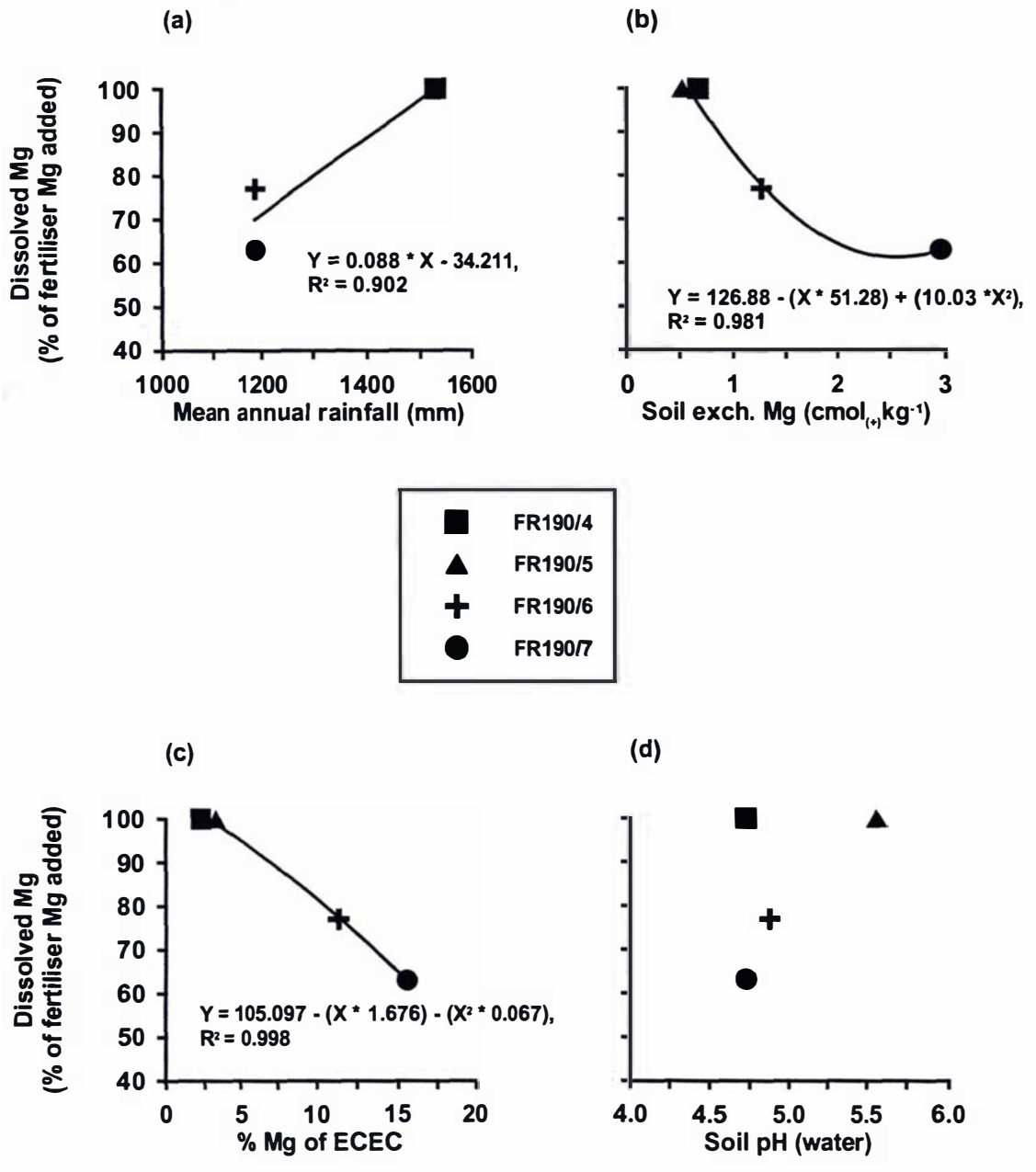

Figure 4.1 Magnesium fertiliser dissolution in 42 months after fertiliser application in the 0-10 cm soil layer versus (a) mean annual rainfall of the site, (b) soil exchangeable Mg, (c) percent Mg saturation of exchange capacity and (d) soil pH.

These relationships are similar to those reported for phosphate rock dissolution in soils (Mackay *et al.* 1986). This is not surprising, as the equations describing Mg fertiliser (equation 4.1) and phosphate rock (equation 4.4) dissolution (White *et al.* 1989) are similar.

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \Rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- \qquad (4.4)$$

It has been reported that the rate of phosphate rock dissolution is also related to the capacity of sinks for the dissolution products (percent Ca saturation of the exchange complex and P sorption capacity) (Mackay *et al.* 1986) and mean annual rainfall (White *et al.* 1989).

Although, strong relationships were found between percent Mg dissolution and (i) mean annual rainfall and initial soil exchangeable Mg, as well as (ii) mean annual rainfall and percent Mg saturation of exchange capacity, the relationships need to be considered with some caution for application to other sites. The analysis is only based on data from four trials and because FR190/6 is reasonably close to FR190/7, and FR190/4 is reasonably close to FR190/5 there are only two independent values for mean annual rainfall. Therefore, a strong relationship between rainfall and percent Mg dissolution was easily obtained. The data sets need to be expanded to a greater range of soils subject to a wider range of annual rainfalls in order to assess the robustness of this relationship. Magnesium fertiliser dissolution is expected to be influenced by factors other than those considered, such as rainfall distribution or, more importantly, soil water content changes during the study period. For example, a sandy loam soil receiving rainfall for a short period followed by a long dry period will probably have a slower rate of Mg fertiliser dissolution than a clay loam soil subjected to the same rainfall pattern because of the higher moisture holding capacity of the clay loam soil. Therefore, future investigations of this nature should consider rainfall at the site of the study, rainfall distribution or soil moisture distribution over the study period, as well as soil chemical properties.

4.4.3 Effect of Mg fertiliser on soil pH, exchange acidity and ECEC

Magnesium fertiliser application increased soil pH in the soils of FR190/1, FR190/6 and FR190/7 (Figure 4.2) as in FR190/4 and FR190/5 trials (Chapter 3). Increases in soil pH are due to the liming effect of the calmag fertiliser. The increase in soil pH was higher at FR190/6 and FR190/7 compared to FR190/1 in spite of higher amounts of fertiliser dissolution in FR190/1. This is probably due to the higher pH buffering capacity at FR190/1 (51 mmol H^+ kg^{-1} pH^{-1}, 0-10 cm soil layer), compared to the other two trials (41 and 42 mmol H^+ kg^{-1} pH^{-1} at FR190/6 and FR190/7, respectively) (Table 4.1). However, none of the increases were significant (Figure 4.2). As the pH buffering capacity and percent dissolution were not widely different among the five trials, there was no relationship between the pH increases due to Mg fertiliser application, and the independent variables of pH buffering capacity and percent Mg dissolution.

In accordance with the soil pH increase at FR190/1, FR190/6 and FR190/7, the exchange acidity reduced following the application of Mg fertiliser (Figure 4.2). However, none of the decreases were statistically significant ($P > 0.05$). Like the soils discussed in Chapter 3, the soils at FR190/1 and FR190/6 probably have a significant concentration of variable charge colloids (Leamy *et at.* 1980). The soil pH at FR190/1, increased because Mg fertiliser application has increased the negative charge on the soil colloids as evidenced by the increased (not significant at $P = 0.05$) effective cation exchange capacity (ECEC) (exchangeable bases Ca, K, Mg, Na plus exchangeable Al, Blakemore *et al.* 1987). ECEC of the 0-5 cm soil layer increased from 7.76 to 10.0 $cmol_{(+)}kg^{-1}$ (Figure 4.1). The ECEC of FR190/6 however, was not affected by the change in soil pH due to Mg fertiliser application although the soil at this site probably have some variable charge soil colloids the amount of variable charge colloids was not determined. The difference in behaviour at FR190/6 and FR190/1 is probably due to the proportions of the variable charge colloids in the respective soils.

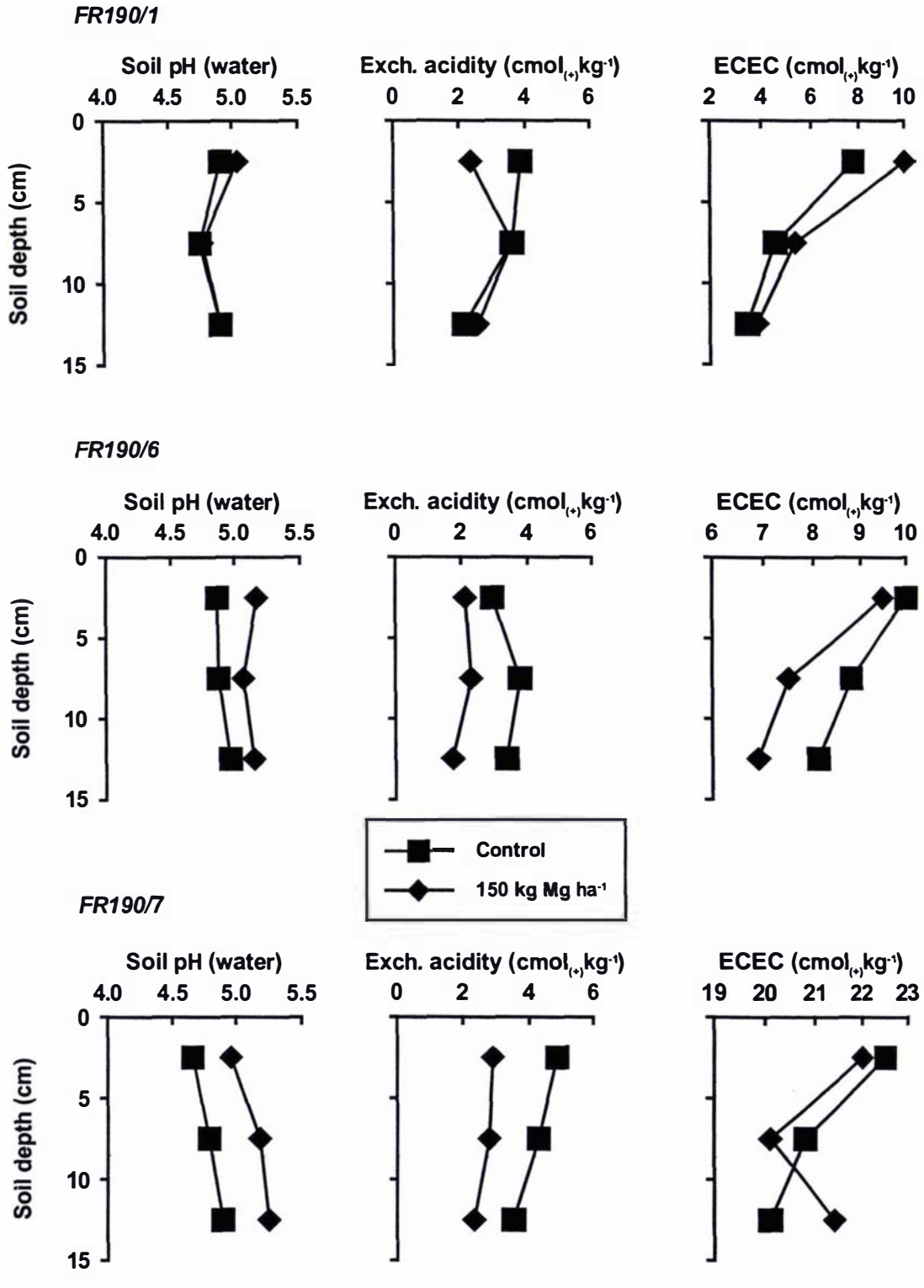

Figure 4.2 Effect of Mg fertiliser application on soil pH, exchange acidity and ECEC at FR190/1, FR190/6 and FR190/7 trials.

4.4.4 Effect of Mg fertiliser on soil exchangeable cations

Magnesium fertiliser application generally increased soil exchangeable Mg in the 0-5 cm depth in all three trials (Figures 4.3, 4.4 and 4.5). At FR190/1, 90 months after fertiliser application, the soil exchangeable Mg recorded in the Mg fertilised plots (approximately 55 kg Mg ha^{-1} above the control) significantly ($P < 0.05$) exceeded the levels within the control plots (Figure 4.3). The increase at FR190/1was less than the increases reported at FR190/4 (approximately 79 kg Mg ha^{-1} above the control) and FR190/5 (approximately 94 kg Mg ha^{-1} above the control) (Chapter 3). Significant ($P < 0.05$) increases in exchangeable Mg were also recorded in the other depths sampled at FR190/1. At FR190/6 and FR190/7, Mg fertiliser application resulted in smaller increases in exchangeable Mg (approximately 32 kg Mg ha^{-1} at FR190/6 and 58 kg Mg ha^{-1} at FR190/7 above the controls) (Figure 4.4 and 4.5) compared to FR190/1, FR190/4 and FR190/5 (Chapter 3). None of the increases in exchangeable Mg at FR190/6 and FR190/7 were significant ($P > 0.05$). The lower increases in exchangeable Mg at FR190/6 and FR190/7 was probably due to the higher levels of exchangeable Mg in the control soils and the lower percentage of fertiliser Mg dissolution, compared to FR190/1. Exchangeable Mg values in the surface soils of FR190/1 would be classed as medium for the Mg fertilised plots and low for the no-fertiliser control plots, based on criteria for a range of New Zealand soils (Metson and Gibson 1977). Exchangeable Mg values at FR190/6, for both the control and Mg treated plots would be classed as medium whereas for FR190/7, both the control and the Mg treated plots would be classed as high. Exchangeable Mg levels in the control plots of all three trials (0-5 cm depth) were well above the critical level of 0.2 $cmol_{(+)}\,kg^{-1}$ suggested by Will (1961) for adequate needle Mg concentrations.

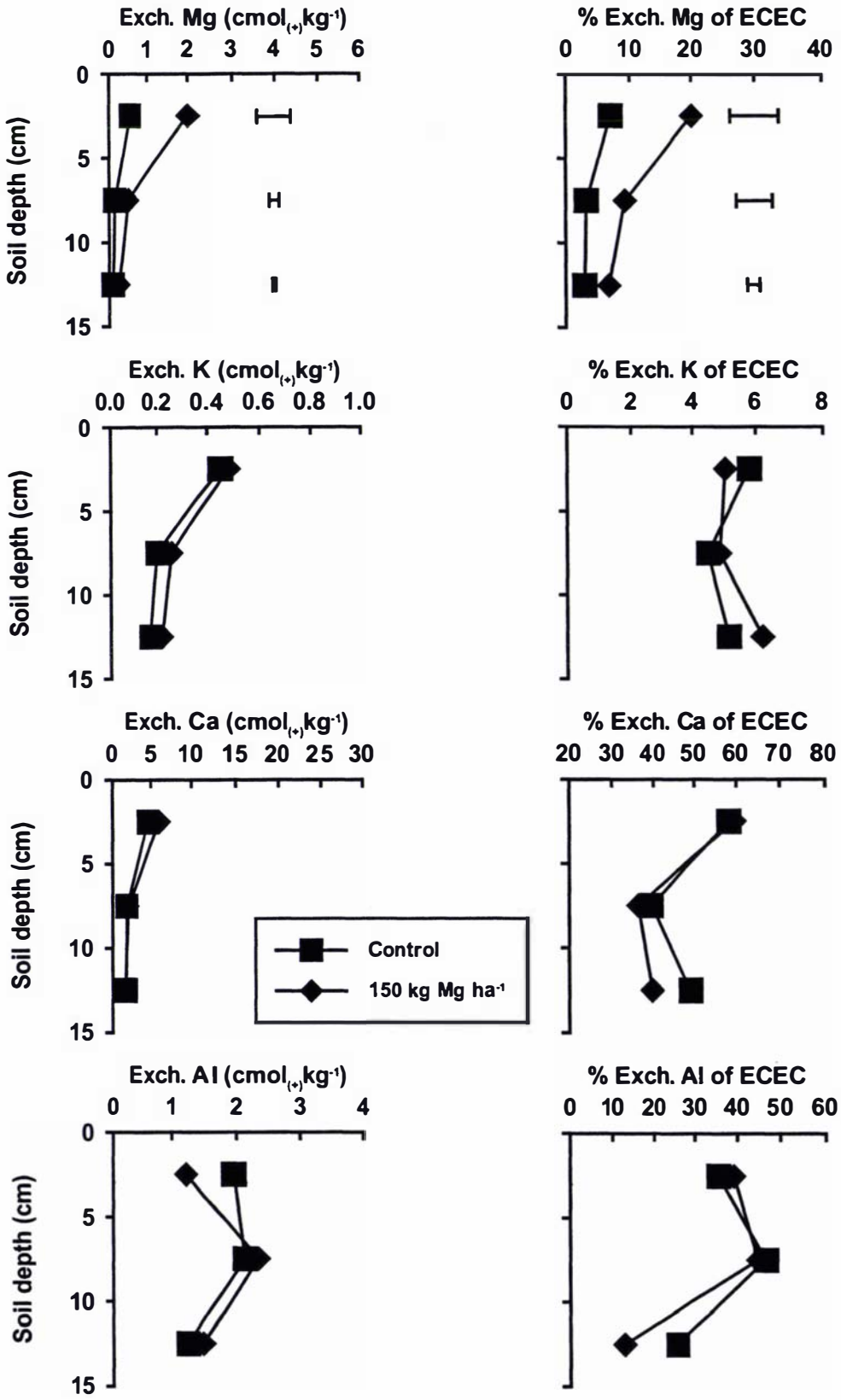

Figure 4.3 Effect of Mg fertiliser application on soil exchangeable cations and cation saturation of ECEC at FR190/1 trial. Horizontal bars represent l.s.d. for treatment means which are significantly different at $P = 0.05$.

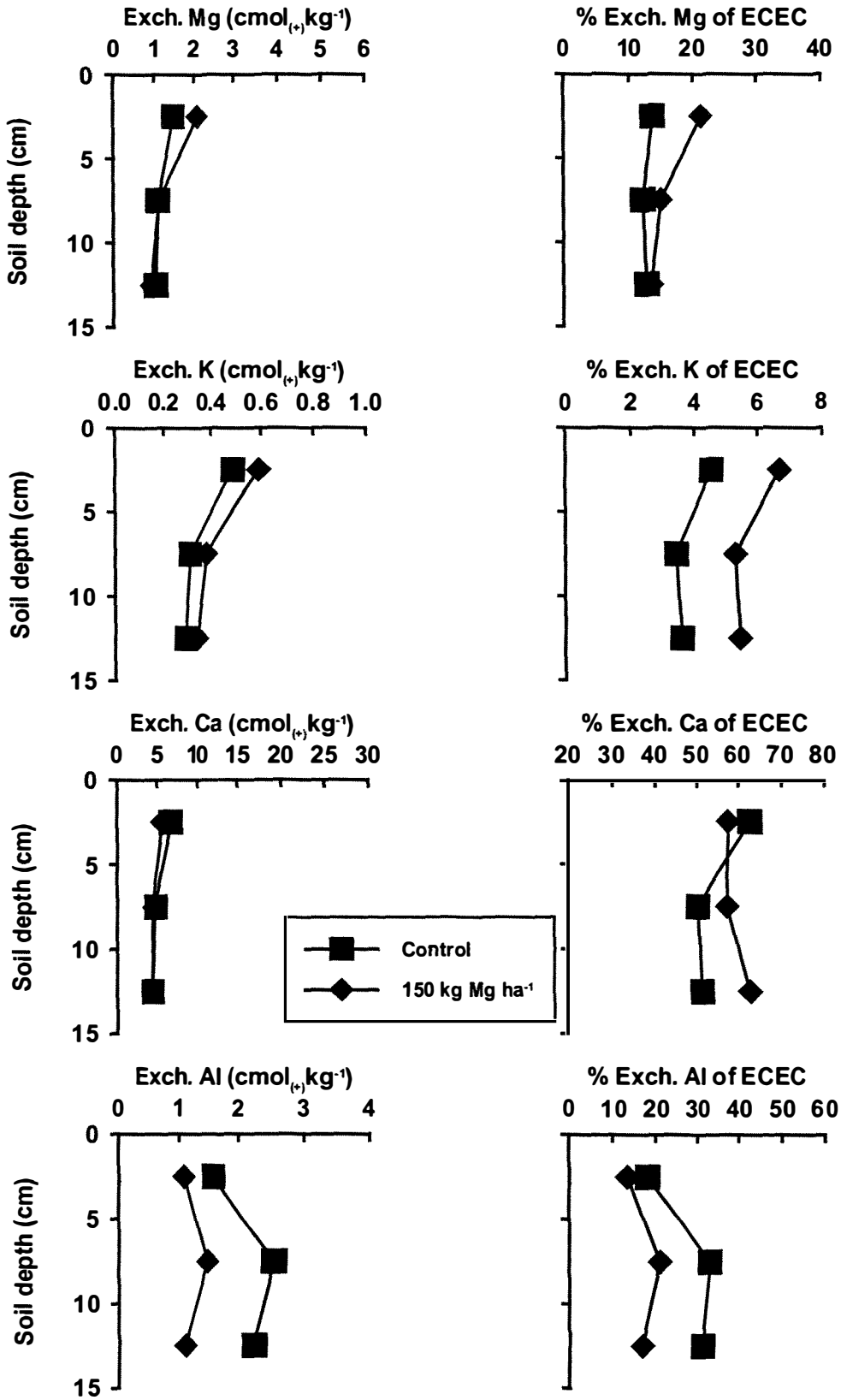

Figure 4.4 Effect of Mg fertiliser application on soil exchangeable cations and cation saturation of ECEC at FR190/6 trial.

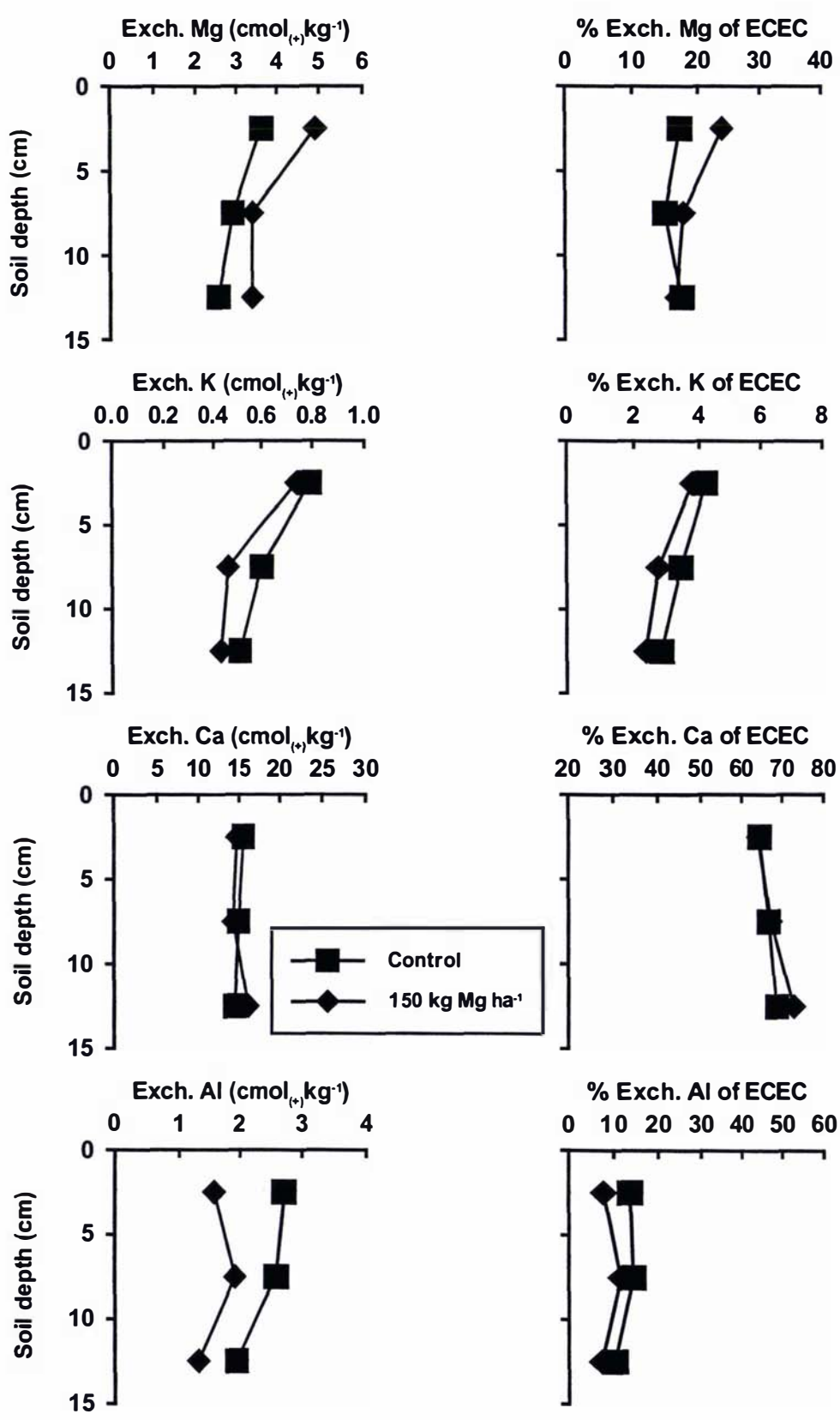

Figure 4.5 Effect of Mg fertiliser application on soil exchangeable cations and cation saturation of ECEC at FR190/7 trial.

The application of calmag fertiliser reduced exchangeable Al in the 0-5 cm layer (Figures 4.3, 4.4 and 4.5) in all three trials, although the reduction is not significant ($P >$ 0.05). These results are similar to those for the FR190/4 and FR190/5 trials (Chapter 3). This is probably because the application of calmag fertiliser increased soil pH, which is known to decrease Al solubility and hence exchangeable Al (Edmeades *et al.* 1983; Manoharan *et al.* 1997). In addition Mg may exchange with part of the exchangeable Al. At FR190/7, exchangeable Al levels on the fertilised plots were reduced to approximately half those in the control plots (Figure 4.5). Calmag application did not effect exchangeable concentrations of Ca and K at any site (Figures 4.3, 4.4 and 4.5).

In Chapter 3, the effect of Mg fertiliser on exchangeable Mg and Al at FR190/5 was found to be similar whether the results were expressed as a percentage of ECEC or not. However, the effect on exchangeable K and Ca was different when expressed as a percentage of ECEC. At FR190/5, calmag application resulted in a marginal increase in exchangeable K and Ca, but significantly ($P < 0.05$) decreased exchangeable K and Ca when expressed as a percentage of ECEC. This suggests that Mg might have exchanged with K and Ca in the exchange complex. Therefore, the effect of Mg fertiliser application on the exchangeable cation concentrations as a percentage of ECEC at FR190/1, FR190/6 and FR190/7 was examined. Generally the effect on exchangeable Mg, K, Ca and Al was similar whether or not ECEC was considered in the analysis (Figure 4.3, 4.4 and 4.5) and only the increase in exchangeable Mg as a percentage of ECEC at FR190/1 was significant ($P < 0.05$).

4.4.5 Effect of Mg fertiliser on soil exchangeable K to Mg molar ratio

The studies at FR190/4 and FR190/5 in Chapter 3 showed that it was possible to significantly ($P < 0.05$) amend the exchangeable K:Mg molar ratio in pumice soils by applying Mg fertiliser. Therefore, the effect of calmag application on the soil exchangeable K:Mg molar ratio was examined at the other three FR190 trials. At FR190/1 the exchangeable K:Mg molar ratio in the Mg treated plots was significantly ($P < 0.05$) lower than in the controls in the top 10 cm soil depth (Figure 4.6). At both

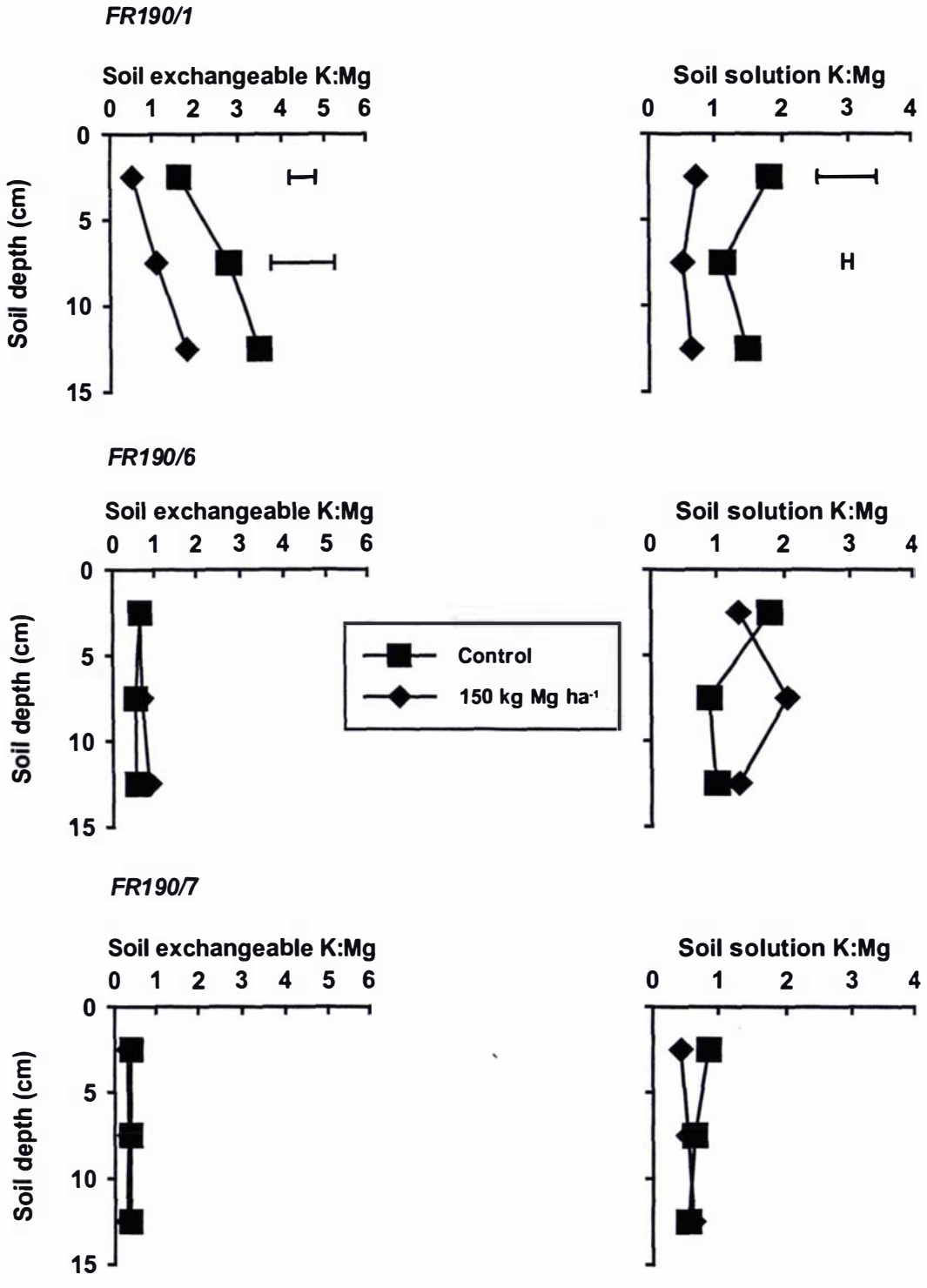

Figure 4.6 Effect of Mg fertiliser application on soil and soil solution K:Mg molar ratios at FR190/1, FR190/6 and FR190/7 trials. Horizontal bars represent l.s.d. for treatment means which are significantly different at $P = 0.05$.

FR190/6 and FR190/7, calmag fertiliser application did not result in any changes in the soil exchangeable K:Mg molar ratio (Figure 4.6).

The differences in the effects of Mg fertiliser application on the exchangeable K:Mg ratio in these trials is due to the relatively high levels of exchangeable Mg in the original soil. The FR190/6 and FR190/7 soils originally had medium and high levels of exchangeable Mg respectively (1.47 $cmol_{(+)}kg^{-1}$ at FR190/6 and 3.63 $cmol_{(+)}kg^{-1}$ at FR190/7, 0-5 cm soil layer), according to the ratings of Metson and Gibson (1977). The application of Mg fertiliser did not significantly ($P < 0.05$) increased concentrations of exchangeable Mg in these two trials. Therefore, the K:Mg molar ratio at FR190/6 and FR190/7 also remains unaffected by Mg fertiliser application.

In contrast, the FR190/1 soils originally had low levels of exchangeable Mg (0.55 $cmol_{(+)}kg^{-1}$, 0-5 cm soil layer). Consequently, Mg fertiliser application has significantly ($P < 0.05$) increased exchangeable Mg concentrations (an increase of about 260% over the control). This is reflected in the significant ($P < 0.05$) decrease in the exchangeable K:Mg molar ratio.

The original soils in the trials reported in Chapter 3 had exchangeable Mg concentrations of 1.03 $cmol_{(+)}kg^{-1}$ at FR190/4 and 0.74 $cmol_{(+)}kg^{-1}$ at FR190/5 (0-5 cm soil layer). These values are considered low and application of Mg fertiliser increased the exchangeable Mg concentrations by 160% and 340% respectively, and significantly decreased the K:Mg molar ratio.

Therefore, based on the results of all five trials it can be concluded that if exchangeable Mg concentrations are below 0.55 to 1.03 $cmol_{(+)}kg^{-1}$ and exchangeable K is below 0.41 to 0.67 $cmol_{(+)}kg^{-1}$, the application of Mg fertiliser at the rate of 150 kg Mg ha^{-1} is expected to significantly reduce the exchangeable K:Mg molar ratio in soils. The importance of changes in the soil exchangeable K:Mg molar ratio of the soils was discussed in Chapter 3.

4.4.6 Fertiliser Mg recovery in soils and Mg leaching loss estimation

Application of Mg fertiliser had increased soil exchangeable Mg ($BaCl_2$ - TEA extraction, Table 4.3) in the topsoil layer (0-10 cm) by 76 kg Mg ha^{-1} in FR190/1, 48 kg Mg ha^{-1} in FR190/6 and 66 kg Mg ha^{-1} in FR190/7, above the levels of control plots. These values represent approximately 51%, 32% and 44% of Mg applied respectively. The increase in soil exchangeable Mg as determined by NH_4OAc at pH 7.0 was 75 kg Mg ha^{-1}, 44 kg Mg ha^{-1} and 85 kg Mg ha^{-1} in FR190/1, FR190/6 and FR190/7 respectively (Figure 4.3, 4.4 and 4.5). These values were similar to those determined by the $BaCl_2$-TEA extraction (Table 4.3).

Total recovery (dissolved plus undissolved) of Mg fertiliser in the 0-10 cm soil layer equated to 64% in FR190/1, 45% in FR190/6 and 85% in FR190/7, indicating that some leaching and/or plant uptake has occurred. The difference in total Mg uptake between the Mg-fertilised and the unfertilised 11-year-old *P. radiata* trees was estimated to be 9 kg Mg ha^{-1} yr^{-1} (Hunter *et al.* 1986; P. Beets pers. com.). Using this figure, the respective leaching losses at FR190/1, FR190/6 and FR190/7 were estimated to be 0%, 20% and 0% of the applied fertiliser Mg during the 90 months (FR190/1) and 42 months (FR190/6 and FR190/7) after calmag application. These are similar to the leaching losses calculated for FR190/4 (11%) and FR190/5 (3%) in Chapter 3. The losses reported here are considerably lower than the 30-40% leaching losses from Mg fertilisation (Epsom salts and dolomite) of Pumice Soils under *P. radiata* in the Central North Island reported by Hunter *et al.* (1986). The lower leaching losses in FR190/7 are much lower than those for FR190/6 probably due to differences in soil type. The soil at FR190/7 is a mudstone with a higher effective cation exchange capacity (29.5 $cmol_{(+)}kg^{-1}$) than the Pumice Soil at FR190/6 (9.5 $cmol_{(+)}kg^{-1}$) (Table 4.1), and is more able to retain Mg released from fertiliser dissolution.

4.4.7 Effect of Mg fertiliser on soil solution concentrations of cations and pH

Changes in exchangeable Mg, K and Ca at FR190/1, FR190/6 and FR190/7 due to calmag fertiliser application were reflected in changes in solution cation concentrations. Calmag fertiliser application has significantly ($P < 0.05$) increased solution Mg at FR190/1 at all depths (Figure 4.7). At FR190/6 and FR190/7 Mg fertiliser application also increased solution Mg in the 0-5 cm soil layer, although none of the increases were significant ($P > 0.05$) (Figures 4.8 and 4.9). Magnesium fertiliser application had no significant effect on soil solution K and Ca at any of the three trials (Figures 4.7, 4.8 and 4.9). This reflected similar findings for soil exchangeable K and Ca (Figures 4.3, 4.4 and 4.5).

At FR190/1 and FR190/6 Mg fertiliser application slightly increased solution pH in the top 5 cm of soil thereby reflecting changes in soil pH (Figures 4.7 and 4.8), but the increases were not significant ($P > 0.05$). As with soil pH, the slightly higher solution pH in the fertilised plots is due to the liming effect of the calmag fertiliser. At FR190/7 Mg fertiliser application had no effect on solution pH (Figure 4.9).

Soil solution K:Mg molar ratios, as with the soil exchangeable K:Mg molar ratio, was significantly ($P < 0.05$) reduced in the top 10 cm of soil at FR190/1 (Figure 4.6), which was the soil with the lowest exchangeable Mg concentration of the three soils reported in this chapter. At FR190/6 Mg fertiliser application had no effect on the soil solution K:Mg molar ratio. At FR190/7 however, soil solution K:Mg molar ratio was reduced in the top 5 cm soil layer but the reduction was not significant ($P > 0.05$) (Figure 4.6).

4.4.8 Effect of Mg fertiliser on Foliar Mg

The application of Mg fertiliser at FR190/1 tended to increase foliar Mg concentrations in the treated plots over the control treatment. However, as reported for FR190/4 and FR190/5 in Chapter 3 none of the increases were statistically significant ($P > 0.05$) (Figure 4.10). At FR190/7, where the soils had much higher exchangeable Mg concentrations than those at FR190/1, the application of Mg had no effect on foliar Mg

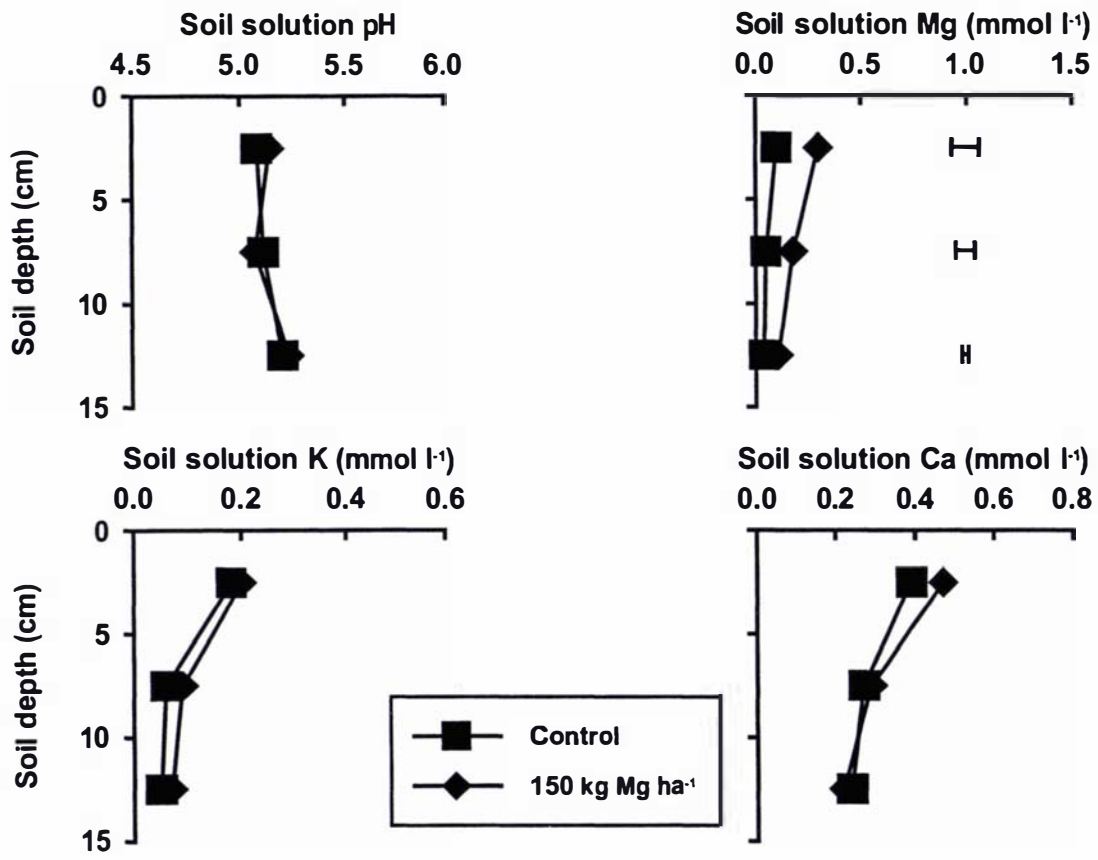

Figure 4.7 Effect of Mg fertiliser application on soil solution cation concentrations at FR190/1 trial. Horizontal bars represent l.s.d. for treatment means which are significantly different at $P = 0.05$.

