POTENTIAL USES OF FLUIDISED BED BOILER ASH AS A LIMING MATERIAL, SOIL CONDITIONER AND SULPHUR FERTILISER

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Abstract

A fluidised bed boiler ash, produced by the New Zealand Dairy Corporation (NZDC FBA) as a by-product resulting from the combined combustion of high S coal and limestone, was chemically characterised and evaluated as a potential liming material, soil conditioner and S source in some representative New Zealand soils.

Chemical analysis showed that slaked NZDC FBA had a pH_{water} of 12.4 and $CaCO_3$ equivalent of 51.8%. The "lime" in FBA is mainly $Ca(OH)_2$, making it a quicker acting, more caustic material than limestone. FBA contained 6.2% S, 25.4% Ca (dry weight basis) and negligible amounts of P, K and Mg. Mineralogical analysis indicated that approximately 50% of the S in the slaked FBA is gypsum ($CaSO_4.2H_2O$) with the remainder being water insoluble ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$).

A field trial was established on a permanent dairy pasture (predominantly ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*)) on peat soil, in Moanatuatua peatland, Waikato, New Zealand, to examine the effectiveness of FBA as a soil conditioner to overcome soil water repellency, a liming material and a S source. The treatments included the untreated control and three rates of FBA (1000, 6616 and 26462 kg FBA ha^{-1}, wet weight basis), which were surface dressed onto the pasture. Three rates of lime, which had the same $CaCO_3$ equivalent as the corresponding rates of FBA, were included for comparison.

Using the molarity of ethanol droplet (MED) test, the air dried peat soil sampled in summer was classified as severely water repellent (MED > 2.2). Fatty acids were identified as the fraction most responsible for the repellent character of the peat soil. Only the high rate (26462 kg ha^{-1}) of FBA significantly reduced water repellency of surface peat soil and increased the rate of water infiltration into the dry peat. The hydrophobic nature of the peat soil was probably modified by the high alkalinity of applied FBA, which removed or saponified fatty acids from the soil particle surface.

However, normal liming and fertiliser rates (6616 kg ha^{-1} or less) of FBA application, as well as all the lime treatments, had negligible effect on the water repellency of the peat soil. Therefore, it is not practical to use FBA as an amendment to minimise water repellency on peat soil.

The FBA treatments significantly increased pasture yield, in the field trial during eight months of the experimental period, mainly by improving herbage S nutrition status. In spring, the S concentrations in herbage from the FBA treatments were raised from a deficient level of 0.20% S (the untreated control) to 0.27 - 0.40% S. The ettringite-sulphate in FBA acted as a slow-release S fertiliser and high rates of FBA application maintained the raised S concentrations in the herbage for the eight month period. The presence of ettringite implies that application of FBA-sulphate has the potential to reduce the leaching loss of sulphate, a common problem in many New Zealand soils.

In a laboratory incubation and leaching study using repacked peat soil cores, the effect of surface applied FBA and lime on base and solute movement in soil was investigated. The results indicated that FBA was an effective alternative to agricultural lime to neutralise the acidity of peat soil. Although surface-applied FBA had no significant effect on decreasing subsurface soil acidity as measured by pH change in the peat soil, the Ca^{2+} ions released by FBA dissolution moved down to subsurface soil much faster than those released from lime. Increased Ca^{2+} ion concentration in subsurface soil can alleviate the acidity constraints on pasture root growth through the antagonistic relationship between Ca^{2+} and H^+ ions. In contrast to the lime treatment, however, FBA caused significant leaching of native soil exchangeable K^+. Therefore, K fertilisers should accompany FBA application to peat soils.

In order to examine the effect of topsoil incorporated FBA on the subsurface acidity in mineral soils, six acidic topsoils (0 - 100 mm) were tested for their ability to "self-lime" through sulphate sorption from gypsum treatment. Two soils, from the yellow-brown loam, or Allophanic soil (the Patua soil) and the yellow-brown earth, or Ultic soil (the Kaawa soil) groups (orders), which contrasted strongly in their reaction to gypsum treatment, were chosen for further study. Lime, FBA and Flue gas desulphurisation gypsum (FGDG) were incorporated in the top 0 - 50 mm of repacked columns of the Patua and Kaawa soils, at rates containing Ca equivalent to 5000 kg ha^{-1} of $CaCO_3$. Each column was leached with 400 mm of water. After leaching, one set of the columns were sliced into sections for chemical analysis, and another set was used for growing lucerne (*Medicago sativa.* L) as a root bioassay.

In the columns of the variable charged, allophanic Patua soil, topsoil incorporated NZDC FBA ameliorated top and subsurface soil acidity through liming and the "self-liming effect" induced by sulphate sorption, respectively. The soil solution pH of the top and subsurface layers of the Patua soil were raised to pH 6.40 and 5.35 respectively, by the FBA treatment, compared with pH 4.80 and 4.65 in the control treatment. Consequently phytotoxic labile monomeric Al concentration in soil solution of the FBA treatment was reduced to less than 0.1 μmol Al dm^{-3}, compared with that of 8 - 64 μmol Al dm^{-3} in the untreated control. These changes were associated with greatly improved lucerne root growth in the subsurface of the Patua soil after FBA treatment. FGDG had a similar "self-liming effect" on subsurface of the Patua soil, but not the topsoil. Whereas FBA raised the pH of the Kaawa topsoil, no "self-liming effect" of subsurface soil by sulphate sorption was observed on the Kaawa soil, which is dominated by permanently charged clay minerals. Application of FBA and FGDG to both soils, however, caused significant leaching of native soil Mg^{2+} and K^{+}. These nutrients were displaced from the exchange sites by the relatively high concentration of Ca^{2+} released from dissolution of gypsum. In contrast, the topsoil incorporated lime had little effect on either the subsurface soil acidity or nutrient leaching.

NZDC FBA is an ideal by-product for correcting topsoil and subsurface soil acidity in yellow-brown loam (allophanic) soils, but only topsoil acidity on yellow-brown earth (Ultic) soils, dominated by clays with permanent charge. Mg and K fertiliser application would be recommended when a soil is treated with FBA or other gypsiferous materials.

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Chapter 1

Introduction

In order to dry milk powder at Anchor Products Ltd., the New Zealand Dairy Corporation's (NZDC) Te Awamutu factory, heat is partly generated through the use of fluidised bed boilers burning high sulphur lignite from the Kawhia coal field. Limestone chip mixed with the fine coal, is burnt in a bed suspended by compressed air. SO_2, released as the coal is burnt, reacts with CaO generated in the furnace therefore minimising SO_2 emissions from the stack. The resulting ash from the boiler bed and trapped flyash, known as fluidised bed boiler ash (FBA, or NZDC FBA), contains $CaSO_4$ and unreacted lime (CaO). Mixing this ash with water, to overcome dust problems, subsequently converts CaO to $Ca(OH)_2$. Hence, FBA has the potential to be used as both a liming material and S fertiliser. However, except one previous chemical analysis of the ash (N. A. Cullen, Unpublished report 1991), there is no quantitative data available to support utilisation of this product on agricultural land, or to evaluate its possible influence on environment. Currently approximately 1.5×10^7 kg of anhydrous FBA are produced annually in New Zealand. It is expected that a number of fluidised bed combustion systems will be introduced into New Zealand in the near future to process wastes as fuels. Thus the availability of FBA will increase.

To meet the Clean Air standard, many North American and European power plants have adopted fluidised bed combustion techniques already. These systems require lower capital investment, to reduce the SO_2 emissions in flue gases, than the wet flue gas desulphurisation process. Although the resulting large volumes of FBA materials are generally disposed of in landfills, limited landfill space and increased costs, however, have stimulated investigations in the US to develop and demonstrate agricultural and environmentally safe uses for FBAs, thereby reducing the cost of SO_2 scrubbing. Land application of FBA as a lime substitute and a source of Ca and S has been studied by a number of US researchers (Korcak 1980; Korcak & Kemper 1993; Stout et al. 1979; Terman et al. 1978). These studies have generally reported positive effects on plant growth and crop yield, with negative effects occurring only at very high application rates (Korcak 1993). The chemical composition of FBA is highly dependent on the efficiency of the boilers and the nature of the fuel and limestone sources and the characteristics of each individual FBA will directly influence its usefulness and effectiveness as a liming material and a fertiliser (Stout et al. 1988). Thus, there is need to characterise NZDC FBA and test its agronomic value in New Zealand farming systems, particularly that of grazed pasture. These studies will also provide a basis for comparing other FBAs likely to be produced in New Zealand in the future. As New Zealand is rich in coal resources, coal plays a significant role in supplying energy. But, some of the coal resources are rich in sulphur and with increasing concern for environmental pollution, low cost techniques, such as fluidised bed combustion, are required to reduce SO_2 emission from the burning of such high S coal. Consequently, large quantities of FBA or similar by-products would be expected.

FBAs containing lime and S should be highly suited to use on pastures, because in recent years, many farmers in New Zealand have increased the use of S-free fertilisers and chemical N fertiliser but reduced lime application onto pasture. These practices have caused S deficiency and soil acidification under pasture (Parfitt et al. 1994) and S particularly has become an increasingly costly input into New Zealand pastoral farming (Phimsarn 1991). Agricultural utilisation of FBA overcomes a waste problem and at the same time provides a liming material and an inexpensive form of S which could reduce the volume of S imports into New Zealand. Full investigation on the potential use of New Zealand FBA is therefore timely.

The overall objective of this thesis is to characterise the NZDC FBA and explore its potential uses as a liming material, soil conditioner and S fertiliser in New Zealand agriculture.

This thesis comprises nine chapters. Following this introduction is a review of literature on aspects of agricultural utilisation of FBAs. Chemical and mineralogical characterisation of the NZDC FBA are reported in Chapter 3. Chapters 4, 5 and 6 will focus on testing the effect of FBA applications onto acid peat soil under pasture, with reporting of changes in the soil physical and chemical properties and pasture growth. Chapter 4 discusses the possible amelioration of water repellency in a peat soil by FBA application, whereas Chapters 5 and 6 mainly investigate the effectiveness of FBA as a liming material and S fertiliser on pasture growth and soil solute movement. The potential use of surface applied FBA as subsurface soil acidity ameliorant on mineral soils is investigated in Chapters 7 and 8, and general conclusions and implications are given in Chapter 9.

Chapter 2

Fluidised bed boiler ash in agriculture: a review

2.1 INTRODUCTION

Fluidised bed combustion is a technology utilised in the burning of high sulphur coal to limit the amount of S expelled into the atmosphere (Fennelly et al. 1977). Coal is burnt in a bed of inert ash and crushed limestone. The bed is fluidised (held in suspension) by injecting air through a perforated floor. Sulphur dioxide (SO_2) released during combustion is converted to calcium sulphate through its reaction with the calcined limestone. Fluidised bed boilers can also utilise waste oil, municipal wastes, sewage sludge, wood wastes and other materials as heat sources (Anonymous 1976; Heynen et al. 1994). Such boilers thus have potential in power plants for meeting air quality standards without the high costs of installing scrubbers to remove SO_2 from stack gases. Fluidised bed furnaces burn coal at lower temperatures (between 815 to 870°C, Lawson 1987) than do conventional coal fired furnaces (1400 to 1600°C) (Terman et al. 1978) because the lower temperatures result in optimum S capture, minimising the limestone usage (Lawson 1987) and reducing nitrogen oxide formation (Anonymous 1976; Fennelly et al. 1977). The chemical reactions involving the limestone charge in a fluidised bed boiler can be described by the following equations:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{(Eqn. 2.1)}$$

$$CaO + SO_2 \rightarrow CaSO_3 \qquad \text{(Eqn. 2.2)}$$

$$2CaSO_3 + O_2 \rightarrow 2CaSO_4 \qquad \text{(Eqn. 2.3)}$$

Because of its relatively low costs, the fluidised bed combustion technique has become widely used for reducing SO_2 emissions from electricity-generating plants, especially in the United States. The fluidised bed combustion techniques are generally smaller in scale, have lower engineering requirements, and require less capital investment than the wet flue gas desulphurisation processes (Fennelly et al. 1977;

Stehouwer et al. 1995b). Existing coal fired power plants can be modified to fluidised bed combustion, and therefore present a simple option for bringing older plants into compliance with clean air legislation (Stehouwer et al. 1995b). One disadvantage, however, is that approximately 200 kg of fluidised bed boiler ash (FBA) is generated per 1000 kg of coal burned (Stout et al. 1979). Thus relatively large amounts of FBA waste are produced in fluidised bed combustion power plants. It is estimated that a 1000 megawatt fluidised bed power plant without regeneration of the bed material would produce about 1.8×10^6 kg of FBA per day (Ruth 1975). Therefore, in addition to installation and operating expenses, significant costs for disposal of FBA material are incurred. Development of beneficial uses for FBA material demonstrated to be environmentally benign or even beneficial would significantly reduce the costs of SO_2 emission (Stehouwer et al. 1995b).

The need for more steam generating capacity at the Anchor Products Ltd. Te Awamutu factory, New Zealand Dairy Corporation (NZDC), the availability of a large reserve of high sulphur coal (Kawhia Deposit), and the ability to burn this coal within environmentally acceptable emission standards resulted in the establishment and operation of the first industrial fluidised bed steam generating plant in New Zealand (Lawson 1987). Approximately 18000 tonnes of anhydrous NZDC FBA is produced annually (P. Shannon, Personal communication 1996).

FBA is a mixture of conventional coal combustion ash (either bed or fly ash), the SO_2 reaction product (primarily anhydrite, $CaSO_4$) and unspent sorbent (generally lime, limestone or dolomite) (Lawson 1987; Stehouwer et al. 1995b). Therefore, the fuel and the limestone source dictate the composition of the FBA. In the United States, FBA is generally disposed of in landfills. Limited landfill space and increased tipping fees are forcing the development and demonstration of beneficial and environmentally safe uses for FBA (Stehouwer et al. 1994a). FBA is usually highly alkaline because of the presence of unspent sorbent, and also contains anhydrite, thus has potential to be used as liming material and S fertiliser (refer Sections 2.4 & 2.6).

2.2 PHYSICAL AND CHEMICAL PROPERTIES OF FBA

The physical and chemical characteristics of FBA depend on a variety of factors, including the composition of the parent coal, SO_2 sorbent and specific boiler configuration used (Carlson & Adriano 1993). However, certain properties are fairly uniform for most FBA. FBA is composed predominantly of small particles, with particle sizes ranging from 2 μm to 4 mm (Stehouwer et al. 1994b; Terman et al. 1978; Wrubel et al. 1982). FBA also exhibits pozzolanic properties, i.e. it can react with water to form cement (Rogbeck & Elander 1994; Stehouwer et al. 1995b) due to its similar composition to cement (ACI 225 Committee 1987; Dawson et al. 1995). It has been observed that the slaked FBA becomes a rock-like material after piling up for a period of several months (P. Shannon, personal communication 1994). Researchers in the USDA-ARS use FBA as a low strength concrete for cattle walkways (W. L. Stout, personal communication 1995) and dairy cattle feedlots (Bossart & Newman 1995). FBA can also be utilised to make synthetic aggregates (Bland & Rowen 1995; Rogbeck & Elander 1994; Wu et al. 1995), to control acid mine drainage and subsidence in underground mines (Bland et al. 1995; Bossart & Newman 1995; Hamric 1995; Gray et al. 1995), to remove CO_2 from multi-component gas (natural gas) streams (Taulbee et al. 1995) and as a substitute for cement in road construction and mine reclamation (Rogbeck & Elander 1994; Bland et al. 1995).

2.2.1 Agronomically useful elements

Chemically, anhydrous FBA is mainly composed of CaO and $CaSO_4$. Table 2.1 shows the chemical analysis of several FBA samples from the United States. The components (elemental analysis) important to agriculture are divided into four groups: liming material, essential plant nutrients, heavy metals and phytotoxic elements (Stout et al. 1988).

FBA has a Ca content ranging from 16% (Stout et al. 1996) to 39% (McCarty et al. 1994; Reichert & Norton 1994). The Mg content of FBA varies from 0.1% (Reichert & Norton 1994; 1996) to 11.4% (Marsh & Grove 1992a; b) depending on whether the sorbent is calcite or dolomite (Table 2.1). Due to the presence of unspent sorbent, FBA

Table 2.1 Chronological summary of chemical characterisation of FBAs (Appendix table).

FBA No.[1]	Sorbent	$CaCO_3$ %	pH	Elemental analysis[2]	Reference
FBA1	Calcite	53-58	12.5	52% $CaSO_4$, 23.6% Ca, 0.5% Mg, 36-112 $\mu g\ g^{-1}$ B, H.M. trace	Korcak 1979; 1980a; b; 1982; 1984; 1985; 1988; 1993; Korcak & Kemper 1993; Stout et al. 1979, 1995; Terman et al. 1978; Wrubel et al. 1982
FBA2	Calcite	51		27% Ca, 7.4% S, 1.1% Mg, 88 $\mu g\ g^{-1}$ B, H.M.≤20 $\mu g\ g^{-1}$	Sidle et al. 1979
FBA3	Dolomite	68		41% $CaSO_4$, 12.9% Ca, 9% Mg	Edwards et al. 1985a
FBA4	Calcite	65		28% $CaSO_4$, 24.3% Ca, 1.1% Mg, 106 $\mu g\ g^{-1}$ B, H.M. ≤715 $\mu g\ g^{-1}$	Edwards et al. 1985a, b
FBA5	Calcite	50		28% Ca, 3.6% S, 0.5% Mg, H.M.≤11 $\mu g\ g^{-1}$	Cochran et al. 1989; 1991
FBA6	Calcite			32% Ca, 10% S, 5.5% Mg, H.M.≤25 $\mu g\ g^{-1}$	Whitsel et al. 1988
FBA7	Calcite & Dolomite	105		4% $CaCO_3$, 31% $CaSO_4$, 29% Ca, 11% Mg, H.M.≤41 $\mu g\ g^{-1}$	Marsh & Grove 1992a, b
FBA8	Dolomite			27% Ca, 5.9% S, 6.1% Mg, 74 $\mu g\ g^{-1}$ B, H.M.≤11 $\mu g\ g^{-1}$	Vona et al. 1992
FBA9	Dolomite	60	10.5	18% Ca, 5.2% S, 11% Mg, 171 $\mu g\ g^{-1}$ B, 5.6 $\mu g\ g^{-1}$ Se, H.M. ≤52 $\mu g\ g^{-}$	Dick et al. 1994; Stehouwer et al. 1994a, b; 1995a, b, c
FBA10	Calcite	97	11.9	39% Ca, 3.8% S, 0.5% Mg	McCarty et al. 1994; Siddaramappa et al. 1994
FBA11	Calcite	46	12.5	39% Ca, 16% S, 0.1% Mg	Reichert & Norton 1994; 1996; Reichert et al. 1994
FBA12	Calcite	31		16% Ca, 0.3% S, 0.9% Mg, H.M. ≤ 6.8 $\mu g\ g^{-1}$	Stout & Priddy 1996

[1] All FBAs are from burning coal except for FBA7 which is generated from burning petroleum coke.
[2] H.M.= heavy metals.

is usually highly alkaline (pH_{water} 12.5, Wrubel et al. 1982) with significant neutralisation potential (Carlson & Adriano 1993; Terman et al. 1978). It has been reported that the best agricultural use of FBA is as a liming source (Korcak 1980b; 1985; Sidle et al. 1979; Stehouwer et al. 1994a; Stout et al. 1988; Terman et al. 1978).

The sulphur content of FBA is also relatively high, being mainly in the form of $CaSO_4$ (anhydrite). Therefore, FBA is a source of both Ca and S for plant nutrition in addition to having liming value (Edwards et al. 1985a; b; Korcak 1979; 1980b; 1982; 1984; McCarty et al. 1994; Stout et al. 1979; Terman et al. 1978). Anhydrite in FBA does not neutralise acidity as does lime but it may ameliorate subsoil acidity (Marsh & Grove 1992b; Ritchey et al. 1995a; Shainberg et al. 1989; Sumner 1993; 1994). This will be discussed in more detail later (Section 2.5).

Compared with Ca and S, the amounts of K and P in FBA are negligible (Stout et al. 1988). Mg and K appear as oxides, hydroxides, or sulphates in FBA. P probably occurs as a form of calcium phosphate (Stout et al. 1988). Since these elements are usually applied to soil in the form of lime or fertiliser, their presence in FBA is desirable.

The micronutrient content in FBA is low except for boron (B) which ranges from 36 - 188 $\mu g\ g^{-1}$ in US FBAs (Table 2.1). B is an essential mineral nutrient for all vascular plants. The functions of B are primarily extracellular, which relates to lignification and xylem differentiation (Lewis 1980; Marschner 1986). Due to the oxidising conditions to which these elements are exposed during combustion, Fe, Mn, Cu and Zn probably occur as oxides in FBA, and B and Mo as borates and molybdates (Stout et al. 1988). With more intensive cropping systems and purer, high analysis fertilisers, the need for micronutrient fertilisation is becoming more apparent, and the presence of these nutrients in FBA may be beneficial.

FBA contains small amounts of selenium (Se, 0.16 - 5.6 $\mu g\ g^{-1}$) (Stehouwer et al. 1995a; b; Stout et al. 1988).) Se is an essential nutrient for animals but not for plants (Marschner 1986). The most economically important animal disease associated with Se deficiency is ill-thrift of both sheep and cattle. Se can be phytotoxic if too much is taken up by plants. Although Se toxicities are common in some areas, such as the Great Plains and Rocky Mountain region in the United States, many regions have Se levels in forages that are too low for grazing animals (Kubota & Allaway 1972), including New Zealand. About 30% of the total farmland in New Zealand is affected by Se deficiency, as determined by lamb growth trials (McLaren & Cameron 1990). In those Se deficient soils, Se fertiliser is applied and the rate of 10 g Se ha^{-1} has been recommended (Cornforth 1984a). Therefore, Se in FBA could be beneficial to grazing animals when FBA is applied onto pastures in these areas.

2.2.2 Potentially phytotoxic elements

The amounts of micronutrients in FBA, except for B, are within the range of these elements usually found in soils (Stout et al. 1988). Korcak 1988 and Korcak & Kemper 1993 observed no phytotoxic effects of micronutrients have been observed when FBA (FBA1, Table 2.1) was used as a lime source even at very high rates. However, the availability of micronutrients to plants depends not only on the amounts applied in FBA, but on the soil properties and the specific crop being grown. Therefore, their entrance into the human food chain via FBA application should be carefully monitored (Stout et al. 1988).