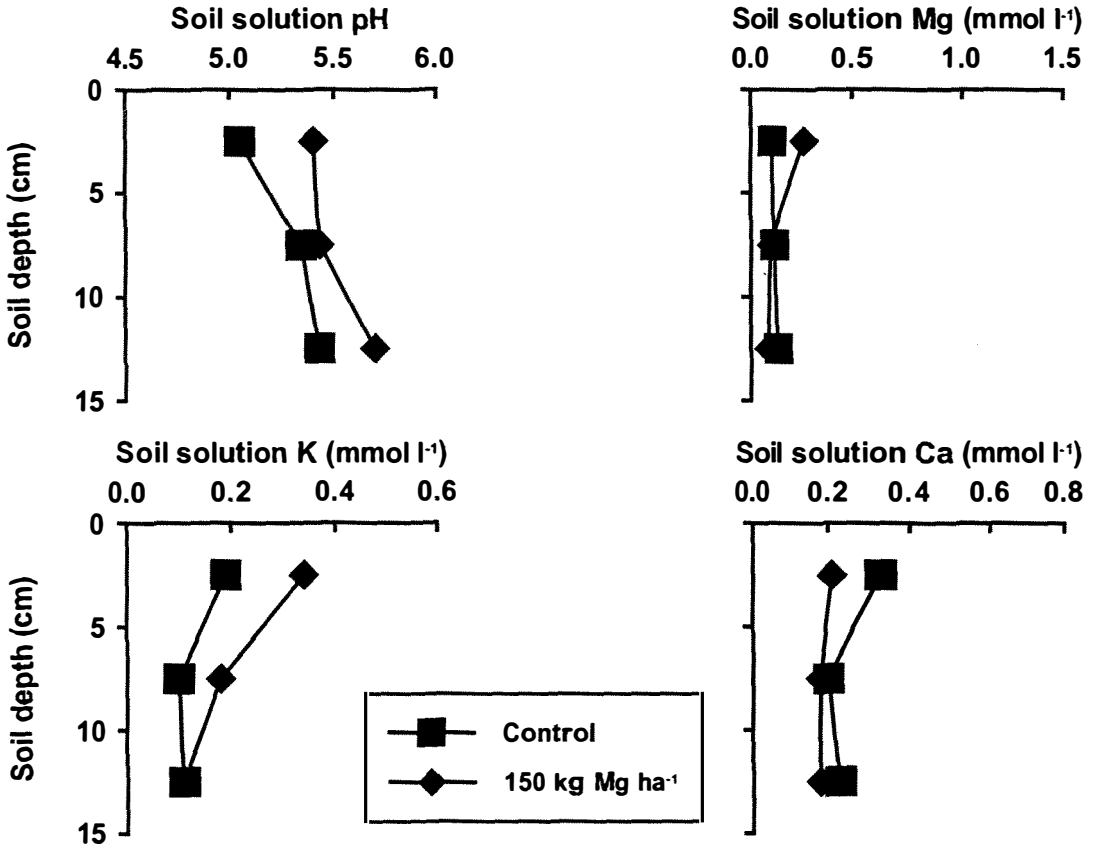

Figure 4.8 Effect of Mg fertiliser application on soil solution cation concentrations at FR190/6 trial.

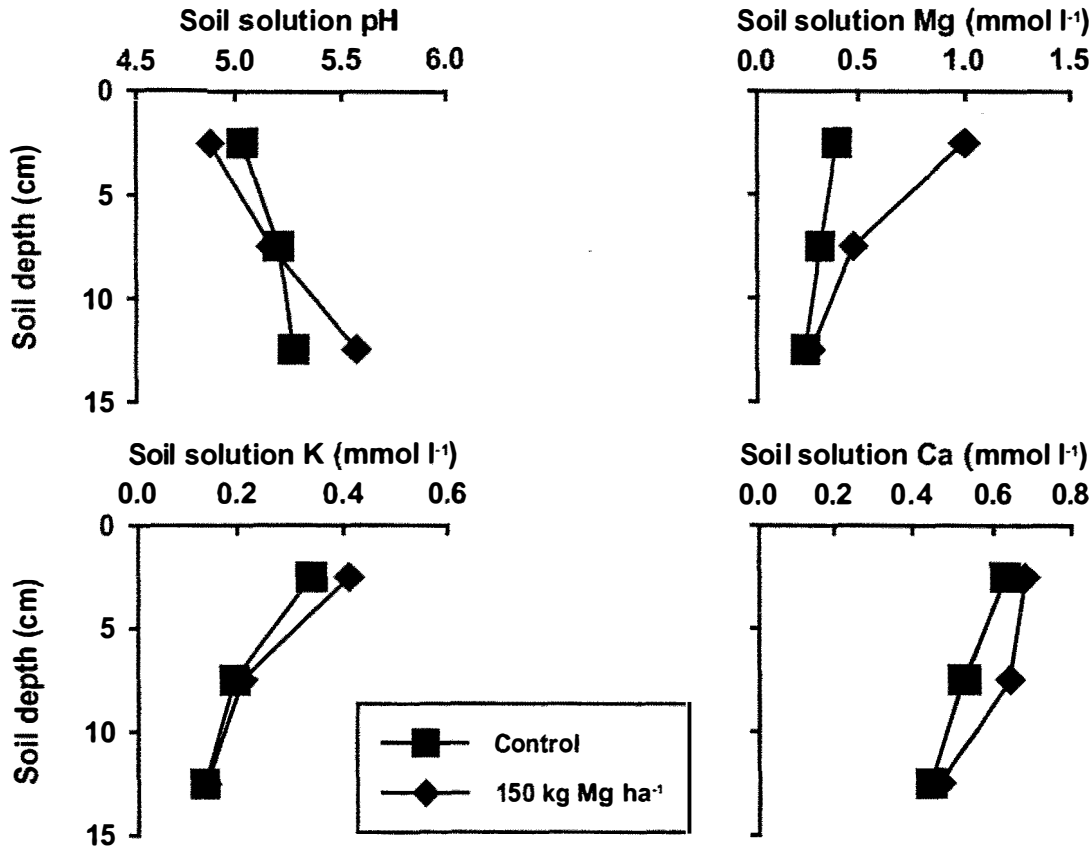

Figure 4.9 Effect of Mg fertiliser application on soil solution cation concentrations at FR190/7 trial.

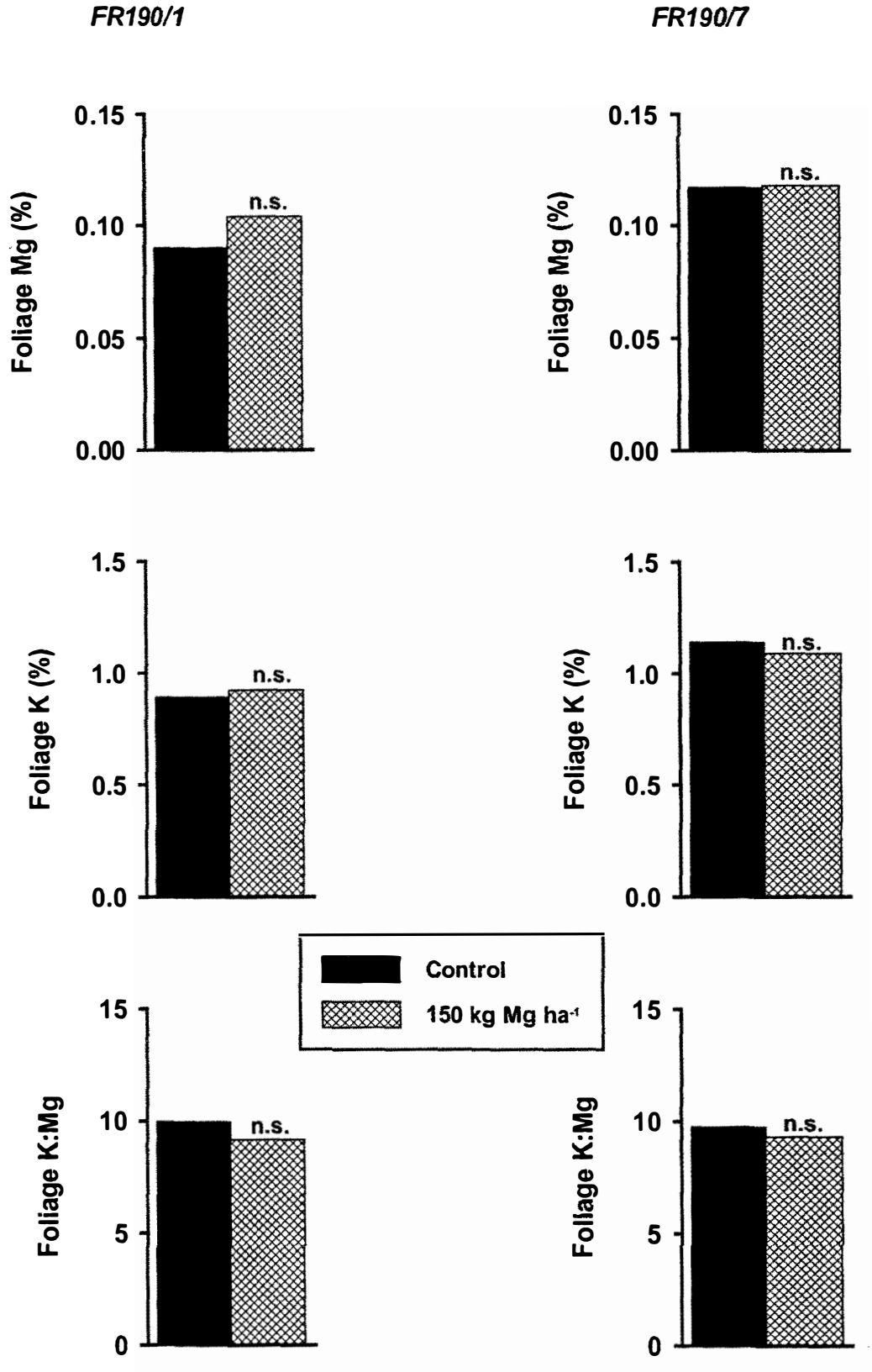

Figure 4.10 Foliar Mg, K and K:Mg in FR190/1 and FR190/7 trials. n.s. - differences not significant.

concentration (Figure 4.10). In addition, foliar Mg concentrations of unfertilised trees at FR190/7 were higher than those at FR190/1, and FR190/4 and FR190/5 reflecting the higher natural concentrations of soil exchangeable Mg at this trial (Figure 4.5). Foliar sampling and analysis was not undertaken at FR190/6. One reason for the absence of significant responses in needle Mg concentration to Mg fertiliser application in all trials studied is probably due to the soil exchangeable Mg concentrations being above the critical exchangeable Mg level of 0.2 $cmol_{(+)}kg^{-1}$ suggested by Will (1961).

The absence of a response to fertilisation by *P. radiata* contrasts strongly with marked increases in exchangeable Mg and soil solution Mg (Figure 4.3, 4.4, 4.5, 4.7, 4.8 and 4.9). These results, with those of Chapter 3, again highlight the apparent slow response of *P. radiata* to elevated soil Mg level through Mg fertiliser application and confirm the earlier findings of Hunter *et al.* (1986), Payn *et al.* (1995) and Hunter (1996).

4.4.9 Effect of Mg fertiliser on foliar K and K to Mg ratio

Magnesium fertiliser application at FR190/1 and FR190/7 had no effect on foliar K concentration (Figure 4.10). At both these trials however, Mg fertiliser application has slightly reduced the foliar K:Mg concentration ratio (Figure 4.10). Once again these findings are similar to the affects observed in Chapter 3.

4.4.10 Correlations between foliage and soil Mg and K concentrations

In FR190/1 and FR190/7, the correlations between foliar Mg and K concentration, and soil Mg and K fractions were generally low and non–significant (Table 4.4). Only the correlation between soil exchangeable K and foliar K:Mg ratio at FR190/1 was found to be significant at $P < 0.1$. Correlations were not improved by considering data from 0-10 cm depth or combining the data sets from these two trials or by combining data from these two trials with data from the two Kaingaroa trials, reported in Chapter 3. A possible reason for the absence of any consistently significant correlations might be due to 90% of foliar Mg concentrations in all four trials (FR190/1, FR190/7, FR190/4 and FR190/5) falling within the narrow range of 0.08 to 0.11% (Figure 4.11). Whereas,

Table 4.4 **Correlation coefficients for linear relationships between various soil (0-5 cm depth) and foliar Mg and K concentrations at FR190/1 and FR190/7 trials**

FR190/1	Soil exch. Mg	Soil exch. K	Soil exch. K:Mg	Solution Mg	Solution K	Solution K:Mg	Foliar Mg	Foliar K:Mg
Soil exch. Mg	1							
Soil exch. K	-0.17	1						
Soil K:Mg	-0.99**	0.24	1					
Solution Mg	-0.96**	-0.17	-0.92**	1				
Solution K	-0.01	0.82*	0.09	0.07	1			
Solution K:Mg	-0.88**	0.40	0.91**	-0.81*	0.39	1		
Foliar Mg	0.36	-0.38	-0.49	0.13	-0.37	-0.41	1	
Foliar K:Mg	-0.55	0.80*	0.65	-0.44	-0.61	0.64	-0.80*	1
FR190/7								
Soil exch. Mg	1							
Soil exch. K	-0.33	1						
Soil K:Mg	-0.84*	0.78*	1					
Solution Mg	0.10	0.21	-0.05	1				
Solution K	-0.26	0.70	0.49	0.80*	1			
Solution K:Mg	-0.51	0.54	0.70	-0.66	-0.15	1		
Foliar Mg	-0.72	-0.36	0.29	-0.46	-0.42	0.33	1	
Foliar K:Mg	0.75	0.36	-0.30	0.33	0.32	-0.21	-0.98**	1

Note: * and ** denotes correlation coefficients statistically significant at $P = 0.1$ and $P = 0.05$ respectively

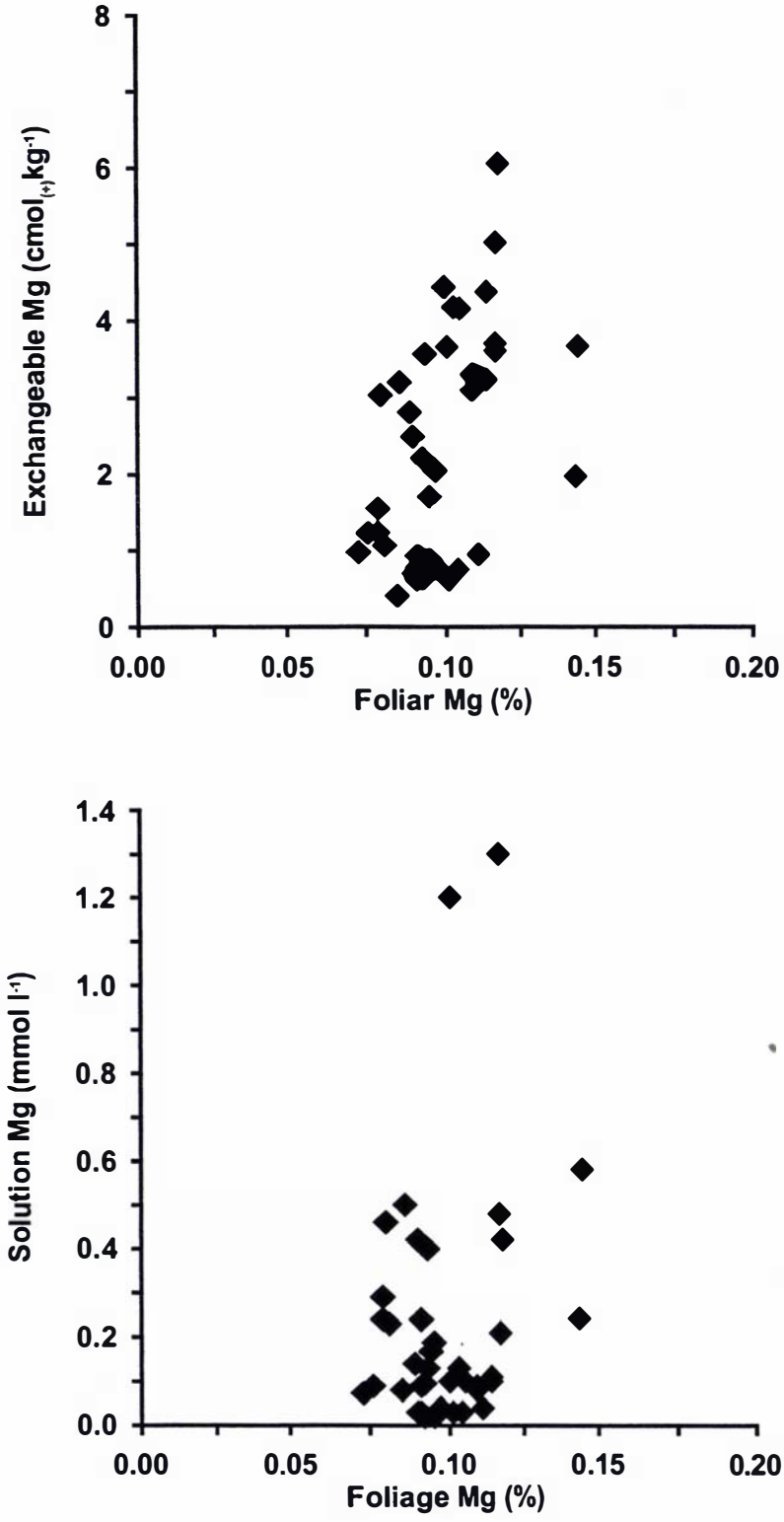

Figure 4.11 Foliar Mg concentrations versus soil exchangeable Mg and soil solution Mg for FR190/1 and FR190/7, and FR190/4 and FR190/5 (Chapter 3).

there was a wider range of exchangeable Mg (0.41 to 6.06 $cmol_{(+)}kg^{-1}$) and solution Mg concentrations (0.08 to 1.30 mmol l^{-1}) recorded for the four trials (Figure 4.11). The correlations were not improved when curvilinear models were fitted to the data. This provides further evidence that the current measures of soil Mg are of little value in predicting foliar Mg levels for a perennial crop like *P. radiata*

4.5 CONCLUSIONS

Results from four of five Mg fertiliser trials on *P. radiata* growing in acidic soils (pH in water of 4.5 to 5.3) in the North Island of New Zealand showed that the rate of Mg fertiliser dissolution varied with rainfall, exchangeable Mg and percent Mg saturation of exchange capacity. In soils with a mean annual rainfall of 1530 mm; exchangeable Mg $\leq$ 0.7 $cmol_{(+)}kg^{-1}$; percent Mg saturation of exchange sites of $\leq$ 3%; more than 95 percent of Mg in calmag fertiliser applied at 150 kg Mg ha^{-1} dissolved in 42 months after application. This compares to the less than 75 percent dissolution in soils with mean annual rainfall of 1190 mm; exchangeable Mg $\geq$ 1.3 $cmol_{(+)}kg^{-1}$; and percent Mg saturation of the exchange sites $\geq$ 11%. The rate of dissolution appeared not to be dependent on soil pH because of the narrow pH range of the soils in these trials. This conclusion should be treated with caution. Only after determining the effects of a wide range of soils with differing Mg status and rainfalls on the rate of dissolution can it be made with any certainty.

Calmag fertiliser application to soils at the rate of 150 kg Mg ha^{-1} was only effective at significantly increasing exchangeable Mg in soils with exchangeable Mg concentrations $\leq$ 1 $cmol_{(+)}kg^{-1}$.

Calculations based on a conservative increase in tree uptake of 9 kg Mg ha^{-1} due to fertiliser application indicate that only 0-20% of the fertiliser Mg had been lost below 10 cm soil layer for all five trials, regardless of the time since fertiliser application.

Calmag fertiliser application increased soil pH in four of the five trials. In general, the extent of increase in pH increased with increases in the rate of dissolution of calmag and decreases in pH buffering capacity of the soils.

The improved Mg fertility of the soil has only resulted in a small but insignificant increase in foliar Mg, even after more than seven years since fertiliser application in one trial and two to three years since application in three other trials. These results further highlight the slow response of *P. radiata* to increased soil Mg concentrations and suggests that for soils where the Mg concentration is high, Mg fertiliser application at 150 kg Mg ha^{-1} may be ineffective at further improving foliar Mg concentrations within two to three years after fertiliser application.

None of the measures of soil Mg produced good correlations with foliar Mg at FR190/1 and FR190/7.

CHAPTER 5

MAGNESIUM FERTILISER DISSOLUTION RATES IN PUMICE SOILS UNDER *Pinus radiata* [1]

5.1 INTRODUCTION

Magnesium deficiency in *P. radiata* can be corrected by the application of Mg fertiliser with time (Will 1961; Hunter *et al.* 1986). However, the effectiveness of most Mg fertilisers in correcting Mg deficiency largely depends on their rates of dissolution in soils. There have been concerns reported in the literature that the slow rate of availability of Mg from fertilisers could be partially responsible for the slow response of *P. radiata* to Mg fertilisation (Hunter 1996). In Chapter 3 and 4 it was shown that calcined magnesite (calmag) applied as 2-5 mm chip at a rate of 150 kg Mg ha^{-1} to forest soils in five sites in the North Island of New Zealand was generally effective in increasing soil exchangeable Mg concentrations. But this fertiliser has not resulted in any significant increases in foliar Mg concentration. Further analysis of soils from these trials indicated that approximately 60-90% of the applied fertiliser had dissolved in the almost two and three and a half years after calmag application. However, these results do not provide any information on the amount of fertiliser dissolved at various times following the fertiliser application, nor any indication of the rate of dissolution of any other Mg fertiliser products currently available.

Dissolution of Mg fertilisers is expected to be influenced by factors such as the composition of the fertiliser, soil acidity, soil moisture, surface area of the fertiliser particle, and diffusion of dissolved constituents away from the fertiliser and protons to the surface of the fertiliser.

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[1]**Mitchell, A. D., Loganathan, P., Payn, T. W., and Tillman, R. W. (2000). Magnesium fertiliser dissolution rates in pumice soils under *Pinus radiata*. *Australian Journal of Soil Research*, 38, 753-767.**

Several of the commonly used Mg fertiliser (e.g. MgO, $MgCO_3$, $CaCO_3.MgCO_3$) are alkaline and have similar reactions in soils to limestone. Therefore, any models developed to describe the dissolution of limestone ($CaCO_3$) could be expected to apply to the dissolution of these Mg fertilisers. To describe limestone dissolution, Elphick (1955) developed the hypothesis of equal reduction, which postulated that the rate of particle-diameter reduction is proportional to the surface area of the limestone particles. From Elphick's work, Swartzendruber and Barber (1965) developed a cubic equation to test this hypothesis. They found that the rate of dissolution of limestone particles followed the cubic equation but the specific fertiliser dissolution rate constant (μg limestone dissolved per cm^2 surface area of limestone particles per day) increased with decreases in particle size. They explained the variation in specific fertiliser dissolution rate constant as probably due to the skewed nature of particle size distribution within a size class.

Laboratory incubation studies conducted on a range of Mg fertilisers of varying particle size, mixed with two Pumice Soils (pH 4.6 to pH 5.1) have shown that the rate of dissolution was in the sequence: Epsom salts ≥ fine calcined magnesite > coarse calcined magnesite, coarse granmag (partially acidulated and granulated calcined magnesite), fine dolomite > fused magnesium phosphate (Loganathan *et al.* 1999). In another incubation study, Heming and Hollis (1995) found that the rate of dissolution of Mg fertilisers added to five soils from the south of England (pH 6.2 to pH 8.2) was in the sequence: kieserite granules (1-3 mm) > calcined magnesite powder (< 1 mm) > calcined magnesite granules (1-3 mm) > magnesian limestone (65% < 1.5 mm and 35% < 150 μm).

However, no long-term studies on determining the rate of dissolution of Mg fertilisers under field conditions have been published to our knowledge. This is probably because the commonly used laboratory method of determining the rate of dissolution of Mg, by measuring the increase in dissolved Mg in soils can not be applied to the field situation where losses of dissolved Mg from the site of application by plant uptake and leaching could lead to errors in determining the amount of dissolved fertiliser. Recently a method has been developed to determine the rate of Mg dissolution by measuring the

amount of undissolved fertiliser Mg remaining in soils and subtracting it from the amount of Mg applied (Loganathan *et al.* 1999). This method is expected to accurately determine the rate of Mg dissolution under field conditions.

5.2 OBJECTIVES

The objectives of the study reported in this chapter were:

1. To compare the rates of dissolution of a range of Mg fertilisers, with and without litter, in a pumice soil under *P. radiata*.
2. To investigate the effect of different forms of Mg fertilisers on soil exchangeable Mg and pH.
3. To test whether Mg fertiliser dissolution can be explained by a cubic model based on the hypothesis of equal reduction.

5.3 MATERIALS AND METHODS

5.3.1 Fertilisers

Fertilisers and their characteristics used in this study are shown in Table 5.1. Calcined magnesite (calmag, MgO) is made by calcining magnesite ($MgCO_3$) to increase the Mg content and to produce a hardened coarser material which is more suitable for blending with other fertilisers and for aerial application. Two particle sizes (1-2 mm and 2-4 mm) of this fertiliser were chosen for this study to investigate the effect of particle size on the rate of dissolution.

Granmag 20™ is a fertiliser made by 20% acidulation of finely divided calmag with H_2SO_4, thereby increasing the water solubility of a portion of the fertiliser Mg and producing a granular material more suitable for blending with other fertilisers and for aerial application (Loganathan *et al.* 1999). Granmag contains both fast release Mg as $MgSO_4$ and slow release Mg as MgO.

Table 5.1 Characteristics of the fertilisers used

Fertiliser	Symbol	Granule size or grade (mm)	Total Mg (%)	Neutralising Power[A] (CaO equivalent per kg fertiliser)	Liming value[B] (CaO equivalent per kg Mg applied)	Price for bagged fertiliser (NZ$/kg Mg)
Calcined magnesite (calmag 1, MgO)	CM1	1-2	51	1.389	2.72	1.0
Calcined magnesite (calmag 2, MgO)	CM2	2-4	51	1.389	2.72	1.0
Granulated calmag 20% acidulation (granmag, $MgSO_4.MgO$)	GM	2-4	34	1.111	3.27	1.8
Dolomite ($CaCO_3.MgCO_3$)	Dol	Forestry[C]	11	0.612	5.56	2.2
Epsom salts ($MgSO_4.7H_2O$)	Eps	<0.25	10	0	0	6.5

[A]Buckman and Brady (1960); for Granmag - 80% of the liming value of CM1 (and CM2) was considered since the 20% $MgSO_4$ component has no liming value. [B]Liming value per kg of fertiliser divided by the fractional weight of Mg in the fertiliser. [C]Particle size distribution: 0.06-0.25 mm 37%; 0.25-0.5 mm 10%; 0.5-1 mm 18%; 1-2 mm 34%; 2-3 mm 1%

Forestry grade dolomite fertiliser consists of a range of particle sizes from very fine (0.06 mm) to coarse (3 mm). A breakdown of the particle size distribution is shown in Table 5.1.

When deciding which fertiliser is best, the fertiliser cost per unit weight of Mg should be considered along with the dissolution characteristics. Of the fertilisers used in this study, Epsom salts was the most expensive per unit weight of Mg and calmag the least expensive (Table 5.1).

5.3.2 Field trial site and soil description

This study was established in Kaingaroa forest (near Rotorua) in the buffer zones of the control plots of FR190/5 trial in compartment 1079. The site is a second rotation stand of 20-year-old *P. radiata* located in northern Kaingaroa Forest and had no history of fertiliser use for at least 20 years. The soil in this trial site belongs to the order Pumice Soils in the New Zealand Soil Classification (Hewitt 1993) and is a member of the Kaingaroa series. It is classified as Typic Udivitrand in US Soil Taxonomy. These soils have developed from rhyolitic flow-tephra deposits from the latter stages of the Taupo eruption (Rijkse 1988), 1800 years BP. The soil (0–10 cm) had a pH in water (1:2.5 w/w soil:water ratio) of 5.6 and organic carbon content of 4.7%. It had exchangeable Mg of 0.6, Ca of 3.4 and K of 0.5 $cmol_{(+)}kg^{-1}$ and effective CEC (exchangeable Mg + Ca + K + Na + Al) of 6.0 $cmol_{(+)}kg^{-1}$.

5.3.3 Field trial establishment

Split plots (2 m by 2 m) with and without litter removed (1 m separating with and without litter plots) were located equidistant from the surrounding trees (Figures 5.1 and 5.2). The trial consisted of five fertiliser treatments (Table 5.1) and a control (no fertiliser) treatment. Each treatment was replicated four times and randomly allocated to the various plots to give a total of 48 plots. Each replicate was located in a different FR trial control plot to give 4 blocks of 12 plots. The as-received fertiliser materials (except for the forestry grade dolomite and Epsom salts) were passed through sieves

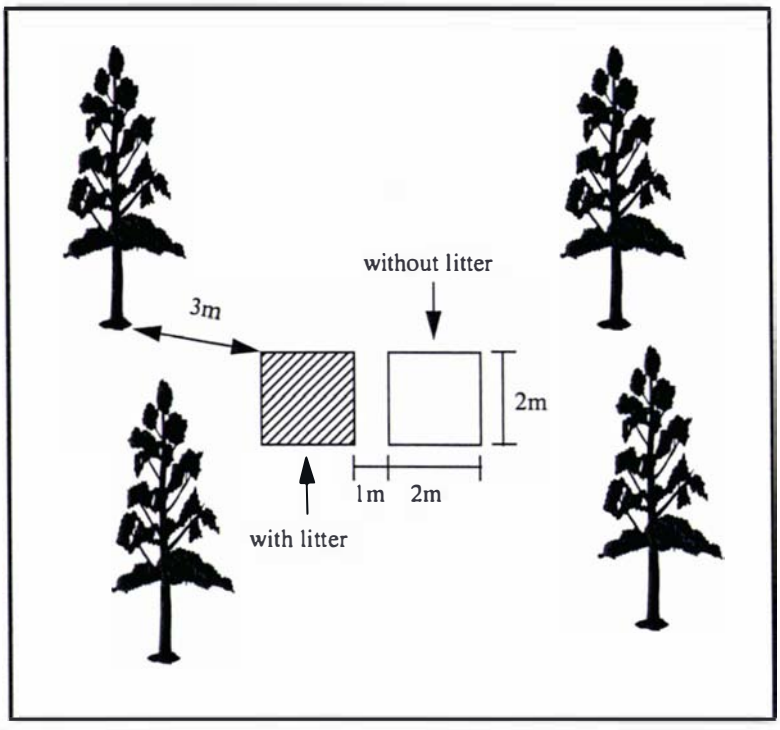


Figure 5.1 Sketch of trial set-up in compartment 1079, Kaingaroa Forest.

Figure 5.2 Trial set-up in compartment 1079, Kaingaroa Forest.

to obtain the specific particle sizes used in this study (Table 5.1). The forestry grade dolomite and Epsom salts were applied in the as-received form. Fertilisers were applied at a rate equivalent to 200 kg Mg ha^{-1}.

5.3.4 Soil sampling and analysis

Soil samples were collected on 20 September 1996, the day after fertiliser application. Eight soil cores (2.5 cm diameter) were taken per plot to a depth of 5 or 10 cm. Soil samples were collected on a regular basis at 3, 6, 12, 18 and 27 months intervals after application of Mg fertilisers. The samplings at 1 day and, 3 and 6 months were collected to a depth of 0-5 cm, the remaining samplings were to a depth of 0-10 cm, as it was believed that the fertiliser might have moved down the soil profile with increased time. The soil samples were air-dried, ground to pass through a 2 mm sieve and analysed for dissolved Mg and undissolved fertiliser Mg using the sequential extraction method of Loganathan *et al.* (1999). In this method the soil samples were extracted with 0.25 *M* $BaCl_2$ – 0.2 M Triethanolamine (TEA) at pH 8.2, to determine apparent Mg dissolution, followed by extraction with 0.5 *M* HCl to determine partially dissolved Mg and finally with 2 *M* HCl to determine undissolved Mg. The amounts of apparent Mg fertiliser dissolution, partially dissolved and undissolved fertiliser Mg in the soils were calculated by subtracting the amounts of Mg extracted by the respective chemicals in the control (no fertiliser) treatment from those in the soils treated with Mg fertilisers. The true dissolution of Mg is determined by subtracting the partially dissolved and undissolved Mg from Mg added in the fertiliser. Soil pH in water (1:2.5 w/w) was also determined (Blakemore *et al.* 1987).

Results were tested for significant differences between treatment means and for interactions among fertiliser source, litter and time of sampling using the analysis of variance statistical package SAS for Windows-Version 6.12 (SAS 1996).

5.3.5 Liming value

The liming value, expressed in terms of the CaO equivalent was calculated for the calmag, Granmag 20™ and dolomite fertiliser treatments by dividing the molecular weight of CaO by the molecular weight of the liming material (MgO or $CaCO_3.MgCO_3$) in the fertiliser (Table 5.1) (Buckman and Brady 1960). This value was used to calculate the liming value of the fertiliser in CaO equivalents expressed per kg of Mg applied. This allows fertilisers of differing composition to be compared on a common basis.

5.3.6 Cubic model of fertiliser dissolution

Swartzendruber and Barber (1965) derived the following cubic equation for the dissolution of limestone assuming that the dissolution follows the equal-reduction hypothesis of Elphick (1955).

$$(1-u)^{1/3} = 1 - ct \qquad (5.1)$$

where:

$$c = 2k/\rho D_g \qquad (5.2)$$

u is the fractional mass dissolution (unit-less), k is the specific limestone dissolution rate constant (μg cm^{-2} day^{-1}), ρ is the particle density (kg m^3) and D_g is the geometric mean particle diameter (mm) and t is time (days). The model assumes that the initial mass of limestone is present in the form of spheres of uniform size, density, and composition, and that the rate of limestone mass dissolution is directly proportional to the total instantaneous surface area of the limestone spheres. The model also assumes that the moisture content of the soil remains constant and that there are always sinks available for the dissolution products. If the equal-reduction hypothesis is valid, a plot of $(1 - u)^{1/3}$ against t should be a straight line of slope $-c$ with an Y intercept of 1. Furthermore, a plot of c *v.* $1/D_g$ should be a straight line through the origin, allowing k to be calculated from the slope of this line.

Dolomite has chemical properties similar to limestone particles, and consequently equation 5.1 could be used to describe the dissolution of this fertiliser.

The rate of oxidation of elemental sulfur (elemental sulfur, S^o) in soils is proportional to the surface area of the sulfur particles. During the last decade cubic equations have been used successfully to describe the rate of S^o oxidation (McCaskill and Blair 1989; Chatupote 1990; Watkinson and Blair 1993; Hedley *et al.* 1995). The dolomite used in this study had a range of particle size fractions and the specific fertiliser dissolution rate constants for this fertiliser, as well as for calmag and granmag were determined using an approach based on the S^o oxidation model derived by Chatupote (1990). This model is able to describe the oxidation of S^o fertilisers with a range of particle size fractions.

The model of McCaskill and Blair (1989) assumed that S^o particles were spheres and that S^o oxidation can be described in terms of the decrease in particle radius (Δr) for each time increment (Δt).

$$\frac{\Delta r}{\Delta t} = \frac{k}{\rho} \tag{5.3}$$

where k is the specific S^o oxidation rate constant and ρ is the density of S^o particles. The radius of particles after t_n days (r_{t_n}) is given by:

$$r_{t_n} = r_{t_0}\left(\frac{S_{t_n}}{S_{t_0}}\right)^{\frac{1}{3}} \tag{5.4}$$

where r_{t_o} is the initial particle radius, S_{t_o} is the initial amount of S^o and S_{t_n} is the amount of S^o remaining after t_n days. As $\Delta r/\Delta t = (r_{t_0} - r_{t_n})/t_n$, Equation 5.4 can be rewritten as follows:

$$\frac{\Delta r}{\Delta t} = \frac{r_{t_0}\left[1-\left(\frac{S_{t_n}}{S_{t_0}}\right)^{\frac{1}{3}}\right]}{t_n} \qquad (5.5)$$

This equation is similar to equation 5.1 of Swartzendruber and Barber (1965) used for limestone dissolution. Chatupote (1990) and Hedley *et al.* (1995) modified this equation and used it with equation 5.3 to develop a computer based iterative procedure for the calculation of k. The iterative procedure requires the user to input an initial estimate for k that fits the S^o oxidation data. The initial estimate of k is used to calculate $\Delta r/\Delta t$ for the observed data using equation 5.3. The amounts of S^o remaining (S_{t_n}) at the end of each day during the trial period are calculated and those relevant to the sampling dates are compared with the observed S_{t_n} values. Using the method of least squares iteration a new estimate is made for k and the iteration continues until changes in $\Delta r/\Delta t$ falls below 0.01% of the r value. The k value at this iteration step is considered to be the specific S^o oxidation rate for the specific fertiliser. The computer program was further modified by Chatupote (1990) and Hedley *et al.* (1995) to take account of S^o fertilisers that consist of a range of particle sizes. The initial geometric mean radius of the particles in each size class was input into the iteration. The constraint here is that the boundaries of each particle class should not differ more than two-fold. The iteration procedure then subtracts Δr from the initial geometric mean radius in each size class to obtain a new mean radius for that size class. This iteration is carried out on a cumulative basis for each day of the trial period. The sum total of all S_{t_n} for all particle sizes is then calculated and compared with measured values. The constant k is calculated in the same way as for a single particle size class as described above. The computer program was used to calculate the Mg fertiliser specific dissolution rate constants in terms of μg fertiliser dissolved per cm^2 of surface area of fertiliser particles per day for the field and laboratory trials.

Using these values for k, the model was used to predict the percent of fertiliser dissolved at various times during the trial, according to the procedure used for determining percentage of S^o oxidation (Hedley *et al.* 1995).

5.3.7 Laboratory incubation of dolomite fertiliser in soils

A laboratory incubation study was undertaken to investigate the effect of particle size on the rate of dissolution of dolomite fertiliser. These data were used to test the effectiveness of the model described by equation 5.1 in explaining the rate of dissolution of the different particle size fractions of dolomite. As-received forestry grade dolomite was passed through sieves of varying fineness to determine its particle size distribution (Table 5.1). A soil sample (0-10 cm) taken from the same site as the field fertiliser dissolution study was air-dried, ground to pass through a 2 mm sieve and sub-samples were used for the incubation study. Three replicates of each size fraction of dolomite fertiliser were mixed with 60 g (oven dry) soil at a rate equivalent to about 200 kg Mg ha^{-1} (10 cm depth of mixing, 700 kg m^3 bulk density). The soil and fertiliser mix were incubated at 60% (w/w) moisture content (approximately field capacity) at 20 ± 2°C. Percentage dissolution (Loganathan *et al.* 1999) was determined at 28, 76 and 120 days after mixing of fertilisers.

5.4 RESULTS AND DISCUSSION

5.4.1 Dissolution of Mg fertiliser in field trial

The percentage of dissolved, and partially dissolved and undissolved (residual) fertiliser Mg, as determined by the sequential extraction method of Loganathan *et al.* (1999), six months after fertiliser application is shown in Figure 5.3. The weakness of the conventional method (Heming and Hollis 1995) of determining Mg dissolution in field trials by only measuring the increases in exchangeable Mg in the fertilised treatments above the control (no fertiliser) treatment can be illustrated using these data. For example, the Epsom salts fertiliser increased the exchangeable Mg by only 20–25% ($BaCl_2$ TEA-Mg in fertilised soil minus those in unfertilised soils). This suggests that between 75-80% of the fertiliser remains undissolved and that Epsom salts have a relatively slow rate of dissolution. This is not true because Epsom salts are highly soluble in water and would have completely dissolved soon after application

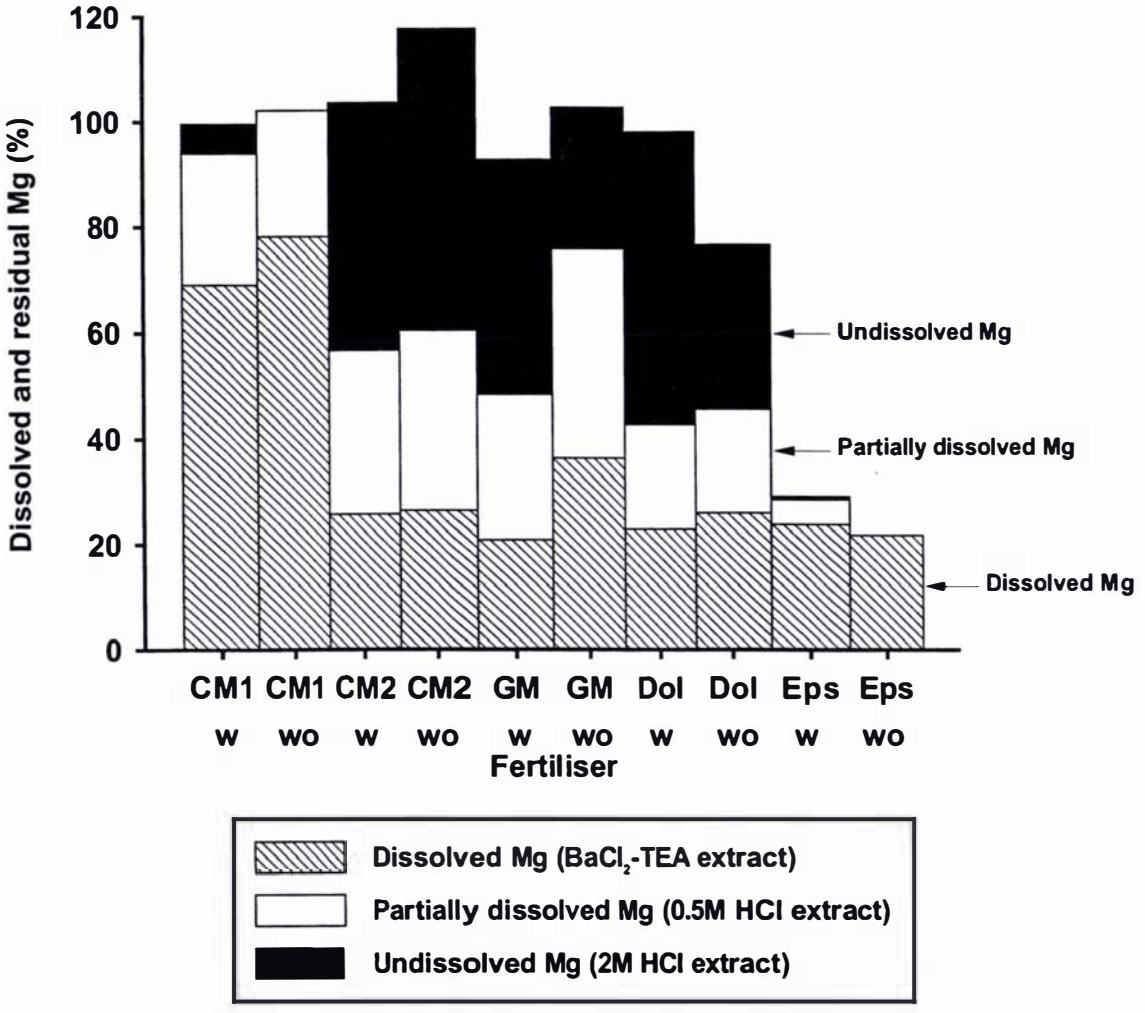


Figure 5.3 Dissolved, partially dissolved and undissolved Mg in the soil as a percentage of Mg fertiliser (200 kg Mg ha^{-1}) six months after application (CM1-calmag 1-2 mm; CM2-calmag 2-4 mm; GM-granmag; Dol-dolomite; Eps-Epsom salts; w-with litter (litter remaining); wo-without litter (litter removed)).