Similar to other coal combustion by-products, the boron concentration in FBA (Table 2.1) is higher than that found in soils, which is averaged at 10 $\mu g\ g^{-1}$ (ranged from 2 - 100 $\mu g\ g^{-1}$) (Baker & Chesnin 1975). B is not toxic in most agricultural soils, unless supplied in excessive amounts by fertilisers (Murphy & Walsh 1972; Stout et al. 1988). Typical B toxicity symptoms on mature leaves are marginal and/or tip chlorosis and necrosis. They reflect the distribution of B in shoots, following the transpiration stream (Marschner 1986). Therefore, care should be taken when applying FBA with high levels of B to sensitive crops such as cherry, peach, lupin, and kidney bean, especially when these crops are growing on sandy soils (Stout et al. 1988).

The increased utilisation of sewage sludge on agricultural lands has raised concern over heavy metal contamination, thus most of the work associated with heavy metals has referred to the use of sewage sludge (Stout et al. 1988). Stout et al. (1995) reported that the heavy metal content in FBA is comparable to that of more traditional agricultural soil amendment products, such as lime and gypsum. Compared to sewage sludge, FBA contains very low levels of heavy metals (Table 2.1). In addition, the oxide form of heavy metals in FBA makes them much less available to plants than the organic forms in sewage sludge (Stout et al. 1988). A number of studies have confirmed that the accumulation of heavy metals in food crops or herbage grown on FBA treated soils has not caused adverse effects on the health of animals consuming these diets (Cahill et al. 1988; Cochran et al. 1991; Stout et al. 1979; Vona et al. 1992; Whitsel et al. 1988). Loading of these metals on agricultural soils through FBA treatment, however, should not exceed loadings recommended for sewage sludge (Department of Health 1992).

Furthermore, any increase in the quantity or availability of these metals in soils should be carefully monitored using appropriate soil tests (Stout et al. 1988).

2.3 CROP RESPONSES TO FBA APPLICATION

Substantial and highly significant plant growth or yield responses have been reported in a number of experiments involving either broadcast application or incorporation of FBA into the soil. The crops studied include corn (Marsh & Grove 1992a; Stehouwer et al. 1994a; b; 1995a; Terman et al. 1978), peanuts (Terman et al. 1978), alfalfa (Stehouwer et al. 1994a; b; 1995a; Stout & Priddy 1996), fescue (Dick et al. 1994), tobacco (Marsh & Grove 1992a), soybean (Marsh & Grove 1992b), apples (Korcak 1979;1980a; b; 1982; 1984; 1985; 1988; Korcak & Kemper 1993; Wrubel et al. 1982), peaches (Edwards et al. 1985b; Wrubel et al. 1982), pecan (Edwards et al. 1985b), red clover, tall fescue, oat and buckwheat (Stout et al. 1979). Typically, yield increases were shown mainly to be associated with reductions in soil acidity and Al phytotoxicity (Dick et al. 1994; Edwards et al. 1985b; Korcak 1980b; Stehouwer et al. 1994b; 1995a; Stout 1995; Terman et al. 1978) and improvements in Ca and S nutrition (Korcak 1979, 1982, 1984; Terman et al. 1978). Improved rooting with depth has also been reported (Marsh & Grove 1992b).

Stehouwer et al. (1994a) concluded that FBA application has the potential to improve growth and yield of pH sensitive crops such as alfalfa on acid soils. With a crop such as corn that is less pH sensitive, the potential yield benefit from FBA application may be less (Stehouwer et al. 1994a).

2.4 FBA AS A LIMING MATERIAL

2.4.1 Effect on soil acidity

Research has focused on the potential for using FBA as liming material to reduce the acidity of low pH soils because it is an alkaline material with $CaCO_3$ equivalence ranging from 31% to 105% (Table 2.1). A number of studies have shown that addition of FBA can increase the pH of acid soils (Edwards et al. 1985a; Korcak 1980b; 1984; 1988; Korcak & Kemper 1993; Marsh & Grove 1992a; b; McCarty et al. 1994; Sidle et al.

1979; Stehouwer et al. 1994a; 1995a; Stout et al. 1979; Terman et al. 1978; Wrubel et al. 1982). Application of FBA at the recommended liming rate effectively neutralised acidity in the zone of incorporation (Korcak 1980b; 1982; Stehouwer et al. 1994a; b) and in some cases increased the pH of underlying soil (Marsh & Grove 1992b).

Marsh and Grove (1992a) evaluated the efficacy of an FBA derived from burning petroleum coke (dolomite as sorbent, FBA7 in Table 2.1) in reducing soil acidity on a silt loam soil (pH_{water} 4.75) compared with limestone and $Ca(OH)_2$. Soil pH rose with increasing rates of application for all liming materials in the experiment. The increase in soil pH was less in the limestone treatment, primarily because the carbonates of the limestone reacted more slowly than the oxides-hydroxides associated with the equivalent liming weights of the other materials. Soil pH measurements were not accurate measures of the amount of soil acidity neutralised because soil pHs measured in water were sensitive to soil salt concentrations. Where higher rates of $Ca(OH)_2$ were used, as well as the sulphate salts in the FBA, pH values may be lower than expected because of the high ionic strength in soil solution. Soil solution electrical conductivity remained constant across rates of limestone, but increased with rate for $Ca(OH)_2$, and especially for the FBA. This necessitated overcoming the salt effect by using 1 M KCl as the measurement medium to obtain pH values permitting comparisons among the amendments (Marsh and Grove 1992a).

Korcak and Kemper (1993) investigated the long term effects of FBA (FBA1, Table 2.1) applied at disposal levels on soil chemical properties. In 1980 FBA was applied as a soil 'cap' about 50 mm thick within the rows of an established, young apple orchard at rates up to 1.12×10^5 kg ha^{-1}. Eleven years after application, soil profile pH was significantly elevated by the FBA treatment to a depth of 660 mm. They suggested that horticultural utilisation of FBA at relatively high rates of application may be a practical consideration for disposing of FBA since the material, in orchard settings, can be surface applied and remain in place for long periods. Results from their original apple study showed, in general, good growth and productivity of the trees (Korcak 1988).

2.4.1.1 Particle size of FBA and reactivity

Not only the $CaCO_3$ equivalence but also the particle size will affect the time required for FBA to be an effective liming material. Terman et al. (1978) compared the neutralising ability of FBA (FBA1, Table 2.1) of different sizes with that of fine calcite. In an incubation experiment, fine $CaCO_3$, and coarse (< 3.4 mm) and fine (< 0.1 mm) FBA (33.1% CaO) were mixed with 1 kg of soil (Typic Paleudult) at rates of 0, 1, 2, 4 and 8 g kg^{-1} soil and incubated for five weeks. After one week, the soil pH response to increasing rates of fine $CaCO_3$ was linear reaching a maximum at pH 7.7 - 7.8. More than 95% of the maximum pH change was achieved with the 4 g kg^{-1} of fine $CaCO_3$. With a rate of 8 g kg^{-1}, coarse FBA increased soil pH linearly from 4.4 to 4.9 and fine FBA to 7.4. They suggested that the immediate liming value of coarse and fine FBA was about 8 and 47%, respectively, that of fine $CaCO_3$. They also cited a liming test on the same soil by D. A. Mays who reported that two locally obtained ground (< 1.6 mm) agricultural limestone (25 and 17% of which was < 0.1 mm) were 58 and 48% as effective for increasing soil pH as was fine $CaCO_3$. Consequently, Terman et al. (1978) suggested that fine FBA has about the same immediate liming value as 1.6 mm ground limestone. They concluded, however, that the coarse FBA has a much lower short-term liming value, probably about equal to similar size ranges of ground limestone.

Edwards et al. (1985a) also confirmed that particle size of FBA (FBA3 & FBA4, Table 2.1) affected its effectiveness in raising soil pH. Their incubation study indicated that FBA from a calcitic sorbent source (ground to pass a 0.15 mm sieve) was more effective in altering soil pH than FBA from a dolomitic source (90% passing through a 2 mm sieve and 25% passing through a 0.15 mm sieve). Both FBA sources, however, were adjusted to equal Ca contents. They suggested that smaller size of the calcitic FBA was more reactive than the bigger sized dolomitic FBA. Thus when comparing FBA liming effectiveness, FBA particle size must be considered as well as the nature of the fuel and sorbent source.

2.4.2 Effect on other soil chemical properties

In the range of studies described in the last section, besides increasing pH, FBA has been shown to modify other soil chemical properties. Changes in soil chemical composition result both from changes in soil pH, affecting elemental solubilities and from soil enrichment with soluble salts and major and trace elements present in the FBA. In general FBA application causes water soluble concentrations of Al, Mn and Fe to decrease and the base status of acid soils to increase. The base status of soil below the zone of incorporation is commonly increased as well owing to transport of Ca^{2+} and Mg^{2+}. Mobility of Ca and Mg (when dolomite is used as the SO_2 sorbent) in FBA is the result of the greater solubility of $CaSO_4$ and $MgSO_4$ compared with that of $CaCO_3/CaMg(CO_3)_2$.

Korcak (1984) reported that FBA (FBA1, Table 2.1) treatments (at one and two times of the soil lime requirement on weight basis) greatly elevated extractable soil Ca compared to the untreated control. Soil extractable metals (Mn, Zn, Cu, Pb and Cd) were not significantly or consistently different, while the KCl extractable soil Al was significantly reduced by FBA treatment and the effect lasted throughout the four-year experimental period (Korcak 1984). Similarly, of the studies to date there was no evidence that land application at the recommended liming rate of the FBA (Table 2.1) would lead to elevated levels of potentially toxic trace elements in soil or water (Stehouwer et al. 1994b; 1995a). Only if the lime sorbent or the fuel contain excessive levels of toxic elements is this likely to occur.

Utilisation of high application rates of FBA materials to agricultural land at disposal level is limited by the high alkalinity produced when the material is mixed within the soil (Terman et al. 1978). However, Korcak (1988) applied rates of FBA (FBA1, Table 2.1) of up to 1.12×10^5 kg ha^{-1} as a within-row cap in an established apple orchard. Over six years, cumulative yields were increased in three of four cultivar/rootstock combinations. Both electrical conductivity (EC) and exchangeable Ca in amended soil were significantly elevated, whereas exchangeable Mg decreased due to the low level Mg in FBA1 (0.8% MgO, Table 2.1). Similarly, extractable Fe, Mn, Zn and Cu plus exchangeable K were significantly decreased with increasing FBA. On a percent-saturation basis, the low and high FBA rates resulted in about 90% Ca saturation of the soil exchange capacity, compared to about 10% for the control soils. Concurrently, exchangeable Mg was significantly reduced by FBA application. Soil Ca/Mg was thus increased from 4.3 for the control soils to 24.3 at the high FBA rate. Foliar Mg levels decreased with time following high FBA application, indicative of the greatly increased soil Ca status and the potential to leach Mg from the surface horizons.

These apple plots were re-examined eleven years after the initial application and five years after the plots were ploughed (Korcak & Kemper 1993). X-ray diffraction patterns of remnant cemented pieces of the applied FBA showed that most of the original CaO has converted to calcium carbonate and some quartz, gypsum and ettringite were present. The formation of calcium carbonate with time is expected and it leads to the maintenance of a relatively high soil pH. Surface pH values from these plots after eleven years is about 7.6. Soil pH is significantly higher in the top 660 mm of the treated sites compared to unamended sites. This has been accompanied by significant increases in extractable and total Ca, B and S with a concomitant reduction in extractable Mg. The higher B levels were not reflected in increased apple tissue concentrations of B throughout the first six years after application (Korcak 1988). Therefore, application of FBA at relatively high rates, 1.12×10^5 kg ha^{-1}, can have long lasting effects on the soil environment. A potential area of concern is the imbalance created in the Ca to Mg ratio when evaluated on an extractable nutrient basis (Korcak & Kemper 1993). This situation can be corrected by application of $MgSO_4$ as a soil amendment or, for orchards, as a foliar spray. Alternatively, the use of dolomitic limestone as part of the absorbent during coal combustion would greatly increase the Mg content of the residue and lessen the potential for Ca:Mg imbalances (Korcak & Kemper 1993).