(Loganathan *et al.* 1999). However, the percentage of undissolved (residual) Mg fraction, is < 5%, which confirms that > 95% of Epsom salts have dissolved.

The recovery of approximately 25% of Mg from Epsom salts treatment as dissolved and undissolved fractions suggests that the remaining 75% of applied Mg was lost from the soil layer sampled either by leaching and/or plant uptake. In contrast to Epsom salts, the sequential extraction method was able to recover nearly 100% of the added Mg for

most of the less soluble fertiliser treatments (Figure 5.3). These results indicate that leaching losses are small for the less soluble fertilisers.

Considering the undissolved Mg fractions, significantly ($P < 0.05$) more calmag 1 fertiliser dissolved compared with calmag 2, granmag and forestry grade dolomite fertilisers during the 18 months of the trial (Figure 5.4). As expected, nearly 100% of the soluble Epsom salts dissolved in one day after application. At 27 months after fertiliser application, between 91-100 % of the Mg in Epsom salts, calmag 1 and granmag had dissolved. The corresponding figure for calmag 2 was 82-85% and forestry grade dolomite was 65-72%. However, only dolomite differed significantly ($P < 0.05$) from Epsom salts in terms of percent dissolution after 27 months.

Comparison of the rates of dissolution of calmag 1 and calmag 2 showed that increases in particle size decreases the rate of dissolution. However, although dolomite had a lower geometric mean particle diameter (0.42 mm) than either calmag 1 (1.41 mm) or calmag 2 (2.83 mm), it dissolved much more slowly than either of these two fertilisers. This reflected its much lower solubility. This is in agreement with the calculations of Lindsay (1979), who used equilibrium constants (K°) for the chemical reactions involved in the dissolution of these two fertilisers (Equations 5.6, 5.7 and 5.8) to demonstrate that over a wide range of pHs and log(CO_2 concentration), the concentration of Mg dissolved from MgO (calmag) was about 10^{10} times that from dolomite.

$$MgO + 2H^+ = Mg^{2+} + H_2O \qquad \log K^\circ = 21.74 \qquad (5.6)$$

$$CaCO_3.MgCO_3 + 4H^+ = Ca^{2+} + Mg^{2+} + 2CO_2(g) + 2H_2O \qquad \log K^\circ = 18.46 \qquad (5.7)$$

$$CaCO_3 + 2H^+ = Ca^{2+} + CO_2(g) + 2H_2O \qquad \log K^\circ = 9.74 \qquad (5.8)$$

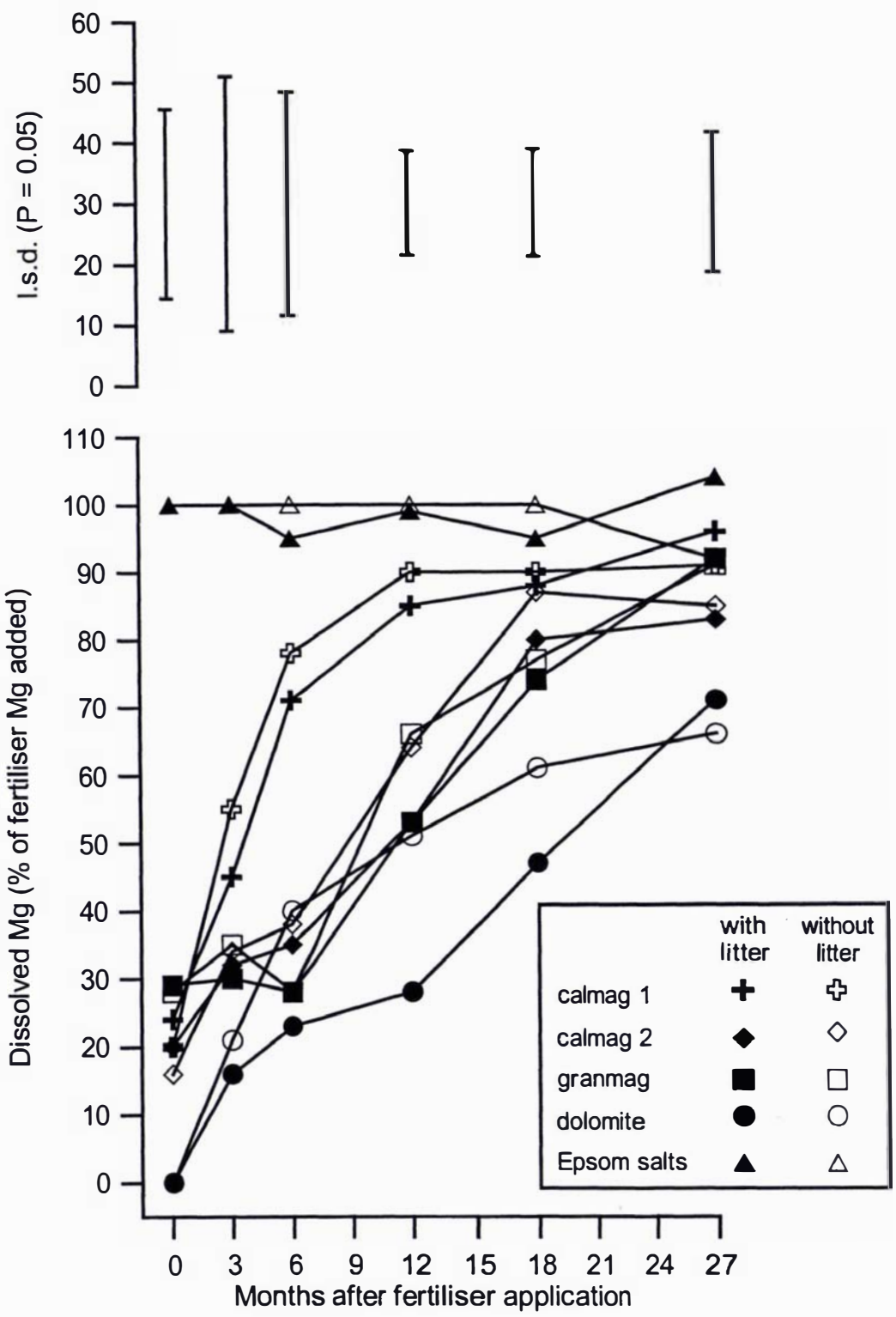


Figure 5.4 Rates of dissolution of Mg fertilisers applied at 200 kg Mg ha^{-1}.

When fertilisers are applied to soil after removing litter they have direct contact with the soil. This helps the soil exchange complex to act as a sink for the dissolution products of the fertilisers (Mg and Ca) and also provides protons for reacting with the fertilisers, thereby increasing the rate of dissolution compared to when fertilisers are applied on to the litter layer. However, the results of this study showed that there was no significant difference ($P < 0.05$) in the amount of Mg fertiliser dissolved between plots with and without litter (Figure 5.4). Only for the dolomite treatment at the 12 month sampling, was the difference between with and without litter plots close to statistical significance at $P = 0.05$. There was no significant ($P < 0.05$) interactions between either litter treatments and time of sampling or litter treatments, fertiliser source treatments and time of sampling.

5.4.2 Soil exchangeable Mg in field trial

All fertiliser treatments except Epsom salts, significantly increased soil exchangeable Mg above the no-fertiliser control treatment, for 12 and 27 months after application (Table 5.2). The increase in soil exchangeable Mg generally follows the rate of dissolution of the fertilisers except for the highly soluble Epsom salts treatment, where the dissolved Mg may have been lost by leaching (Table 5.2, Figure 5.4). In addition, the pH of soils treated with Epsom salts is lower than the pH of soils treated with other fertilisers (Table 5.2, Figure 5.5). Therefore the negative charge density of the soil colloids in the Epsom salts treatment was lower. This would have given rise to lower amounts of Mg retained by the soil and hence greater leaching of Mg in the Epsom salts treatment. The results suggest that soluble Mg fertilisers may not be effective in providing an increased supply of plant-available Mg for a long- period in pumice soils at Kaingaroa Forest. The cost per unit weight of Mg is also much higher for soluble Mg fertilisers (eg Epsom salts, Table 5.1) and this further discourages their use in forestry.

5.4.3 Fertiliser effects on soil pH in field trial

The results show that calmag 1, calmag 2, granmag and dolomite fertiliser treatments have significantly ($P < 0.05$) increased soil pH over the control treatments from six

Table 5.2 **Fertiliser dissolution rate constants calculated using Chatupote's (1990) model andsoil exchangeable Mg and pH (soil depth 0–10 cm) at 12 and 27 months**

Fertiliser symbol	Dissolution rate constant for the "with-litter" plots ($\mu g\ cm^{-2}\ day^{-1}$ of fertiliser)[A]	Exchangeable Mg		Soil pH	
		12 months	27 months	12 months	27 months
		($cmol_{(+)}kg^{-1}$)			
CM1	587	2.62	2.58	5.48	5.52
CM2	426	1.73	1.92	5.51	5.53
GM	385	2.48	2.18	5.51	5.67
Dol	18	1.44	2.18	5.52	5.68
Eps	n.a.	0.73	1.04	5.33	5.41
Control	n.a.	0.65	0.61	5.10	5.30
L.s.d. (P = 0.05)		0.58	1.08	0.22	0.20

[A] Particle density of 3500 kg m^3 for CM1, CM2 and GM and 2800 kg m^3 for Dol used in model calculations.

n.a.; not applicable

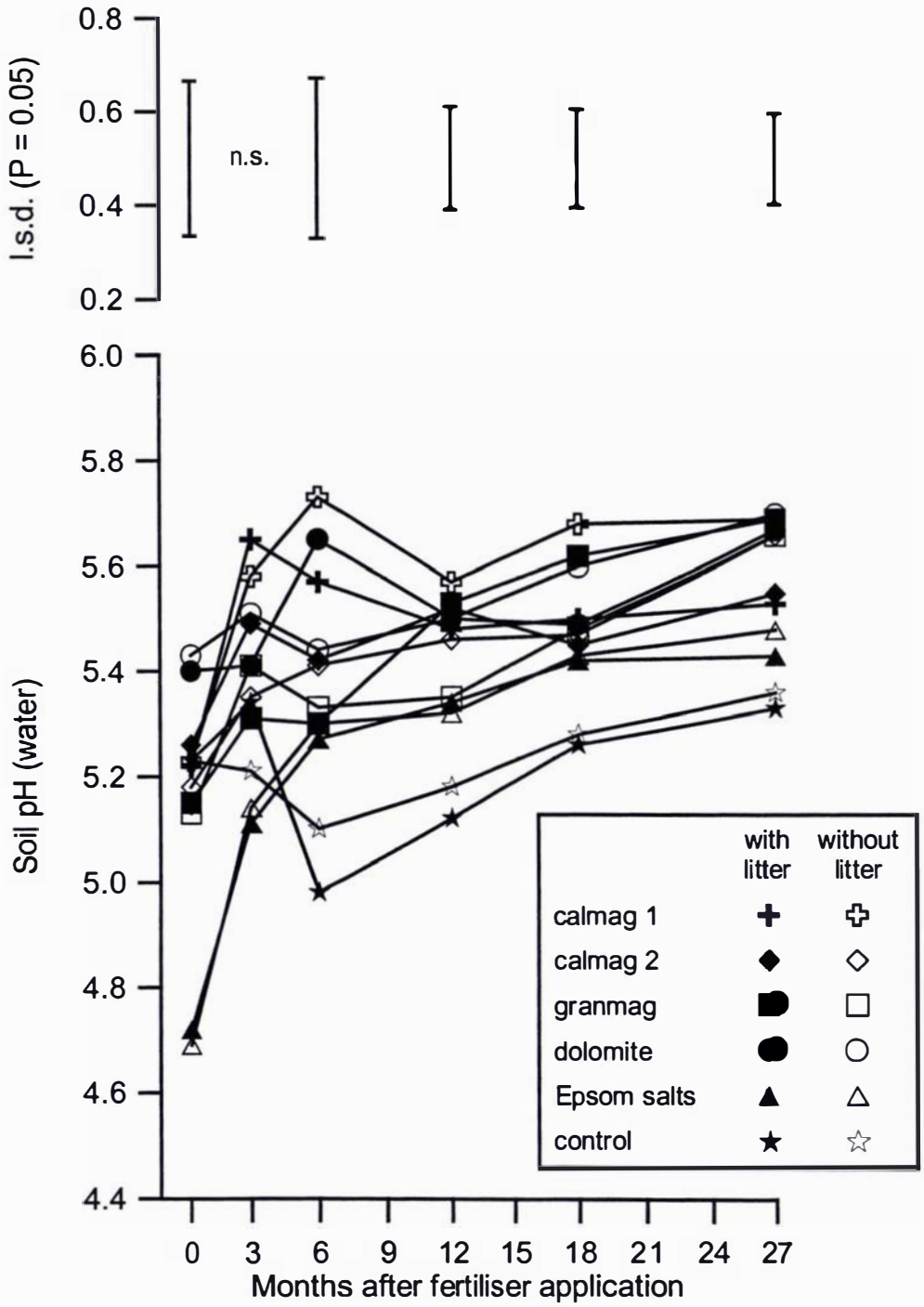


Figure 5.5 Effect of Mg fertilisers applied at 200 kg Mg ha^{-1} on soil pH, n.s. - no significant differences.

months onwards (Table 5.2, Figure 5.5). This is due to the alkalinity of these fertilisers. Generally, the increases in soil pH reflected the higher rates of fertiliser dissolution except for the dolomite treatment (Table 5.2, Figure5.4). Despite the lower percentage dissolution, the dolomite treatments resulted in increases in soil pH similar to the calmag and granmag treatments. This is due to the higher liming value of dolomite relative to its Mg content (Table 5.1). For the sampling immediately after application, the Epsom salts treatment resulted in a significant ($P < 0.05$) decrease in measured soil pH compared to the calmag, granmag, dolomite and control treatments. This is a consequence of measuring soil pH in H_20. The Epsom salts would have increased the ionic strength to cause a reduction in measured soil pH. With increases in time this effect disappeared because most of the dissolved Epsom salts was probably lost by leaching.

5.4.4 Modelling fertiliser dissolution rates

5.4.4.1 Laboratory trial

Plots of $(1 - u)^{1/3}$ versus time (Equation 5.1) (Swartzendruber and Barber 1965) for the range of dolomite size fractions tested in the laboratory incubation study are shown in Figure 5.6a. Although, there are a limited number of samplings and very little of the coarser size fractions (1-2 and 2-3 mm) has dissolved, the data points seem to fit to straight line relationships, as predicted by the cubic model. The results suggest that, within each size class, the rate of dissolution of dolomite over time was controlled by the changing surface area of the particles (Figure 5.6a).

When several size classes (different D_g values) were considered together and c versus $1/D_g$ (Equation 5.2) was plotted (Figure 5.6b), the data points did not fall on a straight line passing through the origin as the equation specified, but curved upwards as $1/D_g$ increased (particle size decreased). The slopes of straight lines drawn from the origin through each data point increased consistently with increases in $1/D_g$, instead of remaining constant. For example, the slope for the 2-3 mm particles is 10% of that for the 0.5-1.0 mm particles. Thus, like Swartzendruber and Barber (1965) reported,

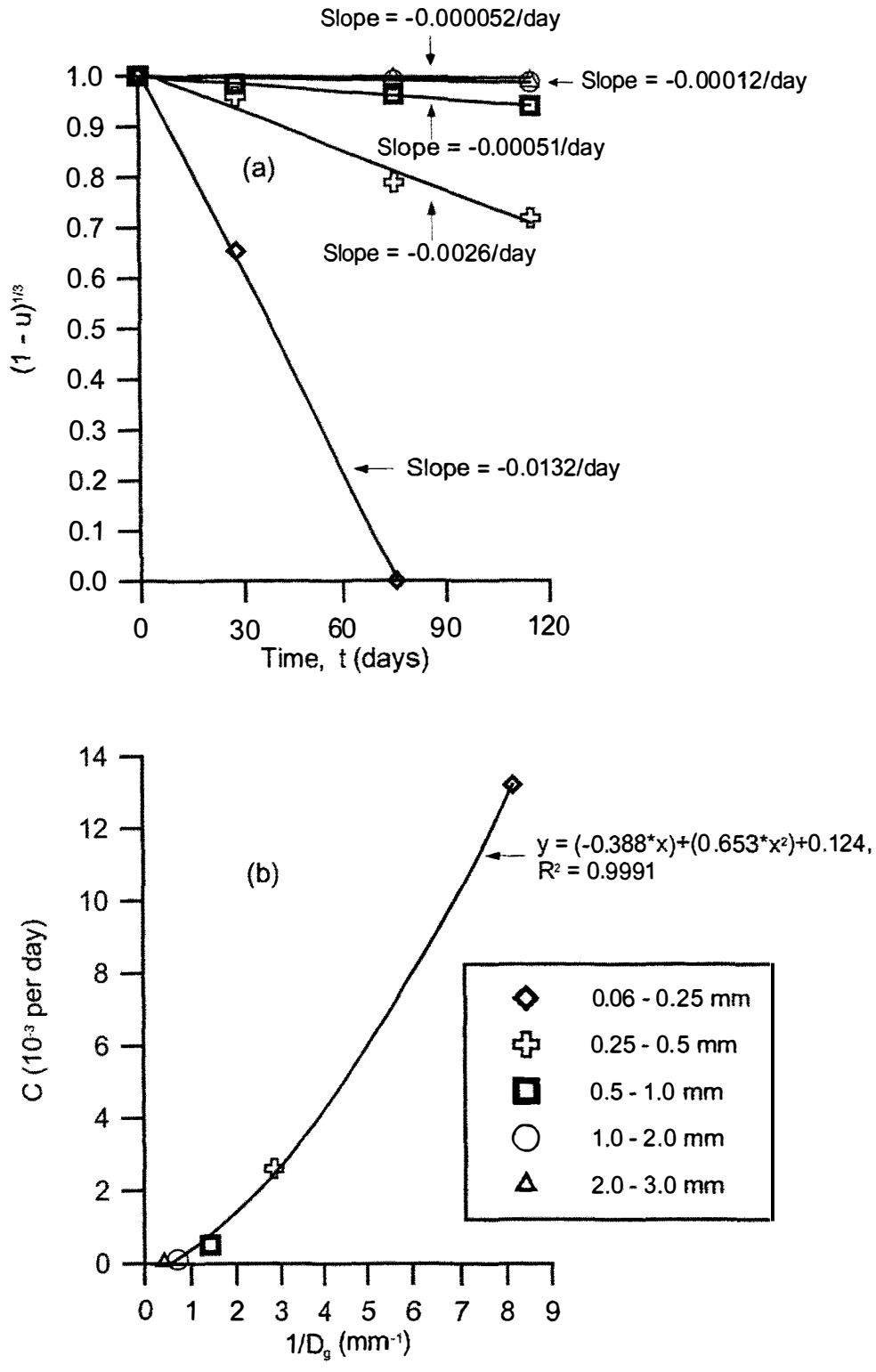


Figure 5.6 (a) Fit of laboratory incubation data to the cubic model of Swartzendruber and Barber (1965) and (b) the slopes of the fitted lines versus geometric means for the five different size fractions of forestry grade dolomite.

the specific fertiliser dissolution rates calculated from the slopes and particle density of dolomite (2800 kg m^3) (Equation 5.2) increased with decreases in particle size (Table 5.3).

Specific fertiliser dissolution rate constants (Table 5.3) for each size fraction as calculated by the computer model of Chatupote (1990) also increased with decreases in particle size. The relationship between the rate constants calculated by the models of Chatupote (1990) (k_1) and Swartzendruber and Barber (1965) (k_2) can be described by the regression equation of $k_1 = 1.05*k_2 - 4.85$, (R^2=0.995, number of data sets 5).

The change in k with fertiliser particle size observed for both Swartzendruber and Barber (1965) and Chatupote (1990) models predictions could be due to a number of reasons. The chemical composition (25% Ca and 11% Mg) and mineralogy (only calcite and dolomite identified by x-ray diffraction) of the dolomite did not vary between particle size classes. These factors do not explain the variability in k. Swartzendruber and Barber (1965) suggested that the variation of k with particle size may be due to the geometric mean of the particle sizes (D_g) not being a representative measure of the range of diameters of the limestone particles within each size fraction. The change in k with fertiliser particle size could also be due to the rate of dissolution of the fertilisers not obeying the zero-order kinetics assumed in the models.

Factors other than surface area of the fertilisers, such as soil pH, soil pH buffering capacity, Ca and Mg concentrations in soil solution and the exchange complex may be changing differentially among the different particle size classes as the particles dissolve. For example, consider two fertiliser particle size classes where the sum total surface area for the small and large fertiliser particles is the same. Then, for the smaller particles, the sum total soil volume surrounding the fertiliser particles, where diffusion gradients of the fertiliser dissolution products (Mg, Ca) and protons between soil solution and the fertiliser particles surface (diffusive volume) exist, is proportionally larger than that for the larger fertiliser particles. If we assume that the fertiliser particles are spherical and diffusion gradients in the soil extend to a distance of 1 mm from the surface of the fertiliser particles, then, a simple calculation would show that the

Table 5.3 Dissolution rate constants for dolomite size fractions investigated in the laboratory incubation study as calculated by (A) the computer based cubic model for S^o oxidation of Chatupote (1990) and (B) the cubic model for limestone dissolution of Swartzendruber and Barber (1965)

Dolomite size fraction	Specific fertiliser dissolution rate constants	
	A	B
(mm)	($\mu g\ cm^{-2}\ day^{-1}$ of fertiliser)	
0.06 - 0.25	239	226
0.25 - 0.5	119	129
0.5 - 1.0	49	50
1.0 - 2.0	22	24
2.0 - 3.0	18	18

diffusive volume in the soil for fertiliser particles of 0.25 mm diameter is 26 times higher than that for 2.0 mm diameter particles. Therefore, there would be a proportionally greater number of sinks for dissolution products and a larger source of protons available in the soil for the smaller fertiliser particles compared to the larger particles. This would increase the specific dissolution rate for the smaller particles.

Any future work on the modelling of Mg fertiliser dissolution should consider both fertiliser and soil properties. A model similar to the mechanistic model developed by Kirk and Nye (1986) and modified by Bolland and Barrow (1988) to explain phosphate rock dissolution could be developed.

5.4.4.2 Field trial

The order of fertiliser dissolution in the field trial was generally reflected in the specific dissolution rate constants generated by the cubic model (Chatupote 1990) (Figure 5.7, Table 5.2). Specific fertiliser dissolution rate constants for the "with-litter" plots ranged from 587 μg cm^{-2} day^{-1} of fertiliser for calmag 1 to 18 μg cm^{-2} day^{-1} of fertiliser for dolomite. There was little difference in the rate constants calculated for calmag 1 and calmag 2 (587 and 426 μg cm^{-2} day^{-1} of fertiliser respectively) suggesting that the rate at which a fertiliser dissolved expressed in terms of unit surface area of the fertiliser particle was predominantly independent of fertiliser particle size within 1–4 mm size range. The granmag dissolution during the six months after application was higher than that predicted by the computer model. This is due to the fast–release of Mg from the readily

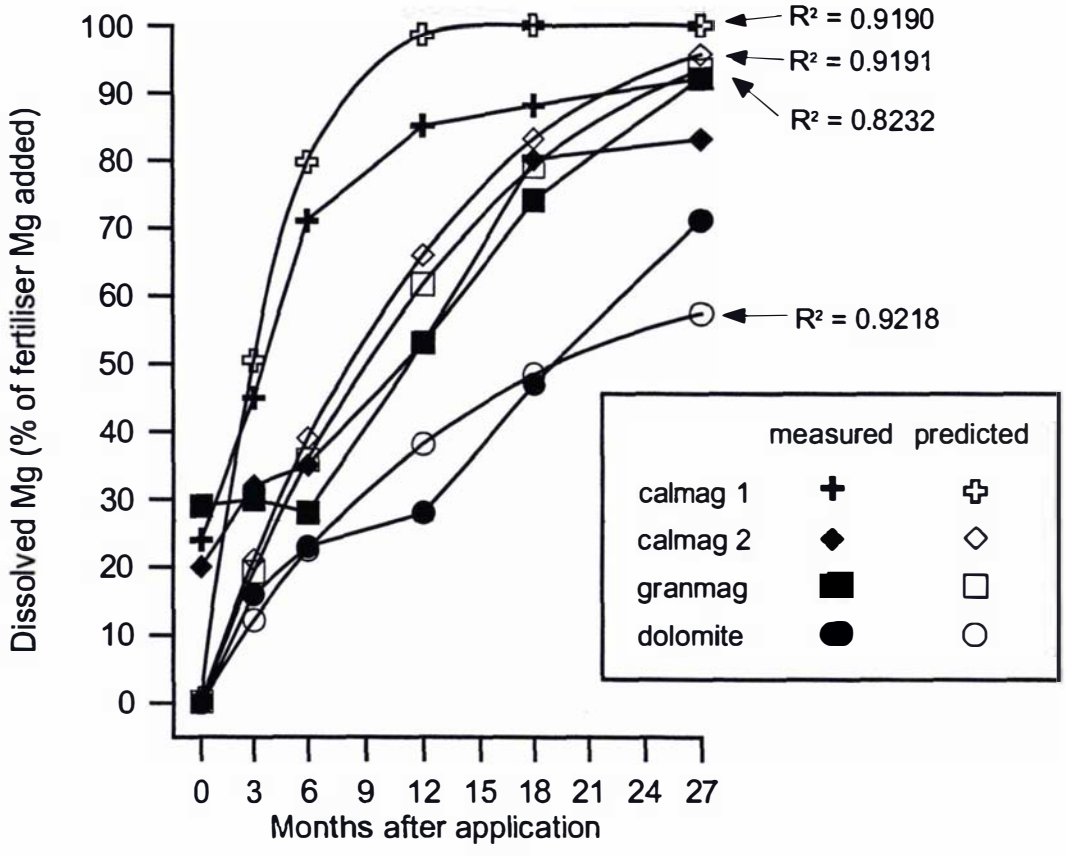


Figure 5.7 Predicted and measured rates of dissolution of Mg fertilisers applied at 200 kg Mg ha^{-1} for the 'with-litter' plots.

soluble $MgSO_4$ component in granmag. However, the overall dissolution rate constant of 385 μg cm^{-2} day^{-1} of fertiliser was similar to that of the calmag fertilisers reflecting the dissolution characteristics of the unacidulated MgO in the granmag fertiliser (Table 5.2, Figure 5.7). Dolomite had the lowest dissolution rate constant of 18 μg cm^{-2} day^{-1} of fertiliser because of differences in its chemical composition compared to calmag and granmag fertilisers (Equation 5.6, 5.7, and 5.8).

5.5 CONCLUSIONS

In Pumice Soils under *P. radiata* the rates of Mg fertiliser dissolution after 27 months followed the sequence: Epsom salts > calcined magnesite (1-2 mm) > granmag > calcined magnesite (2-4 mm) > forestry grade dolomite (0.06-3.00 mm; geometric mean 0.42 mm). The rate of dissolution depended on the particle size of the fertiliser and increased with decreases in particle size. The rate of fertiliser dissolution was little affected by whether fertiliser is applied directly on to the soil surface (litter removed) or on to the forest litter layer.

The alkaline, slowly soluble Mg fertilisers (calcined magnesite, granmag and dolomite) have a significant liming effect on the soil. Dolomite with its highest liming value relative to its Mg content has a proportionally greater effect on soil pH than the other fertilisers, despite a slower overall dissolution rate. The slowly soluble Mg fertilisers are more effective in increasing soil exchangeable Mg over a long-period than the easily soluble and more expensive (per unit weight of Mg) Epsom salts. Therefore, the slowly soluble fertilisers are more suitable for *P. radiata* except where trees are severely deficient in Mg, where more soluble fertiliser like Epsom salts may be considered.

A computer program based on an S oxidation cubic model can explain the rate of dissolution of Mg fertilisers within a narrow fertiliser particle size range but fails when a wide range of particles sizes are considered. The specific fertiliser dissolution rate constant (μg cm^{-2} day^{-1} of fertiliser) increases with decrease in particle size suggesting that the rate of dissolution depends on factors other than surface area when particle size varies widely.

CHAPTER 6

PLANT INDUCED CHANGES IN MAGNESIUM AVAILABILITY IN THE RHIZOSPHERE OF *Pinus radiata* SEEDLINGS FERTILISED WITH VARIOUS FORMS AND RATES OF MAGNESIUM AND POTASSIUM FERTILISERS

6.1 INTRODUCTION

Magnesium availability to *P. radiata* is affected by soil type, ionic imbalances, leaching losses of Mg and by the uneven distribution of plant-available Mg in the root zone. Application of Mg fertilisers has been suggested as a means of improving the Mg availability to *P. radiata.* However, it has been reported that *P. radiata* is slow to respond to Mg fertiliser application (Hunter *et al.* 1986; Hunter 1996; Payn *et al.* 1995) and this could be due to the slow availability of Mg from fertilisers (Hunter 1996). But the results from Mg fertiliser trials reported in Chapter 3 suggested that, about 90% of Mg in slowly-soluble calcined magnesite (calmag) fertiliser became plant available (soil exchangeable Mg) in the soils within two years of application. This indicates that the rate of release of Mg from fertilisers is rapid. Therefore, this should not be limiting tree uptake. In Chapters 3 and 4 it was reported that the application of calmag fertiliser to a range of soils was very effective at increasing soil exchangeable Mg within two to three and a half years, particularly where natural concentrations of soil exchangeable Mg were low to medium. However, analysis of *P. radiata* foliage from these trials shows that increases in concentration of soil exchangeable Mg due to fertiliser application has not resulted in any significant increases in foliar Mg concentrations. This further indicates, as Schaaf (1997) has suggested for Norway spruce (*Picea abies*), that *P. radiata* is inefficient, and/or slow in responding to the increased concentrations of soil Mg.

Leaching losses of Mg have also been cited as reasons for the slow response of *P. radiata* to Mg fertiliser application (Will 1961; Hunter 1996). But the results presented

in Chapter 3 showed that leaching losses of Mg from the top 10 cm of soil after calmag application were very low, estimated at between 3-11% of applied fertiliser Mg. Even though fertiliser application increased bulk soil Mg, it is not known whether this increase is also reflected in the soil at the root-soil interface. The root-soil interface is commonly called the rhizosphere and is the narrow soil cylinder (about 0-2 mm radius) that surrounds the root. The rhizosphere soil is the region of soil where uptake of nutrients takes place.

There is considerable evidence in the literature to show that usually the chemistry of the root-soil interface is considerably different from and has a greater influence on plant growth, than that of the bulk soil (Kuchenbuch and Jungk 1982; Youssef and Chino 1988; Youssef and Chino 1989; Gijsman 1990a; Gijsman 1990b; Zoysa *et al.* 1997; Zoysa *et al.* 1998). Many of the previous studies of plant rhizospheres have concentrated on soil pH changes, in relation to the bulk soil, as affected by the nitrogen nutrition and cation-anion balance within the plant (Nye 1981; Youseff and Chino 1989; Gijsman 1990a; Gijsman 1990b; Haynes 1990). Other studies have concentrated on P depletion patterns in the rhizosphere of a range of plants (Youssef and Chino 1989; Gahoonia and Nielson 1991; Hedley *et al.* 1994; Wang *et al.* 1995; Zoysa *et al.* 1997; Zoysa *et al.* 1998). However, there has been very little research to date on cation chemistry of plant rhizospheres and of particular interest to foresters in New Zealand, studies of the behaviour of Mg in the rhizosphere of *P. radiata.*

Changes in the rhizosphere chemistry may be influencing the uptake of Mg by *P. radiata.* In order to better understand the Mg chemistry in the root zone of *P. radiata,* a study investigating the effects of *P. radiata* seedlings on the Mg chemistry of rhizosphere soil was undertaken using rhizosphere study containers (RSC) as described by Kuchenbuch and Jungk (1982) and Hedley *et al.* (1994), and further modified by Zoysa *et al.* (1997). The study used a Pumice Soil (0-10 cm) amended with a range of Mg fertilisers and *P. radiata* GF16 seedlings. As a consequence of the results from the first study, a second study was carried out using soil from 10-20 cm of the same Pumice Soil that has a lower pH buffering capacity and lower exchangeable Mg concentrations. In the second study, the soils were amended with two rates of Mg fertiliser. As mentioned previously in Chapters 2 and 3, K and the K:Mg ratio have been implicated

as contributing factors in Mg deficiency in *P. radiata*. Therefore, a K and a Mg plus K fertiliser treatments were also included in the second study.

6.2 OBJECTIVES

The objectives of the investigation reported in this chapter are:
To determine the plant induced changes in soil exchangeable Mg and K, and soil pH in the rhizosphere of *P. radiata* seedlings and to measure the Mg uptake by the seedlings:

1. When fertilised with different forms of Mg fertiliser (Experiment 1).
2. When fertilised with different rates of K_2SO_4 and $MgSO_4.7H_20$ (Experiment 2).

6.3 MATERIALS AND METHODS

A Pumice Soil (0-10 cm and 10-20 cm depth) from the control plots of FR190/5, compartment 1079, Kaingaroa Forest (near Rotorua), and described in Chapter 3 was used in these studies. The properties of the soils are presented in Table 6.1 and appendix 1.

6.3.1 Experiment 1

The fertilisers used in Experiment 1 were calcined magnesite (calmag, MgO), Granmag 20™ (20% acidulated and granulated calmag, granmag, $MgO.MgSO_4$), dolomite ($CaCO_3.MgCO_3$), and Epsom salts ($MgSO_4.7H2O$). All fertilisers had particle sizes within the range 0.25-0.50 mm (granmag granules were ground to this particle size). Soil from 0-10 cm depth was air dried and ground to pass through a 2 mm sieve and mixed with the fertilisers at a rate of 75 mg Mg kg^{-1} soil (equivalent to about 53 kg Mg ha^{-1}; soil depth of 10 cm at a bulk density of 760 kg m^3).

Table 6.1 Characteristics of soils used

Property (unit)		
Pedology details		
NZ Soil Classification[A]	Pumice Soil	
Soil type[B]	Kaingaroa loamy sand	
US Soil Taxonomy	Typic Udivitrand	
Selected soil chemical properties		
Depth (cm)	0-10	10-20
pH (water)	5.6	5.9
pH buffering capacity	36	20
(mmol H^+ kg^{-1} pH^{-1})		
Total C (%)	9.1	2.7
Total N (%)	0.4	0.1
Exchangeable cations		
($cmol_{(+)}kg^{-1}$)		
Mg	0.6	0.2
K	0.5	0.4
Ca	3.4	2.2
Al	1.8	0.8
ECEC ($cmol_{(+)}kg^{-1}$)[C]	6.0	3.7

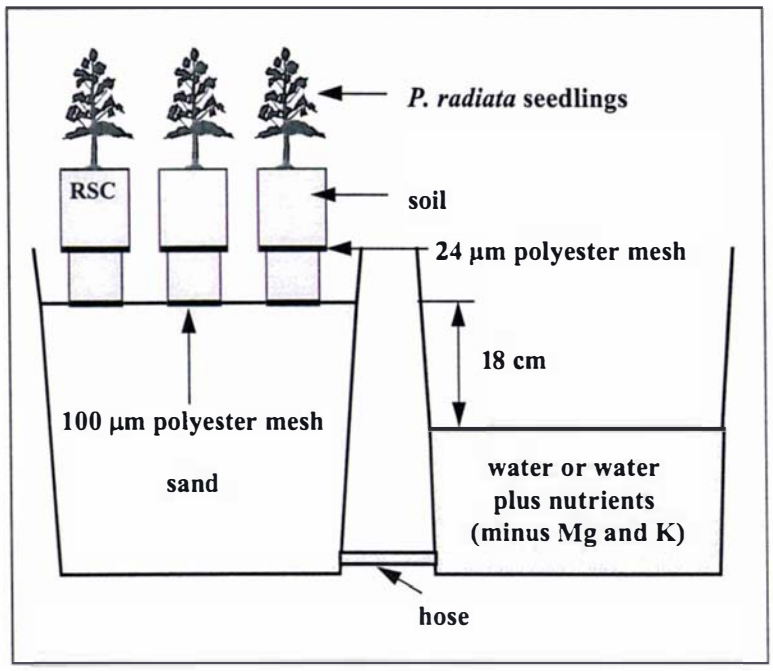
[A] Hewitt (1993), [B] Rijkse (1988), [C] Exchangeable bases plus exchangeable Al, Blakemore *et al.* (1987)

A RSC technique as used for tree crops by Zoysa *et al.* (1997) was used in this study. The RSC technique involves growing a plant in containers that consist of two compartments made-up of two (PVC) cylinders, the upper and lower compartments having an internal diameter of 75 mm. The upper compartment has a depth of 70 mm and the lower compartment a depth of 50 mm. A 24 μm pore-diameter polyester mesh separates the two compartments. The upper and lower compartments were packed with 220 g and 170 g of soil (equivalent to bulk densities of about 760 kg m^3) respectively. Two-month-old GF16 *P. radiata* seedlings were transplanted into the upper compartments of the RSCs (one seedling per container) (Figure 6.1a). Plant roots in the upper compartment striking the mesh were unable to penetrate the mesh and grew horizontally along the mesh forming a root mat. Therefore, the soil immediately below the polyester mesh represents the rhizosphere and the zone of transition demarcating the bulk soil. The RSCs were placed on top of a series of sand baths, which were kept moist by a water reservoir (Figures 6.1a and b) The water table was maintained at 180 mm below the base of the RSCs. This allowed the soil within the RSCs to be kept at constant water potential of approximately -1.8 kPa.

The experiment consisted of four fertiliser treatments and a no-fertiliser treatment. The treatments were replicated five times and the RSC container were arranged in a completely randomised block design in a glass house maintained at 26° C. maximum and 15° C. minimum.

Four RSCs without seedlings and fertilisers were also included in this experiment to allow approximate values for seedlings transpiration to be calculated.

(a)



(b)

Figure 6.1 (a) Schematic representation of the root study container (RSC) technique and (b) experimental setup in the glasshouse.

6.3.2 Experiment 2

The RSC technique used in Experiment 1 was repeated in Experiment 2 but with soil from 10-20 cm depth. The soils were treated with two fertilisers at a range of application rates. The fertilisers and rates used were as follows:

Epsom salts: (Treatments 1 and 2)	37.5 and 75 mg Mg kg^{-1} soil (equivalent to about30 and 60 kg Mg ha^{-1} respectively; soil depth of 10 cm at a bulk density of 800 kg m^3).
Potassium sulfate: (Treatment 3)	150 mg K kg^{-1} soil (equivalent to about 120 kg K ha^{-1}; soil depth of 10 cm at a bulk density of 800 kg m^3).
Epsom salt and Potassium sulfate: (Treatment 4)	75 mg Mg kg^{-1} soil and 150 mg K kg^{-1} soil (equivalent to about 60 kg Mg ha^{-1} and 120 kg K ha^{-1}; soil depth of 10 cm at a bulk density of 800 kg m^3).

A no-fertiliser treatment (with seedling) (Treatment 5) was also included.

The upper compartment was packed with 228 g of soil and the lower compartment was packed with 185 g of soil (equivalent to a bulk density of about 800 kg m^3). The four fertiliser treatments and the no-fertiliser treatment were replicated five times and arranged in a completely randomised block design in a glass house maintained at 26° C. maximum and 15° C. minimum. Four RSCs without seedlings and fertilisers were also included to allow approximate values for seedlings transpiration to be calculated, as in Experiment 1. Root study containers were watered with an otherwise complete, but without K and Mg, nutrient solution (Middleton and Toxopeus 1973) via the sand bath watering system, so essential plant nutrients other than Mg and K were not limiting seedling growth (Table 6.2).

Table 6.2 Ion concentrations in solution used to water the RSCs in the second rhizosphere study (Middleton and Toxopeus 1973)

Macro nutrient (mmol l^{-1})		**Micro nutrient** (μmol l^{-1})	
NO_3^-	3.4	H_3BO_3	3.9
NH_4^+	3.4	Co^{2+}	0.1
$H_2PO_4^-$	1.1	Cu^{2+}	0.3
SO_4^{2-}	0.6	Mn^{2+}	6.1
Ca^{2+}	1.4	MoO_4^{2-}	0.1
Mg^{2+}	0	Zn^{2+}	0.5
K^+	0	Fe^{2+}	0.01

6.3.3 Height and transpiration measurements

Seedling heights were measured at the start of both experiments and at regular intervals during the course of both experiments. The transpiration of the seedlings was estimated at regular intervals by removing the RSCs from the sand baths and measuring the change in weight due to water loss over a 24-hour period. The water loss due to the seedlings was calculated by subtracting the mean weight change for the RSCs without seedlings from the weight change of each of the RSCs with seedlings.

6.3.4 Soil and plant sampling

6.3.4.1 Experiment 1

Experiment 1 was ended 75 days after transplanting of seedlings into RSCs and seedling heights were measured. Seedlings were cut 2 mm above the soil and the

weights recorded after drying at 70^{O} C. The soil in the lower compartment was then sliced into thin sections using a piston microtome starting at the inter-compartment boundary (24 μm polyester mesh) (Figures 6.2a and b). The first six sections were sliced at 0.5 mm thickness and a second set of six slices were taken at 1 mm thickness in order to study the root induced changes in soil chemical properties with increasing distance from the rhizoplane. The remaining soil was regarded as the bulk soil. White ectomycorrhizal hyphae were observed on the soil surface of slices of the bottom compartments up-to about 2 mm from the mesh. Photographs were taken of the soil surface of the lower compartments and of the soil surface after the removal of each soil slice (to 2 mm from the inter-compartment boundary) in one lower compartment chosen at random to show the presence of ectomycorrhizal hyphae with distance from the rhizoplane. A 2.0 mm thick soil and root slice from the upper compartment immediately above the inter-compartment boundary (24 μm polyester mesh) was also sampled. Roots were separated from the soil and washed in distilled water. The remaining roots were removed from the soil in the upper compartment and washed in distilled water.

The root volumes were determined by the amount of water displaced when the roots were immersed in water. The roots were then weighed after drying at 70^{O} C. The root surface area was determined using the formula $2\sqrt{(\pi LV)}$ where π: 22/7, L: length of roots and V: volume of roots and assuming the roots are a cylindrical tube with a constant radius. The lower surface area of the roots immediately above the mesh (the root surface in direct contact with the mesh) was considered responsible for the observed changes in cations and pH in the lower compartment.

6.3.4.2 Experiment 2

Experiment 2 was ended 100 days after transplanting the seedlings and seedling heights were recorded. Seedlings were cut 2 mm above the soil surface and weighed after drying at 70^{O} C. As in Experiment 1, photographs were taken of the soil surface of the lower compartments of one replicate of each treatment, chosen at random, to show the

(a)

(b)

Figure 6.2 (a) Piston microtome and (b) slicing soils from the bottom RSC.

presence of ectomycorrhizal hyphae. However, no photographs were taken with distance from the rhizoplane, as there was no further visual evidence of hyphae once the first slice had been removed. The soil in the lower compartment was sliced into thin sections using a piston microtome starting at the inter-compartment boundary (24 μm polyester mesh), as in Experiment 1. The first four sections were sliced at 0.5 mm thickness and a second set of three slices were taken at 1.0 mm thickness in order to study the root induced changes with increasing distance from the rhizoplane. The remaining soil was regarded as the bulk soil. A 2.0 mm thick soil and root slice from the upper compartment, immediately above the inter-compartment boundary (24 μm polyester mesh) was also sampled, as in Experiment 1. The roots were separated from the soil and washed in distilled water. The remaining roots were removed from the upper compartment soil and washed in distilled water. Root volumes and weights were measured, and surface areas calculated, as in Experiment 1.

6.3.5 Plant and soil analysis

The roots and shoots from both experiments were finely ground and sub-samples were digested in concentrated nitric acid. The resulting residue was taken up in 2 *M* HCl. The concentrations of Mg, K, Ca and Na in the digests were measured by atomic absorption spectrometry (AAS). Root and shoot samples from both studies were also analysed for total N, P, Cl and S. Total N and P were extracted by Kjeldahl digestion (Jackson 1958) followed by colorimetric determination of N by alkali-phenol (Markus *et al.* 1985) and P by vandomolybdate method (Colwell 1965), using an auto-analyser. Chloride in the samples was extracted by demineralised water and the Cl concentration in extracts measured by a Tecator FIA star 5020 model chloride analyser (Troelstra 1983). Total plant S was determined by digesting plant samples in sodium hypobromite (NaOBr) and the resulting residue was taken up in concentrated formic acid (Tabatabai and Bremner 1970). Concentrations of S in extracts were measured by the bismuth sulfide method (Dean 1966), using an auto-analyser.

The soil samples from both experiments were air-dried and analysed for soil pH (0.5 g soil in 1.25 ml distilled water) using a micro-electrode and exchangeable Mg, K and Ca (1 *M* NH_4OAc buffered at pH 7.0, Blakemore *et al.* 1987). Concentrations of Mg, K

and Ca in extracts were measured by AAS. Because of poor growth of the seedlings in some replicates, soils and seedlings from only four of the five replicates from Experiment 1 and three of the five replicates in Experiment 2 were analysed for Mg, K and Ca, and soil pH, as described above.

6.3.6 Analysis of covariance

Because of the variation in seedling growth, analysis of variance of shoot and root dry matter yields, shoot to root dry matter ratios, increase in height, root length and Mg, K and Ca uptake for both experiments was adjusted for the covariate of initial seedling height.

6.4 RESULTS AND DISCUSSION

6.4.1 Ectomycorrhizal growth

Upon separation of the upper and lower compartments of the RSCs in both experiments, fungal hyphae were observed on the surface of the lower compartments (Figures 6.3, and 6.4). The hyphae were assumed to be from ectomycorrhizal fungi associated with roots of *P. radiata* (Foster and Marks 1967; Skinner and Bowen 1974; Bowen 1983; Comerford and Skinner 1989). Figure 6.5 shows a root mat of two replicates chosen at random from Experiment 2 and the mycorrhizal hyphae associated with the seedling roots.

From these photographs (Figures 6.3, 6.4, and 6.5), it can be seen that the 24 μm pore-diameter polyester mesh which was successful in preventing root hairs of grasses, clover and tea from growing into the lower compartment (Youssef and Chino 1988; Jungk and Claassen 1989; McLaughlin and James 1991; Gahoonia *et al.* 1992; Hedley *et al.* 1994; Zoysa *et al.* 1997), failed to stop mycorrhizal hyphae of *P. radiata* penetrating the lower compartment.

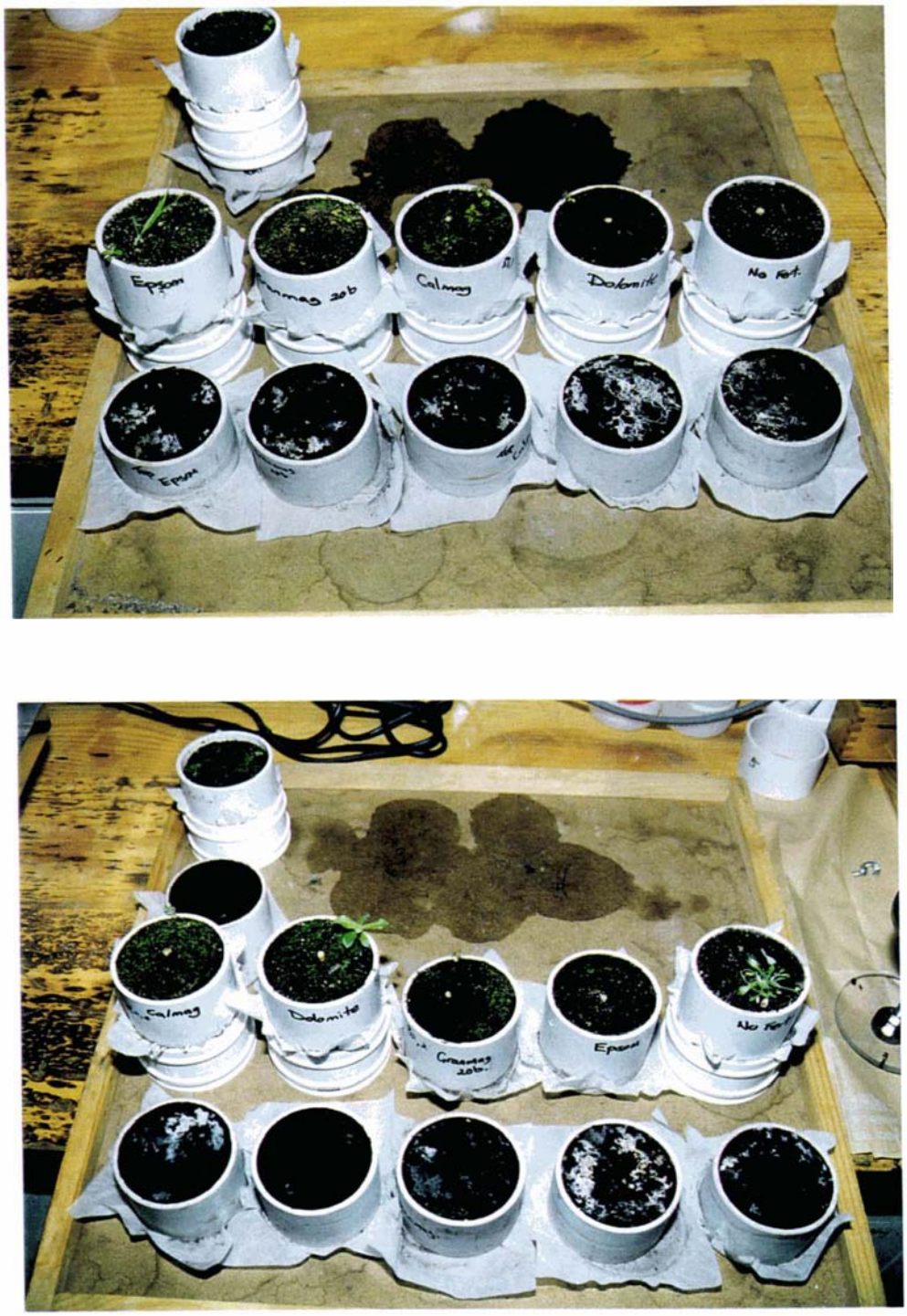


Figure 6.3 Top view of ectomycorrhizal hyphae on the surface of the bottom RSCs of two sets of replicates from Experiment 1.

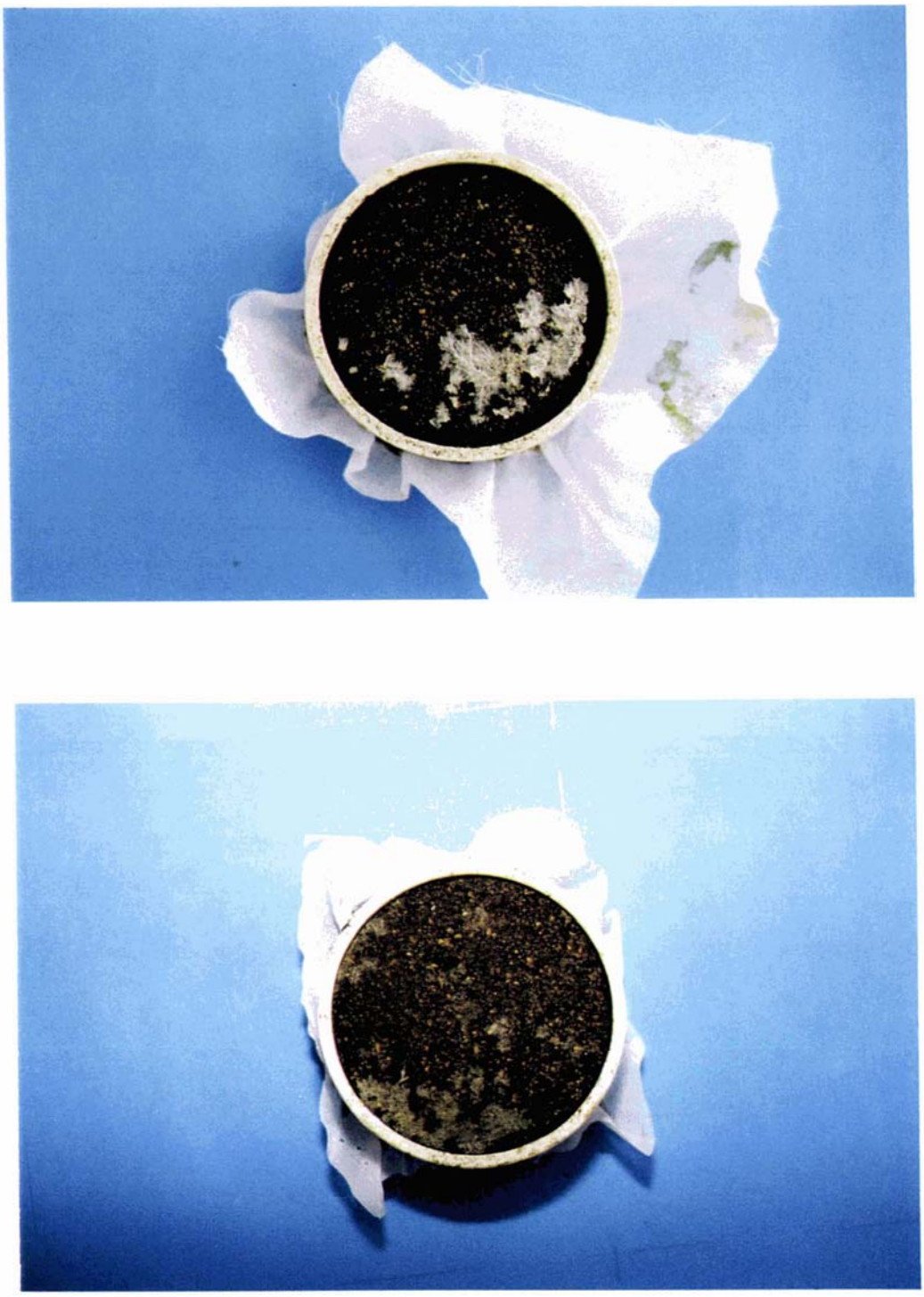


Figure 6.4 Top view of ectomycorrhizal hyphae on the surface of the bottom RSCs of two replicates chosen at random from Experiment 2.

Figure 6.5 Bottom view of the root mats formed above the polyester mesh in RSC and associated ectomycorrhizal hyphae of two replicates chosen at random from Experiment 2

In Experiment 1, it was found that hyphae had grown into the lower RSC compartment to a considerable depth. Figure 6.6a shows the upper surface of the lower compartment of one replicate from Experiment 1, chosen at random. Figures 6.6b through to 6.6d show the same compartment after successive 0.5 mm soil slices had been removed. From this series of photographs it can be seen that, in this particular replicate, hyphae were visible 2 mm from the rhizoplane. Similarly, hyphae were found to have grown into the bottom RSC compartment in most of the replicates of all treatments in Experiment 1. However, in Experiment 2 hyphae were only able to be seen on the top surface of the bottom RSC compartment, although they may have grown further into the bottom compartment but were not obvious to the naked eye.

There is little information available on the role of ectomycorrhiza in forest trees (George and Marchner 1996). However, generally ectomycorrhiza have been shown to increase tree seedling dry weights and improve foliage nutrient concentrations in a range of forest species, compared to non-mycorrhizal seedlings (Bowen 1973; Marschner 1995; George and Marchner 1996). The improved growth and nutrition was usually associated with greater nutrient availability to mycorrhizal plants because of a higher effective root area. Therefore, the plants are able to explore a greater volume of soil for nutrient absorption (Marschner 1995).

Ectomycorrhiza are also known to produce and excrete organic acids into soil. These acids can enhance the plant-availability of nutrients by dissolution of fixed forms of nutrients (Malajczuk and Cromack 1982; Comerford and Skinner 1989; George and Marschner 1996) and weathering of soils (Marschner 1995).

The presence of mycorrhizal hyphae in the bottom RSC compartment is likely to make the interpretation of changes in nutrient concentrations in soil with distance from the rhizoplane difficult. The growth of the hyphae into the bottom compartment was highly variable (Figures 6.3, 6.4 and 6.5) and effectively increases the distance of soil away from the roots over which the plant has an influence. It has been reported by Bowen (1983) that mycorrhizal types and populations change over time. These factors are also likely to contribute to variability in seedling growth and nutrient uptake.

(a)

(b)

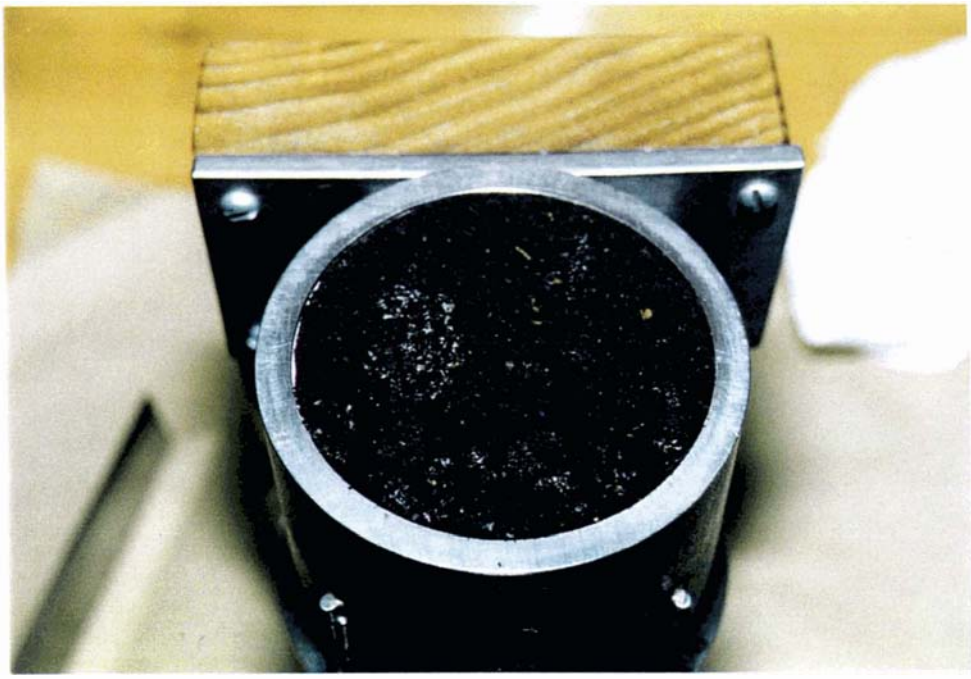
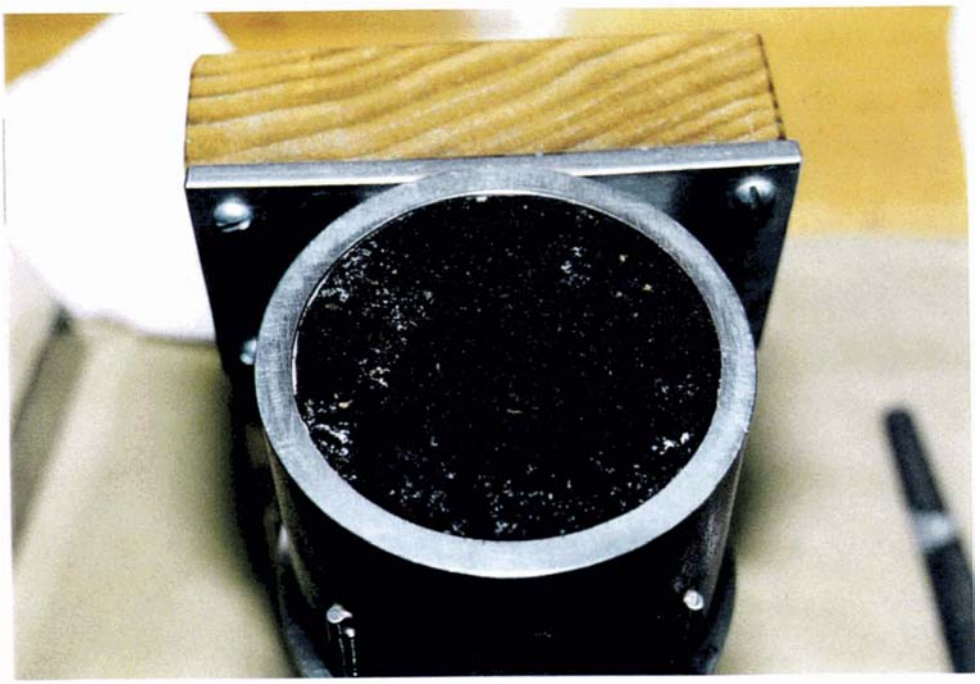


Figure 6.6 (a) Top view of ectomycorrhizal hyphae on the surface of the bottom RSC of a replicate chosen at random from Experiment 1 and (b) the same compartment after a 0.5 mm soil slice has been removed.

(c)



(d)

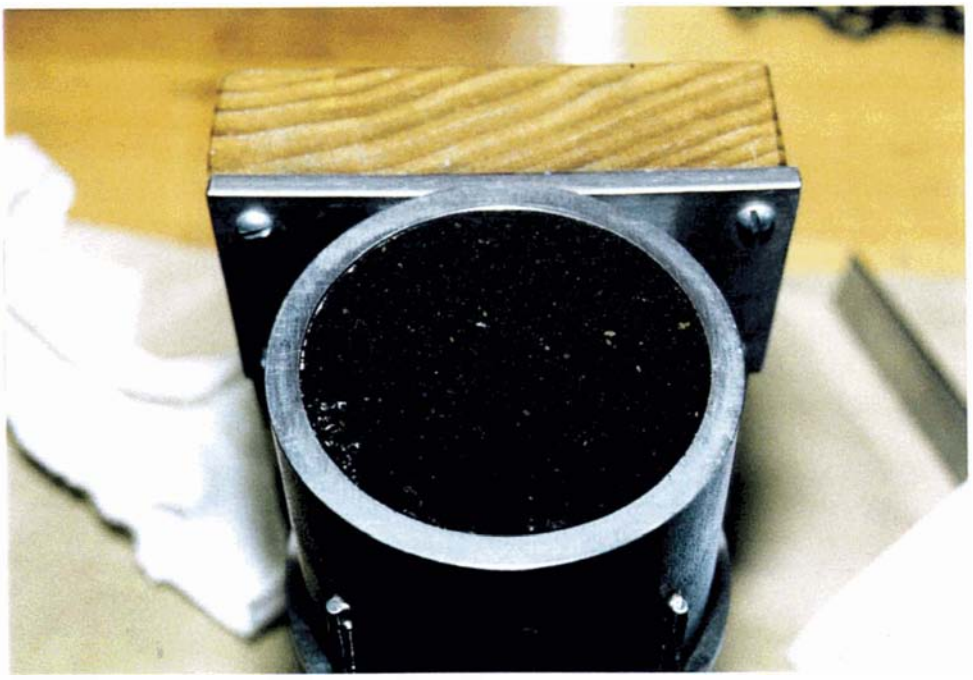


Figure 6.6 (c) and (d) the same compartment as in Figure 6.6a and b after successive 0.5 mm soil slices have been removed.

6.4.2 Effect of Mg and K fertilisers on seedling growth

Dry matter yields of the shoots and roots (in both experiments) were determined from final dry weights of the seedlings minus the dry weights of the shoots and roots of four seedlings in Experiment 1 and three seedlings in Experiment 2, having similar height as those used at the start of the experiments. Results of the two experiments showed that Mg and K fertiliser application had no significant ($P > 0.05$) effects on seedling growth (Table 6.3).

6.4.3 Effect of Mg and K fertilisers on seedling cation concentrations

Potassium was the dominant cation in the shoots of the *P. radiata* seedlings, followed by Ca, while Mg concentrations are approximately a tenth of those of K in both experiments (Figure 6.7a and 6.8a). Magnesium was evenly distributed between shoots and roots, whereas greater concentrations of K can be found in the shoots compared to the roots and generally half as much Ca was found in the shoots compared to the roots (Figure 6.7a and 6.8a).

Calcium concentrations in the roots of Experiment 2 were significantly ($P < 0.05$) higher in the Mg- and K-fertilised seedlings than the no-fertiliser treatment. However, Ca concentrations in the shoots were not affected by these treatments (Figure 6.8a). Magnesium and K fertiliser application appears to have stimulated the uptake of Ca by the roots. Calcium was supplied to the seedlings via the nutrient solution. However, the addition of Mg and K fertilisers may have caused additional Ca from the exchange sites to be replaced by Mg and K ions, thereby increasing Ca concentrations in solution and making it more available for seedling uptake. Calcium is essential for the proper growth and function of root caps (McLaren and Cameron 1990), but as to why the shoots were not affected in the same manner as the roots by the treatments was unclear. It could be that higher concentrations of Mg in the shoots are retarding the translocation of Ca from the roots to shoots (Marschner 1995). As mentioned previously, Lowe (1999) also reported higher concentrations of Ca in the roots compared to the shoots of Mg fertilised seedlings but she gave no explanation for this.

Table 6.3 Effect of (a) various Mg fertilisers and (b) Epsom salts and K_2SO_4 fertilisers on increase[A] in shoot and root dry matter yields, shoot to root dry matter ratio and increase[A] in seedling height. Data represent means of four replicates in Experiment 1 and three replicates in Experiment 2. Means are adjusted for the covariate of initial seedling height

Treatment	Increase in Shoot DM (g plant)	Increase in Root DM (g plant)	Shoot: Root DM ratio	Increase in Height (mm plant)
(a)		Experiment 1		
Calmag	2.39	0.56	4.68	57
Granmag 20™	2.21	0.48	5.02	44
Dolomite	2.38	0.67	3.16	70
Epsom salts	2.54	0.64	4.42	57
No fertiliser	2.07	0.45	5.20	47
	n.s.	n.s.	n.s.	n.s.
(b)		Experiment 2		
37.5 mg Mg kg^{-1}	0.95	0.37	4.69	76
75 mg Mg kg^{-1}	0.54	0.20	3.01	50
Mg plus K[B]	0.70	0.25	3.27	52
150 mg K kg^{-1}	0.75	0.42	1.89	62
control	1.23	0.90	0.41	53
	n.s.	n.s.	n.s.	n.s.

n.s. - indicates that treatment means are not significant at $P = 0.05$. [A] dry weight or height at harvest minus dry weight or height at start of experiment. [B] 75 mg Mg kg^{-1} plus 150 mg K kg^{-1}.

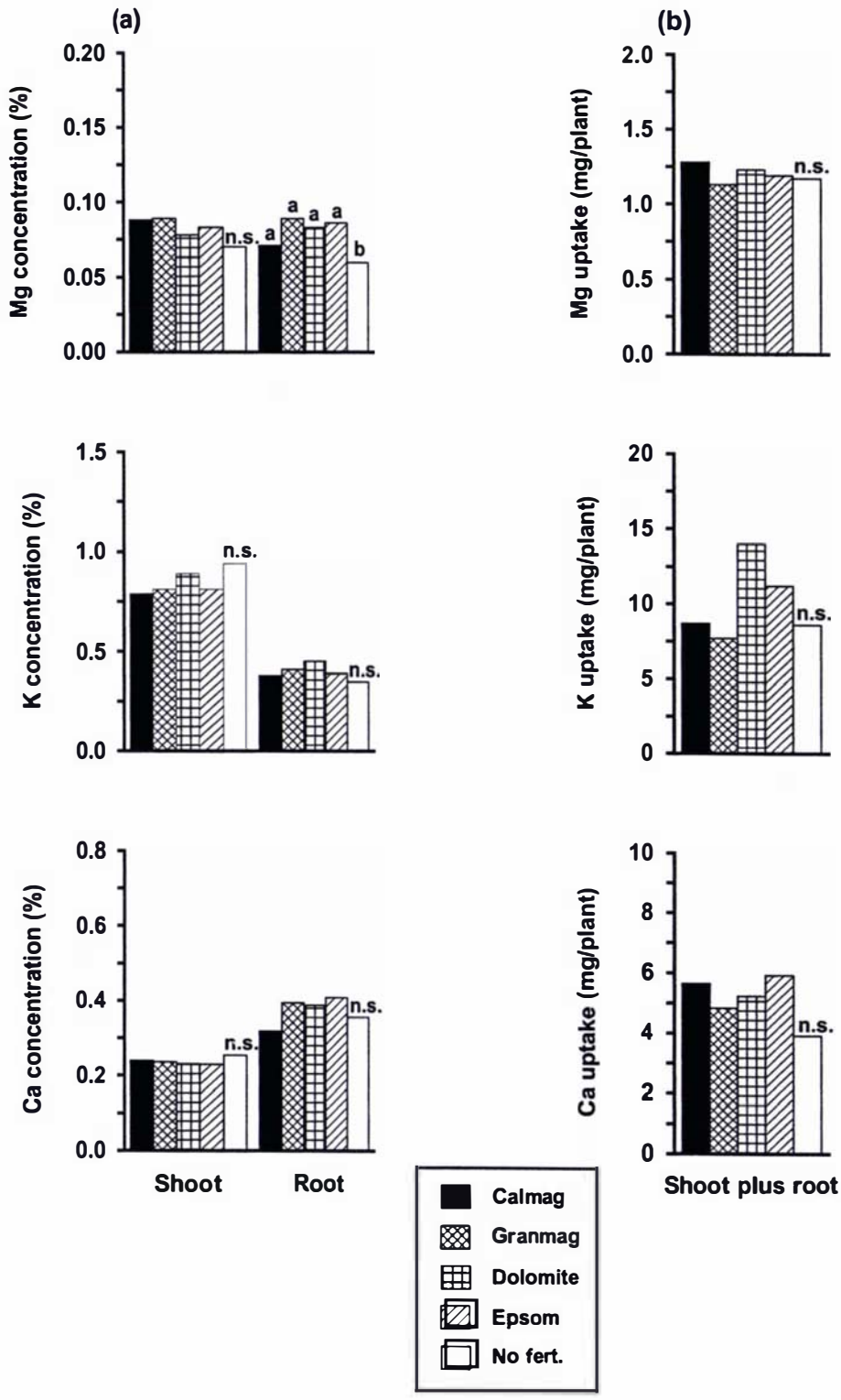


Figure 6.7 Effect Mg fertiliser types on shoot and root Mg, K and Ca (a) concentrations and (b) uptake in Experiment 1. Means with the same letter are not significantly different at $P = 0.05$, n.s. - differences not significant at $P = 0.05$.

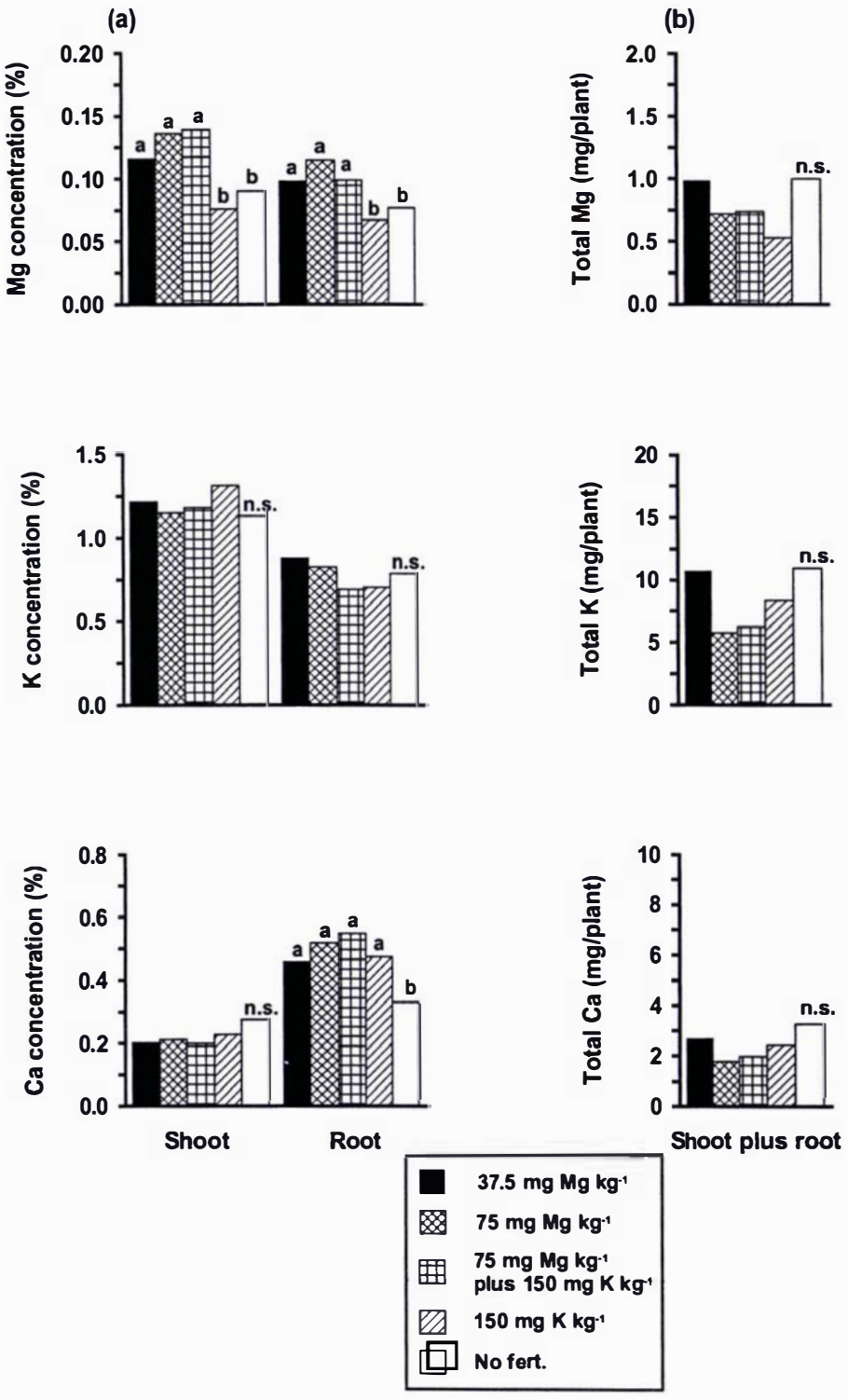


Figure 6.8 Effect of rates of Mg and K applied as Epsom salts and K_2SO_4 respectively on shoot and root Mg, K and Ca (a) concentrations and (b) uptake in Experiment 2. Means with the same letter are not significantly different at $P = 0.05$, n.s. - differences not significant at $P = 0.05$.

6.4.4 Effect of Mg and K fertilisers on seedling cation uptake

Magnesium fertiliser application had no significant ($P > 0.05$) effect on Mg uptake (shoots plus roots) of the seedlings in spite of significant increases in Mg concentrations of the roots in Experiment 1. Potassium and Ca uptake of the seedlings were also generally unaffected by Mg fertiliser application (Figure 6.7b).

In Experiment 2, in spite of Mg fertiliser application significantly ($P < 0.05$) increasing both shoot and root Mg concentrations, Mg uptake (shoots plus roots) of seedlings was not significantly ($P > 0.05$) affected. This is probably due to wide variations in dry matter yield (Figure 6.8b), even after covariance adjustment. Potassium alone (without Mg) produced lower Mg uptake (50% lower) than the no-fertiliser treatment, although the difference was not significant ($P > 0.05$). Potassium and Ca uptake, was unaffected by K and Mg fertiliser application, similar to K and Ca concentrations in the seedlings (Figure 6.8b).

6.4.5 Effect of Mg and K fertilisers seedling K to Mg ratio

A high foliar K:Mg concentration ratio has been implicated as a factor responsible for the occurrence of UMCY (Beets *et al.* 1993). Therefore, the effect of Mg and K fertiliser application on shoot and root K:Mg concentration ratios was examined. Shoot K:Mg concentration ratios were lower (by 20-53%) in the Mg-fertilised seedlings than the no-fertiliser treatment in Experiment 1 (Figure 6.9a). However, none of the changes were significant at $P = 0.05$, although decreases in shoot K:Mg concentration ratio for Epsom salts, calmag and granmag treatments were significant at $P = 0.1$.

In Experiment 2, shoot K:Mg concentration ratios were lower ($P < 0.1$) in the Mg- and Mg plus K- fertilised seedlings than in the no-fertiliser treatment (20-48% lower) and the 150 mg K kg^{-1} fertiliser treatment (66-106% lower). The 150 mg K kg^{-1} fertiliser treatment increased by 40% ($P < 0.1$) the shoot K:Mg concentration ratios over the no-fertiliser treatment (Figure 6.9b).

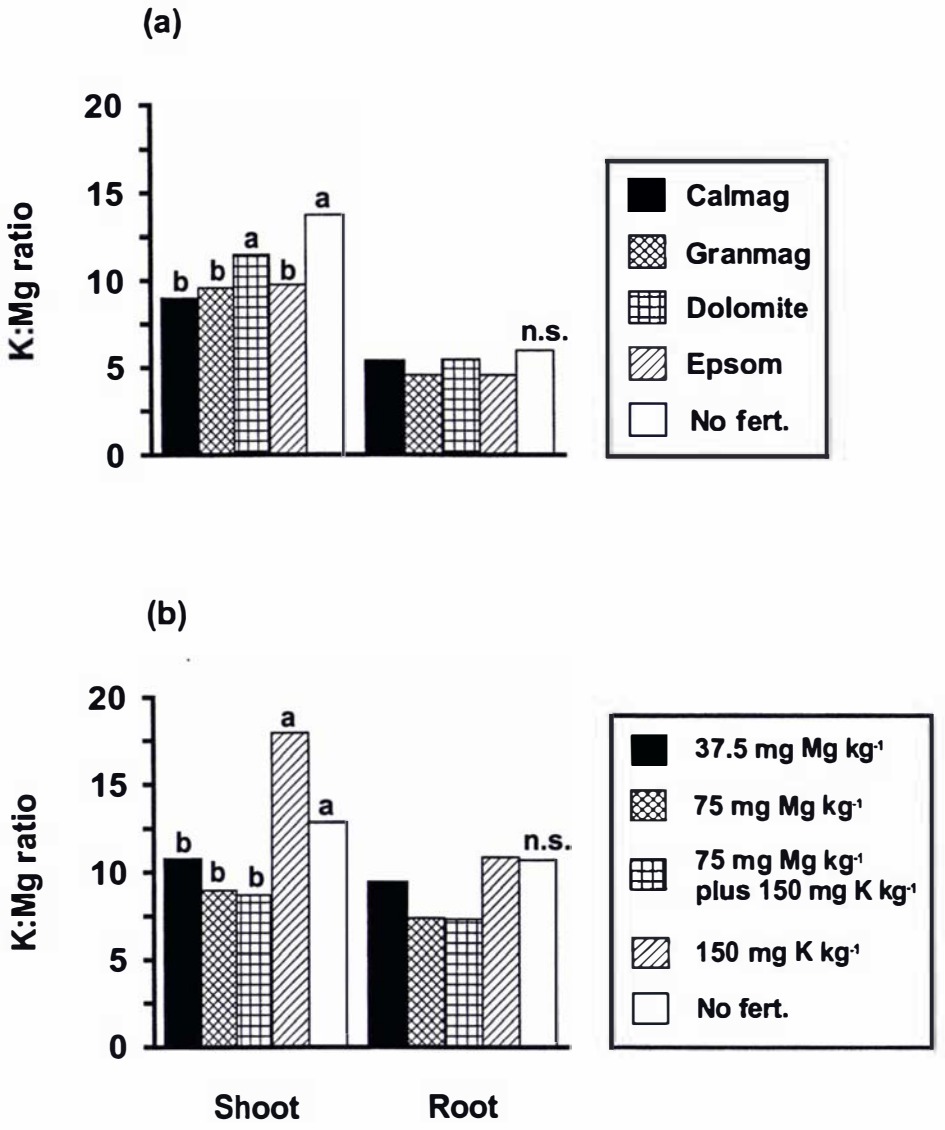


Figure 6.9 Effect of (a) Mg fertiliser types (Experiment 1) and (b) rates of Mg and K applied as Epsom salts and K_2SO_4 (Experiment 2) respectively on shoot and root K to Mg concentration ratios of *P. radiata* seedlings. Means with the same letter are not significantly different at $P = 0.1$, n.s. - differences not significant at $P = 0.1$.

These results show that K:Mg concentration ratios in the shoots of *P. radiata* seedlings can be manipulated by applying K and Mg fertilisers. Upper mid crown yellowing (UMCY) is related to the K:Mg concentration ratio in needles. Therefore, the incidence of UMCY may be increased or decreased by application of K or Mg fertilisers respectively. As the effects were only statistically significant at $P = 0.1$, further studies need to be conducted to confirm these results. A field experiment (described in Chapter 7) is currently in progress to test these observations. It is also interesting to note that the Mg plus K treatment in Experiment 2 has decreased the K:Mg concentration ratios in the shoot compared to the no-fertiliser treatment by 48%, suggesting that Mg has been taken up by the seedlings in preference to K. This was in spite of K being added to the seedlings at twice the rate of Mg.

Root K:Mg concentration ratios in Experiment 1 and 2 were marginally lower in the Mg fertilised seedlings compared to the no-fertiliser treatment, as for the shoot K:Mg concentration ratios. Potassium fertiliser application had no effect on K:Mg concentration ratios in the roots in spite of increases ($P < 0.1$) in the shoot K:Mg concentration ratios. None of the changes in root K:Mg concentration ratios, in both experiments were significant, even at $P = 0.1$ (Figure 6.9).

6.4.6 Effect of Mg and K fertilisers, and plant roots on soil exchangeable Mg

Magnesium fertiliser application has significantly ($P < 0.05$) increased exchangeable Mg concentrations in the bulk soil and at all distances from the rhizoplane sampled, compared to the no-fertiliser treatment in Experiment 1 (Figure 6.10). However, the dolomite treatment has resulted in a lower concentration of exchangeable Mg compared to the other fertiliser treatments. The difference was significant ($P < 0.05$) for the first 2 soil layers from the rhizoplane (0-1.0 mm). These results reflect the lower solubility of dolomite compared to the other fertilisers, as observed in field soils (Chapter 5).

Exchangeable Mg appears to have accumulated in the rhizosphere soil layers (0-1.5 mm) of the granmag and Epsom salts fertiliser treatments (Figure 6.10). The ratios of rhizosphere soil Mg concentration to that in the bulk soil, presented in Table 6.4, show the magnitude of the Mg accumulation in the rhizosphere for these two treatments.