Therefore, for horticultural utilisation, FBA appears to be one of the better coal combustion products due to lower metallic concentration (FBA1, Table 2.1) (Korcak 1993). When not soil-incorporated, the pH and alkalinity effects are reduced, allowing the use of higher rates. When the situation is not suitable for surface applications that can remain in place for several years, application rates need to be at or near the lime requirement of the soil to prevent detrimental effects on crop growth (Korcak 1993).

In addition to the application of FBA to soils, FBA has potential to be added to mixtures containing organic materials such as sewage sludges or sludge composts. The high pH of the FBA materials would assist in maintaining a low availability of heavy metals such as Cd. A greenhouse experiment on apple seedlings was conducted using FBA at application rates of one or two times greater than the soil lime requirement mixed with composted sewage sludge at 0, 2.5 and 5.0 × 10^4 kg ha^{-1} (Korcak 1980a). The mixtures reduced Mn uptake from an indigenously high-Mn soil and increased apple tissue Ca concentration after 15 weeks (Korcak 1993).

2.4.3 Effect on plant elemental composition

Application of FBA not only changes the chemical properties of the soil but affects plant root uptake of nutrients from soil. The results from a number of studies showed that when FBA is applied to soil at the rate of its lime requirement, FBA treatment may increase concentrations of Ca and S in plant tissue, but no detrimental effect on plant growth has been reported.

When relatively large quantities of FBA (FBA1, Table 2.1) were disposed of on an established apple (*Malus domestica* Borkh) orchard at two rates (either 9.2 kg m^{-2} (low rate), 36 kg m^{-2} (high rate) or untreated control) no nutrition related problems were noted for any of four tree types used (Korcak 1988). Although leaf Ca concentrations were significantly increased by FBA treatment, little if any influence of applied FBA was noted on peel and flesh Ca concentrations throughout the study. One of the concerns of applying a high Ca product to orchard soils is the effect on the Mg status of the trees. The applied FBA, due to the calcitic limestone used in combustion, had a relatively low Mg content (0.8% MgO) and Korcak (1988) found that leaf Mg was significantly lowered by the high FBA rate for the last two growing seasons. Peel Mg was unaffected. Fruit flesh Mg was little affected by treatments throughout the study (Korcak 1988). Leaf Mg was generally within the acceptable range of 0.15-0.25% for apple trees (Shear & Faust 1980). Foliar concentrations of N, P, K, S, Mn, Fe, Ca, B, Al and Zn were generally little affected by treatment or apple tree type throughout the study and found to be within normal concentration ranges (Shear & Faust 1980). Similar results were noted for elemental concentrations in both fruit peel and flesh (Korcak 1984; 1988).

Using FBA as a minespoil amendment, Stehouwer et al. (1996) found high rates application of FBA (FBA9, Table 2.1) of up to 120 g kg^{-1} increased tall fescue growth, and chemical analysis of plant tissue indicated that concentrations of the main nutrients were generally within sufficiency ranges. Although tissue Ca, Mg and S were increased by FBA treatment, tissue concentrations of most trace elements were decreased.

Stout et al. (1979) compared FBA with $Ca(OH)_2$ as a lime source in a greenhouse study with red clover (*Trifolium pratense* L.), tall fescue (*Festuca arundinacea* Schreb.), oat (*Fagopyrum sagittatum* Gilib.) and buckwheat (*Avena sativa* L.). The FBA (FBA1, Table 2.1) treatment was applied at a rate to give sufficient alkali to adjust the pH of Westmoreland silt loam (Ultic Hapludalf, mixed, mesic) up to 6.5. FBA treatments increased Ca levels in red clover more than did $Ca(OH)_2$. This did not occur in the non-legumes. All species had higher tissue Mg and S concentrations when grown with FBA rather than $Ca(OH)_2$. In spite of the increased Zn loading, Zn levels in herbage decreased relative to the control as soil pH increased as a result of FBA application. Cochran et al. (1989) also reported that application of FBA (FBA5, Table 2.1) (6760 kg ha^{-1}) to a *Festuca arundinacea/Lotus corniculatus* sward on reclaimed coal mine spoil increased herbage Ca, Fe, Zn, S and Cu and lowered herbage Mg and P compared with dolomitic limestone (3380 kg ha^{-1}). In a similar experiment, Vona et al. (1992) found there were no differences in micronutrient concentrations in herbage due to treatment. The above experiments and a number of other studies on the effect of FBA treatment on plant tissue elemental composition are summarised in Table 2.2. As expected, therefore, when Ca and Mg rich alkaline materials are added to soil-plant systems, the herbage concentrations of the base cations generally increase while concentrations of the transition metals decrease or show no change.

2.4.4 Implications to food chains

FBA contains heavy metals that may be toxic to animals and humans if they entered into the human food chain. Research on possible effects of FBA application to soils on the nutritional quality of food crops has been conducted with a number of animal species, such as the chick (*Gallus gallus*) (Mitchell et al. 1983), rat (*Rattus rattus*) (Cahill et al.

Table 2.2 Summary of effect of FBA on plant elemental composition.

FBA type[1]	Plant species	Trial type	Plant tissue analysis relative to Control[2]	Reference
FBA1	Apple	Sand culture	Leaf: Ca, S, Sr, ↑; N, K, n.c.; P, Mg, B, Mn, Zn, Cu, Fe, ↓ Peel & flesh: n.c.	Korcak 1982
FBA1	Apple	Pot	Leaf: Ca, ↑; Mn, Zn, ↓; K, N, P, S, B, n.c.	Korcak 1980b
FBA1	Apple	Pot	Root: Ca, ↑; P, Mn, Cu, Al, n.c.	Korcak 1985
FBA1	Apple	Field (Control aglime)	Leaf: Ca, n.c.; Mg, ↓ Peel & flesh: n.c.	Korcak 1984
FBA1	Apple	Field	Leaf: Ca, ↑; Mg, ↓ Peel & flesh: n.c.	Korcak 1988
FBA1	Apple	Field	Leaf, peel & flesh: Ca, P, B, n.c.	Wrubel et al. 1982
FBA1	Peach	Field	Leaf: Ca, B, ↑; Mn, Fe, Cu, Zn, Sr, Pb, n.c. Peel & flesh: Ca, n.c.	Wrubel et al. 1982
FBA3	Peach	Pot	Leaf: Mg, ↑; Mn, Zn, Al, ↓	Edwards et al. 1985a
FBA4	Pecan	Pot	Leaf: Ca, P, K, ↑; Mn, Zn, Al, ↓	Edwards et al. 1985b
FBA1	Vegetables, corn, wheat, peanuts	Field	Total content: Ca, P, Mg, N, K, Zn, B, Cu, Cd, Mn, Fe, n.c.	Cahill et al. 1988
FBA1	Red clover Tall fescue Oat Buckwheat	Pot (Control: $Ca(OH)_2$)	Mg, S, ↑; Zn, ↓	Stout et al. 1979
FBA5	Tall fescue Lotus	Field (Control: dolomite)	Ca, Fe, S, Zn↑; Mg, P, ↓	Cochran et al. 1989
FBA5	Tall fescue	Field	Ca, Fe, S, ↑; Mn, Zn, ↓	Cochran et al. 1991
FBA6	Corn, wheat	Field (Control: dolomite)	Ca, Fe, ↑; Mg, ↓ K, Mn, Cu, Zn, n.c.	Whitsel et al. 1988
FBA7	Tobacco	Pot (Control aglime)	Leaf: Cl, P, S, ↑; N, K, Cd, Ni, Zn, ↓;	Marsh & Grove 1992a
FBA7	Corn		Shoot tissue: Cl, Cu, ↑; Pb, ↓;	Marsh & Grove 1992a
FBA8	Orchardgrass & white clover	Field	Ca, Mg, S, ↑; N, P, K, Mn, Zn, Al, n.c.	Vona et al. 1992
FBA9	Tall fescue	Pot	Ca, Mg, S, K, ↑; N, P, B, Mn, Zn, Al, Cd, Cr, Cu, Ni, Se, ↓	Stehouwer et al. 1995c
FBA12	Alfalfa	Field	S, ↑; N/S, ↓; Heavy metals, n.c.	Stout & Priddy 1996

[1] Refer to Table 2.1 (Appendix table).

[2] ↑, increase; ↓, decrease; n.c., no change, relative to the untreated control unless control is stated.

1988; Fashandi et al. 1985), pig (*Sus scrofa*) (Whitsel et al. 1988), hamster (*Mesocricetus auratus*) (Fashandi et al. 1985), sheep (*Ovis aries*) (Cochran et al. 1991; Vona et al. 1992) and cattle (*Bos taurus*) (Cochran et al. 1989; Smedley et al. 1985). All these studies confirm that treatment of agricultural soils for up to six years with high levels of FBA (up to 9080 kg ha^{-1}) as a liming or fertilising agent causes no measurable adverse effects on composition of food crops or herbage, or on the health and productivity of animals consuming diets produced on such soils.

The work of Vona et al. (1992), who evaluated effect of FBA on the health and performance of sheep grazing pastures, has direct relevance to the use of FBA on grazed pastures in New Zealand. Forage analysis showed increases in Ca concentration in FBA (8960 kg ha^{-1}) and dolomitic limestone (4480 kg ha^{-1}) treated herbage vs. the control, a higher level of S in FBA vs. lime treated herbage, but no differences in microelement concentrations due to treatment. They studied the effects of FBA on the health and performance of sheep grazing pastures and found that there were no differences in weight gains of either ewes or lambs within years due to treatment and no effect of treatment on blood hematocrit levels. Similarly, there were either no differences or small differences in the concentrations of macro- and micro-elements in the carcass, liver and kidney of ewes and lambs associated with treatment, and tissue concentrations of elements were within normal ranges (Vona et al. 1992). Based on this experiment and other relevant studies, including rat (*Rattus rattus*) (Cahill et al. 1988; Fashandi et al. 1985), pig (*Sus scrofa*) (Whitsel et al. 1988) and hamster (*Mesocricetus auratus*) (Fashandi et al. 1985), Vona et al. (1992) concluded that treatment of agricultural soils with high levels of FBA as a liming or fertiliser agent causes no adverse effects on composition of food crops or herbage, or on the health and productivity of animals consuming diets produced on such soils.

Cochran et al. (1991) evaluated nutrient utilisation by sheep fed forage grown on soil treated with dolomitic limestone (11.26% Mg, 4540 kg ha^{-1}) and FBA (0.08% Mg, 9080 kg ha^{-1}). Forage analysis indicated that the FBA treatment greatly increased Ca and S concentration but had no effect on Mg concentration in forage, compared with untreated control, whereas the limestone treatment increased Ca and Mg concentration. They found that apparent digestibility of cellulose was higher for amended forages than for the non-amended control and in addition the apparent digestibility of hemicellulose was higher for limestone amended forage than for FBA amended forage. Apparent absorption of S was higher for lambs on the FBA treatment than for those on the limestone treatment. These differences were related to differences in mineral concentrations of the forages. Therefore, Cochran et al. (1991) concluded that FBA treatment may have enhanced utilisation of Ca and S and improved digestibility of some fibre components by lambs.