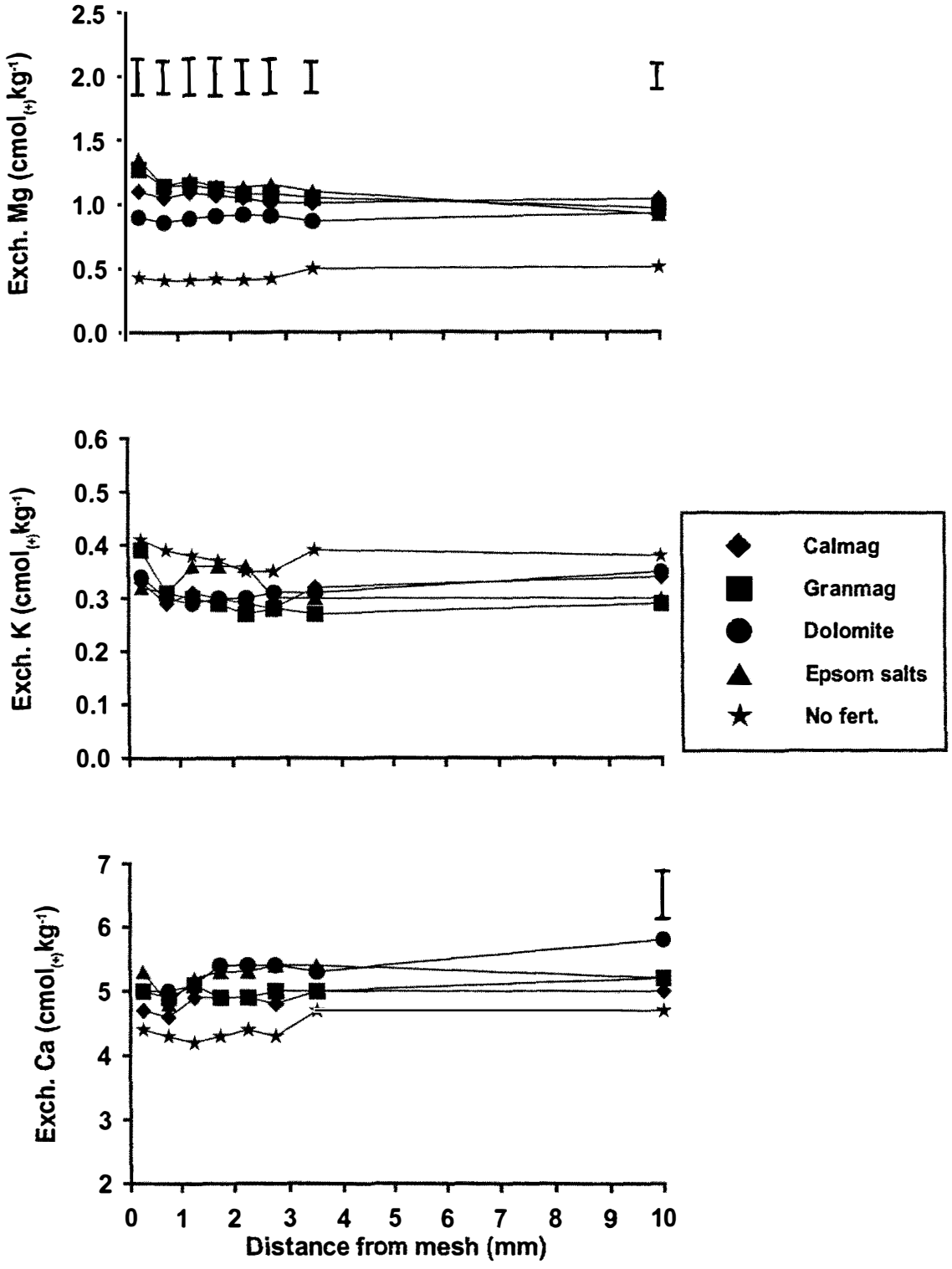


Figure 6.10 Effect of Mg fertiliser types on soil exchangeable Mg, K and Ca in the rhizosphere of *P. radiata* seedlings in Experiment 1. Vertical bars correspond to l.s.d. at $P = 0.05$ for fertiliser source comparisons.

Table 6.4 Ratio of pH(water) and nutrient concentrations at various distances from the roots to those in the bulk soil in Experiment 1

Treatment	pH/Nutrient	0-0.5	0.5-1.0	1.0-1.5
			(mm)	
Calmag	pH	1.00	1.00	0.97
	Mg	1.04	1.00	1.03
	K	0.93	0.80	0.88
	Ca	0.93	0.92	0.98
	K:Mg	0.90	0.81	0.86
Granmag	pH	1.02	1.00	1.00
	Mg	1.33	1.19	1.19
	K	1.14	0.93	0.91
	Ca	1.03	0.99	1.03
	K:Mg	0.87	0.80	0.77
Dolomite	pH	1.00	0.96	0.97
	Mg	0.97	0.92	0.95
	K	0.85	0.75*	0.73*
	Ca	0.85*	0.84*	0.87
	K:Mg	0.89	0.82	0.77
Epsom	pH	1.02	1.00	0.98
	Mg	1.53*	1.30	1.35
	K	1.18	1.13	1.30
	Ca	1.13	1.02	1.09
	K:Mg	0.78	0.90	0.86
No fertiliser	pH	1.00	0.98	0.99
	Mg	0.87	0.83	0.83
	K	1.05	0.99	0.97
	Ca	0.92	0.90	0.86
	K:Mg	1.25	1.21	1.19

Note: Ratios > 1 indicate alkalisation or nutrient accumulation, ratios < 1 indicate acidification or nutrient depletion. * Indicates difference between rhizosphere soil layer and the bulk soil (at 10 mm from the roots) is significant at $P = 0.05$

However, only the difference between the exchangeable Mg in the 0-0.5 mm soil layer and the bulk soil for the Epsom salts treatment was significant at $P = 0.05$ (Table 6.4).

In Experiment 2, application of Mg and K fertiliser had no significant ($P < 0.05$) effect on soil exchangeable Mg concentration in the bulk soil (Figure 6.11). This is not consistent with the results of Experiment 1 (Figure 6.10) where, Mg fertiliser application significantly ($P < 0.05$) increased soil exchangeable Mg in the bulk soil.

The reason for the absence of any significant response in soil exchangeable Mg in the bulk soil due to fertilisation in Experiment 2 is unclear. It may be due to the low ECEC of the soil in Experiment 2. This indicates a limited number of ion exchange sites in the soil (ECEC of 6.0 $cmol_{(+)}kg^{-1}$ in Experiment 1 and 3.7 $cmol_{(+)}kg^{-1}$ in Experiment 2) (Table 6.1). Therefore, the bulk soil will have only limited ability to retain Mg released from the Mg fertiliser. Another reason for the lack of response to Mg fertilisation in Experiment 2 could be because of the Ca supplied in the nutrient solution used to water the RSCs. Calcium in the solution may have competed with Mg for the exchange sites.

The results reported for Experiment 2 indicate that the dissolved Mg from fertiliser application has moved from the bulk soil. However, it is unlikely that the dissolved Mg has been leached from the lower compartment. The RSCs were being watered from the bottom and transpiration by the seedlings and evaporation from the soil surface means that water would be moving up through the RSCs (from bottom to top). Therefore, the dissolved Mg has probably also moved up through the RSCs by mass flow. Figure 6.10 provides evidence of this, as concentrations of exchangeable Mg increase in the soil slices closer to the rhizoplane. Some of the dissolved Mg has accumulated in the rhizosphere soil (Figure 6.10) and this is discussed further in the next paragraph. Some dissolved Mg will have been taken up by the seedlings at the rhizoplane immediately above the mesh separating the two RSC compartments. The balance of the dissolved Mg has probably moved into the soil in the upper RSC. However, this can not be proven as the soil in the upper RSC was not sampled and analysed.

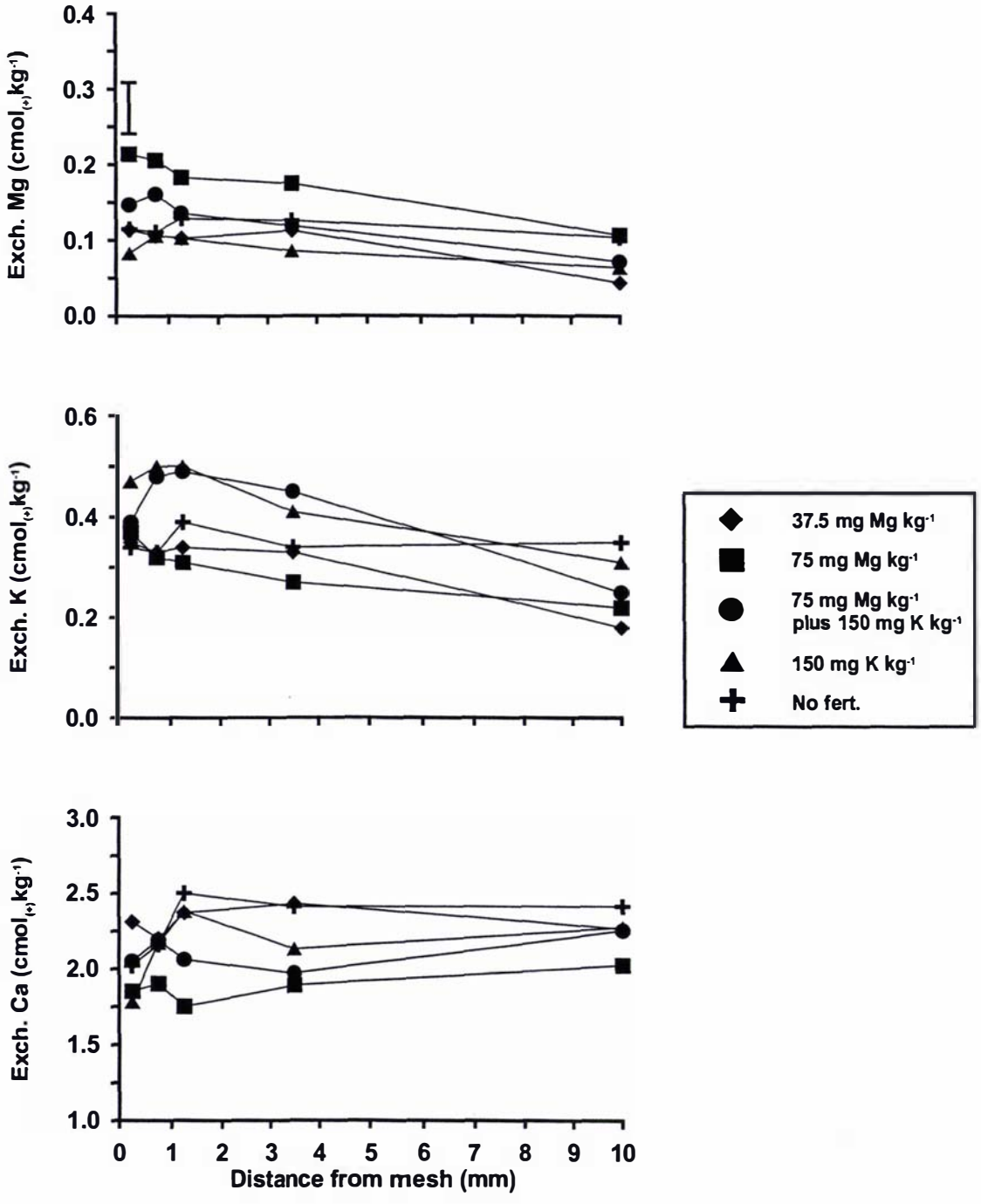


Figure 6.11 Effect of rates of Mg and K applied as Epsom salts and K_2SO_4 respectively on soil exchangeable Mg, K and Ca in the rhizosphere of *P. radiata* seedlings in Experiment 2. Vertical bars correspond to l.s.d. at $P = 0.05$ for fertiliser treatment comparisons.

There appears to be a build up of exchangeable Mg in the rhizosphere layers for the 37.5 mg Mg kg^{-1} (0-1.5 mm layers), 75 mg Mg kg^{-1} (0-1.0 mm layers) and Mg plus K (0-1.0 mm layers) treatments in Experiment 2 (Figure 6.11; Table 6.5). The concentrations of exchangeable Mg in these layers were significantly ($P < 0.05$) higher than those in the bulk soil. The results are similar to the Epsom salts and granmag treatments in Experiment 1 (Figure 6.10; Table 6.4).

The results of both experiments, where Mg has accumulated in the rhizosphere, suggests that the soil is not limiting the uptake of Mg by the seedlings, particularly when Mg fertiliser has been applied. The seedlings appear to somehow be limiting their uptake of Mg. The ability of *P. radiata* to restrict its uptake of Mg may be an adaptation to survival on soils where Mg can be expected to accumulate (Beets *et al.* 1993).

Other studies have also recorded an accumulation of Mg in rhizosphere soils in a range of different plants. Yousseff and Chino (1988) recorded accumulation of soluble Mg in the rhizosphere soil layers (0-3 mm) of barley (var. dorirumugi) and they suggested this was related to increases in soil pH near the roots but did not discuss this further. Wang and Zabowski (1998) also recorded higher concentrations of solution Mg in the rhizosphere of Douglas fir (*Pseudotsuga menziesii*) compared to the bulk solution. They attributed this increase in Mg concentration in the rhizosphere to the rate of supply of Mg to the rhizosphere, from mineral weathering and organic matter decomposition, exceeding the rate of plant uptake. Rengel and Robinson (1990) demonstrated, by modelling the uptake of Mg by annual ryegrass from an acid soil, that calculated concentrations of solution Mg can be higher at the root surface than concentrations in the bulk soil because of relatively large supply of Mg by mass flow compared with plant uptake. A similar study of Mg uptake by loblolly pine seedlings using the Barber-Cushman mechanistic nutrient uptake model also showed that Mg would accumulate at the root surface (Kelly *et al.* 1992). Like Rengel and Robinson

Table 6.5 Ratio of pH(water) and nutrient concentrations at various distances from the roots to those in the bulk soil in Experiment 2

Treatment	pH/Nutrient	0-0.5	0.5-1.0	1.0-1.5
			(mm)	
37.5 mg Mg kg^{-1}	pH	0.96*	0.95*	0.94*
	Mg	2.66*	2.51*	2.43*
	K	1.92*	1.81*	1.85*
	Ca	1.03	0.99	1.06
	K:Mg	0.73	0.74	0.79
75 mg Mg kg^{-1}	pH	0.96*	0.94*	0.95*
	Mg	2.05*	1.95*	1.74
	K	1.73*	1.49	1.48
	Ca	0.92	0.95	0.87
	K:Mg	0.84	0.76	0.84
75 mg Mg kg^{-1}	pH	0.96*	0.95*	0.95*
plus 150 mg K kg^{-1}	Mg	2.11*	2.34*	1.97
	K	1.60	1.92*	1.97*
	Ca	0.93	0.98	0.92
	K:Mg	0.89	0.98	1.16
150 mg K kg^{-1}	pH	0.96	0.95*	0.95*
	Mg	1.35	1.30	1.74
	K	1.58	1.64	1.67*
	Ca	0.80	0.96	1.06
	K:Mg	1.21	0.99	1.00
No fertiliser	pH	0.95	0.94*	0.94*
	Mg	1.42	1.25	1.40
	K	1.04	0.99	1.06
	Ca	0.84*	0.90	1.04
	K:Mg	0.93	0.89	0.96

Note: Ratios > 1 indicate alkalisation or nutrient accumulation, ratios < 1 indicate acidification or nutrient depletion. * indicates difference between rhizosphere soil layer and the bulk is significant at $P = 0.05$

(1990), Mg accumulation in the study of Kelly *et al.* (1992) was due to the rate of supply of Mg by mass flow exceeding the rate of seedling Mg uptake.

From the literature cited in the preceding paragraph, the difference in the rate of Mg supply to the rhizosphere and the rate of plant uptake seems to be a major factor in determining whether Mg accumulates in the rhizosphere or not. Generally, it was assumed in the literature that Mg moves to the roots by mass flow. However, mass flow and diffusion to the root surface usually occur simultaneously and it is not possible to separate these processes (Nye and Tinker 1977).

The contribution of mass flow to the supply of Mg to a plant depends on factors such as plant age, plant transpiration rate, soil moisture content and concentration of the nutrient in solution (Marschner 1995; Jungk 1996). The driving force behind diffusion is concentration gradient. Soil water content also plays an important part, affecting effective path lengths and the cross sectional area available for diffusion.

Under field conditions, when the soil water content is at field capacity, plant transpiration rates are high as are solution Mg concentrations (when Mg fertiliser has been applied), mass flow of Mg would be the main process of nutrient supply. However, as the soil water content falls, the rate of nutrient uptake by the roots may exceed the supply by mass flow and concentration gradients develop between the root surface and the surrounding soil. Therefore, diffusion can then become the main mechanism for the movement of nutrients (Nye and Tinker 1977; Marschner 1995). Under the conditions imposed by the RSC technique (constant supply of water, warm temperatures maintaining high transpiration rates, and Mg fertiliser application), mass flow is likely to be the main process involved in the supply of Mg to the roots.

6.4.7 Estimation of Mg movement to roots by mass flow

To explain some of the accumulation of Mg in the rhizosphere soil layers of both experiments, the amount of Mg supplied by mass flow was calculated. The amount of Mg that moved to the root surface by mass flow was determined for both experiments by calculating the total volume of water transpired by each seedling and multiplying it

by an estimate of the concentration of solution Mg moving to the rhizosphere. This calculation is based on the assumptions that: concentrations of solution Mg were uniform over the duration of the experiments, the calculated total volume of water transpired reflects actual seedling transpiration and transpiration by the seedling is the only driving force moving water and nutrients to the roots.

Soil solution Mg concentrations were not determined in either experiment because of the difficulty in extracting sufficient volume of soil solution for chemical analysis from the small weight of the soil slices. Therefore, they were estimated from the mean soil exchangeable Mg in the bulk and original soil, and using data on the relationships between soil exchangeable and soil solution Mg concentrations from FR190/5 (Chapter 3) and FR190/8 (Chapter 7) (Figure 6.12). Soils from FR190/5 and FR190/8 are the same type as the soils used in this study. Although, this will provide a reasonable estimation of solution Mg concentrations, this needs to be considered with some caution. Factors other than soil exchangeable Mg can influence solution concentrations. These include soil moisture, soil depth, pH, cation-exchange capacity, redox potential, quantity of soil organic matter and microbial activity, season of the year and fertiliser application (Marschner 1995). For example, Figure 6.12 shows how soil depth can influence the relationship between soil exchangeable and soil solution Mg. While the soil used for both experiments are the same type as those at FR190/5 and FR190/8 and collected in the same vicinity under forest trees some factors such as soil moisture, redox potential, microbial activity and fertiliser types and rates of application may differ. In addition, exchangeable Mg values used in the calculations were measured at the end of the experiments and may not represent the soil conditions for the entire duration of the studies. Therefore, the estimated soil solution concentrations, as described above, may not reflect accurately those that occurred in both experiments.

In spite of possibility of errors caused by the above factors, Mg supplied by mass flow was calculated using the best possible estimate of the concentration of Mg in soil solution and these values were compared to the Mg uptake (Mg content at the end of the experiments minus Mg content at start of the experiments) of each seedling. The mean soil solution Mg concentration required to meet the measured Mg uptake of the seedlings was also predicted by dividing net Mg uptake by the volume of water

transpired, assuming that all Mg transported to the roots is by mass flow and uptake of Mg by the seedlings was constant. This allowed comparisons to be made with the soil solution Mg concentrations estimated from the soil exchangeable Mg/soil solution Mg concentration data of FR190/5 and FR190/8 trials.

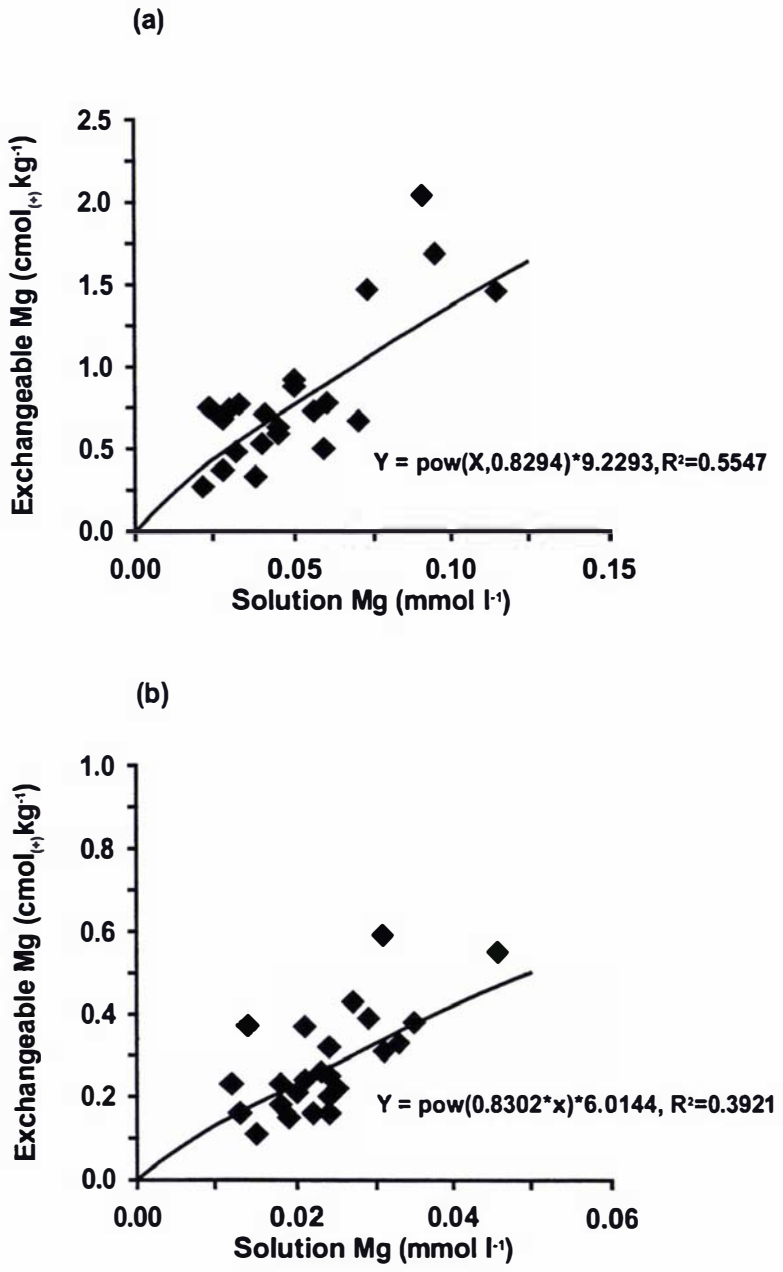


Figure 6.12 Relationship between soil solution and exchangeable Mg in (a) 0-10 and (b) 10-20 cm soil depths at FR190/5 and FR190/8.

The calculations showed that excess of supply of Mg by mass flow compared to seedling uptake was likely to be responsible for the significant (P <0.05) accumulation of Mg in the 0-0.5 mm rhizosphere soil layer for the granmag and Epsom salts treatment in Experiment 1 (Tables 6.4 and 6.6). For the Epsom salts treatment, estimated Mg supplied by mass flow as a percentage of Mg uptake was 146% and for granmag it was 156%. For the dolomite treatment there was no accumulation in the rhizosphere (Table 6.4) but, estimated Mg supplied as a percentage of Mg uptake, was 156%.

In Experiment 2, the estimated Mg supplied by mass flow was below that of seedling Mg uptake for all treatments (Table 6.7). This indicates that there should not be any accumulation of Mg in the rhizosphere. In fact, a significant (P <0.05) accumulation of Mg was observed for 3 treatments (Table 6.5). The accumulation of Mg (Table 6.5) suggests that the actual solution Mg concentration was greater than that estimated from the relationship in Figure 6.12b (Table 6.7, last column). The fertilisers (Epsom salts and K_2SO_4) used in Experiment 2 are both highly soluble in water and would have completely dissolved soon after addition to the soil. Therefore, initial concentrations of Mg in soil solution were probably higher than those estimated, based only on final exchangeable Mg concentrations. If so, the estimated Mg supplied by mass flow would have been higher than seedling uptake. This would explain the Mg accumulation in the rhizosphere.

It should be noted that the standard errors in the above calculations were too high (Tables 6.6 and 6.7) to make any strong conclusions. The reasons for the high standard errors include those stated previously and those discussed in the next section.

Table 6.6 Estimation of the proportions of seedling uptake of Mg as supplied by mass flow in Experiment 1

Treatment	Estimated soil solution Mg[A] (mmol l^{-1})	Total volume of water transpired (l^{-1} seedling)	Estimated Mg supplied by mass flow[B] (mmol)	Measured Mg uptake (mmol)	Estimated Mg supplied by mass flow as a % of measured Mg uptake (%)	Predicted soil solution Mg concentration for uptake to equal supply by mass flow[C] (mmol l^{-1})
Calmag	0.054±0.005	1.16±0.12	0.063±0.007	0.054±0.001	120±28	0.047
Granmag 20™	0.051±0.007	1.40±0.12	0.071±0.006	0.046±0.010	156±13	0.033
Dolomite	0.049±0.004	1.67±0.21	0.082±0.010	0.062±0.007	156±69	0.038
Epsom salts	0.047±0.002	1.52±0.01	0.072±0.000	0.054±0.032	146±60	0.036
No fertiliser	0.033±0.002	1.21±0.10	0.040±0.004	0.051±0.018	78±6	0.042

[A] Estimated form the mean soil exchangeable Mg in the bulk and original soils and using data on the relationship between soil exchangeable Mg and soil solution Mg from FR190/5 and FR190/8 (Figure 6.12). [B] Estimated soil solution Mg multiplied by total volume of water transpired.

[C] Measure Mg uptake/total volume of water transpired

Table 6.7 Estimation of the proportions of seedling uptake of Mg as supplied by mass flow in Experiment 2

Treatment	**Estimated soil solution Mg[A]** (mmol l^{-1})	**Total volume of water transpired** (l^{-1} seedling)	**Estimated Mg supplied by mass flow[B]** (mmol)	**Measured Mg uptake** (mmol)	**Estimated Mg supplied by mass flow as a % of measured Mg uptake** (%)	**Predicted soil solution Mg concentration for uptake equal to supply by mass flow[C]** (mmol l^{-1})
37.5 mg Mg kg^{-1}	0.009±0.001	1.72±0.50	0.016±0.008	0.045±0.016	35±3	0.026
75 mg Mg kg^{-1}	0.012±0.001	1.35±0.42	0.017±0.008	0.027±0.015	68±18	0.020
Mg plus K[D]	0.010±0.000	1.40±0.35	0.014±0.006	0.033±0.006	42±4	0.024
150 mg K kg^{-1}	0.010±0.000	1.39±0.39	0.014±0.007	0.023±0.002	60±12	0.017
No fertiliser	0.012±0.002	1.50±0.28	0.018±0.005	0.037±0.017	57±27	0.024

[A] Estimated form the mean soil exchangeable Mg in the bulk and original soils and using data on the relationship between soil exchangeable Mg and soil solution Mg from FR190/5 and FR190/8 (Figure 6.12). [B] Estimated soil solution Mg multiplied by total volume of water transpired. [C] Measure Mg uptake/total volume of water transpired. [D] 75mg Mg kg^{-1} plus 150 mg K kg^{-1}

6.4.8 Influence of ectomycorrhizal hyphae on the accumulation of Mg in the rhizosphere

The presence of ectomycorrhizal hyphae in the first few soil slices of both rhizosphere experiments could also be responsible for some of the accumulation of exchangeable Mg in these soil slices (Figures 6.3 and 6.4). It may be that the Mg is concentrated in the hyphae and is solubilised during determination of soil exchangeable Mg and this is showing up as increases in exchangeable Mg in the rhizosphere soil. Rygiewicz and Bledsoe (1984), found that ectomycorrhizal fungi associated with seedlings of Douglas fir (*Pseudotsuga menziesii*), western hemlock (*Tsuga heterophylla*) and Stika spruce (*Picea sitchensis*) increased the rate of uptake of rubidium-86 (^{86}Rb), used as a tracer for potassium uptake by the seedling. Rygiewicz and Bledsoe (1984), also found that mycorrhizal roots had higher concentrations of ^{86}Rb than non-mycorrhizal roots, presumably because ^{86}Rb was being stored in the vacuoles of the mycorrhiza. It has been demonstrated that *P. radiata* mycorrhiza mycelial strands were capable of uptake and translocation of orthophosphate labelled with P-32 (Skinner and Bowen 1974). Ectomycorrhizal hyphae have been shown to absorb both NH_4^+ and NO_3^-, assimilate the nitrogen and transport it to the host plant (George and Marschner 1996). Therefore, it is possible that ectomycorrhizal hyphae are capable of taking-up and concentrating the Mg before transporting it to the host seedling.

6.4.9 Effect of Mg and K fertilisers, and plant roots on soil exchangeable K

The application of Mg and K fertilisers had no significant effects on soil exchangeable K concentrations in the bulk soil in Experiment 2 (Figure 6.11). The lack of any increase in soil exchangeable K due to K fertiliser application was probably because of the limited exchange capacity of the soil used in Experiment 2. This is similar to the effect of Mg fertilisers on soil exchangeable Mg discussed previously in Section 6.4.6. In addition, the monovalent nature of K makes it difficult for K to exchange with the divalent Mg and Ca, and trivalent Al ions in the exchange complex preventing a significant increase in exchangeable K at the rates applied in this experiment (Table 6.1). Furthermore, Ca supplied in the nutrient solution would have also competed with K for the exchange sites. The results indicate that dissolved fertiliser K may have

moved from the bulk soil probably with the water moving up through the lower RSC as was discussed for the dissolved fertiliser Mg in Section 6.4.6. This suggests that under the conditions imposed by the RSC technique, mass flow of K might have occurred as found by Hylander *et al.* (1999). Therefore, a significant proportion of the dissolved K could have moved into the upper RSC. However, this can not be confirmed as the soil from the upper RSC was not sampled and analysed.

In Experiment 2, there was an accumulation of exchangeable K in the rhizosphere soil slices (0-1.5 mm) compared to the bulk soil, for all treatments except the no-fertiliser treatment (Figure 6.11). The difference between concentration of exchangeable K in the bulk and the 0-0.5 mm soil layer was statistically significant ($P < 0.05$) for the 37.5 and 75 mg Mg kg^{-1} fertiliser treatments (Table 6.5).

Other studies have recorded accumulation of exchangeable K in rhizosphere soils. Kuchenbuch and Jungk (1982) observed accumulation of K in the soil layers close to the rhizoplane. They attributed the accumulation of K to the K content of root hairs and other biomass in the rhizosphere layers. As discussed in section 6.4.8, Rygiewicz and Bledsoe (1984), reported that ectomycorrhiza associated with seedlings of Douglas fir (*Pseudotsuga menziesii*), western hemlock (*Tsuga heterophylla*) and Stika spruce (*Picea sitchensis*) took-up and stored ^{86}Rb (used as tracer used for K). Therefore, the accumulation of K in the rhizosphere of Experiment 2 could be due to the presence of mycorrhizal hyphae in these layers (Figure 6.4). Hylander *et al.* (1999) recorded increases in exchangeable K in the soil layer close to the rhizoplane of cotton and soybean. However, Hylander *et al.* (1999) attributed the accumulation of exchangeable K to the excess supply of K by mass flow, which the cotton and soybean plants were not able to take-up because of their poor growth. Similarly to results of Hylander *et al.* (1999), the excess supply of K by mass flow and the poor growth of *P. radiata* seedlings in Experiment 2 study could be reasons for the observed accumulation of K in the rhizosphere soil.

In Experiment 1, Mg fertiliser application had no significant ($P > 0.05$) effect on exchangeable K concentrations in the bulk soil (Figure 6.10). Exchangeable K concentrations in the rhizosphere soil layers (0-1.5 mm) and all other soil layers were

unaffected by Mg fertiliser application (Figure 6.10). There was no significant ($P > 0.05$) differences between exchangeable K in the rhizosphere soil layers and the bulk soil.

6.4.10 Effect of Mg and K fertilisers, and plant roots on soil exchangeable Ca

The application of Mg and K fertilisers had no significant ($P > 0.05$) effect on soil exchangeable Ca in the bulk or rhizosphere soil in both experiments (Figures 6.10 and 6.11).

6.4.11 Effect of Mg and K fertilisers, and plant roots on soil exchangeable K to Mg molar ratio

The symptoms of UMCY are worse in trees with to high foliar K:Mg concentration ratios. Changes in foliar K:Mg concentration ratios generally reflect changes in soil exchangeable K:Mg ratios (Beets and Jokela 1994). Analysis of the *P. radiata* seedlings showed that Mg and K fertiliser application resulted in changes in the K:Mg concentration ratios of the shoots and roots in both experiments (Figure 6.9). Therefore, the effect of Mg and K fertiliser application on the soil exchangeable K:Mg molar ratio was also examined.

The application of Mg fertilisers to the soil has significantly ($P < 0.05$) decreased the exchangeable K:Mg molar ratio in both the bulk and rhizosphere soils compared to the no-fertiliser treatment in Experiment 1 (Figure 6.13a). This was a result of the increases in soil exchangeable Mg due to Mg fertiliser application (Figure 6.10). These results are not surprising as similar decreases in K:Mg molar ratio were also recorded after application of Mg fertilisers to soils in the field trials reported in Chapters 3 and 4.

In Experiment 2, the highest rate of Mg fertiliser treatment (75 mg Mg kg^{-1}) decreased the exchangeable K:Mg molar ratio in both the bulk and rhizosphere soils compared to the no-fertiliser treatment but the decrease was significant ($P < 0.05$) only for soil layers closer to the rhizoplane (0-4 mm) (Figure 6.13b). These results are similar to those recorded in Experiment 1. The highest rate of K fertiliser application (150 mg K kg^{-1})

significantly ($P < 0.05$) increased the exchangeable K:Mg molar ratio compared to the no-fertiliser treatment in the soil layers close to the rhizoplane (Figure 6.13b). This reflects increases in exchangeable K due to K fertiliser application and movement of solution K from the bulk towards the roots of the seedlings (Figure 6.11).

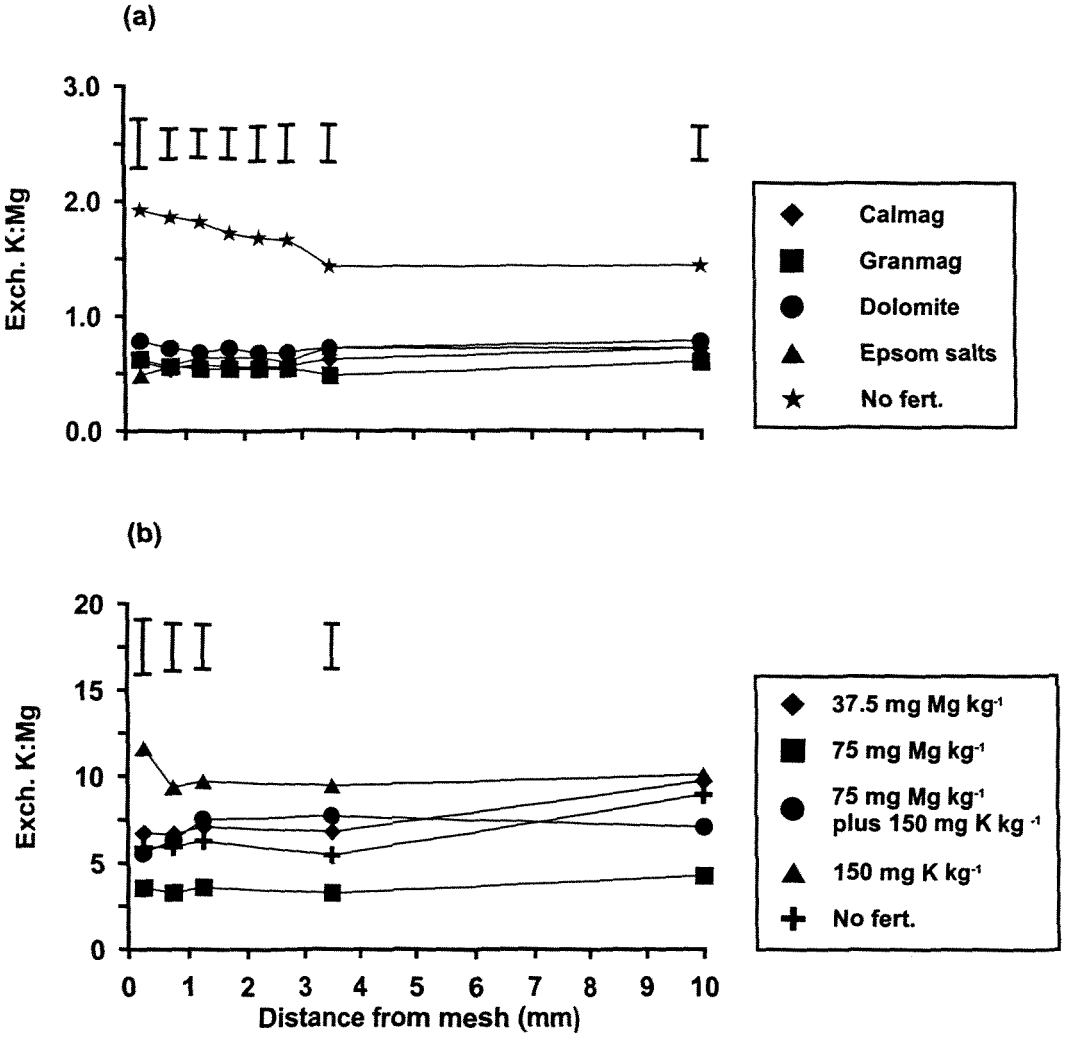


Figure 6.13 Effect of (a) Mg fertiliser types (Experiment 1) and (b) rates of Mg and K applied as Epsom salts and K_2SO_4 respectively (Experiment 2) on soil exchangeable K to Mg molar ratio in the rhizosphere of *P. radiata* seedlings. Vertical bars correspond to l.s.d. at $P = 0.05$ for fertiliser source comparison.

Application of Mg and K fertilisers in both experiments had no significant ($P > 0.05$) effect on differences between K:Mg molar ratios in the bulk soil and the rhizosphere soil, probably because the relative accumulation of Mg and K in the rhizosphere soils is approximately in the same proportions as the concentrations of those cations in the bulk soil (Tables 6.4 and 6.5).

6.4.12 Effect of Mg and K fertilisers, and plant roots on soil pH

The application of Mg fertilisers had no significant ($P > 0.05$) effect on soil pH(water) in the bulk soil in Experiment 1 (Figure 6.14a). These results are in contrast to those observed in the field where the application of calmag, granmag and dolomite significantly increased soil pH (Chapters 3, 4 and 5). One reason for the difference in the behaviour of the fertilisers in the glasshouse and field studies is the low rate of fertiliser application in the laboratory study (53 kg Mg ha^{-1} in the glasshouse versus 150 and 200 kg Mg ha^{-1} in the field). Another reason is that only a fraction of the applied fertiliser may have dissolved to cause any significant increase in soil pH, during the 75 days of the glasshouse study as opposed to greater than 70% dissolution in the two or more years duration of the field trials.

Soil pH(water) near the roots of *P. radiata* seedlings (0-1.5 mm soil layer) in Experiment 1 was the same or similar to soil pH values observed in the bulk soil for all treatments (Figure 6.14a, Table 6.4). Examination of the results in Table 6.4 showed that the ratios of pH in the first 3 soil slices to those in the bulk soil were 1.00 or close to 1.00 indicating that neither alkalisation nor acidification has occurred.

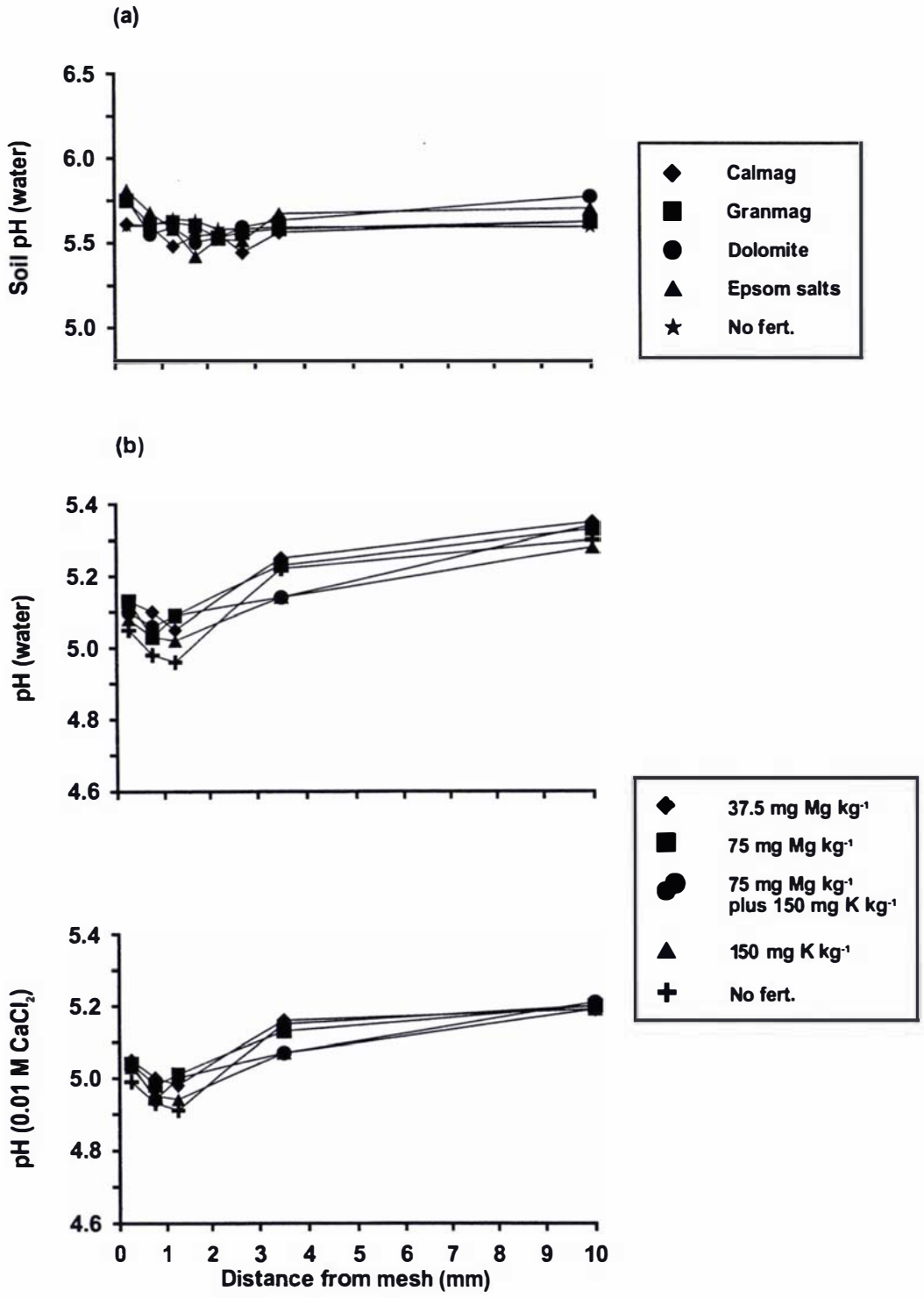


Figure 6.14 Effect of (a) Mg fertiliser types (Experiment 1) on soil pH (water, 1:2.5 soil to solution w/w ratio) and (b) rates of Mg and K applied as Epsom salts and K_2SO_4 respectively (Experiment 2) on soil pH (water and 0.1 *M* $CaCl_2$; 1:2.5 soil to solution w/w ratio) in the rhizosphere of *P. radiata* seedlings.

In Experiment 2, subsoil from the same pumice soil profile utilised in Experiment 1 was used (10-20 cm soil depth). This subsoil has a lower pH buffering capacity, compared to the surface soil used in Experiment 1 (20 mmol H^+ kg^{-1} pH^{-1} in Experiment 2 *vs* 36 mmol H^+ kg^{-1} pH^{-1} in Experiment 1). Also in Experiment 2, in addition to measuring soil pH in water, pH was also measured in 0.01 *M* $CaCl_2$ because it was thought that the ionic strength in the rhizosphere and the bulk soils might have changed due to fertiliser application or root processes. Soil pH in 0.01 *M* $CaCl_2$ solution is not affected by such ionic strength changes because the addition of $CaCl_2$ brings the ionic strength of all samples to approximately 0.03 *M* (Blakemore *et al.* 1987).

The application of Mg and K fertilisers had no significant ($P > 0.05$) effect on soil pH(water and 0.01 *M* $CaCl_2$) in the bulk soil in Experiment 2 (Figure 6.14b). This is as expected because the Mg and K salts used in the Experiment 2 ($MgSO_4.7H_2O$ and K_2SO_4) were not alkaline, so did not have any liming effect to cause any significant changes in soil pH. Soil pH(water) of the bulk soil for all treatments were within a narrow range of 5.28 to 5.35. However, in contrast to Experiment 1, a reduction in soil pH(water) of between 0.24 to 0.30 units was observed near the roots (0-1.5 mm) of the *P. radiata* seedlings compared with the bulk soil for all treatments (Figure 6.14b; Table 6.5). This reduction was significant ($P < 0.05$) for the first 3 soil layers (0-1.5mm) for both the Mg treatments and the K plus Mg treatment, and the second and third soil layers (0.5-1.5 mm) for the K and no-fertiliser treatments (Table 6.5). Of these 3 layers, the greatest reduction in soil pH occurred in the soil slices where ectomycorrhizal activity was not evident (1.0-1.5 mm). The results tend to suggest that *P. radiata* roots acidify the soil but the magnitude and the zone of pH reduction is difficult to quantify because of the variability in the growth of mycorrhizal hyphae.

Ectomycorrhiza associated with forest tree species including *P. radiata*, *Eucalyptus marginata* and Douglas fir (*Pseudotsuga menziesii*), are known to produce and excrete oxalic acid (Malajczuk and Cromack 1982; George and Marschner 1996). Comerford and Skinner (1989) have also shown that *P. radiata* roots excrete oxalic acid, which causes acidification of rhizosphere soils. Oxalic acid, having pk_1 and pk_2 values of 1.25 and 4.28 respectively (Butler 1964) results in the release of H^+ ions to the soil and therefore, a reduction in soil pH. If the zone of the hyphae which is responsible for the

excretion of organic acids occurs at or near the hyphae tip, and the active hyphae tips were concentrated in the second and third soil layers (0.5-1.5 mm), the greatest reduction in soil pH is likely to occur in these layers. Rhizosphere pH measurements along root axes of Douglas fir (*Pseudotsuga menziesii*) have shown that pH can be variable along the root axis (Gijsman 1990c). This depends on the ratio of cation to anion concentrations in various parts of the root system, the form of N taken up and excretions of organic acids at the root apex. The same may be true for ectomycorrhizal hyphae of *P. radiata* resulting in the pattern of changes in soil pH in the 0-1.5 mm soil layers (Figure 6.14b).

Reductions in soil pH in the rhizosphere of plants are also the result of extrusion of protons by plant roots to maintain electro-neutrality of plant tissues as plant roots take up excess cations over anions (Barber 1984; Haynes 1990). Results of cation and anion analysis for the *P. radiata* seedling from both experiments (Table 6.8) show that there is surplus of cations (C) taken up compared to anions (A), when N nutrition is ignored. The resulting effect should be a net efflux of H^+ ions into the rhizosphere soil. However, if N nutrition is considered, the form in which N is taken up by the plant also influences whether acidity (H^+) or alkalinity (OH^-/HCO_3^-) is excreted by the plant to maintain electro-neutrality. The uptake of NH_4^+ causes the release of H^+ to the rhizosphere, whereas NO_3^- uptake results in OH^- or HCO_3^- release (Gahoonia *et al.* 1992; Gijsman 1990 a and b; Nye, 1981). As the proportions of N taken-up as NO_3^- and NH_4^+ are not known, it was not possible to determine the contribution of N uptake towards acidity produced in the rhizosphere.

Table 6.8 Cation and anion balance in *Pinus radiata* seedlings grown in pumice soil treated with (a) various Mg fertilisers applied at 75 mg Mg kg^{-1} of soil (Experiment 1) and (b) different rates of application of Epsom salts and K_2SO_4 (Experiment 2)

Treatment	Mg	K	Ca	Na	Cl	P	S	(C - A)[A]	N_{org}
				(μeq/plant)					
				Experiment 1					
No fertiliser	98.4±8.3	224.0±83.8	202.0±62.4	54.0±17.3	98.2±11.8	34.4±19.6	18.1±12.8	425±128	805±225
Calmag	102.6±18.7	207.6±76.2	252.9±43.6	22.8±7.9	55.1±31.2	37.5±22.6	43.6±7.7	450±122	993±179
Granmag	93.1±11.1	192.2±87.7	233.1±134.5	23.4±13.8	42.5±24.5	31.1±20.0	52.6±37.5	416±194	1117±504
Dolomite	106.9±63.0	376.6±185.2	293.3±156.7	33.1±29.4	83.0±57.6	39.3±37.5	50.4±40.4	637±296	1221±811
Epsom	99.0±34.6	285.9±164.8	296.1±139.2	29.8±14.4	65.9±22.4	27.6±13.3	56.4±30.1	561±300	1039±447
				Experiment 2					
No fertiliser	73.7±33.0	264.9±114.8	154.4±67.6	42.0±20.5	82.5±40.2	24.7±11.4	29.2±33.5	399±162	963±468
37.5 mg Mg kg^{-1}	90.1±32.4	288.1±115.8	141.8±34.4	32.0±9.2	91.7±38.2	25.3±0.1	32.4±12.6	403±140	1066±442
75 mg Mg kg^{-1}	54.7±29.7	140.6±73.2	84.9±47.3	17.1±9.6	44.8±22.8	11.6±9.0	25.5±13.4	216±121	521±265
Mg plus K[B]	66.5±11.2	167.6±25.8	103.1±18.0	17.7±0.9	57.5±12.7	14.9±6.1	32.5±7.0	250±49	669±147
150 mg K kg^{-1}	45.6±3.3	216.3±45.9	122.5±11.5	25.6±6.2	69.9±15.6	26.7±8.9	20.9±23.1	293±43	814±182

[A] (Mg + K + Ca + Na) - (Cl + P + S). [B] 75 mg Mg kg^{-1} plus 150 mg K kg^{-1}

6.5 CONCLUSIONS

Magnesium fertiliser application can cause exchangeable Mg accumulation in the rhizosphere soil of *P radiata* seedlings grown at −1.8 kPa soil moisture content. This is probably because the supply of Mg to the roots by mass flow exceeds the rate of Mg uptake by *P radiata* seedlings. Therefore, exchangeable Mg concentrations in the rhizosphere should not be limiting the uptake of Mg by the trees. Exchangeable K, has also accumulated in the rhizosphere probably because K uptake was less than the K moved to the root. Potassium also moved to the roots by mass flow under the conditions of the experiment. Another reason for the accumulation of Mg and K near the roots could be due to the mycorrhizal hyphae growth in the rhizosphere soils. Ectomycorrhizal hyphae may be concentrating these nutrients and when extracted with 1 *M* NH_4OAc for exchangeable cation determination shows up as exchangeable Mg and K. If the accumulation of Mg in the rhizosphere was due to uptake and storage of Mg by the mycorrhizal hyphae, and this also occurred under field conditions, this might be a factor limiting the supply of Mg to the trees. This could be a reason for the slow response to Mg fertiliser application observed in the field trails reported in Chapter 3 and 4. The results reported in this Chapter require confirmation through further investigation testing the role of ectomycorrhiza on the concentration of cations in the rhizosphere soil compared to the bulk soil under different moisture conditions and in subsequent studies under field conditions. It is also recommended that in future studies that soil solution K and Mg concentrations be measured to better understand the reasons for the differences in cation concentrations between the bulk and rhizosphere soil and the reason why the trees are not responding to changes in exchangeable Mg concentrations brought about by Mg fertiliser application.

Pinus radiata seedlings acidified the rhizosphere soil. This was explained as due to removal by seedlings of an excess of cations compared to anions and synthesis of organic acids (e.g. oxalic acid) within the plant and their excretion to the soil. However, the contributions of NO_3^--N and NH_4^+-N uptake towards the cation-anion balance and the acidity produced is unknown. Mycorrhizal hyphae growth in the rhizosphere soil would have also influenced the results reported here. These results also require confirmation through further investigation similar to the ones suggested in the

preceding paragraph. It is recommended that in future studies, NH_4^+ and NO_3^- in soil be measured at various periods during the trials, possibly using ^{15}N labelled NH_4^+ and NO_3^- fertilisers, comparing NH_4^+ and NO_3^- as N sources while minimising nitrification by adding nitrifying inhibitors. The contribution of organic acid excretion to changes in rhizosphere soil pH needs quantifying.

CHAPTER 7

EFFECT OF MAGNESIUM AND POTASSIUM FERTILISERS ON LEACHING, AND SOIL AND SOIL SOLUTION CONCENTRATIONS OF MAGNESIUM AND POTASSIUM IN A PUMICE SOIL UNDER *Pinus radiata*

7.1 INTRODUCTION

The review of literature presented in Chapter 2 shows that the worst Mg deficiency symptoms and highest upper mid crown yellowing (UMCY) scores in *P. radiata* have been recorded for trees with high foliar K and low foliar Mg concentrations (Beets *et al.* 1993). An increase in foliar K:Mg concentration ratios has been observed after repeated harvesting of *P. radiata* on Pumice Soils of the central North Island (Will 1966; Ballard 1978). These changes in foliar K:Mg concentration ratios reflect changes in pools of exchangeable Mg and K caused by the removal of organic topsoils, during harvesting operations (Ballard 1978; Beets and Jokela 1994). Magnesium is adsorbed preferentially to soil organic matter compared to K (Parfitt 1991). The effect of Mg deficiency on tree growth has been established by Forest Research (Institute Ltd) (FR), in trials at Purukohukohu Experimental Catchment located near Rotorua. It was concluded that Mg deficiency symptoms were causing a decrease in productivity and that this was related to low soil exchangeable Mg:K concentration ratios (Beets unpublished data).

Given the apparent importance of the K status of the soil and that field trials using Mg fertilisers have been widely studied (Chapters 3, 4, and 5), there was a need for a clearly defined field experiment that manipulated the soil exchangeable K:Mg ratios by the addition of K and Mg fertilisers and investigating their effects on tree nutrition.

Therefore, FR initiated a field trial, FR190/8, in September 1996 on a Pumice Soil at compartment 1079 of Kaingaroa Forest, near Rotorua. The objective of this trial was to

change the soil K:Mg balance, by applying Mg and K fertiliser and studying the effects of the treatments on Mg and K uptake by *P. radiata*, and on the development and severity of UMCY symptoms.

This new trial offered an opportunity to study the leaching losses of Mg in a Pumice Soil as influenced by Mg and K fertiliser application. Studies by Will (1961) and Hunter *et al.* (1986) showed that Mg deficiency symptoms in *P. radiata* could be corrected by applying Mg fertiliser. But when soluble Mg fertilisers were used a large portion of the applied Mg was reported to have been lost due to leaching. However, the studies of Will (1961) and Hunter *et al.* (1986) did not specifically determine the quantities of fertiliser Mg lost and how quickly after application it was lost. Therefore, a suction cup lysimeter study was initiated in 1996 to run alongside the FR study described in the preceding paragraph to monitor the effects of Mg and K fertilisers on soil solution concentrations of Mg and K in the topsoil, where most of the active roots are, and the leaching losses of these cations below the root zone.

7.2 OBJECTIVES

The objectives of the study reported in this chapter were:

1. To study the effects of kieserite ($MgSO_4.H_20$) applied at 200 kg Mg ha^{-1} and K_2SO_4 applied at 200 and 400 kg K ha^{-1} on soil solution concentrations of Mg and K over 18 months.
2. To determine Mg and K leaching losses below the upper root zone using suction cup lysimeters after application of Mg and K fertilisers.
3. To investigate the effect of the Mg and K fertiliser treatments on the soil cation balances and foliar Mg and K concentrations.

7.3 MATERIALS AND METHODS

7.3.1 Site and soil description

The site of FR190/8 is adjacent to FR190/5 in Cpt1079, Kaingaroa Forest, near Rotorua described in Chapter 3. Soil and stand details were presented in Chapter 3.

7.3.2 Treatments

The trial consists of 4 treatments: 200 kg Mg ha^{-1} applied as kieserite ($MgSO_4.H_2O$), 200 and 400 kg K ha^{-1} applied as K_2SO_4, and a no-fertiliser control. Each treatment was replicated 5 times to give 20 plots in total and arranged in a randomised complete block design. Treatments were broadcast applied on 19 September 1996. The plot size was 50 x 50 m^2 with a 10 m buffer around each 30 x 30 m^2 inner measurement plot consisting of approximately 20 measurement trees.

7.3.3 Suction cup lysimeter installation

The suction cup lysimeters consisted of a round-bottomed porous ceramic cup cemented to an appropriate length of PVC pipe. The lysimeters were cleaned by flushing with 0.5 *M* HCl followed by several flushes with distilled water. Two suction cup lysimeters were installed on 18 September 1996 in each of the 20 plots at 2 depths, 10 cm and 45 cm from the soil surface (Figure 7.1). The 10 cm lysimeters were installed by drilling a hole with an auger of slightly smaller diameter than the lysimeters to ensure close contact between the soil and the lysimeter. The lysimeters at 45 cm were installed by digging a hole to about 30 cm with a spade then drilling a hole to 45 cm with an auger as described for the 10 cm lysimeter. Soil was then carefully returned to the hole in the order it was removed, maintaining as close as possible the original make-up of the soil profile. The lysimeters were positioned, under a gap in the canopy and equidistant from the surrounding trees. The position of the lysimeters, as much as possible, avoided any rain fall that had passed through the canopy and stem flow. They were also located away from any shrubby under-growth and any obvious areas of soil disturbance (e.g. old skidder tracks).

Figure 7.1 Lysimeter installation at FR190/8 trial.

The lysimeters were left to equilibrate for 21 days before sampling commenced.

7.3.4 Solution and soil sampling, and sample analysis

Soil solution samples were first collected from the lysimeters on 11 October 1996. Lysimeters were evacuated to an average tension of -50 kPa (0.5 bar), the maximum tension possible, to ensure an adequate volume of soil solution was removed from the surrounding soil over a period of 24 hours. At this tension, readily available soil water from pores >6 μm would have been sampled (Loveday 1973). The resulting solutions were siphoned off into vials the next day and stored in a refrigerator for chemical analysis. Initially, samples were collected at about 20 day intervals up to 90 days after fertiliser application and subsequently at about six weekly intervals till March 1998. Samples were not collected during the drier summer months as the soil water content was expected to be below field capacity and leaching is unlikely to have taken place.

Concentrations of Mg, K and Ca in the solution were measured by atomic absorption spectrometry (AAS).

Soil samples were collected in March 1997 (approximately 180 days after fertiliser application) from the top 10 cm of each plot. Twenty 2 cm diameter soil cores were collected at random and combined to make a bulk sample for each plot. A second set of soil samples was collected in March 1998 (approximately 550 days since fertiliser application) from the top 10 cm of each plot by randomly taking six, 18 x 18 x 10 cm^3 blocks of soil. Smaller sub-samples from these blocks of soil were sampled for chemical analysis after thorough mixing. Samples collected in 1998 were part of another study where the chemical compositions of bulk soils were compared with rhizosphere soils of *P. radiata*. In this study the bulk soils had to be collected in blocks close to the rhizosphere soils and hence the difference in the sampling procedure to that of the 1997 samples.

Soil solutions were extracted from one portion of the field moist soils by centrifugation at 12,000 rpm (17200 RCF) in a refrigerated centrifuge at 4^0C within two days of sample collection. This would yield solutions held at tensions of ~0-3600 kPa. At this tension range, solution would be extracted from soil pores greater than at least 0.08 μm in diameter (Loveday 1973). The pH of the resulting solutions was measured immediately after centrifugation. Concentrations of Mg, K and Ca in the solution were measured by AAS.

The remaining portion of the field moist soil was air-dried and ground to pass through a 2 mm sieve. Soils were analysed for pH, exchangeable Mg, K and Ca (extraction with 1 *M* NH_4OAc buffered at pH 7.0, Blakemore *et al.* 1987), exchange acidity and exchangeable Al (Yuan 1959). Concentrations of Mg, K, Ca and Al in the extracts were measured by AAS and exchange acidity by NaOH titration using phenolphthalein indicator.

7.3.5 Foliar sampling and analysis

Foliage samples were taken from the trial in March 1997, 1998 and 1999. Fully extended needles from the current season from secondary branches in the upper third of the crown were sampled at random from 12 trees per plot (Beets and Jokela 1994). Samples were oven - dried at 70° C. and analysed for Mg and K by AAS after digesting in H_2SO_4/H_2O_2 mix (Nicholson 1984).

7.4 RESULTS AND DISCUSSION

7.4.1 Effect of Mg and K fertilisers on concentrations of soil solution Mg, K and Ca in the lysimeters at 10 cm depth

7.4.1.1 Soil solution Mg

Immediately after fertiliser application there was a significant ($P < 0.05$) increase in soil solution Mg concentrations for all fertiliser treatments compared to the control treatment (Figure 7.2). This was a direct result of the Mg fertiliser treatment and also the K fertiliser treatments causing exchange of Mg by K from the exchange sites. The application of Mg fertiliser at 200 kg Mg ha^{-1} has resulted in the greatest increase in solution Mg concentrations followed by the K fertiliser application at 400 kg K ha^{-1}. The significant ($P < 0.05$) increase in solution Mg concentrations for the Mg fertiliser treated plots was maintained up to and including the sampling at 60 days, although solution concentrations have progressively declined over this period. From 180 days to the last sampling at about 550 days solution Mg concentrations were maintained at levels close to those for the control treatment (Figure 7.2). Increases in solution Mg concentrations due to the application of K fertiliser also declined, but more rapidly than those for the Mg fertiliser treatment and by 90 days had returned to levels similar to those in the control treatment.

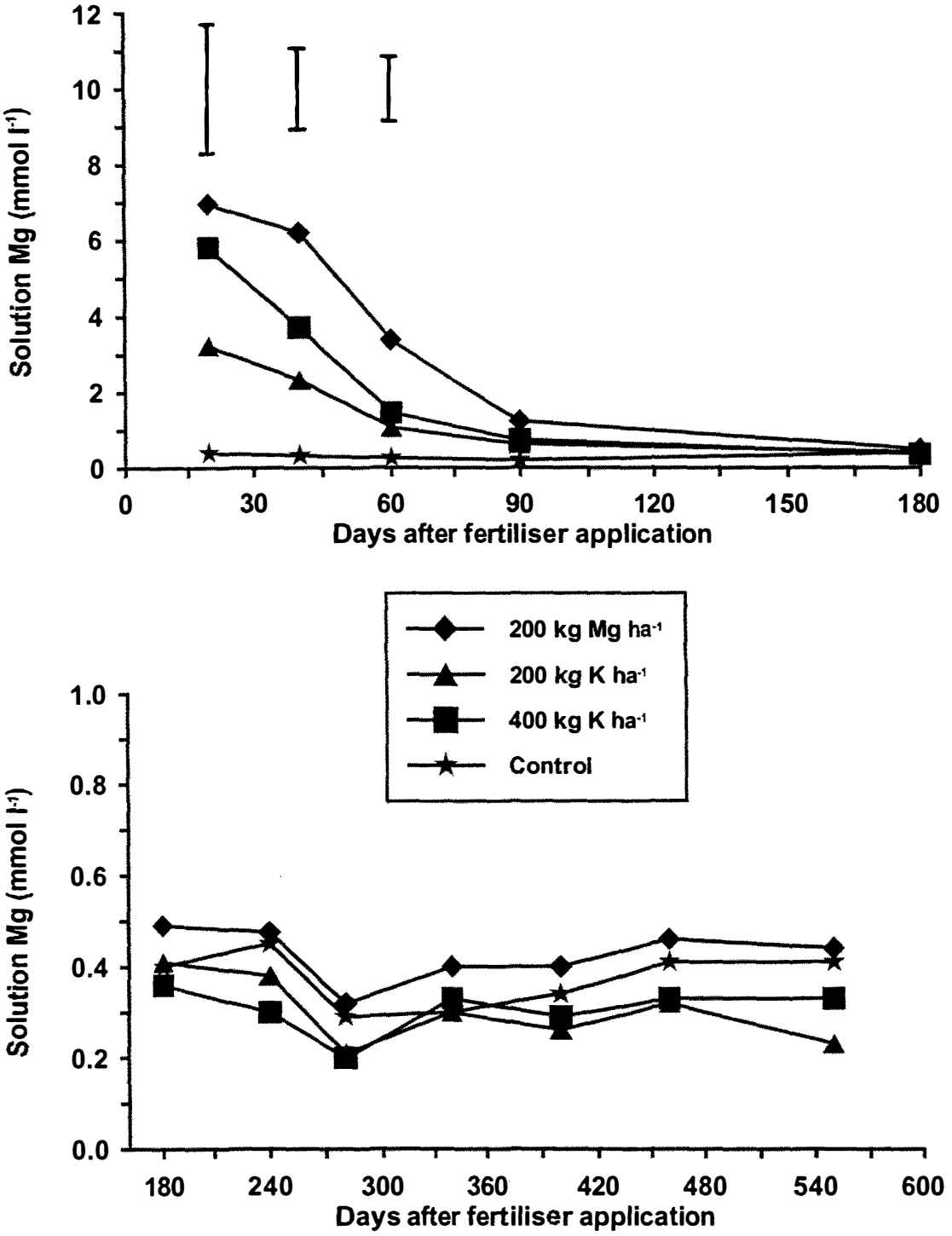


Figure 7.2 Effect of Mg and K fertilisers on soil solution concentrations of Mg in lysimeters at 10 cm soil depth in FR190/8. Vertical bars represent l.s.d. at $P = 0.05$. (Note change of scale after day 180).

Derome and Saarsalmi (1999) have reported similar results in a stand of Scots pine (*P. sylvestris*) on an Orthic Podzol at Harjavalta, Finland. Magnesium fertiliser applied as dolomitic limestone at 100 kg Mg ha^{-1} and at 61 kg Mg ha^{-1} in combination with other major macro and micro nutrients (P, K, Ca, S, B, Cu and Zn) applied as both slow-release powdered minerals and fast-release, water-soluble salts, resulted in strong increases in concentrations of solution Mg within a month after application. Derome and Saarsalmi (1999) reported that concentrations of solution Mg declined sharply within one-year of application. But, in contrast to the results FR190/8, solution Mg concentrations remained higher than those in the no-fertiliser control plots.

7.4.1.2 Soil solution K

In the first sampling after fertiliser application, soil solution K concentrations were significantly ($P < 0.05$) increased compared to the control treatment, by K fertiliser application at 400 kg K ha^{-1}. However, increases in the soil solution K concentrations for the 200 kg K ha^{-1} fertiliser treatment were not statistically significant ($P < 0.05$) compared to the control treatment (Figure 7.3). There was a sharp decline in solution K concentrations with time for the 400 kg K ha^{-1} fertilised plots, similar to the decline in solution Mg concentrations. However, the differences in solution K concentrations between this treatment and the 200 kg K ha^{-1} plots, Mg fertilised plots, and control plots remained significant up to and including the sampling at 180 days (Figure 7.3). From 240 days to the final sampling, K concentrations declined to levels similar to those for the control treatment.

Although, K fertiliser application increased Mg concentrations in solution (Figure 7.2), Mg fertiliser application did not increase solution K concentration (Figure 7.3). The reason for this is unclear. However, examining the data presented in Figure 7.4 indicates that Mg has exchanged with Ca on the exchange sites in preference to K. There was a significant ($P < 0.05$) increase in solution Ca concentration due to the Mg fertiliser treatment compared to the control treatment.

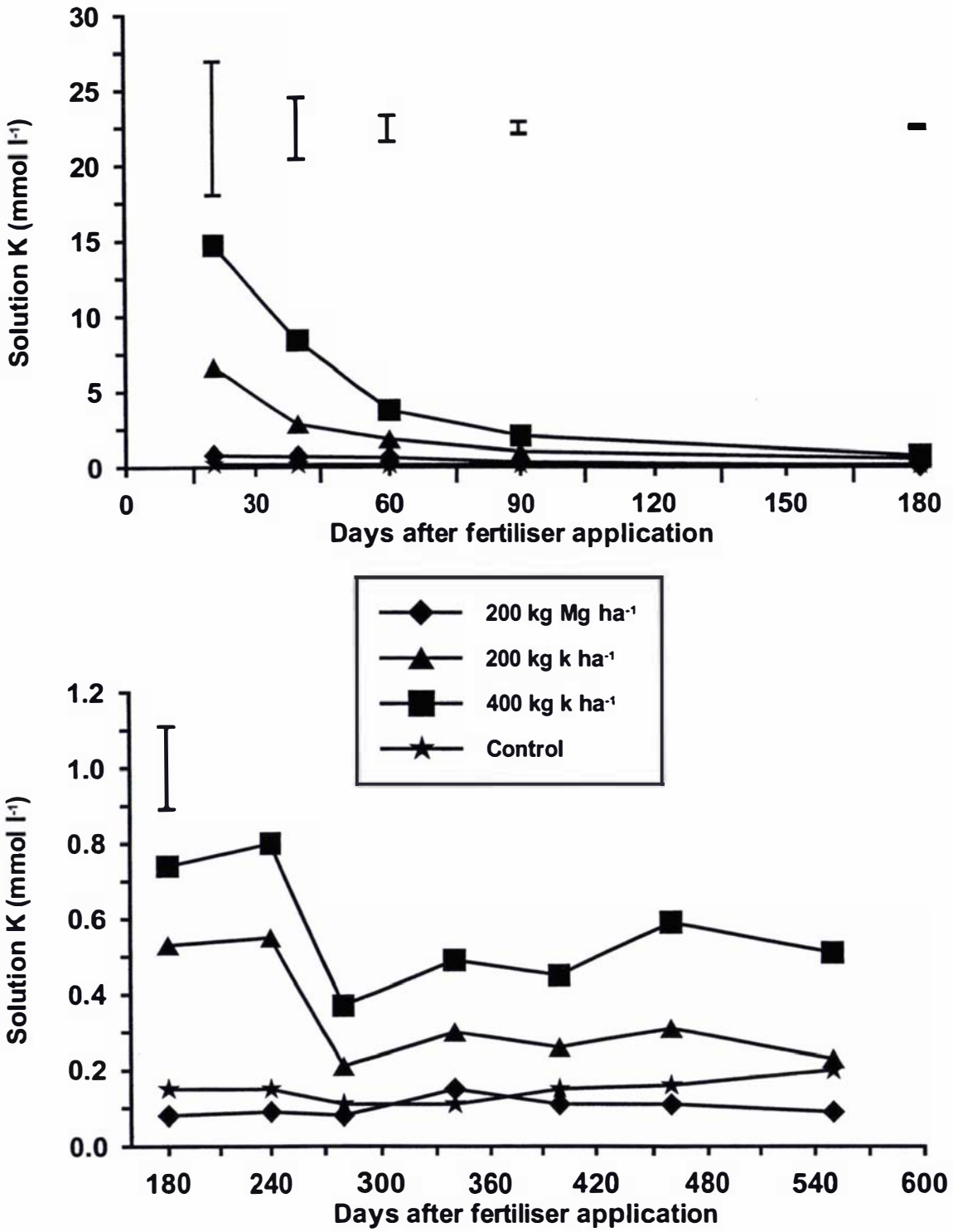


Figure 7.3 Effect of Mg and K fertilisers on soil solution concentrations of K in lysimeters at 10 cm soil depth in FR190/8. Vertical bars represent l.s.d. at $P = 0.05$. (Note change of scale after day 180).

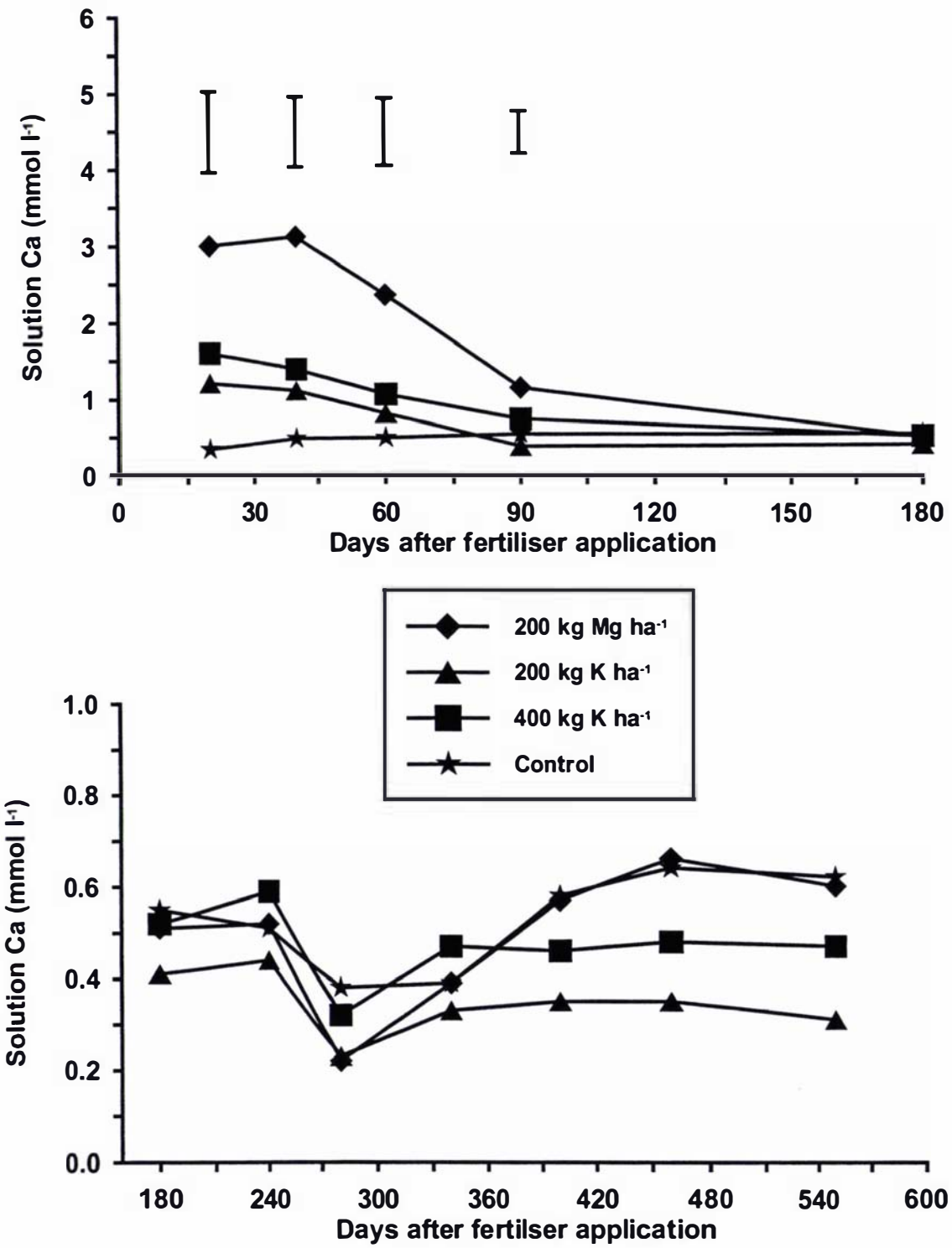


Figure 7.4 Effect of Mg and K fertilisers on soil solution concentrations of Ca in lysimeters at 10 cm soil depth in FR190/8. Vertical bars represent l.s.d. at $P = 0.05$. (Note change of scale at day 180).

As discussed for solution Mg under Section 7.4.1.1, Derome and Saarsalmi (1999) also reported a strong increase in solution concentrations of K within one month of application of P, K, Ca, Mg, S, B, Cu and Zn fertilisers, where K was applied at a rate of 56 kg K ha^{-1}. There was a sharp decline in solution K concentrations in the year after fertiliser application, as reported for solution Mg. However, solution K concentrations were maintained at levels greater than those for the no-fertiliser control.

7.4.1.3 Soil solution Ca

Soil solution Ca concentrations in the first four samplings (up to 90 days after fertiliser application) were significantly ($P < 0.05$) increased by the application of Mg compared to the control treatment. As explained in a previous paragraph, Mg from the fertiliser has replaced Ca on the exchange sites and Ca has been released into solution (Figure 7.4). However, Ca concentrations, as with solution Mg and K, progressively declined over this period. By the sampling at 180 days after fertiliser application, solution Ca concentrations returned to levels similar to those of the control treatment. Potassium fertiliser application also increased Ca concentrations in solution in the first four samplings, although the increase in Ca concentration over the control treatment was significant ($P < 0.05$) only at the highest rate of K application (400 kg Mg ha^{-1}). Potassium from fertiliser application has replaced Ca on the exchange sites, releasing Ca into solution, as was reported for Mg fertiliser application. The increases in concentrations of solution Ca due to K fertiliser application declined over time and returned to levels close to those of the control treatment by 90 days (Figure 7.4).

7.4.2 Effect of Mg and K fertilisers on soil solution K to Mg molar ratios in the lysimeters at 10 cm depth

One of the objectives of this trial was to amend the K:Mg ratio in the soil to investigate the effects of a range of soil K:Mg ratios on the incidence and severity of UMCY. Therefore, the effect of Mg and K application on soil solution K:Mg molar ratios was examined. The application of Mg and K fertilisers has produced a range of soil solution K:Mg molar ratios (Figure 7.5).

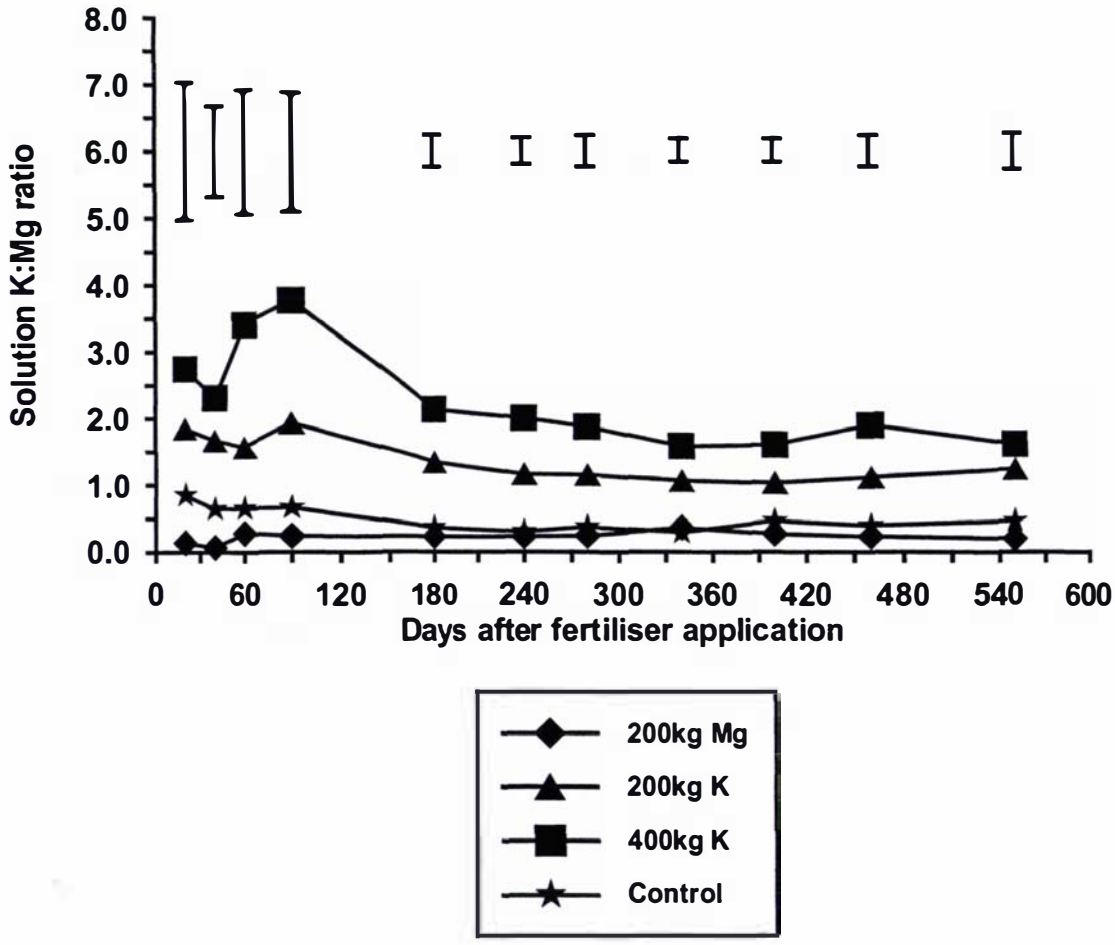


Figure 7.5 Effect of Mg and K fertilisers on soil solution K:Mg molar ratio in lysimeters at 10 cm soil depth in FR190/8. Vertical bars represent l.s.d. $P = 0.05$.

Application of Mg fertiliser has generally reduced solution K:Mg molar ratios compared to the control treatment at all samplings although, none of these decreases were significant ($P > 0.05$) (Figure 7.5). However, the application of K fertiliser at both rates has significantly ($P < 0.05$) increased solution K:Mg molar ratios compared to the control treatment at all samplings times (Figure 7.5). Potassium fertiliser application at 400 kg K ha^{-1} has also increased K:Mg molar ratio over the 200 kg K ha^{-1} treatment. Potassium to Mg molar ratios for both K fertiliser treatments have declined over time, but they have remained significantly ($P < 0.05$) greater than those in the control treatment up to and including the sampling at 550 days (Figure 7.5). The effect of the

change in solution K:Mg molar ratio caused by fertiliser application, on foliar K:Mg concentration ratios will be examined in section 7.4.11.

7.4.3 Effect of Mg and K fertilisers on soil pH, exchange acidity and ECEC in 0-10 cm soil layer

Magnesium and K fertiliser application had no effect on soil pH in both years (Figure 7.6). This is due to the sulfate forms of fertiliser (kieserite and K_2SO_4) used in the trial. Neither of these fertilisers has appreciable acid nor alkaline properties, nor do they react in soil to produce significant acidity or alkalinity. These contrasts with the findings reported in Chapter 3 and the dissolution study reported in Chapter 5 where, alkaline Mg fertiliser applications significantly increased soil pH.

In accordance with the lack of response in soil pH due to fertilisation, exchange acidity was unaffected by the Mg and K fertilisers (Figure 7.6). Magnesium and K fertiliser application also had no significant ($P > 0.05$) effect on ECEC (Figure 7.6).

7.4.4 Effect of Mg and K fertilisers on soil exchangeable Mg in 0-10 cm soil layer

Magnesium fertiliser application significantly ($P < 0.05$) increased soil exchangeable Mg over the control treatment in the 0-10 cm soil layer in both years of sampling (Figure 7.7). The increases in exchangeable Mg equate to approximately 124 kg Mg ha^{-1} in 1997 and 88 kg Mg ha^{-1} in 1998 (representing increases of the control value of approximately 240% and 170% in 1997 and 1998 samplings, respectively) above the control plots. However, the increases in exchangeable Mg were less than those recorded at FR190/5 (152 kg Mg ha^{-1} in 1997) (Chapter 3), which has similar ECEC to FR190/8 and in spite of a lower rate of Mg fertiliser application at FR190/5 (150 kg Mg ha^{-1} at FR190/5 and 200 kg Mg ha^{-1} at FR190/8). The lower increase in exchangeable Mg at 190/8 may be due to considerably greater leaching of Mg at this site because of the use of soluble Mg fertiliser.

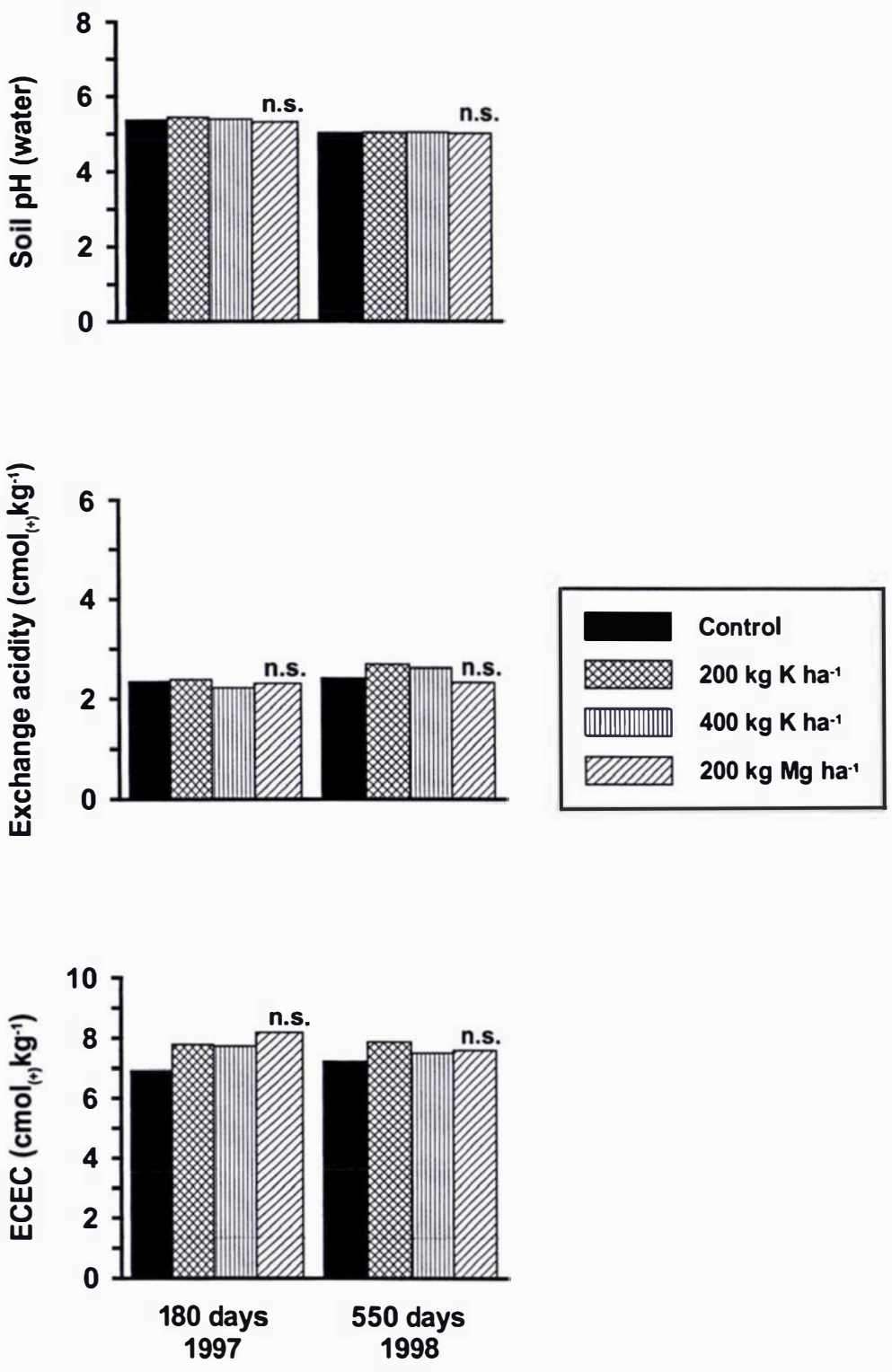


Figure 7.6 Effect of Mg and K fertilisers on soil pH, exchange acidity and ECEC in the top 10 cm soil layer at FR190/8, 180 and 550 days after application. n.s. - no significant difference between treatment means.