Thus previous work indicates that heavy rates of FBA (approximately 9000 kg FBA ha^{-1} year^{-1}) can be applied to grazed pastures without causing increased mobilisation of toxic elements into the food chain.

2.4.5 Acid mine spoil reclamation

Large volumes of FBA are required when FBA is used to reclaim acidic surface mine spoils (Dick et al. 1994; Sidle et al. 1979; Stehouwer et al. 1995b; Terman et al. 1978). Many mine spoils are high in pyrite (FeS_2), which oxidises to form sulphuric acid, resulting in highly acidic ($pH \leq 3.5$) spoil (Carlson & Adriano 1993). Therefore, it can be difficult or impossible to establish vegetation on these sites without altering the strongly acidic environment. Lack of vegetative cover causes these areas to be highly erosive and drainage waters from such sites can cause severe off-site environmental damage because of acidity, high salt content and sedimentation (Sutton & Dick 1987). The amount of alkaline amendment needed for reclamation of acidic mine spoils can be five to ten times greater than is used in agricultural soils (Stehouwer et al. 1995b). Furthermore, the use of FBA on these sites is attractive because it helps solve the FBA disposal problem while alleviating some of the problems associated with another coal waste product (Carlson & Adriano 1993).

Stehouwer et al. (1995b) investigated the efficacy of FBA as amendment for acidic mine spoils and the potential for adverse environmental impacts from salts and trace elements when FBA was applied in high rates needed for mine spoil reclamation. In their eight month column leaching and greenhouse study, they found that FBA (60% $CaCO_3$ equivalence) was effective in neutralising acid conditions in the mine spoils when FBA was added to spoil at 30 to 60 g kg^{-1} spoil weight. With FBA rates at greater than 30 to

60 g kg^{-1} spoil high leachate pH and Ca and Mg concentrations indicated some potential for amelioration of phytotoxic conditions below the zone of incorporation. In addition, leachate electrical conductivity, dissolved organic C, and S, tended to increase with increased FBA rate. FBA also reduced leachate concentrations of Al, Fe, Mn and Zn that are frequently phytotoxic in acid soils. Decreased solubility and mobility of these metals would also improve water quality. They found that with FBA of 160 g kg^{-1} spoil or less, leachate concentrations of trace elements of environmental and regulatory concern remained very small. In fact, most were less than primary drinking water standards. Improved plant growth (tall fescue) was observed when FBA was mixed with acid spoils (Dick et al. 1994). Therefore, Stehouwer et al. (1995b) concluded that FBAs are very suitable for mine spoil amendment if amendments are limited to amounts that will not cause excessively high pH or phytotoxic salt concentrations. Provided leachates are not highly alkaline, there is little potential for adverse effects on water and soil quality from trace elements. This agrees to the findings by Sidle et al. (1979), who used lower rates of FBA in their column leaching experiment.

2.5 POTENTIAL USE OF FBA AS A SUBSOIL ACIDITY AMELIORANT

2.5.1 Background

In many parts of the world acid conditions in subsoil horizons pose a major limitation to the successful production of many important crop species (Adams & Moore 1983; Doss et al. 1979; Farina & Channon 1988a; Loganathan & Hedley 1996; McKenzie & Nyborg 1984; Parfitt et al. 1994; Simpson et al. 1979; Stout & Priddy 1996; Sumner et al. 1986). Furthermore, intensive cropping accompanied by high nitrogen use may lead to subsurface acidification of soils that are not naturally prohibitively acidic (Abruna et al. 1964; Adams 1984; Adeoye & Singh 1985; Bolan et al. 1991a; Pearson et al. 1962; Stumpe & Velk 1991). It becomes more common therefore that plant rooting is limited by the subsurface soil acidity and the problem is often manifested as drought intolerance and/or poor use of nutrients associated with shallow rooting (Foy 1992; McCray & Sumner 1990; Sumner et al. 1991). It is a common practice to incorporate lime into the plough layer to raise the pH of acid soils and neutralise and precipitate plant-toxic Al.

Unfortunately, downward movement of base after liming is extremely slow because OH^- and HCO_3^- ions are consumed by acidity in the topsoil and no mobile anions remain. In addition the increased pH generates more negative charge on soil particle surfaces, which acts to retain more Ca^{2+} ions in the surface soil (Alva et al. 1990). The most effective procedure for promoting root growth in the acidic subsoil is to mix lime throughout the entire soil volume in which roots are desired (Coventry 1991; Coventry et al. 1987; Jayawardane et al. 1995; McKenzie & Nyborg 1984; Hammel et al. 1985; Sumner et al. 1986). However, in most situations this procedure is not economically feasible (Foy 1992; Sumner 1994).

The expense and difficulty of mixing lime into the subsoil have led researchers to examine surface applied amendments, such as gypsum, in the amelioration of subsoil acidity. Reeve & Sumner (1972) found that surface incorporated gypsum moved through a simulated profile of a Natal Oxisol and reduced the level of exchangeable Al in the subsoil more effectively than surface incorporated lime. Since then, a number of studies have been conducted on the surface incorporation of gypsum and gypsiferous waste materials (Ritchey et al. 1980; 1995a; Shainberg et al. 1989). In all the experiments that have been conducted, it is clear from the cumulative responses obtained that very appreciable yield increases of maize and soybeans (Farina & Channon 1988b; Hammel et al. 1985; Marsh & Grove 1992b; Ritchey et al. 1995a), alfalfa (Sumner et al. 1986), wheat (McLay et al. 1994a; Zaifnejad et al. 1995), apple (Pavan et al. 1987), sorghum (Ritchey et al. 1995a), coffee, rice, beans, peaches, cotton (Shainberg et al. 1989) can be obtained.

Increased yields of crops grown on acid soils with surface incorporated gypsum have been attributed to increased root length density in the subsoil (Farina & Channon 1988b). Confirmatory evidence for the benefits of deeper rooting following gypsum use is to be found in water extraction pattern down the profile. Sumner & Carter (1988) studied the effect of gypsum on alfalfa root distribution in the profile of a Ultisol. Gypsum treatment resulted in substantial penetration of roots to deeper than 1 m, whereas in the control plots few roots penetrated beyond 0.6 m. On both a mass and length basis, the quantity of roots in the subsoil of the gypsum treatment exceeded that of the control three to five fold, which is reflected in the alfalfa yield response (Sumner et al. 1986). Reports corroborating this type of response have been published for maize, apples, beans and rice (Shainberg et al. 1989). In all cases, the gypsum treatment increased the Ca level in the subsoil, decreased the Al level and promoted root growth, so the roots were able to extract more water from subsoil and had lower leaf water potential than in control treatments. This increased water uptake allows the plant to better overcome drought stress and therefore accumulate dry matter more successfully on the gypsum treated soils (Shainberg et al. 1989).

In a number of cases, however, there is no yield response to gypsum application (Black & Cameron 1984; Simpson et al. 1979; Wright et al. 1985), and a relative decrease in root growth has been observed at intermediate depths in the subsoil (Farina & Channon 1988b; Sumner & Carter 1988). At present there is no entirely satisfactory explanation for this effect.

2.5.2 Mechanisms of subsoil acidity amelioration by using gypsum

Although gypsum does not have the ability to neutralise soil acidity in the same way as limestone, it does produce a number of effects which can partially or fully mitigate the severity of several detrimental aspects of soil acidity. The mechanisms by which gypsum ameliorates subsoil acidity by Ca^{2+} exchange and SO_4^{2-} sorption will be discussed in detail in Chapter 7 (refer Section 7.1).

2.5.3 Criteria for identification of gypsum-responsive soils

In order to make efficient use of gypsum, it is necessary to be able to predict which soils will respond to its application. Characteristics of soil below the plough layer which affect the likelihood of crop rooting improvement include the subsoil exchangeable Ca^{2+} level, the exchangeable Al level and the response of soil minerals to sulphate addition (Ritchey et al. 1995a). Where exchangeable Ca^{2+} levels are less than 0.1 cmol $_{(+)}$ kg^{-1}, there is a high probability of root growth responses to gypsum, regardless of Al levels, because of root growth response to Ca^{2+} as a nutrient. At higher levels of Ca^{2+} where the nutritional needs of the plant roots are met, the probability of response to gypsum is controlled more strongly by the percentage Al saturation of effective cation exchange capacity

(ECEC) of the soil (Ritchey et al. 1995b). Ritchey et al. (1995a) reported that for low ECEC soils of central Brazil, gypsum responses were usually high for Al saturation levels of 65% or greater and low where Al saturation was less than 35%.

Ritchey et al. (1995a; b) and Shainberg et al. (1989) found that mineralogy of soils and resulting charge characteristics may influence the reactions of gypsum and, therefore, may vary the effectiveness of gypsum in alleviating acidic soil infertility in various soils. Determining mineralogical composition is, however, more expensive and time-consuming than measuring extractable Ca^{2+} and Al^{3+} levels which are routinely assessed in soil analytical laboratories. To avoid this problem, Sumner (1994) published a simple method to predict whether a subsoil will respond to gypsum. It is based on the capacity of the soil to sorb SO_4^{2-} and raise the pH through displacement of hydroxyl groups. If the pH of the supernatant of a soil shaken intermittently overnight with 0.005 M $CaSO_4$ (10 g soil to 25 ml solution) is higher than the pH when shaken with 0.005 M $CaCl_2$, and the electrical conductivity (EC) of the 0.005 M $CaSO_4$ solution is lower after shaking than before (indicating sorption of Ca^{2+} and SO_4^{2-}), then the subsoil is considered a good candidate for gypsum treatment.

An alternative is the bioassay method that is originally used to detect plant responses to Ca^{2+} deficiency and Al toxicity (Ritchey et al. 1989; 1995a). In the biological method, four-day root lengths of seedlings of the actual cultivar being used on the farm are compared in subsoil with and without the addition of 1% by volume of gypsum. Where growth in the gypsum treated soil is improved by 15% or less, limited benefit is expected from field use of gypsum. Where the improvement is 30% or more, gypsum application may be beneficial (Ritchey et al. 1995a).

2.5.4 FBA - A prospective ameliorant for subsoil acidity

Topsoil incorporated gypsum is able to increase base status and reduce exchangeable Al in the subsoil much more effectively than lime. At the topsoil level, however, gypsum is less effective than lime in totally eliminating exchangeable Al (Shamshuddin et al. 1991). When gypsum is used as a subsoil acidity amendment, it is necessary to incorporate lime into the plough layer to mitigate the acidity in the topsoil (Shainberg et al. 1989). Because FBA contains both ‘lime’ and gypsum, it may not only neutralise topsoil acidity, but act as an effective ameliorant for subsoil acidity. The 'lime' in FBA is CaO (Stout et al. 1979) or $Ca(OH)_2$ in slaked FBA, which has the advantage of being quicker reacting with topsoil acidity than ordinary lime and the Ca^{2+} and SO_4^{2-} from gypsum can readily move into subsoil to ameliorate Al toxicity there. Therefore, application of FBA to topsoil has the potential to rectify both surface and subsurface soil acidity.

2.6 FBA AS A SULPHUR SOURCE

Sulphur is essential to plant nutrition. In general, plants contain as much S as P, the usual range being from 0.2 to 0.5% on a dry-weight basis. Sulphur ranks in importance with N as a constituent of the amino acids cysteine, cystine, and methionine in proteins that account for 90% of S in plants. It is also involved in the formation of oil in crops such as peanut (*Arachis hypogaes* L.), soybean [*Glycine max* (L.) Merr.], flax (*Linum usitissimum*), and rapeseed (*Brassica campestris*) (Tisdale et al. 1985). In the past three decades, S deficiencies have been reported with increasing frequency throughout the world, including New Zealand (The Sulphur Institute 1982; Tisdale et al. 1986).

The reasons given for the increasing S deficiencies world wide are: (1) the shift from low analysis to high analysis fertilisers containing little or no S, (2) use of high-yielding crop varieties that remove greater amounts of S from the soil, (3) reduced industrial S emission into the atmosphere due to pollution-control measures (eg. production of FBA, and decreased use of high S content fossil fuels, (4) decreased use of S in pesticides, and (5) declining S reserves in soil due to erosion, leaching, and crop removal. Increased consumption of sulphur free, high analysis fertilisers is seen as the most important reason for the increasing S deficiency worldwide (Morris 1986). Thus, with increasing S deficiencies worldwide, some industrial by-products such as waste gypsum and FBA deserve serious consideration for agricultural applications where mined gypsum has traditionally been used.

Because the S in FBA is mainly in the form of anhydrite ($CaSO_4$) or gypsum ($CaSO_4.2H_2O$) after hydration, FBA and gypsum should have, as an S source, similar effect on crops in S deficient soils. Gypsum, including industrial by-products, such as phosphogypsum, has been successfully used as a S fertiliser to increase the yields of winter wheat (Oates & Kamprath 1985), rice (Chien et al. 1987) and pasture

(Woodhouse 1969). Use of gypsum as a source of S has been extensively reviewed by Alcordo & Rechcigl (1993). To date, data on the use of FBA as a S fertiliser is limited, although Terman et al. (1978) demonstrated that FBA is an effective S source for growing corn and peanuts.

2.7 EFFECT OF FBA ON SOIL PHYSICAL PROPERTIES

Surface applied phosphogypsum has been successfully used to reduce soil dispersion and erosion (Agassi et al. 1981; Charters et al. 1985; Miller 1987). FBA has been utilised to increase water infiltration into soil, reduce soil surface sealing and control soil erosion (Balla & Edwards 1995; Norton 1995; Reichert et al. 1994; Reichert & Norton 1994; 1995; 1996) because gypsum is one of the main components in FBA. It is possible to use FBA to ameliorate the restrictive nature of fragipan horizons (Rhoton et al. 1995). With dissolution, gypsum increases the electrolyte and Ca concentrations of the soil solution and runoff thus reducing swelling of soil and dispersion of clay particles (Reichert & Norton 1994). In the case of FBA, which is rich in $CaSO_4$ and CaO, this material is a source of electrolytes and of alkalinity as well. Increases in soil pH enhance dispersion, particularly of variable-charge soils, and the electrolytes released by FBA may be insufficient to flocculate clay particles, therefore FBA may actually increase erosion of variable-charge soils. For soils with a predominance of permanent charge colloids, such as soils with 2:1 type clays, increases in pH have less effect on surface negative charge. Therefore, FBA can be utilised for controlling soil erosion on agricultural land and construction sites, especially those with permanently charged clays (Reichert & Norton 1994; Reichert et al. 1994). Reichert & Norton (1994) measured the steady-state infiltration rates (I_s) for five soils, with and without addition of 5000 kg ha^{-1} surface applied FBA (74% CaSO4, 23% CaO, total dissolved salts 4700 mg litre^{-1}). They found that surface sealing and erosion were significantly reduced by the surface applied FBA on all studied soils, but with a lesser effectiveness on the illitic and smectitic soils. For infiltration, FBA was most effective on the smectitic soil, except when swelling is high. The values of the steady-state infiltration rates (I_s) for the control ranged from 1.8 to 5.8 mm h^{-1} and were increased 3.6 to 5.0 fold with the FBA. They explained that the increased electrolyte concentration reduced swelling and enhanced flocculation and possibly sedimentation of soil clays, thus decreasing sediment concentration in the runoff and sediment yield. Reichert et al. (1994) suggested that FBA has great potential for reducing sealing and erosion on permanent charge soils. The FBA effectiveness on variable charge soils was dependent on soil pH, its buffering capacity and flocculation (Reichert et al. 1994; 1996).

Care needs to be taken, however, because compositionally, FBA is similar to Portland cement (ACI Committee 1987; Dawson et al. 1995; Korcak 1988). When applied at high rates as a soil amendment, FBA exhibits strong pozzolanic properties and can limit water infiltration and root penetration (Dick et al. 1994; Stehouwer et al. 1995b). The pozzolanic nature of FBA can create large cemented 'chunks' of the material in the field. Pozzolans are siliceous materials containing Al that react with CaO to form a slow-hardening cement. This pozzolanic property of FBA can benefit apple orchards (Korcak 1988), where rates of FBA up to 1.12×10^5 kg ha^{-1} were applied as a within-row cap in an established apple orchard. The surface applied material formed a porous cement that prohibited weed growth for up to four years after application, but had no adverse effects on crop yields.

2.8 SUSTAINING OF SOIL FERTILITY IN RELATION TO FBA APPLICATION

As more stringent emission regulations for coal fired power plants are enforced, it is likely that the use of fluidised bed combustion and other desulphurisation technologies will increase dramatically and will result in the production of increasing amounts of FBA and similar by-products. If vast amounts of FBA and other coal combustion by-products are produced, however, it seems unlikely that there will be sufficient demand for liming materials in agricultural production to consume these amounts and there is considerable interest in the use of land for disposal of these by-products by application at rates much higher than those required to lime soil (Carlson & Adriano 1993). Although very high rates of FBA applied (up to 1.12×10^5 kg ha^{-1} FBA1, Table 2.1) to orchards improved the apple productivity and had no detrimental effect on the soil (Korcak 1988; Korcak &

Kemper 1993), there are concerns that this use of FBA harms the quality of the soil (Siddaramappa et al. 1994).

Some reports reflect considerable interest in the concept of soil quality as it relates to sustainable productivity in agricultural systems and in the development of indices to assess changes in such quality (Haberern 1992; Papendick & Parr 1992; Parr et al. 1992; Reganold et al. 1993). It has been suggested that measurement of changes in soil enzyme activities may provide useful measures of the changes in soil quality (Dick 1992; Visser & Parkinson 1992). McCarty et al. (1994) investigated the influence of FBA (FBA10, Table 2.1) (up to 22400 kg ha^{-1}) and $CaCO_3$ on soil pH urease, phosphatase, arylsulphatase and dehydrogenase activities in soil. They found that the effect of both liming materials on the enzyme activities studied was largely due to their influence on soil pH and FBA functioned as soil liming material in a manner similar to that of $CaCO_3$ and seemed to have little adverse effect on enzyme activities (McCarty et al. 1994).

The importance of maintaining soil organic matter for the maintenance of good soil quality is well established because of its central role in establishing the physical structure, fertility and biological activity of soil (Karlen et al. 1992; Parr et al. 1992). For example, organic N in soil provides the majority of N for plant growth (Keeney 1982; Stanford 1982) and it seems obvious that destruction of this organic N would degrade the fertility of soil. In addition, it has been suggested that monitoring the rate of various N transformations in soil can provide useful measures of soil quality and indicate the changes in the quality that can result from environmental disturbances (Visser & Parkinson 1992). To determine the influence of FBA on the transformation and fate of soil N and to assess the potential impact of land disposal of FBA on soil quality, Siddaramappa et al. (1994) studied the effect of FBA (FBA10, Table 2.1) (at the rates of 22.5, 45, 90 and 180 × 10^3 kg ha^{-1}) on mineralisation and volatile loss of N in soil. The results showed that FBA treatments, except at 22.5 × 10^3 kg ha^{-1}, caused substantial mineralisation of organic soil N and volatile loss of this N as NH_3 due to the highly alkaline environment (up to pH 12.8). The authors suggested that such extreme alkaline conditions caused chemical degradation and volatile loss of as much as 10% of the organic N in soil. Therefore, improper disposal of FBA on land can have a substantial negative impact on the quality of soil organic matter (Siddaramappa et al. 1994).

2.9 CONCLUSIONS AND RESEARCH PRIORITIES FOR THIS THESIS

Increasing concern about emissions of SO_2 in flue gas and associated problems with acid rain world wide has promoted the development of desulphurisation technologies that reduce these emissions and result in the production of new by-products, such as FBA. As more stringent emission regulations for high-S coal fired industries are enforced, it is likely that the use of fluidised bed boilers will increase dramatically and will result in the production of increasing amounts of FBA materials and other similar by-products.

The literature review has indicated that FBA application to soils should ameliorate soil acidity and S deficiency without causing adverse effects. FBAs are sufficiently variable in composition and their reaction with different soil types, however, that New Zealand FBAs require chemical characterisation and their use on New Zealand pasture soils needs further investigation. Then accurate recommendations for FBA use can be given. In particular this thesis investigates the possibility that FBA can be used to neutralise subsurface soil acidity without the need for pasture cultivation and renovation.

Chapter 3

Chemical properties of fluidised bed boiler ash relevant to its use as a liming material and fertiliser

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3.1 INTRODUCTION

Fluidised bed boiler ash (FBA) is a waste from fossil fuel-fired boilers. The fluidised bed boiler is very similar in construction to a modern day conventional coal fired boiler except that it has a bed of finely divided fuel and sorbent, supported by compressed air in stead of a grate (Lawson 1987). An advantage of fluidised bed boilers is that granular limestone can be used as the sorbent to reduce sulphur emissions from the stack. When the temperature is raised, the limestone calcines and the sulphur dioxide, released during burning of the coal, is chemically captured by the calcium oxide resulting in the formation of calcium sulphate (Equations 3.1 - 3.3).

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{(Eqn. 3.1)}$$

$$CaO + SO_2 \rightarrow CaSO_3 \qquad \text{(Eqn. 3.2)}$$

$$2CaSO_3 + O_2 \rightarrow 2CaSO_4 \qquad \text{(Eqn. 3.3)}$$

The efficiency of the chemical reaction is temperature dependent so the fluidised bed is operated at temperatures between 815 and 870°C to obtain optimum sulphur capture, thus minimising the limestone usage. The bed inventory is continuously replenished with fresh limestone at a rate to provide a calcium:sulphur weight ratio of two. This results in 75% sulphur dioxide (SO_2) absorption and minimises SO_2 emission from the stack (Lawson 1987). Such boilers thus have a potential for meeting air quality standards without the high costs of installing scrubbers to remove SO_2, resulting from combustion of high-sulphur coal, from stack gases.

Fluidised bed boiler ash (FBA) commonly includes both bed discharge and trapped fly ash. In the United States, large quantities of FBA are produced as a waste product of electrical power generation plants. Agricultural uses are required for its disposal because of its high content of calcium sulphate and calcium oxide (Korcak 1988; Korcak & Kemper 1993). Various FBAs have been used as liming material and as calcium and sulphur sources (Cochran et al. 1991; Edwards et al. 1985a; Korcak 1979; 1980b; 1982; 1984; McCarty et al. 1994; Sidle et al. 1979; Stehouwer et al. 1994; Stout et al. 1979; Terman et al. 1978; Wrubel et al. 1982). However, their specific characteristics, and therefore uses are mainly influenced by the fuel source used.

The establishment and operation of New Zealand's first industrial fluidised bed steam generating plant came from a need for more steam generating capacity at the New Zealand Dairy Corporation (NZDC), Anchor Products Ltd.'s Te Awamutu factory, the availability of a large reserve of high sulphur coal (Kawhia Deposit), and the ability to burn this coal within environmentally acceptable emission standards (Lawson 1987). Approximately 1.5×10^7 kg of anhydrous NZDC FBA is produced annually (P. Shannon, Personal communication 1994).