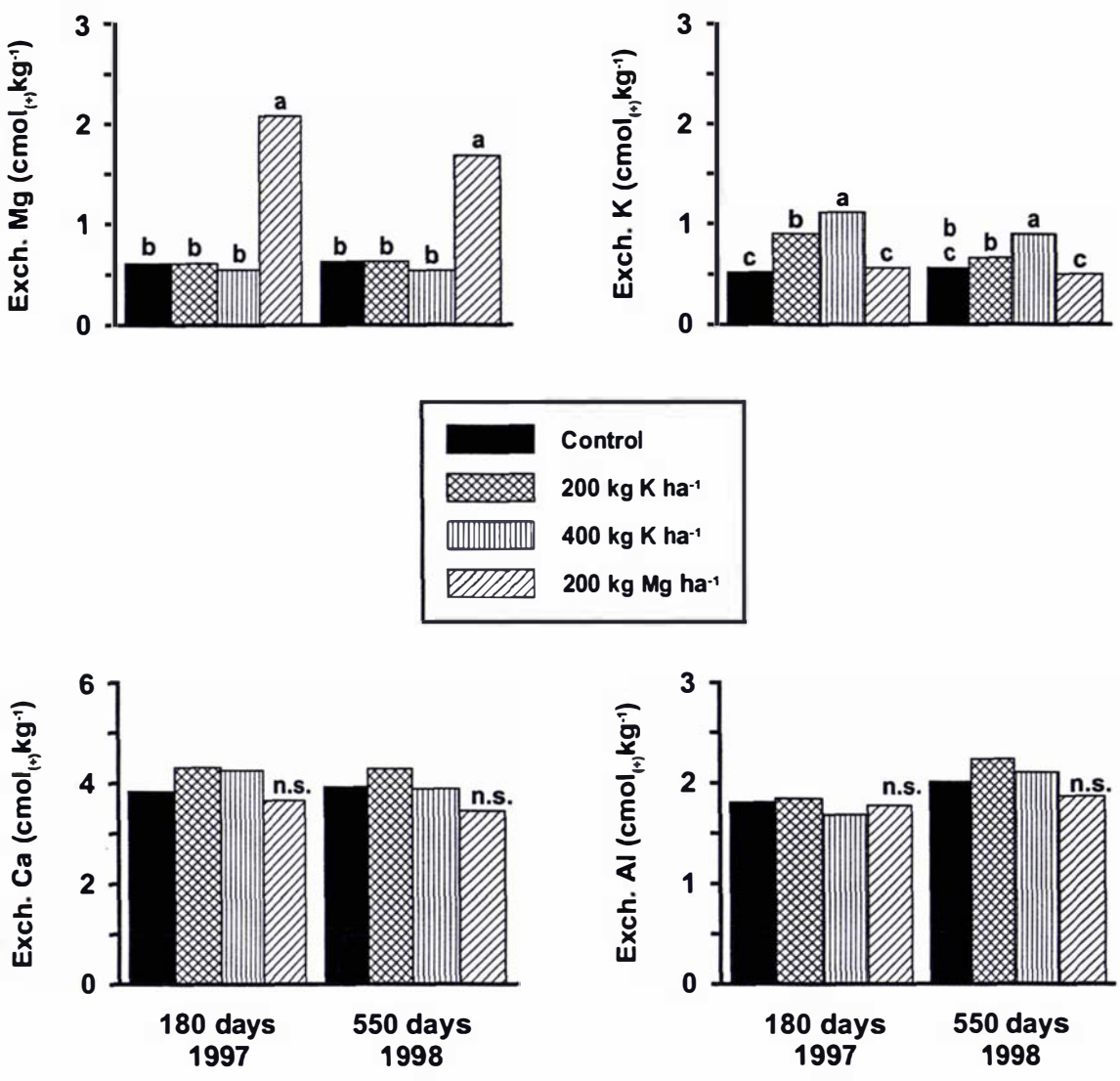


Figure 7.7 Effect of Mg and K fertilisers on soil exchangeable cations in the top 10 cm soil layer at FR190/8, 180 and 550 days after application. Means with the same letter are not significantly different at $P = 0.05$. n.s. - no significant difference between treatment means.

Based on the difference in total Mg uptake between Mg-fertilised and unfertilised 11-year-old *P. radiata* of 9 kg Mg ha^{-1} $year^{-1}$, as used in Chapters 3 and 4 (Hunter *et al* 1986; Beets pers. com.), estimated uptake by the trees for the 18 months following fertiliser application was 14 kg Mg ha^{-1} (9 kg Mg ha^{-1}/12 months*18 months). The increase in exchangeable Mg due to fertiliser application in 1998 was 88 kg Mg ha^{-1} (exchangeable Mg in Mg fertilised plots, 141 kg Mg ha^{-1} minus exchangeable Mg in control plots, 53 kg Mg ha^{-1}). Therefore, estimated losses of applied fertiliser Mg from

the top 10 cm of soil due to leaching in 18 months after fertiliser application, was calculated to be about 98 kg Mg ha^{-1} or 49% of applied fertiliser Mg (Mg applied as fertiliser, 200 kg Mg ha^{-1} minus increase in exchangeable Mg due to fertiliser application, 88 kg Mg ha^{-1} minus estimated tree uptake, 14 kg Mg ha^{-1}). This is considerably more than the estimated losses reported in Chapters 3 and 4 from trials fertilised with calmag fertiliser. The estimated leaching losses in these two chapters were between 0-20% of applied fertiliser Mg. That there were greater estimated losses of Mg in this study compared to the studies reported in Chapters 3 and 4, is not surprising. The kieserite ($MgSO_4.H_2O$) fertiliser applied in the FR190/8 trial is highly soluble compared to the calmag used in the studies reported in Chapter 3 and 4. In addition, a mobile anion (SO_4) was also added as a component of the fertiliser in this trial.

The loss reported in this chapter for FR190/8 was much less than the losses from the top 10 cm of soil of approximately 78% of the applied fertiliser Mg reported by Payn (1991) for Epsom salts ($MgSO_4.7H_2O$) applied at 400 kg Mg ha^{-1} to a Pumice Soil under three-year-old *P. radiata*. The difference in estimated leaching losses between FR190/8 and the study of Payn (1991) was because of the higher rate of application of Epsom salts, compared to Kieserite applied in FR190/8. In addition, greater leaching losses are also likely in the study of Payn (1991), because canopy closure had not yet occurred, resulting in less interception and transpiration of rainfall by the trees and therefore, greater drainage through the soil profile.

Although there appears to be a considerable loss of fertiliser Mg below 10 cm, this does not necessarily mean that this portion of applied Mg has been lost to tree uptake. The soil at the FR190/8 trial has topsoil (A- and B-horizons, loamy sand texture) with an average depth of about 28 cm (Rijkse 1988). Therefore, a large portion of the fertiliser Mg which has moved below 10 cm depth may still remain in the topsoil layer and available for tree uptake. Exchangeable Mg concentrations were not measured in the soil below 10 cm to investigate this.

The application of K fertiliser had no significant ($P > 0.05$) effect on exchangeable Mg concentrations at 180 and 550 days after application (Figure 7.7) in spite of significant increases in solution Mg concentration up to 60 days following application (Figure 7.2).

7.4.5 Effect of Mg and K fertilisers on soil exchangeable K in 0-10 cm soil layer

Potassium fertiliser application at 400 kg K ha^{-1} significantly ($P < 0.05$) increased soil exchangeable K over the no-fertiliser treatment for both years (approximate 115% increase in 1997 and 60% increase in 1998) (Figure 7.7). Potassium fertiliser applied at 200 kg K ha^{-1} also significantly ($P < 0.05$) increased soil exchangeable K over the control but, only in the 1997 sampling (by approximately 80%).

In the 1997 soil samples, the increase in exchangeable K (102 kg K ha^{-1}) above the no-fertiliser control, due to application of K fertiliser application at 200 kg K ha^{-1} was less than the increase in exchangeable Mg (124 kg Mg ha^{-1}) at the same rate of Mg application (200 kg Mg ha^{-1}). Application of K fertiliser at the high rate (400 kg K ha^{-1}) not surprisingly, resulted in a greater increase exchangeable K (159 kg K ha^{-1}) above the no-fertiliser control, than the increase in exchangeable Mg due to Mg fertiliser application. In the 1998 soil samples, the increase in exchangeable K, above the control, due to K fertiliser application at 200 kg K ha^{-1} declined to 26 kg K ha^{-1}. The increase in exchangeable K, above the no-fertiliser control for K fertiliser application at the high rate (400 kg K ha^{-1}) has also declined to 88 kg K ha^{-1}. This was similar to the increase over the no-fertiliser control of exchangeable Mg due to Mg fertiliser application (Section 7.4.4).

The decreases in exchangeable K (76 kg K ha^{-1} decrease for low rate of K and 71 kg K ha^{-1} for the high rate of K) from K fertiliser application between the two years of sampling were greater than decreases in exchangeable Mg (36 kg Mg ha^{-1}) from fertiliser application (Figure 7.7). The reduction in exchangeable K indicates there were greater losses of K between the two years from the top 10 cm of soil due to tree uptake and leaching compared to Mg. *Pinus radiata* take up considerably more K than Mg (Madgwick *et al.* 1977). They reported uptake of 44 kg K ha^{-1} yr^{-1} by eight- to 10-year-old trees growing on pumice soil at Kaingaroa Forest of whereas, the uptake of Mg

was only 5.9 kg Mg ha^{-1} yr^{-1}. Whether the uptake of K by the trees was increased by K fertiliser application at FR190/8 trial is unknown. Increased leaching of K due to fertiliser application from the top 10 cm of soil was also likely. Soils derived from Taupo pumice have the ability to tightly retain K up to about 150 kg K ha^{-1} in the top 10 cm, above this capacity, further K retention is very weak (During 1984). Leached K may have been retained in the subsoil (Parfitt 1991), but this needs to be confirmed by soil analysis.

Magnesium fertiliser application had no significant ($P < 0.05$) effect on exchangeable K concentrations (Figure 7.7).

7.4.6 Effect of Mg and K fertilisers on soil exchangeable Ca and Al in 0-10 cm soil layer

Application of Mg fertiliser reduced exchangeable Ca although the difference was not statistically significant ($P > 0.05$) (Figure 7.7). When exchangeable Ca was expressed as a percentage of ECEC, Mg fertiliser application has significantly ($P < 0.05$) reduced Ca saturation of ECEC (Figure 7.8). Potassium fertiliser application had no significant ($P > 0.05$) effect on exchangeable Ca or exchangeable Ca expressed as a percentage of ECEC (Figures 7.7 and 7.8). Application of Mg and K fertilisers had no significant ($P > 0.05$) effect on exchangeable Al or exchangeable Al expressed as a percentage of ECEC (Figures 7.7 and 7.8).

7.4.7 Effect of Mg and K fertilisers on soil exchangeable K to Mg molar ratio in 0-10 cm soil layer

As mentioned in Section 7.4.2, a major objective for this trial was to manipulate the soil exchangeable K:Mg ratio to study its effect on nutrient balances in the trees and the severity of UMCY. Analysis of soils from other FR190 series trials (Chapters 3 and 4) shows that the soil exchangeable K:Mg molar ratio could be amended through the application of Mg fertiliser (Chapters 3 and 4). Therefore, the effect of Mg and K fertiliser applications on the soil exchangeable K:Mg molar ratio was examined.

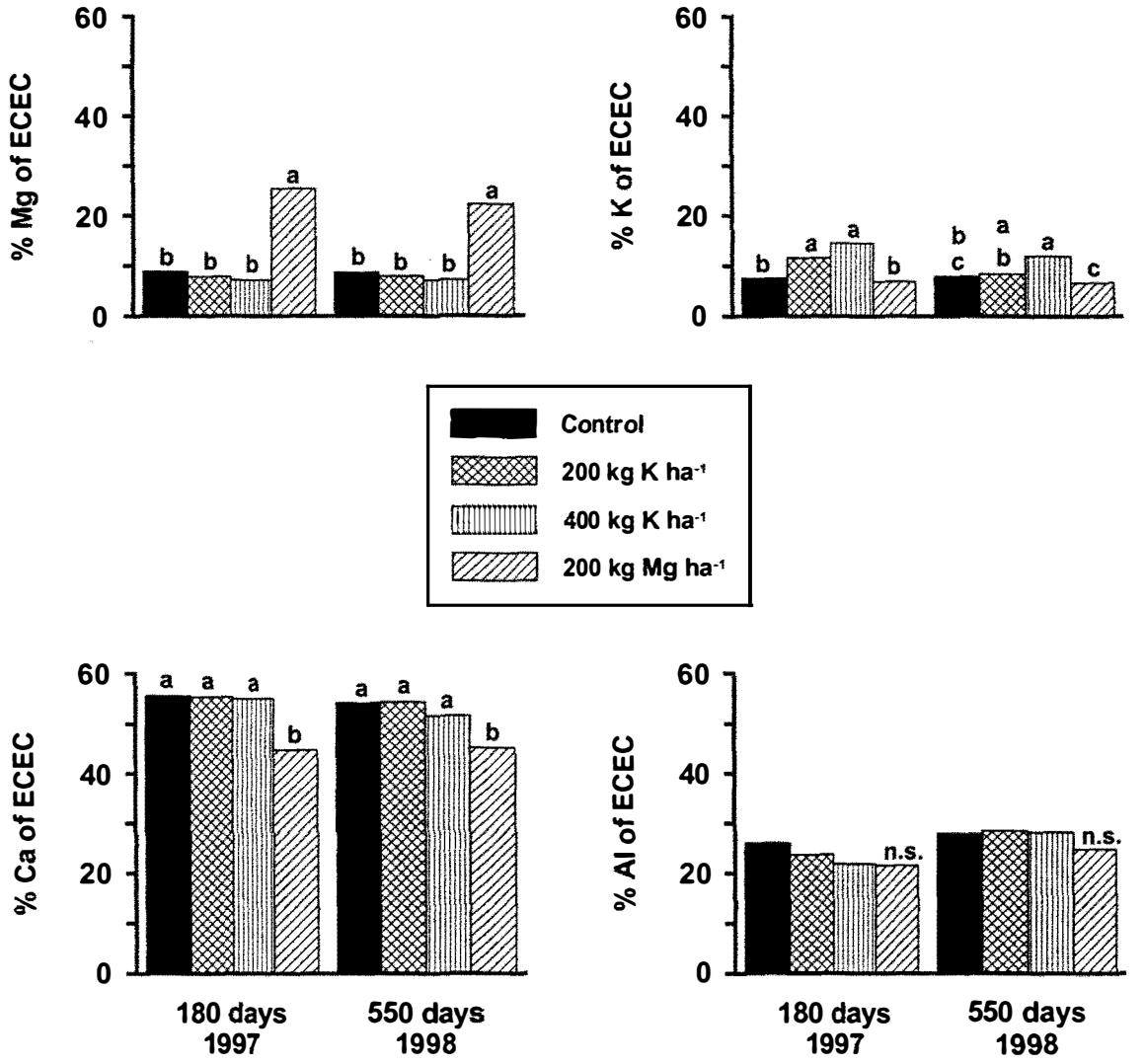


Figure 7.8 Effect of Mg and K fertilisers on cation saturation of ECEC in the top 10 cm soil layer at FR190/8, 180 and 550 days after application. Means with the same letter are not significantly different at $P = 0.05$. n.s. - no significant difference between treatment means.

Magnesium fertiliser application significantly ($P < 0.05$) decreased the soil exchangeable K:Mg molar ratio from 1.70 in the control treatment to 0.54 in 1997. In 1998, Mg fertiliser application significantly ($P < 0.05$) decreased the soil exchangeable K:Mg molar ratio from 1.84 in the control treatment to 0.60. This reflects increases in exchangeable Mg due to Mg fertiliser application (Figures 7.9 and 7.7). Potassium fertiliser application at both rates significantly ($P < 0.05$) increased the soil exchangeable K:Mg molar ratio (from 1.70 to 2.96 for the 200 kg K ha^{-1} and to 4.07 for

the 400 kg K ha^{-1}) in 1997 (Figure 7.9). Therefore, a greater increase in the exchangeable K:Mg molar ratio was observed due to 200 kg K ha^{-1} fertiliser treatment compared to the decrease in the K:Mg molar ratio due to the same rate of Mg fertiliser application (200 kg Mg ha^{-1}) in 1997.

However in 1998, due to smaller effects of the 200 kg K ha^{-1} treatment on exchangeable K, the exchangeable K:Mg molar ratio for the 200 kg K ha^{-1} treatment was not significantly ($P > 0.05$) different from that of the control treatment. Magnesium fertiliser application reduced the exchangeable K:Mg molar ratio from 1.84 in the control treatment to 0.60, whereas K fertiliser application at the same rate as Mg fertiliser application increased the exchangeable K:Mg molar ratio from 1.84 to 2.14. However, at double the rate of K (400 kg K ha^{-1}) fertiliser application the K:Mg molar ratio significantly ($P < 0.05$) increased from 1.84 to 3.43. This increase was greater than the decrease due Mg fertiliser application (Figure 7.9).

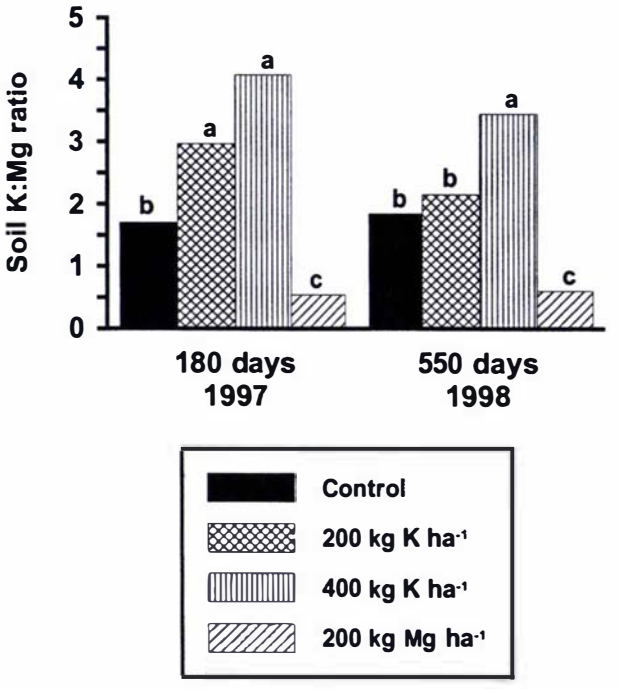


Figure 7.9 Effect of Mg and K fertilisers on soil exchangeable K:Mg molar ratio in the top 10 cm soil layer at FR190/8, 180 and 550 days after application. Means with the same letter are not significantly different at $P = 0.05$.

The results show that through Mg and K fertiliser application, a range of soil exchangeable K:Mg ratios (from 0.6 to 3.43 based on 1998 data) could be obtained at this site. In addition, the application of Mg fertiliser appears to be proportionately more effective at amending the exchangeable K:Mg molar ratio in the top 10 cm of soil over a longer period, as only the higher rate of K fertiliser has maintained a significant increase in the exchangeable K:Mg ratio over the control treatment for both years. Magnesium fertiliser at half the rate of application caused significant ($P < 0.05$) decreases in K:Mg ratio in both years.

7.4.8 Comparison of concentrations of cations in soil solutions extracted by lysimeters and centrifugation

A comparison of the concentrations of Mg, K and Ca in solution samples collected from the lysimeters at 10 cm 180 days and 550 days after fertiliser application with those extracted by centrifugation shows that there are considerable differences in concentrations of ions extracted by the two methods (Table 7.1). Concentrations of Mg and Ca were higher in the lysimeter solutions compared to those extracted bycentrifugation, whereas, concentrations of K were generally higher in the centrifuged solutions (Table 7.1).

Other studies have also reported differences in the concentrations of ions in solutions extracted by lysimeters compared to centrifugation. Parfitt *et al.* (1997) reported ion concentrations in soil solutions extracted by lysimeters (from pores greater than 0.06 mm diameter) and by centrifugation (pore size sampled 0.003-0.06 mm) from Typic Orthic Brown soils at 0-20 cm depth under a stand of *P. radiata.*

Table 7.1 Comparison of concentrations of Mg and K in soil solutions (mean ± standard errors) extracted by lysimeters and centrifugation

Treatment	Lysimeter solution			Centrifuged solution		
	Mg	K	Ca	Mg	K	Ca
		($mmol.l^{-1}$)			($mmol.l^{-1}$)	
			180 days			
Control	0.41	0.14	0.55	0.06	0.28	0.15
	±0.08	±0.08	±0.25	±0.02	±0.08	±0.03
200 kg K ha^{-1}	0.41	0.53	0.41	0.07	0.81	0.20
	±0.13	±0.26	±0.25	±0.02	±0.17	±0.06
400 kg K ha^{-1}	0.36	0.74	0.52	0.14	1.90	0.41
	±0.12	±0.08	±0.10	±0.09	±0.71	±0.25
200 kg Mg ha^{-1}	0.46	0.08	0.51	0.42	0.48	0.31
	±0.16	±0.04	±0.23	±0.14	±0.07	±0.10
			550 days			
Control	0.41	0.20	0.62	0.05	0.19	0.11
	±0.06	±0.17	±0.11	±0.01	±0.05	±0.02
200 kg K ha^{-1}	0.23	0.23	0.31	0.05	0.36	0.11
	±0.12	±0.06	±0.20	±0.01	±0.10	±0.01
400 kg K ha^{-1}	0.33	0.51	0.49	0.06	0.53	0.13
	±0.07	±0.09	±0.05	±0.02	±0.21	±0.06
200 kg Mg ha^{-1}	0.44	0.09	0.60	0.12	0.21	0.11
	±0.06	±0.01	±0.07	±0.06	±0.05	±0.03

They found that the concentrations of Mg, K and Ca in centrifuged solutions to be greater than those in lysimeter solutions. The reason for this was not clear, but Parfitt *et al.* (1997) thought it might have been due to preferential flowpaths in the macropores or non-equilibrium between macropores and micropores. In the study by Zabowski and Ugolini (1990) solutions collected by centrifugation showed strong seasonal differences in concentrations of cation whereas, few seasonal changes were recorded for cation

concentrations collected by lysimeters. A reason for this difference suggested by Zabowski and Ugolini (1990), which is in agreement with that of Parfitt *et al.* (1997), was that there was only limited interchange between micropore water and water moving through the macropores. Water held in the micropores is retained in the pores for longer periods than water in the macropores. Therefore, water in the micropores can have a longer equilibration period resulting in higher concentrations of cations in solution. The centrifuged method extracts solution from more micropores than the lysimeter method and therefore results in higher concentrations of cations in solutions.

This reason could explain the differences recorded in the study at FR190/8 for solution K but, the results for solution Mg and Ca recorded by Parfitt *et al.* (1997) contrast to those at FR190/8. The study of Parfitt *et al.* (1997) used lysimeters consisting of a 25 mm diameter Millipore GFC filter with a 90 mm glass filter paper (GFC) wick. Solutions sampled through glass filter are known not to significantly alter solutions passing through them compared to ceramic cups (Silkworth and Grigal 1981; Bottcher *et al.* 1984). This suggests that the ceramic cups used in the study at FR190/8 may be influencing the Mg and Ca composition of the solution. Wolff (1967) found that ceramic cups increased the Mg and Ca content of water passing through the cup, in spite of rinsing of the cups with 1 *M* HCl prior to use. Rasmussen *et al.* (1986) have also shown that soil leachates and blank solutions (distilled water at pH 3.0) were enriched with considerable amounts of Mg and Ca after passing through ceramic cups. The ceramic cups used in this study were rinsed with acid followed by distilled water before use. But still Ca and Mg could have been released over a period of time from the ceramic cup material. This might be a reason for the higher concentrations of these ions in lysimeter solutions compared to centrifuge solutions.

However, the concentrations of cations in soil solutions extracted in the lysimeters at 45 cm (Figure 7.11) (discussed in the next section), suggests that any Mg and Ca coming into solution from the ceramic cup material is minimal, as concentrations of Mg and Ca in the lysimeters in the no-fertiliser plots are consistently low (< 0.1 mmol l^{-1}) in all samplings. If the higher concentrations of Mg and Ca in the top soil lysimeters, compared to centrifuged samples, was due to release of Mg and Ca from the ceramic cup material, concentrations of these ions would have been much higher in the

lysimeters at 45 cm. Grossmann and Udluft (1991) reviewed the literature on extraction of soil water by suction-cup lysimeters. They suggested that the presence of colloids in soil water, either organic substances or hydroxide complexes of some metals, if not filtered out by the suction cup, could be a cause of contamination. The soil in the top 10 cm is high in organic matter. The lysimeters in this soil layer may have not filtered out these colloids from solution during extraction. This may be a possible reason for the higher concentrations of Mg and Ca in the lysimeter solutions. Solutions extracted by centrifugation were filtered through a 0.45 μm filter, which would have removed any colloids in solution, whereas lysimeters solutions were not filtered.

In a study by Nagpal (1982), porous ceramic cups were found to retain solution K from a prepared nutrient solution as it passed through the cups. This could be another reason for the lower K concentrations in solution extracted from lysimeters compared to those from centrifugation at least in the initial stages of the trial where the ceramic cups were largely free of adsorbed K.

Magnesium concentrations in centrifuged solution at 180 days and 550 days after Mg fertiliser application were significantly ($P < 0.05$) higher in the Mg fertilised plots than those in the no-fertiliser control plots at both times (Figure 7.10). However, there was no effect of Mg fertiliser application on solution Mg concentration in the lysimeter samples for the same two times (Table 7.1). In contrast to the behaviour of Mg fertiliser, the effect of K fertiliser application on K concentrations of solutions extracted by both lysimeters and centrifugation, and for both times were mostly similar (Table 7.1 and Figure 7.10). Significant ($P < 0.05$) increases in concentrations of solution K were recorded for both K fertiliser treatments compared to the control treatment for both solution extraction methods at 180 days. At 550 days, only the increase in solution K concentrations due to K fertiliser application at 400 kg K ha^{-1} in the centrifuged solutions was significant ($P < 0.05$) (Table 7.1 and Figure 7.10).

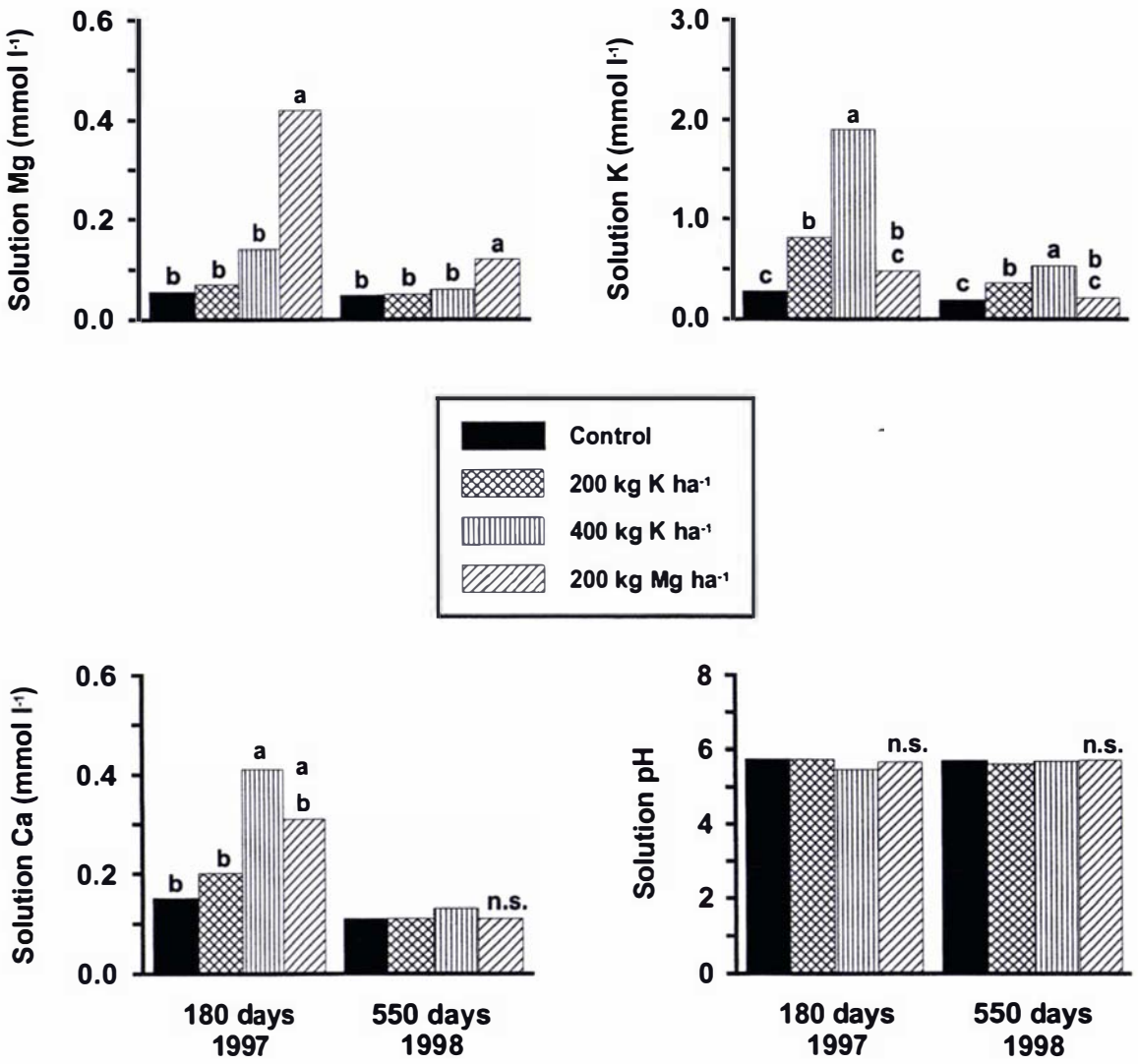


Figure 7.10 Effect of Mg and K fertilisers on centrifuged soil solution Mg, K and Ca concentrations, and pH in the top 10 cm soil layer at FR190/8, 180 and 550 days after application. Means with the same letter are not significantly different at $P = 0.05$. n.s. - no significance difference between treatment means.

7.4.9 Effect of Mg and K fertilisers on concentrations of soil solution Mg, K and Ca in the lysimeters at 45 cm depth

Results from the lysimeter soil solution analysis at 10 cm have shown that there has been a rapid decline in both solution Mg and K concentrations within 90 to 180 days of

fertiliser application. This indicates that there has been adsorption of Mg and K onto the exchange sites, tree uptake of nutrients and possibly some leaching out of the top 10cm. Examining the data presented in Figure 7.11 indicates significant amounts of Mg, K and Ca had been lost below 45 cm.

Magnesium fertiliser application appears to have increased the leaching of Mg as generally higher concentrations of solution Mg were found in the lysimeters at 45 cm in the Mg-fertilised plots compared to the control plots for all times of sampling (Figure 7.11). Mean concentrations of solution Mg in the first sampling were 0.2 mmol l^{-1} in the Mg-fertilised plots, compared to 0.07 mmol l^{-1} in the no-fertiliser control plots. Concentrations of solution Mg have peaked at 240 days at 0.58 mmol l^{-1} for the Mg fertilised plots. Whereas, mean concentrations of solution Mg have remained relatively constant in the control plots at all sampling times. At the peak at 240 days, the difference between the Mg concentrations for the Mg-fertilised plots and the control plots was significant ($P < 0.05$). From 240 days concentrations of solution Mg have slowly declined and were not significantly different to those of the control treatment (Figure 7.11).

Potassium fertiliser application at both rates of application has also increased the leaching of solution Mg probably due to exchange of Mg by K from the fertiliser and pushing exchangeable Mg into solution in the soil layers above 45 cm as reported in Section 7.4.1.1. However, the difference in Mg concentration in solution between these treatments and the control treatment was not statistically significant at any of the sampling times.

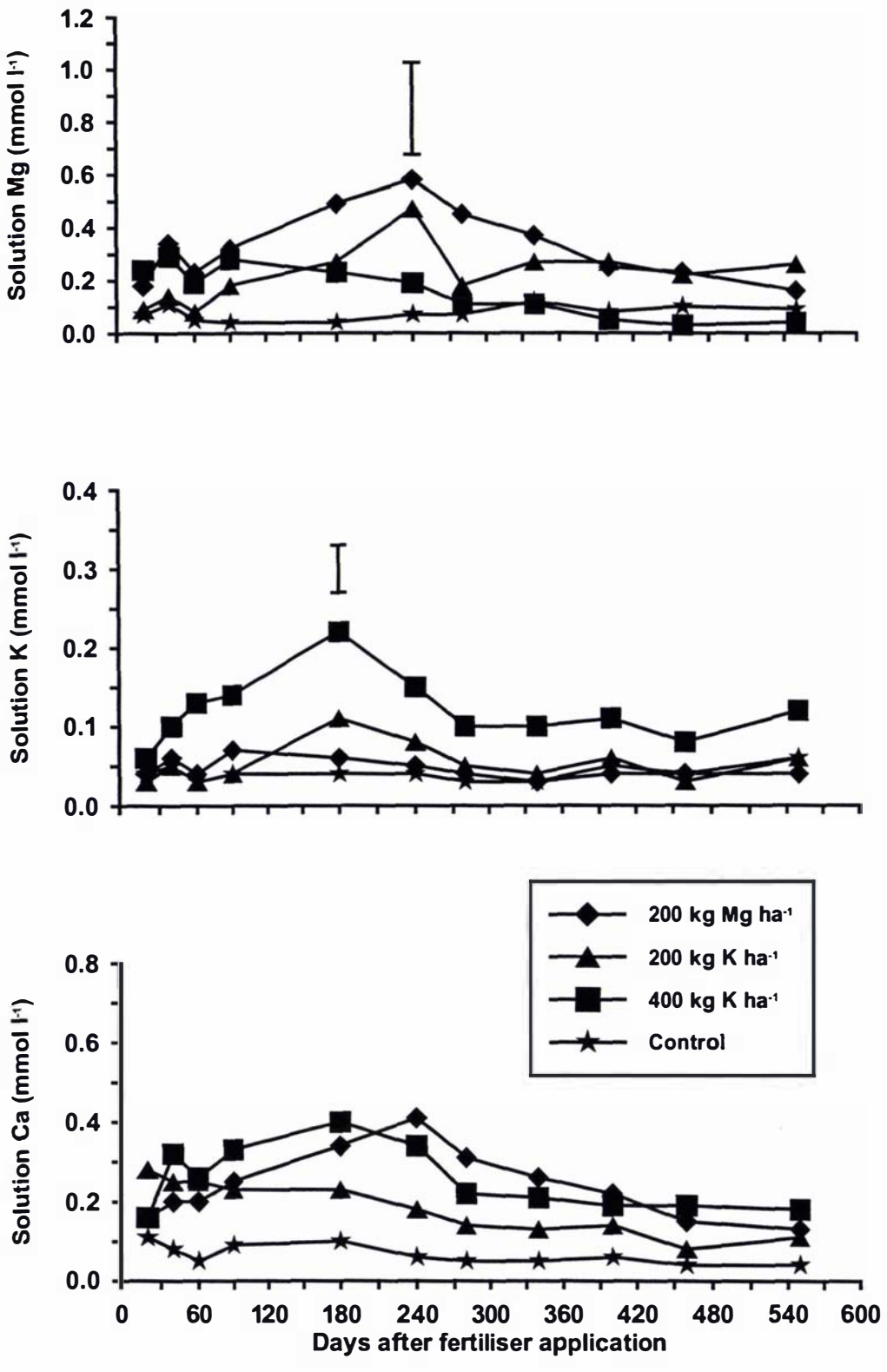


Figure 7.11 Effect of Mg and K fertilisers on concentrations of Mg, K and Ca in soil solution in lysimeters at 45 cm soil depth in FR190/8. Vertical bars represent l.s.d. at $P = 0.05$.

The application of K fertiliser has increased the rate of leaching of K, but only for K fertiliser applied at 400 kg K ha^{-1} (Figure 7.11), similar to the effect of Mg fertiliser application on Mg leaching. Potassium fertiliser application at 400 kg K ha^{-1} has resulted in consistently higher concentrations of solution K in the lysimeters at 45 cm compared to the no-fertiliser control treatment. The difference was significant ($P < 0.05$) between these treatments at the peak in solution K concentration at 180 days after fertiliser application.

Khanna *et al.* (1992) also recorded generally higher concentrations of solution Mg compared to K in lysimeters at 40 cm corresponding to greater leaching of Mg compared to K (67 kg Mg ha^{-1} compared to 28 kg K ha^{-1}) in a Yellow Podzolic soil under *P. radiata.* This was recorded in the year following the application of NPK fertiliser (400 kg N ha^{-1} as ammonium sulfate, 200 kg P ha^{-1} as superphosphate and 100 kg K ha^{-1} as potassium sulfate) applied in equal amounts in September and the following November. Khanna *et al.* (1992) reported that the application of NH_4-N in the NPK fertiliser mix resulted in significant exchange of cations from the exchange complex and the subsequent leaching probably with SO_4^{2-}.

Arnold *et al.* (1993) also recorded greater leaching losses of Mg compared to K below the root zone (100-150 cm) of a stand of Scots pine (*P. sylvestris*) for 55 months since application of Mg and K fertilisers. The experiment was located near Harderwijk, the Netherlands and the soil was developed in a coarse sandy fluvioglacial deposit covered by a fine sandy layer. The Mg was applied as kieserite at 100 kg Mg ha^{-1}, split into even amounts and applied in September 1986, 1987 and 1988, and the K applied as potassium sulfate at 100 kg K ha^{-1} also split between 3 years of application as per that for kieserite. The greater leaching losses of Mg was considered to be due to a larger crop demand for K than Mg although, it was suggested that large quantities of K could have been leached between the time of fertiliser application and the start of sampling of the experiment.

In contrast to the results reported here and those of Khanna *et al.* (1992) and Arnold *et al.* (1993), Derome and Saarsalmi (1999) reported greater leaching losses of K than Mg under a stand of Scots pine on an Orthic Podzol soil in Harjavalta, SW Finland,

fertilised with P, K, Ca, Mg, S, B, Cu and Zn as slow-release powdered minerals and fast-release, water-soluble salts over a 54 month period after application. Derome and Saarsalmi (1999) attributed the greater leaching of K than Mg to a greater proportion of K added in a fast release form (KCl) than Mg, which was applied as slow-release powdered dolomite.

Magnesium and K fertiliser application appears to have also increased leaching losses of Ca. Concentrations of Ca in the lysimeters at 45 cm in the Mg and K fertilised plots were generally greater than those in the no-fertiliser control plots (Figure 7.11). However, none of the increases in concentrations of Ca were significant ($P < 0.05$).

7.4.10 Estimation of leaching losses of Mg and K below 45 cm soil depth

In order to determine the quantities of Mg and K lost below 45 cm soil depth the amount of water draining through the profile needs to be determined. This involves calculation of a soil water balance for the soil profile and period of interest. For this investigation the amount of water drainage was calculated on a daily basis from 1 October 1996 to 31 March 1998, the duration of the trial. To estimate the soil water balance for this trial the following parameters were required: daily rainfall (P) in mm, evapotranspiration (E_r) in mm and the readily available soil water holding capacity (W_R) in mm for the soil depth of interest. Rainfall (P) measurements were taken from a weather station at Fletcher Challenge Forests office at Waiotapu, near Rotorua. A value of 120 mm, as estimated for the readily available soil water holding capacity (W_R) of the top 45 cm by Will and Stone (1967) for a pumice soil in the central region of Kaingaroa Forest was used in the soil water balance calculation at FR190/8. Average daily canopy transpiration (E_t) was estimated using the equation of Priestley-Taylor (1972). This equation is normally used to compute potential evapotranspiration for well-watered pasture (reference crop), so its use for a forest canopy is not accurate. To accurately determine evapotranspiration for a coniferous forest it is necessary to determine separately, the transpiration from the "dry canopy", and the evaporation of intercepted water from the wet canopy and stems, and evapotranspiration from the understorey (Whitehead and Kelliher 1991a). The Penman-Monteith equation (Monteith 1965) along with models of canopy conductance has been combined with the Rutter model of

interception loss (Rutter *et al.* 1971; Rutter and Morton 1977) to allow estimates of water balances for *P. radiata* stands to be made (Kelliher *et al.* 1986; Whitehead and Kelliher 1991a; Whitehead and Kelliher 1991b). However, this approach requires some complex calculations and accurate, site-specific climatic data, so is beyond the scope of this investigation. However, by allowing for a rainfall interception factor (E_i) of 15% of daily rainfall, based on the work of Whitehead and Kelliher (1991a; 1991b), and by adjusting the empirical factor used in the Priestley-Taylor equation to better suit forest conditions, estimates of evapotranspiration from the forest canopy at FR190/8 were made.