Although NZDC FBA is being used as sulphur (S) fertiliser and liming material, which is usually surface-broadcast onto pastures, there is little known about the chemical properties of NZDC FBA and its potential value in agriculture. The objective of this study was to examine the properties of NZDC FBA relevant to agricultural utilisation. In this paper, the nutrient release characteristics of FBA are compared to those of single superphosphate (SSP).

3.2 MATERIALS AND METHODS

3.2.1 Chemical analysis of coal

A typical analysis of the Pirongia coal, used as fuel (Table 3.1), shows its characteristically high sulphur and relatively high sodium content (refer coal ash analysis). The fuel mixture for the combustion chamber is approximately 6:1, coal to limestone. This maintains the required Ca:S ratio of 2 for efficient SO_2 capture. The resultant ash, which is slaked with whey effluent, is described below.

Table 3.1 Typical analysis of Pirongia coal (Kawhia Deposit)[1].

Coal		Coal ash	
Item	% (As received)	Element	% (Dry basis)
Moisture	27.5	Si	12.4
Ash	9.1	Al	4.8
Volatile Matter	33.1	Fe	7.5
Fixed Carbon	30.3	Ca	12.4
Sulphur	2.3	Mg	1.9
		Na	3.1
		K	0.2

[1] Source: T. MacRae, Anchor Products, Te Awamutu, N. Z.

3.2.2 Fluidised bed boiler ash (FBA) material

The FBA utilised in this study was obtained from Te Awamutu Milk Powder Factory, NZ Dairy Co (NZDC). It was initially an anhydrous product in a dry, dusty state. To make it more acceptable to farmers and spreading contractors, Foremost Fertilisers Ltd slaked the FBA with another liquid waste material from the factory, the whey sludge from the oxidation pond. The whey waste and FBA are mixed using a pug mill and allowed to stand in a bin to cool for 24 hours. During slaking, the major chemical components of anhydrous FBA, anhydrous $CaSO_4$ and CaO change to gypsum ($CaSO_4 \cdot 2H_2O$) and calcium hydroxide [$Ca(OH)_2$] (Equations 3.4 & 3.5). Before it is sold to farmers, the slaked FBA is usually crushed with a hammer mill (Maiden 1992). This study used a sample of the slaked and crushed commercial product.

$$CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad \text{(Eqn. 3.4)}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad \text{(Eqn. 3.5)}$$

3.2.3 Analysis of FBA

The moisture content of FBA was measured by oven drying at 105°C and the pH was determined in water suspension (FBA:water = 1:5). Elemental compositions were analysed by inductively coupled, argon plasma, atomic emission spectrometry (ICP-AES). The sample for total elemental analysis was prepared by HF-HNO_3 digestion (Lee

1993). Acid soluble elements were extracted by shaking 0.5 g FBA in 25 ml 10% HCl (1:3 V/V) overnight.

Liming value ($CaCO_3$ equivalent) was measured by neutralisation: 0.500 g FBA sample was gently boiled with 50 ml of 0.5 M HCl in a 300 ml conical flask for 5 minutes. The mixture was allowed to cool and 3 drops of phenolphthalein indicator was added and titrated against 0.5 M NaOH to the end point (pH 8.0). A similarly boiled control containing only 0.5 M HCl was prepared as a blank.

Particle size distribution was determined using dry sieving with a set of stainless steel sieves (0.075 mm, 0.150 mm, 0.250 mm, 0.50 mm, 1.0 mm and 2.0 mm).

Sub-samples of FBA were ground to < 1 mm particle size and the mineralogical characteristics were determined by X-ray diffraction analysis using a Phillips P W 9840 Diffractometer.

3.2.4 Sequential aqueous extraction of FBA and SSP

The main use of FBA is as a source of S, present as gypsum. The other, traditional source of S, also present as gypsum, is SSP. The SSP used in this study contained 12.0% S. The rate of dissolution of each material in deionised water was measured. Aqueous extracts of these two fertilisers were prepared by shaking 5.08 g of FBA and 2.08 g SSP (both containing 250 mg S) with 20 ml water (S:water = 1:80) for 1 hour at approximately 20°C. The extracts were then centrifuged and the supernatant liquids filtered through a Whatman No. 40 filter paper. The extraction was repeated maintaining a constant ratio of fertiliser:water until the concentration of S in FBA extracts decreased markedly.

After measuring the pH and electrical conductivity (EC) each collected filtrate was acidified with 5 ml concentrated HCl to prevent microbial growth. The concentration of sulphur, calcium, magnesium, potassium and sodium was measured in the acidified filtrate. Sulphur concentration was determined by a bismuth sulphide precipitation method on an auto analyser (CSIRO Division of Forest Research, Method No PS17). The concentration of Ca, Mg, K and Na was determined using atomic absorption/emission spectrophotometry.

3.3 RESULTS AND DISCUSSION

3.3.1 Physical and chemical properties of FBA

NZDC FBA used in this study had a moisture content of 27.1% and was mostly sand size particles (76%, 0.075 - 2 mm; Table 3.2). The $CaCO_3$ equivalents and sulphur content varied with changes in particle size; the finer particles contained less lime and sulphur, suggesting more coal ash in these fractions (Table 3.2) whereas the bigger particles are probably residual limestone grains.

The major elements in FBA were Si, Al, Fe, Ca and S, together with lesser amounts of Na, Mg, B, Sr and K. The concentrations of potentially toxic elements, such as Cd, Cr, Ni, Pb and As were very low in NZDC FBA (Tables 3.1 & 3.3) and are unlikely to cause problems for animal health at normal maintenance rates of fertiliser S and lime application. As an example, even at a very high application rate of 5,000 kg anhydrous FBA per hectare, only 32.5 g As ha^{-1} are added to soil, much less than the threshold level suggested for the heavy metal loading in agricultural soils (200 g ha^{-1} $year^{-1}$, Department of Health 1992). Similar elemental composition and lack of toxicity to animals in feeding

Table 3.2 Particle size distribution of fluidised bed boiler ash and its composition (27.1% moisture content).

Particle size (mm)	Weight (%)	Sulphur[1] (%)	$CaCO_3$ Equivalent (%)
<0.075	5.4	4.5	29.1
0.075 - 0.150	9.7	4.6	33.1
0.150 - 0.250	12.2	4.6	36.5
0.250 - 0.50	20.4	5.0	37.0
0.50 - 1.0	19.9	5.3	36.8
1.0 - 2.0	14.2	5.6	40.0
>2.0	18.2	4.2	35.4

[1] 10% HCl extractable S.

Table 3.3 Main elemental concentration of fluidised bed boiler ash.

Element	Concentration[1]	
	Total	HCl-extractable
	%	
Ca	25.4	25.4
S	6.2	6.2
Fe	3.6	2.2
Al	1.8	1.4
Na	0.7	0.7
Mg	0.6	0.6
K	0.3	0.3
	mg kg^{-1}	
B	1360	1360
Sr	1250	1250
P	875	875
Mn	88	88
Zn	72	65
As	6.5	6.5
Se	< 3	< 3
Pb	< 2	< 2
Cu	< 0.3	< 0.3
Sn	< 0.3	< 0.3
Ni	< 0.2	< 0.2
Co	< 0.2	< 0.2
Cr	< 0.1	< 0.1
Mo	< 0.1	< 0.1
Cd	< 0.1	< 0.1

[1] Dry matter basis.

and grazing trials has been found in studies with American FBA (Cahill et al. 1988; Cochran et al. 1991; Marsh & Grove 1992a; Vona et al. 1992; Whitsel et al. 1988). All the elements in NZDC FBA were fully HCl extractable, excepting aluminium, iron and zinc which were only partially HCl insoluble (Table 3.3). This suggests that most of the elements in FBA are not in insoluble silicate compounds.

Gypsum ($CaSO_4 \cdot 2H_2O$), ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$], portlandite [$Ca(OH)_2$] and quartz ($SiO_2$) were the major diffracting minerals in slaked NZDC FBA (Table 3.4). Both gypsum and portlandite could be removed by sequential water extraction. In comparison, mineralogical analysis of anhydrous FBA in the United States has indicated that calcium oxide, calcium sulphate and quartz were the major minerals (Edwards et al. 1985b; Korcak 1980a; Terman et al. 1978). During slaking, some gypsum can be converted to the water insoluble ettringite that forms a protective coating material (ACI 225 committee 1987; Table 3.4).

An aqueous suspension of FBA is very caustic (pH_{water} = 12.4), due to the presence of basic oxides and hydroxides, e.g. calcium hydroxide. FBAs commonly have high $CaCO_3$ equivalent values (51.8% $CaCO_3$ in NZDC FBA) and are considered as good liming agents in the USA (Edwards et al. 1985a; Terman et al. 1978).

Table 3.4 Effect of water extraction on the main mineralogical composition of fluidised bed boiler ash[1].

Mineral	Before extraction	After extraction
Quartz	Present	Present
Gypsum	Present	Absent
Portlandite	Present	Absent
Ettringite	Present	Present
Calcite	Not major peak	Present

[1] Examined using a X-ray diffractometer.

3.3.2 pH value of the aqueous extracts

The objective of the aqueous extraction experiment was to investigate the time sequence of elemental dissolution from FBA, particularly with respect to the caustic nature of the fertiliser suspension and the release of useful plant available S. The dissolution pattern of FBA was compared with that of a standard S fertiliser, superphosphate (SSP).

The possible existence of Na_2CO_3 and K_2CO_3 may account for the high pH of 9.39 in the first FBA extract, which was much higher than those in subsequent extracts (between 8.37 - 8.47, Fig. 3.1). The pH buffered in the latter range indicates a CaO-CO_2-H_2O system in equilibrium with atmospheric CO_2 gas (0.0003 parts CO_2, Lindsay 1979).

The major alkaline material in anhydrous FBA is calcium oxide (CaO), which hydrates to form $Ca(OH)_2$ (portlandite) during slaking. $Ca(OH)_2$ is readily transformed into $CaCO_3$ (calcite) through absorption of atmospheric CO_2. The CO_2 level at which calcite and portlandite can coexist is calculated as follows (Lindsay 1979):

$$\begin{array}{lr} & pK \\ CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2(g) + H_2O & -9.74 \\ Ca^{2+} + 2H_2O \rightarrow Ca(OH)_2 + 2H^+ & 22.80 \\ \hline CaCO_3 + H_2O \rightarrow Ca(OH)_2 + CO_2(g) & 13.06 \end{array} \qquad \text{(Eqn. 3.6)}$$

Where pK (-logK) is the equilibrium constant expressed in terms of chemical activities. From Equation 3.6,

$$CO_2(g) = 10^{-13.06} \qquad \text{(Eqn. 3.7)}$$

Thus, when $CO_2(g)$ drops to $10^{-13.06}$ atm, both calcite and portlandite can coexist, and only if $CO_2(g)$ drops below this level, does calcite become metastable to portlandite. In this study the reaction of Equation 3.6 would be to form $CaCO_3$ since the CO_2 in the air (about 0.0003 atm) is much more than the equilibrium criterion. Thus it is expected that all portlandite particles would be coated with calcite. Therefore, it was calcite that had a dominating influence on the pH of the FBA extracts. The pH of the extracts remained around 8.40, even after 24 extractions when there was little portlandite left in the residue (Table 3.4).