The Priestley-Taylor equation developed for daily reference crop evapotranspiration is

$$E_r = \frac{1.26 s R_n}{\rho_w L(s+\gamma)} \tag{7.1}$$

where s is the slope of the relationship between the saturated vapour density and temperature, R_n is the net radiation over the 24 period (MJ m^{-2}), ρ_w is the density of water (1000 kg m^{-3}), L is the latent heat of vaporisation of water at ambient temperature (2.5 MJ kg^{-1}) and γ is the psychrometric constant. A quadratic equation fitted to tabulated values for the dimensionless ratio of $s/(s+\gamma)$ at an air pressure of 100 kPa over the temperature range 5 to 20°C (D. Scotter pers. com.) gives

$$s/(s+\gamma) = 0.403 + 0.0164 T_{av} - 0.00012 T_{av}^2 \tag{7.2}$$

where T_{av} (°C) is the average screen air temperature for the month. The net radiation for pasture may be estimated from the daily incoming solar radiation (R_s) (Scotter *et al.* 1979) as

$$R_n = 0.62 R_s - 1.47 \tag{7.3}$$

where both R_n and R_s are in units MJ m^{-2}. Values for mature *P. radiata* forest would be higher due to the lower albedo, but this is taken into account by changes to the empirical factor. The average daily solar radiation is estimated from the average

number of sunshine hours per day for the month as described below. First the solar declination angle (all angles are in radians), δ is approximated as (Rosenberg 1974)

$$\delta = 0.41\sin\left[2\pi\left(M - 80\right)/365\right] \tag{7.4}$$

where M is the Julian day for the midpoint of the month. The half-day length, H expressed as an angle is determined from

$$H = \cos^{-1}\left(-\tan\varphi\tan\delta\right) \tag{7.5}$$

where φ is the latitude. The solar radiation received by a horizontal surface outside the earth's atmosphere (R_o) in a day in MJ m^{-2} is found as (Sellers 1965)

$$R_o = 38.5\left(H\sin\varphi\sin\delta + \cos\varphi\cos\delta H\right)\left(d_{av}/d\right)^2 \tag{7.6}$$

where d is the distance of the earth from the sun on the day in question and d_{av} is the average distance. Fitting values from Robinson (1966) to a sine wave gives

$$\left(d_{av}/d\right)^2 = 1 + 0.0334\sin\left(0.0172M - 4.81\right) \tag{7.7}$$

The maximum number of sunshine hours measurable on the mid-month day (N) is calculated from

$$N = 24H/\pi - 0.5 \tag{7.8}$$

where N is the actual maximum, less half an hour, due to the inability of the Campbell-Stokes sunshine recorder to register at low solar elevations (de Lisle 1966). Lastly the incoming solar radiation is estimated from

$$R_s = R_o\left(0.25 + 0.54n/N\right) \tag{7.9}$$

where n is the average number of sunshine hours measured. Once R_s has been estimated, equations (7.3) and (7.1) then allow average daily reference crop potential evapotranspiration for the month to be estimated.

The use of the above equations in determining a water balance at FR190/8 is illustrated by the following example. Taking average screen air temperature (T_{av}) of 10.4°C and total sunshine hours of 191 for the month of October 1996, the month following fertiliser application, the average daily value for E_r in October can be calculated. Substituting the T_{av} in equation (7.2) gives a value of 0.56 for $s/(s+\gamma)$. The middle of the month, 16 October, is Julian day 290, (1996 was a leap year). Therefore, equation (7.4) gives δ as -0.193. Sunshine hours were taken from Rotorua airport (not available from Waiotapu) and the latitude is 38°07′ S or -0.6653 radians, so equation (7.5) gives H as 1.56. Equation (7.7) gives $(d_{av}/d)^2$ as 1.00 and equation (7.6) gives R_o as 37.6 MJ m^{-2}. Equation (7.8) gives N as 12.7 h. As n is 191/31 or 6.2 h, equation (7.9) gives R_s as 19.3 MJ m^{-2}. Equation (7.3) then gives R_n as 10.5 MJ m^{-2} day^{-1} and equation (7.1) gives the average daily value of E_r for October 1996 as 3.0 mm/day or 94 mm/month. The above calculations were done for each month of sampling to March 1998, the results of which appear in the soil water balance (expressed as E_t) in Table 7.2.

From the soil water balance using the unadjusted Priestley-Taylor equation (7.1), total transpiration (E_t) from the tree canopy for the 1997 year was calculated to be 933 mm (Table 7.2). This was approximately the same as total rainfall (P) for this period (1116 mm). Based on studies on 11 and 13 year old closed canopies of *P. radiata* at Longmile, Rotorua and Puruki Rua catchment in the Purukohukohu Experimental Catchment located about 30 km south of Rotorua, both sites subject to rainfall and sunshine hours similar to FR190/8, Whitehead and Kelliher (1991a and b) found tree canopy transpiration for 12 months was 636 mm for Longmile beginning July 1, 1984 and 704 mm for Puruki Rua beginning August 1, 1986. As a percentage of rainfall, canopy transpiration at Longmile was 39% and at Puruki Rua was 50 %. The studies of Whitehead and Kelliher suggest that the Priestley-Taylor equation may be over-estimating canopy transpiration at FR190/8. The Priestley-Taylor equation includes an empirical coefficient of 1.26 (see equation 7.1). This factor was used for pasturelands

Table 7.2 Soil water balance for the top 45 cm soil layer using Priestley-Taylor equation (equation 7.1) to estimate E_t at FR190/8 (P - rainfall; E_i - canopy interception; E_t - dry canopy transpiration; W_A - readily available soil water; D - drainage)

Month/year	P (mm)	E_i (mm)	P- E_i (mm)	E_t (mm)	W_A (mm)	D (mm)
1996						
October	54	8	46	94	72	0
November	83	12	71	126	16	0
December	129	19	110	130	0	0
1997						
January	30	5	25	140	0	0
February	82	12	70	114	0	0
March	126	19	107	84	23	0
April	102	15	87	64	46	0
May	91	14	77	33	90	0
June	109	16	93	25	120	42
July	125	19	106	31	120	80
August	72	11	61	42	120	16
September	127	19	108	50	120	54
October	101	15	86	102	89	13
November	79	12	67	111	45	0
December	72	11	61	137	0	0
1998						
January	52	8	44	139	0	0
February	88	13	75	110	0	0
March	78	12	66	86	0	0
Total	1600	240	1360	1618		205

and takes into account some transfer of energy by advection (the transference of heat energy in a horizontal stream of air) (Kutilek and Nielson 1994). For dry forest canopies the factor will be lower because of generally lower stomatal conductance compared to pasture (Kelliher and Scotter 1992). The ratio of total transpiration (E_t) as calculated by Whitehead and Kelliher (1991a and b) (636 and 704 mm) and that calculated using the Priestley-Taylor equation (7.1) for FR190/8 (983 mm) suggests that the empirical factor should be between 0.65 to 0.70 times (636/983 mm and 704/983 mm) that used for pasture. Therefore, a slightly lower factor of 0.82 (1.26 * 0.65) was used and tree canopy transpiration (E_t) for the 1997 year was reduced to 607 mm, about 54% of rainfall and is closer to the values calculated by Whitehead and Kelliher (1991a and b), and therefore, was probably closer to the true canopy transpiration (E_t) (Table 7.3).

From the soil water balance presented in Table 7.3 total drainage (D) below 45 cm for the 18 months from October 1996 to March 1998 was 385 mm. Drainage (D) will occur when a soil is at field capacity, that is when readily available soil water (W_A) equals the readily available soil water holding capacity (W_R) and rainfall (P) minus interception (E_i) exceeds canopy transpiration (E_t) (McLaren and Cameron 1990). For example, drainage (D) for 1 July 1997 was calculated as follows. Rainfall (P) was 33 mm and interception (E_i) was 5 mm, so P- E_i = 28 mm. Canopy transpiration (E_r) was estimated at 0.65 mm/day and the soil was near field capacity, W_A = 118 mm, so drainage (D) equals 28+118-120-0.65 = 25.4 mm. The values for drainage presented in Table 7.3 are total monthly drainage values, calculated on a daily basis. W_A is calculated from W_A for the previous day plus P minus E_i minus E_t till W_R is reached. From the concentrations of Mg and K in the lysimeters at 45 cm for the different sampling times, losses of Mg and K were estimated by multiplying the drainage from the preceding 6 weeks by the concentration of Mg and K in the lysimeters.

The results show that both Mg and K fertiliser applications have increased the leaching losses of Mg compared to the control (Tables 7.4). Leaching losses of Mg for the 18 months after fertiliser application were 39.4 kg Mg ha^{-1} (16% of added fertiliser) for the 200 kg Mg ha^{-1} application rate, 26.9 kg Mg ha^{-1} for the 200 kg K ha^{-1} application rate

Table 7.3 Soil water balance for the top 45 cm soil layer using amended* Priestley-Taylor equation (equation 7.1) to estimate E_t at FR190/8 (P - rainfall; E_i - canopy interception; E_t - dry canopy transpiration; W_A - readily available soil water; D - drainage)

Month/year	P (mm)	E_i (mm)	P-E_i (mm)	E_t (mm)	W_A (mm)	D (mm)
1996						
October	54	8	46	61	105	0
November	83	12	71	82	94	0
December	129	19	110	84	120	0
1997						
January	30	5	25	91	54	0
February	82	12	70	74	50	0
March	126	19	107	55	102	0
April	102	15	87	42	120	18
May	91	14	77	22	120	53
June	109	16	93	17	120	76
July	125	19	106	20	120	85
August	72	11	61	27	120	36
September	127	19	108	32	120	73
October	101	15	86	66	120	39
November	79	12	67	72	115	5
December	72	11	61	89	87	0
1998						
January	52	8	44	90	41	0
February	88	13	75	71	45	0
March	78	12	66	56	55	0
Total	1600	240	1360	1051		385

*Empirical factor in the Priestly-Taylor equation reduced from 1.26 to 0.82 (equation 7.1).

and 11.2 kg Mg ha^{-1} for the 400 kg K ha^{-1} application rate. The reason for higher leaching losses of Mg for the low rate of K fertiliser application compared to losses of Mg for the high rate of K fertiliser application is unclear. It is possible that a considerable pulse of the Mg from the 400 kg K ha^{-1} treatment has moved below 45 cm in drainage events during the 21 days prior to the collection of the first samples. There may have also been drainage events during the first couple of months that were not determined by the water balance calculations. This would also increase the Mg losses due to 400 kg K ha^{-1} as initially, concentrations of Mg in solution in the 45 cm lysimeter for the 400 kg K ha^{-1} fertiliser treatment were higher than those for the 200 kg K ha^{-1} fertiliser treatment (Figure 7.11).

Only K fertiliser treatments increased leaching losses of K, 17.4 kg K ha^{-1} for the 400 kg K ha^{-1} application rate and 8.9 kg K ha^{-1} for the 200 kg K ha^{-1} application rate compared to the control at 5.7 kg K ha^{-1}. Leaching losses of K were not affected by Mg fertiliser application (Table 7.5). The results reflect the effect of fertiliser application on K and Mg concentrations in soil solutions at 45 cm described in Section 7.4.9.

The losses of Mg due to Mg fertiliser application estimated from data from the 45 cm lysimeter reported in this section (13% of added fertiliser-Mg) were considerably less than those reported earlier in this chapter (Section 7.4.4) (49% loss calculated earlier) based on the exchangeable Mg concentration differences between fertilised and unfertilised soil in the 0-10 cm soil layer and tree uptake of Mg. This indicates that a large proportion of applied fertiliser Mg may have been retained in the 10-40 cm soil layer. In addition, the difference in the uptake of Mg between fertilised and unfertilised trees may be greater than the value of 9 kg Mg ha^{-1} yr^{-1} assumed in the calculation reported in Section 7.4.4. It is also possible that considerable pulses of fertiliser Mg may have moved down below 45 cm soil depth during heavy rainfall events, which were not picked up during the infrequent sampling of this trial. To increase the accuracy of estimates of leaching losses of Mg and K, solution samples should be collected on a daily basis or at least the day after each rainfall event. However, this was not practical for this study. Another error could be in the value for the empirical factor used in the Priestley-Taylor equation (equation 7.1).

Table 7.4 Estimates of Mg leached from the top 45 cm of soil from 1 April 1997 to 30 November 1997 at FR190/8

		Solution Mg concentrations (mmol l^{-1})				Mg losses** (kg Mg ha^{-1})			
Month/ year	**Drainage*** (mm)	**Control**	**200 kg Mg ha^{-1}**	**200 kg K ha^{-1}**	**400 kg K ha^{-1}**	**Control**	**200 kg Mg ha^{-1}**	**200 kg K ha^{-1}**	**400 kg K ha^{-1}**
1997									
April	18	0.05	0.53	0.37	0.21	0.2	2.3	1.6	0.9
May	53	0.07	0.58	0.47	0.19	0.9	7.4	6.0	2.4
June	76	0.07	0.51	0.32	0.15	1.3	9.3	5.8	2.7
July	85	0.07	0.45	0.18	0.11	1.4	9.2	3.7	2.2
August	36	0.12	0.37	0.27	0.11	1.0	3.2	2.3	1.0
September	73	0.10	0.31	0.27	0.08	1.8	5.4	4.7	1.4
October	39	0.08	0.25	0.27	0.05	0.8	2.3	2.5	0.5
November	5	0.09	0.24	0.24	0.04	0.1	0.3	0.3	0.1
Total	385					7.5	39.4	26.9	11.2

* From Table 7.3 (data and leaching calculations only shown for months when drainage occurred)

** Drainage (mm)/1000 (mm m^{-1}) * 10000 (m^2 ha^{-1}) = Drainage (m^3 ha^{-1}) * 1000 = Drainage (l ha^{-1})* solution Mg concentration (mmol l^{-1})*atomic weight of Mg(24 g/mol)/1000000 = Mg losses (kg Mg ha^{-1})

Table 7.5 Estimates of K leached from the top 45 cm of soil from 1 April 1997 to 30 November 1997 at FR190/8

		Solution K concentrations (mmol l^{-1})				K losses** (kg K ha^{-1})			
Month/ year	**Drainage*** (mm)	**Control**	**200 kg Mg ha^{-1}**	**200 kg K ha^{-1}**	**400 kg K ha^{-1}**	**Control**	**200 kg Mg ha^{-1}**	**200 kg K ha^{-1}**	**400 kg K ha^{-1}**
1977									
April	18	0.04	0.05	0.10	0.19	0.3	0.4	0.7	1.3
May	53	0.04	0.05	0.08	0.15	0.8	1.0	1.7	3.1
June	76	0.04	0.04	0.06	0.12	1.2	1.2	1.8	3.6
July	85	0.03	0.03	0.05	0.10	1.0	1.0	1.7	3.3
August	36	0.03	0.03	0.04	0.10	0.4	0.4	0.6	1.4
September	73	0.04	0.03	0.05	0.10	1.1	0.9	1.4	2.8
October	39	0.05	0.04	0.06	0.11	0.8	0.6	0.9	1.7
November	5	0.05	0.04	0.05	0.10	0.1	0.1	0.1	0.2
Total	385					5.7	5.6	8.9	17.4

* From Table 7.3 (data and leaching calculations only shown for months when drainage occurred)

** Drainage (mm)/1000 (mm m^{-1}) * 10000 (m^2 ha^{-1}) = Drainage (m^3 ha^{-1}) * 1000 = Drainage (l ha^{-1}) * solution K concentration (mmol l^{-1}) * atomic weight of K (39 g/mol)/1000000 = K losses (kg K ha^{-1})

To achieve leaching losses of Mg close to that calculated in Section 7.4.4, drainage over the 18 month period of the experiment would need to be approximately 1100 mm. This amount of drainage would be unlikely given that rainfall over the same period was 1600 mm. However, the estimated leaching losses of Mg reported in this section are comparable to those reported in Chapters 3 and 4, where losses of Mg were between 0-20% of the Mg applied as slowly-soluble calmag fertiliser in the 18 to 42 months following fertiliser application.

The leaching losses recorded in the control plots at FR190/8 were less than those reported for an unfertilised stand of *P. radiata* on a silt loam soil in the Manawatu by Parfitt *et al.* (1997). They estimated the leaching losses of 14.7 kg Mg ha^{-1} and 7.8 kg K ha^{-1} from the top 20 cm soil depth over the winter/spring period. The drainage recorded by Parfitt *et al.* (1997) during this period was 347 mm compared to 385 mm in FR190/8. Parfitt *et al.* (1997) estimated drainage based on potential evapotranspiration (E_r) for pasture calculated from meteorological data collected from a weather station near the trial site and allowing for an interception factor of 27%. How E_r was calculated, was not specified. The higher leaching losses reported by Parfitt *et al.* (1997) were because of generally higher concentrations of Mg (0.09 to 0.30 $mmol.l^{-1}$) and K (0.03 to 0.11 $mmol.l^{-1}$) compared to those recorded in lysimeters at 45 cm in FR190/8 (Figure 7.11).

The estimated losses of Mg and K recorded in the FR190/8 trial were also much less than those recorded by Khanna *et al.* (1992). They reported leaching losses of 67 kg Mg ha^{-1} and 28 kg K ha^{-1} below 40 cm from a stand of 11 year old *P. radiata* growing in a yellow podzolic soil (soil pH(water) 5.7, exchangeable Mg 0.47 $cmol_{(+)}$ kg^{-1}, exchangeable Ca 3.0 $cmol_{(+)}$ kg^{-1}) near Canberra, Australia in the year following fertilisation with NPK fertiliser (400 kg N ha^{-1} as ammonium sulfate, 200 kg P ha^{-1} as superphosphate and 100 kg K ha^{-1} as potassium sulfate) applied in equal amounts in September and the following November and subject to irrigation equivalent to annual rainfall of 800-900 mm. The high leaching losses in the study of Khanna *et al.* (1992) were because of generally higher soil solution concentrations of Mg and K compared to the FR190/8 trial. Khanna *et al.* (1992), calculated the amount of water draining through the profile using a water balance equation, and measurements of throughfall,

soil hydraulic properties and changes in soil water content which were measured using a neutron probe, although no drainage value was reported in the paper.

The results reported in this section show that there was greater leaching of Mg below 45 cm compared to K, due to Mg and K fertiliser application. Concentrations of solution Mg in the lysimeters at 45 cm in the Mg and K fertilised plots were generally greater than the concentrations of solution K.

7.4.11 Effect of Mg and K fertilisers on foliar Mg, K and K to Mg molar ratio

In the 18 months following application, Mg fertiliser had no significant ($P > 0.05$) effect on foliar Mg concentrations (Figure 7.13), although there is a general trend of increased foliar Mg concentration in each subsequent year in the Mg fertilised trees. These results are consistent with those reported in Chapter 3 and 4 where, up to about 30 to 42 months after application, calmag Mg fertiliser at 150 kg Mg ha^{-1} was largely ineffective at increasing foliar Mg concentrations. These results provide further evidence of the slow and poor response of *P. radiata* to elevated soil Mg concentrations in marginally Mg deficient soils, as was found by Hunter *et al.* (1986), Payn *et al.* (1995) and Hunter (1996). Potassium fertiliser application had no significant ($P > 0.05$) effect on foliar K or Mg concentrations.

In spite of significant ($P < 0.05$) changes in soil K:Mg molar ratios due to Mg and K fertiliser application (Figure 7.9), in the three years of samples to date, there has been no significant ($P > 0.05$) changes in foliar K:Mg concentration ratios (Figure 7.13). There is a general trend of lower foliar K:Mg concentration ratios in the Mg fertilised trees and this effect seems to be increasing with time.

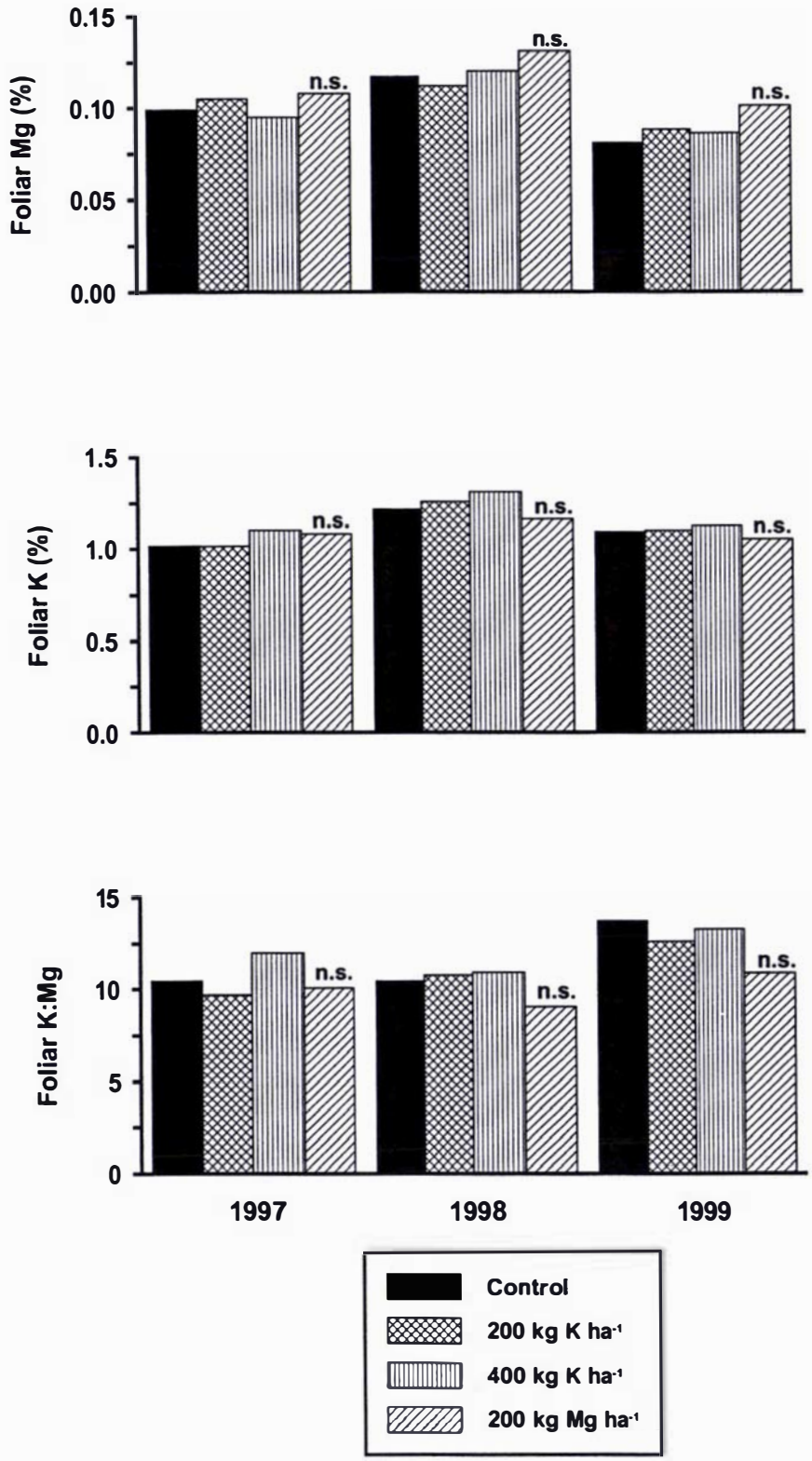


Figure 7.12 Foliage Mg and K concentrations, and K:Mg concentration ratios in FR190/8, in each of the three years after fertiliser application. n.s. - no significant difference between treatment means.

7.5 CONCLUSIONS

Kieserite , a soluble Mg fertiliser, applied to a Pumice Soil under *P. radiata* at a rate of 200 kg Mg ha^{-1} has significantly increased concentrations of Mg in soil solution at 10 cm soil depth up to 90 days after application but has been largely ineffective at significantly affecting concentrations of Mg in soil solution at45 cm soil depth. A soluble K fertiliser, K_2SO_4, applied at 200 and 400 kg K ha^{-1} has also significantly increased solution Mg concentrations up to 60 days after application at 10 cm soil depth. This is probably due to the exchange of Mg by K on the exchange sites and releasing Mg into solution.

Potassium fertiliser applied at rates of 200 and 400 kg K ha^{-1} has significantly increased solution K concentrations at 10 cm soil depth up to 180 days after application and at 45 cm soil depth at 180 days after application. However, Mg fertiliser application had no effect on solution K concentrations at the two soil depths.

Magnesium from Mg fertiliser application exchanged with Ca on the exchange sites as solution Ca concentrations were significantly increased by Mg fertiliser application in the top 10 cm soil layer.

Solution K:Mg molar ratios in the top 10 cm of soil were reduced by Mg fertiliser application, although the decreases were not significant. However, solution K:Mg molar ratios were significantly increased by K fertiliser application at all sampling times.

Magnesium and K fertiliser application increased soil exchangeable Mg and K respectively in each year although, concentrations of exchangeable Mg and K had declined in the second year. Magnesium fertiliser application resulted in proportionally greater increases in exchangeable Mg concentrations compared to increases in exchangeable K concentrations due to K fertiliser application at the same rate.

The soil exchangeable K:Mg molar ratio was significantly decreased by Mg fertiliser application in the two years of sampling. Potassium fertiliser application increased soil exchangeable K:Mg molar ratio in the two years of sampling, but only the increase due to K fertiliser at 400 kg K ha^{-1} was significant for both years of sampling. These results show that the exchangeable K:Mg balance in a Pumice Soil can be significantly amended by the application of K and Mg fertilisers, and the changes can be maintained for over 18 months. However, continued monitoring of the soil is required to establish whether these changes can be maintained over a complete rotation of *P. radiata* and beyond.

Leaching losses of Mg and K below 45 cm, estimated from drainage and soil solution cation concentrations in the lysimeters at 45 cm, were low compared to the amount of these cations applied in fertiliser. The amounts of Mg lost were higher than the amounts of K. Estimated leaching losses of Mg in 18 months since application were 39.4 kg Mg ha^{-1} for the Mg fertiliser application rate of 200 kg Mg ha^{-1}. Potassium fertiliser application at 200 and 400 kg K ha^{-1} resulted in estimated leaching losses of Mg of 26.9 and 11.2 kg Mg ha^{-1}, respectively. It should be noted that the leaching losses of Mg were the result of application of a readily soluble Mg fertiliser. If a less soluble Mg fertiliser such as calmag (Chapters 3 and 4) was applied, the leaching losses would probably be smaller than that for Kieserite and reported in this Chapter. Estimated leaching losses of K were 17.4 kg K ha^{-1} for the application rate of 400 kg K ha^{-1} and 8.9 kg K ha^{-1} for the application rate of 200 kg K ha^{-1}. Magnesium fertiliser application did not have any effect on leaching losses of K.

The application of kieserite, in spite of significantly increasing solution and exchangeable Mg in 0-10 cm soil layer, has not resulted in any significant increases in foliar Mg concentrations, in the 30 months following application. There is however, a general trend of increasing foliar Mg concentrations in the Mg-fertilised trees. Like the effect of Mg fertiliser application on foliar Mg concentrations, K fertiliser application has not increased foliar K concentrations. Foliar K:Mg concentration ratio has also not been significantly affected by either Mg or K fertiliser application in the 30 months following fertiliser application although, there is a trend of decreases in this ratio with time due to Mg fertiliser application.

CHAPTER 8

SUMMARY AND CONCLUSIONS

8.1 REQUIREMENT FOR THE STUDY

The literature review (Chapter 2) showed that magnesium (Mg) deficiency and the associated condition 'upper mid crown yellowing' (UMCY) are widespread problems in many of New Zealand's *Pinus radiata* plantations forests, but are most severe in the large forests growing on Pumice Soils of the central North Island. Magnesium deficiency is an issue affecting the long-term sustainable productivity of New Zealand's forest estate.

Correction of Mg deficiency in *P. radiata* has been the subject of many investigations since deficiency symptoms were first recorded in the late 1950's. However, most of the studies have been concerned with improving foliar concentrations in the trees and increasing growth rate through application of Mg fertilisers. These investigations have shown that Mg deficiency can be corrected by application of Mg fertilisers, but the response in the trees was generally slow and growth rates were only improved in severely Mg deficient trees. The reason for the slow responses was unknown. Past research has also highlighted that UMCY symptoms are worst in trees with high foliar K:Mg ratios.

The literature highlighted a general lack of knowledge of the Mg fertility of forest soils, particularly the Pumice Soils, and their response to the application of Mg fertilisers. In particular, there is little current information on the performance of Mg fertilisers, other than Epsom salts and dolomite, in increasing plant availability of Mg. Currently, calcined magnesite (calmag) is being used by Forest Research (Institute Ltd) in a series of trials to test whether Mg fertiliser application can improve foliar K:Mg ratios and reduce the incidence of UMCY in *P. radiata*.

However, there is little information to date on the effectiveness of calmag in increasing plant available Mg. The rate of dissolution of Mg fertilisers under field conditions is unknown and this may be limiting the rate at which Mg becomes available to the trees.

There is considerable evidence in the literature to show that the chemistry of the rhizosphere differs greatly from the bulk soil. The cation chemistry of the rhizosphere of *P. radiata* may therefore, be influencing the uptake of Mg. In addition, concerns have been expressed as to the extent that leaching losses of Mg are contributing to Mg deficiency problem.

The objectives of this thesis therefore, were to investigate whether calcined magnesite fertiliser applied to a range of forest soils was effective in increasing tree available Mg in soils and improving foliar Mg concentrations of *P. radiata*. The rates of dissolution of a range of Mg fertilisers were determined to investigate whether the rate of availability of fertiliser Mg was limiting the uptake of Mg by the trees. The rhizosphere chemistry of *P. radiata* seedlings was studied to test if changes in the Mg, K and Ca chemistry of the rhizosphere were limiting Mg availability to the trees. Finally, the leaching losses of Mg after application of soluble Mg and K fertilisers were investigated.

8.2 DISSOLUTION AND EFFECTIVENESS OF CALMAG IN FIELD CONDITIONS

Five Forest Research (FR) 190 series trials located throughout the North Island were sampled. All of the trials had received, as one of their treatments, calmag applied at 150 kg Mg ha^{-1}. Three trials were on Pumice Soils derived mostly from Taupo pumice, two at Kaingaroa Forest and the other at Kinleith Forest, all in the central North Island. One trial was on soils derived from mudstone and crushed argillite at Waipaoa Forest, north of Gisborne. The last one was on a Pumice Soil derived from Waiohau ash deposits at Mangatu Forest, also north of Gisborne.

Calcined magnesite was generally effective at increasing the soil exchangeable concentrations of Mg in all trials two to three years after application. The increases in

exchangeable Mg were significant at three of the five trials. At the two trials where Mg fertiliser application did not significantly increase exchangeable Mg, the exchangeable Mg concentrations were medium to high in the control plots. Soils sampled in consecutive years in two trials showed no real changes in exchangeable Mg concentrations with time. *P. radiata* has a rotation time of between 25-30 years. Whether these increases in exchangeable Mg will be maintained over this length of time and longer requires the further monitoring of these trials.

Of the applied fertiliser Mg, between 8% and 37% remained undissolved after two to three years at four of the five trials and 13% remained undissolved after seven and a half years in the fifth trial. In spite of a rapid rate of dissolution in at least four of the five trials sampled, and increases in soil exchangeable Mg, there were no significant increases in foliar Mg concentrations. Foliar Mg concentrations were marginally deficient to adequate at all the trials prior to Mg fertiliser application. This may have been a reason for the trees in the trials not responding to the increases in soil exchangeable Mg. These results confirm the inability of *P. radiata* to respond within a few years to Mg fertiliser application, as reported by others.

Studies of the FR190 series trials indicate that the rate of Mg fertiliser dissolution varied with rainfall, exchangeable Mg and percent Mg saturation of the exchange complex. Faster rates of dissolution can be expected at sites with high rainfall, low levels of exchangeable Mg and low percent Mg saturation of the exchange capacity. Mathematical relationships were obtained between percent Mg fertiliser dissolution, and initial soil exchangeable Mg and mean annual rainfall, and also between percent Mg fertiliser dissolution, and percent Mg saturation of exchange complex and mean annual rainfall. To strengthen the relationships found in this study requires further investigation. Magnesium fertiliser dissolution in a greater range of soils, with a range of soil exchangeable Mg concentrations and subject to a range of annual rainfalls needs to be considered.

8.3 COMPARISON OF DIFFERENT MAGNESIUM FERTILISERS IN A PUMICE SOIL

A study was carried out to determine the rate of dissolution of a range of Mg fertilisers applied to a Pumice Soil under *P. radiata* at Kaingaroa Forest, near Rotorua. The amount of fertiliser Mg dissolution was determined periodically by measuring the amount of undissolved Mg and subtracting it from the amount of fertiliser Mg applied.

The rate of dissolution was little influenced by whether the fertiliser was applied directly onto the soil surface (litter removed) or onto the litter layer. Twenty-seven months following fertiliser application, the mean (with and without litter) percentage of fertiliser Mg dissolved was in the sequence: Epsom salts > calcined magnesite 1-2 mm > granmag > calcined magnesite 2-4 mm > forestry grade dolomite. An elemental sulfur (S^o) oxidation cubic model, developed on the presumption that the rate of S^o oxidation depends on the surface area of the particles, was adapted to predict the specific dissolution rate constants ($\mu g\ cm^{-2}\ day^{-1}$ of fertiliser) of the slowly soluble Mg fertilisers. The specific dissolution rate constants for the slowly soluble Mg fertilisers were 587 for calcined magnesite 1-2 mm, 426 for calcined magnesite 2-4 mm, 385 for granmag and 18 for forestry grade dolomite (0.06-0.25 mm 37%; 0.25-0.5 mm 10%; 0.5-1.0 mm 18%; 1-2 mm 34%; 2-3 mm 1%). In a laboratory incubation study the elemental S^o oxidation cubic model also described the rate of dissolution of Mg fertilisers within narrow fertiliser particle size ranges. However, the specific fertiliser dissolution rate constants increased with decreases in particle size suggesting the rate of dissolution depends on factors other than surface area when the particle sizes varied widely. The modelling of Mg dissolution requires further work. A model similar to the mechanistic model used to explain phosphate rock dissolution could be developed.

The slowly soluble, alkaline Mg fertilisers had a significant liming effect on the soil. They were also more effective at increasing soil exchangeable Mg than soluble Mg salts over a long period. Therefore, they are better fertilisers for a perennial crop such *as P. radiata.*

8.4 MAGNESIUM CHEMISTRY IN THE RHIZOSPHERE OF *Pinus radiata* SEEDLINGS

Two glass house studies were carried out on a Pumice Soils 0-10 cm and 10-20 cm, taken from Kaingaroa Forest, Rotorua to understand how GF16, *P. radiata* seedling roots were influencing the availability of Mg in the rhizosphere, using a modified root study container (RSC) technique. In the first study the soil was fertilised with a range of Mg fertilisers. In the second study there were four fertiliser treatments: Epsom salts at two rates of application, K_2SO_4 fertiliser and Epsom salts plus K_2SO_4 fertiliser.

In both studies, ectomycorrhizal hyphae penetrated into the soil that had been separated from the root mass by a fine nylon mesh (ie. into the rhizosphere soil). This makes the interpretation of the results difficult, as it effectively increased the volume of soil over which the roots had an influence.

In both studies, seedling growth was not affected by Mg or K fertiliser application. Concentrations of Mg in the shoots and roots were generally increased by Mg fertiliser application in both studies, although net uptake of Mg was not significantly different from the unfertilised seedlings. In the second study, K fertiliser application had no effect on K or Mg concentrations or uptake of K or Mg by the shoots and roots.

Magnesium was found to accumulate in the rhizosphere soil of the Mg-fertilised seedlings in both studies. This was probably due to the rate of Mg supply to the roots, mostly by mass flow, exceeding the rate of Mg uptake by the seedlings. Under the conditions imposed by the RSC technique, mass flow of K seems to also have occurred as K was also found to have accumulated in the rhizosphere soil of the Mg and K fertilised seedlings in the second study. The accumulation of Mg and K could also have been due to the presence of ectomycorrhizal hyphae in the first few soil slices from the bottom RSC. These results require confirmation, particularly under field conditions. In addition, the role ectomycorrhizal fungi play in the Mg nutrition of P. radiata requires further investigation.

Pinus radiata seedlings were found to have acidified the rhizosphere soil in the second study. This probably was as a result of an excess of uptake of cations compared to anions. It could also be due to the release of organic acids, such as oxalic acid, by the seedling roots and the ectomycorrhizal hyphae. These results also require confirmation under field conditions.

8.5 LEACHING LOSSES OF MAGNESIUM

A field study using suction cup lysimeters was carried out in a Pumice Soil under *P. radiata* at FR190/8 trial, Kaingaroa Forest to determine the leaching losses of Mg in the 18 months after application of soluble Mg (kieserite at the rate of 200 kg Mg ha^{-1}) and K (K_2SO_4 at the rate of 200 and 400 kg K ha^{-1}) fertilisers. Lysimeters were installed at two depths (10 cm and 45 cm), to monitor changes in soil solution concentrations of Mg, K and Ca in the topsoil, where a majority of the roots are, and to allow an estimation of the amounts of Mg and K lost below 45 cm.

Magnesium fertiliser application resulted in a significant increase in soil solution Mg concentrations in the top 10 cm of soil. Potassium fertiliser application also increased concentrations of Mg in soil solution - the increase was significant for the 400 kg K ha^{-1} treatment. But there was no increase in solution K concentrations due to Mg fertiliser application. Potassium fertiliser application significantly increased K concentrations in soil solution in the top 10 cm of soil. Calcium concentrations in soil solution were significantly increased by Mg fertiliser application in the top 10 cm of soil.

Concentrations of Mg, K and Ca in the top 10 cm of soil declined over time and by 180 days after fertiliser application were at levels similar to those in the control treatment.

Magnesium and K fertiliser application increased the amount of loss due to leaching of Mg and K, respectively. Estimated leaching losses of Mg below 45 cm from the Mg fertilised plots following fertiliser application were 39.4 kg ha^{-1}, compared to only 7.5 kg ha^{-1} in the no-fertiliser control plots. Estimated leaching losses of K were less than those for Mg and were 8.9 kg ha^{-1} for the 200 kg ha^{-1} fertiliser treatment, and 17.4 kg

ha^{-1} for the 400 kg ha^{-1} fertiliser treatment. Estimated leaching losses of K from the no-fertiliser control plots were 5.7 kg ha^{-1}.

The application of soluble Mg fertiliser, in spite of large increases in solution concentration soon after application, has not significantly increased foliar Mg concentrations. However, there is a general trend of increasing foliar Mg concentrations in the Mg fertilised trees in each year of sampling. Potassium fertiliser application, as for Mg, had no significant effects on foliar K concentrations or foliar Mg concentrations. Foliar K:Mg ratios were also unaffected by the application of Mg and K fertilisers, although there is a general trend of declining foliar K:Mg ratios in the Mg-fertilised trees.

8.6 OVERALL CONCLUSION

Repeatedly, throughout this thesis it has been shown that Mg fertiliser application significantly and quickly increased soil exchangeable Mg. However, the increases in soil exchangeable Mg, which are considered to be plant available, has not increased foliar Mg concentrations, even after three years. The reason for this was not because the fertiliser has remained undissolved or large leaching losses of Mg occurred, as has been reported by previous workers. The reason appears to be because of some mechanism hindering Mg uptake and/or translocation. Whether *P. radiata* is capable of luxury uptake of Mg when growing on soils which are marginally deficient in Mg when the supply of Mg is increased by fertiliser application is unknown. The current Forest Research Mg fertiliser trials are on soils that are marginally deficient in Mg. Had the trees been severely deficient in Mg, perhaps they would have responded to the increases in soil Mg concentrations. In future studies, sites should be selected which include severely deficient trees. However, the present sites should continue to be examined to determine the changes in soil Mg levels and foliar Mg concentrations over a long period of time. In addition the role ectomycorrhizal fungi play in the uptake of Mg and K needs to be examined.

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APPENDIX 1: Brief soil profile descriptions for Pekepeke sand and Kaingaroa loamy sand (Rijkse 1988).

Pekepeke sand

A	0-7 cm	black (10YR 2/0) sand; friable; weakly developed coarse and medium nut structure; many fine white grains and fine lapilli; many roots; distinct smooth boundary,
Bw	7-20 cm	dark brown (10YR 3/3) and pale yellow (2.5Y 7/4) coarse sand; loose; single grain; many roots; distinct irregular boundary,
CB	20-35 cm	pale yellow (2.5Y 7/4) coarse sand (1000-2000 μm); loose; single grain; few fine roots; sharp smooth boundary, (Kaharoa lapilli)
2Ab	35-47 cm	brown (10YR 4/3) loamy sand; slightly greasy; friable; weakly developed coarse nut to massive structure; sharp smooth boundary,
2Bw	47-80 cm	olive brown (2.5Y 4/4) loamy sand; slightly greasy; friable; weakly developed coarse nut to massive structure; sharp smooth boundary,
2CB	80-132	cm pale yellow (2.5Y 7/4) pumice gravel; loose; single grain (Taupo lapilli)

Kaingaroa loamy sand

A	0-15 cm	very dark brown (10YR 2/2) loamy sand; friable; moderately developed medium nut and crumb structure; many roots; distinct smooth boundary,
Bw1	15-22 cm	dark yellowish brown (10YR 4/4) loamy sand; firm; weakly developed medium nut and crumb structure; many rots; distinct irregular boundary,
Bw2	22-28 cm	yellowish brown (10YR 5/8) loamy sand; firm; weakly developed coarse nut to massive structure; many fine lapilli; distinct smooth boundary,
C1	28-78 cm	pale yellow (2.5y 7/4) sand; compact; firm massive; few roots in upper 20 cm; few fine lapilli; sharp smooth boundary, (Taupo lapilli)
C2	78-125 cm	white (10YR 8/2) fine pumice gravel; loose; single grain; lapilli (vary from 0.25 to 2 cm dia.); sharp smooth boundary, (Taupo lapilli)

Appendix 2: Description of the UMCY scores for P. radiata and their corresponding numeric value (P. Beets pers. Com.)

Score	Observations in upper crown region	Value
A+	No yellow tipped needles in any age class (Must have at least 2 age classes in the upper crown)	1
A-	2 yr needles are yellow tipped	2
B+	2yr old needles are absent, or very sparse, with yellowing	3
B-	Looks like C+ but 2^{o} twigs still alive – with yellow 1 yr old needles	4
C+	Crown hollowing out – dead 2^{o} twigs present in UMCY zone	5
C-	Large dead zone of 2^{o} twigs expanded to over half the width of the upper crown – clearly hollow	6
D+	Some 1^{o} branches dead	7
D-	All 1^{o} branches in a cluster are dead	8