In contrast to FBA extracts, the first extract of SSP had a pH (pH 3.15), much lower than those of the rest (pH 4.30 - 5.56). This first SSP extract had pH, phosphate and calcium concentrations similar to the stable triple-point solution (TPS) when monocalcium phosphate monohydrate [MCP, $Ca(H_2PO_4)_2{\cdot}H_2O$] dissolves in water (Lindsay 1979). During dissolution, MCP initially reaches a metastable triple-point solution (MTPS) (Lindsay et al. 1959). MTPS is the solution approaching equilibrium with dissolving MCP and precipitating dicalcium phosphate dihydrate (DCPD, $CaHPO_4{\cdot}2H_2O$). The solution composition remained at MTPS for more than 24 hours, then slowly shifted up the MCP isotherm to the TPS that represented final equilibrium with MCP and dicalcium phosphate (DCP, $CaHPO_4$).

The solution resulting from the dissolution of pure MCP is highly acidic since, during the dissolution of MCP, the precipitation of DCPD releases H_3PO_4 according to the reaction:

$$Ca(H_2PO_4)_2 \cdot H_2O + H_2O \rightarrow CaHPO_4 \cdot 2H_2O + H_3PO_4 \qquad \text{(Eqn. 3.8)}$$

The released H_3PO_4 accounts for the low pH of MTPS (pH 1.48). Similarly precipitation of DCP to give TPS reflects even greater release of H_3PO_4 as the pH drops to 1.01 (Lindsay 1979).

Using superphosphate (SSP) instead of pure MCP, Williams (1971) reported that the pH of saturated aqueous extracts of SSP at MTPS (pH 1.60 - 1.92) was higher than in pure MCP solution (pH 1.45). He explained that the higher pH (0.15 - 0.47) was probably due, in part, to the presence of calcium sulphate in SSP, since adding anhydrous calcium sulphate or gypsum to pure MCP increased the pH of the equilibrium solution by 0.15 units (Williams 1971). The initial pH value in this study (Fig. 3.1) was higher than the data reported by Williams (1971) and may be attributed to the higher SSP:water ratio which resulted in more gypsum dissolution.

3.3.3 Sulphate concentration in the aqueous extracts

Gypsum and ettringite were the major sulphate compounds in FBA (Table 3.4). Ettringite is an acid soluble but water insoluble material. Gypsum was, therefore, the main water soluble sulphur containing compound in FBA. FBA might also contain small amounts of Na_2SO_4 and K_2SO_4, that are more soluble than gypsum, because the SO_4^{2-} concentration of the first extract was higher than those in the subsequent extracts (Fig. 3.2). It was also higher than the equilibrium concentration maintained by pure gypsum,

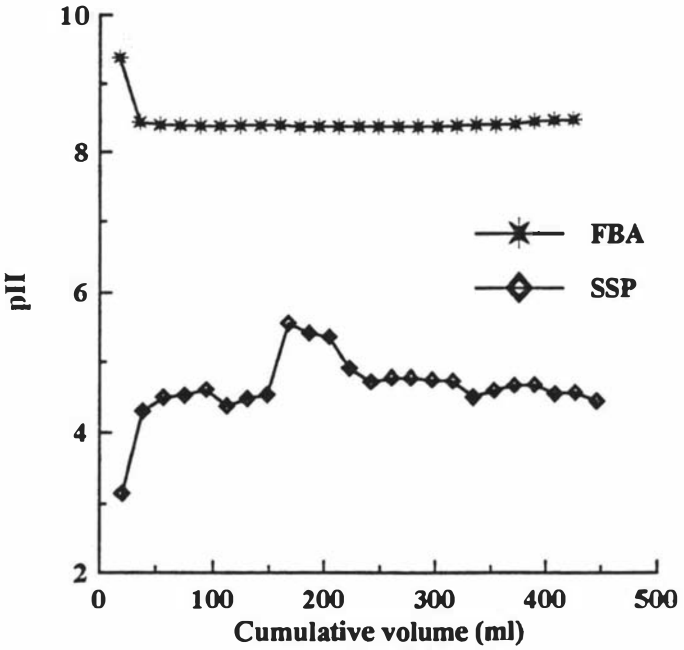


Fig. 3.1 pH change in sequential water extracts of FBA and SSP.

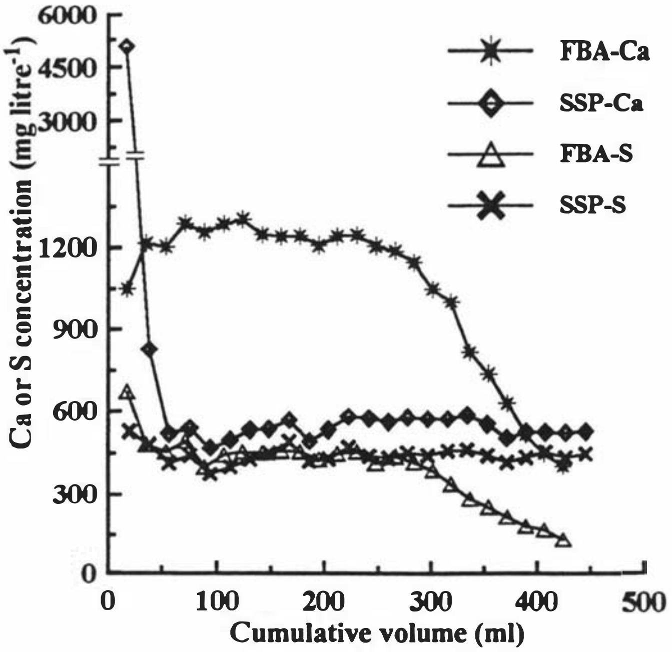


Fig. 3.2 Ca and S concentrations in sequential water extracts of FBA and SSP (The equilibrium concentration of Ca and S maintained by pure gypsum is about 611 and 489 mg litre^{-1}, respectively, Glas et al. 1979).

about 489 mg S litre^{-1} (Glas et al. 1979) . From the second to twelfth extracts, the sulphate concentrations were around 450 mg S litre^{-1} (between 400 - 494 mg S litre^{-1}), a range expected for a saturated solution of gypsum containing minor contaminants (Bolan et al. 1991b).

The S concentration in a pure system containing only water and excess solid gypsum is between 476.8 - 505.6 mg S litre^{-1} (Glas et al. 1979). However, lower values in FBA extracts could result from the high pH and a Ca common-ion effect (Kemper et al. 1975), i.e. the calcium ions dissociated from portlandite may reduce the dissolution of gypsum. When the cumulative extract volume reached 300 ml (17 extractions), the S concentrations in subsequent extracts decreased drastically (Fig. 3.2). It was probable that the gypsum in the residue was coated by some less soluble materials such as calcite and ettringite, two of the main minerals remaining in the residue. These materials could coat and thereby slow down the dissolution rate of the gypsum (Bolan et al. 1991b).

For the SSP extracts, S concentrations were maintained at the same levels (around 450 mg S litre^{-1}) for all the extracts. Unlike FBA, which contained considerable amounts of ettringite (water insoluble), gypsum was the only S source of SSP and in 24 extractions, 74% of the S in SSP was extracted, a greater percentage of total S than that recovered from the FBA water extracts (Fig. 3.3).

3.3.4 Calcium concentration in the aqueous extracts

Both FBA and SSP are rich in calcium, but the Ca^{2+} concentrations in the sequential water extracts were quite different (Fig. 3.2). In FBA, calcium was present in several forms of compounds, from water soluble calcium hydroxide (portlandite) and gypsum, through less soluble calcite to acid soluble ettringite (Table 3.4). Despite alkaline conditions (Fig. 3.1), a substantial amount of Ca^{2+} was dissolved in the FBA extracts. The Ca^{2+} concentrations in the extracts from the first to the seventeenth extract were well above the equilibrium concentration maintained by gypsum (about 611 mg Ca litre^{-1}, Glas et al. 1979) due to the presence of more soluble portlandite in FBA. In the last extract, however, it fell to 404 mg Ca litre^{-1} because little gypsum and portlandite remained in the residue (Table 3.4).

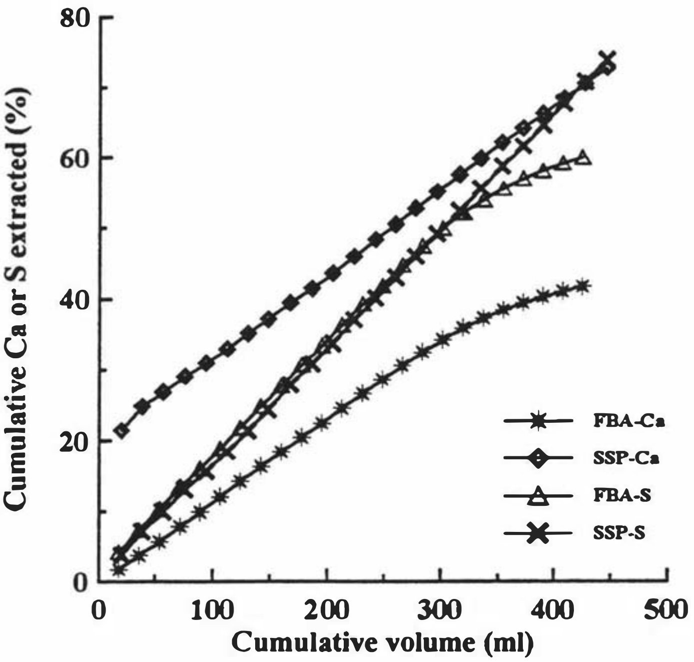


Fig. 3.3 Cumulative Ca and S in FBA and SSP water extracts.

In order to account for the calcium concentration in FBA extracts, the following equilibrium reactions would be expected.

$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$ (Eqn. 3.9)

$Ca(OH)_2 \rightarrow CaOH^+ + OH^-$ (Eqn. 3.10)

$CaOH^+ \rightarrow Ca^{2+} + OH^-$ (Eqn. 3.11)

$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$ (Eqn. 3.12)

$Ca^{2+} + CO_2 + H_2O \rightarrow CaCO_3 + 2H^+$ (Eqn. 3.13)

Dissociation of gypsum, portlandite and calcite in Equations 3.9, 3.11 and 3.12 contributes Ca^{2+} to the solution during extraction. But, because the solubility of gypsum (2.41 g litre^{-1} cold water) and portlandite (1.85 g litre^{-1}) are much higher than that of calcite (0.0143 g litre^{-1}) (CRC 1971), Ca^{2+} in the FBA extracts resulted mainly from the dissolution of gypsum and portlandite. However, the Ca common-ion effect would limit their complete dissolution in the presence of each other. Furthermore, formation of calcite in Equation 3.13 could reduce the Ca^{2+} concentration in the extracts, especially in this alkaline environment with such high Ca^{2+} concentration (Lindsay 1979).

Similar to the sulphate situation, with the exeption of the first two extracts, the Ca^{2+} concentration in SSP extracts was around 500 mg Ca litre^{-1} - accounted for by the gypsum (Fig. 3.2). The first extract was nearly saturated with MCP and DCPD. Being more soluble than gypsum MCP accounted for the extremely high calcium concentration (5029 mg Ca litre^{-1}; Lindsay 1979).

3.3.5 Mg, K and Na concentrations in the aqueous extracts

In addition to calcium and sulphur, some amounts of HCl extractable magnesium, potassium and sodium existed in FBA as well (Table 3.3). Though total K in FBA was small, most of the K was present in soluble form and more than 80% of the K was extracted in the first 3 extractions (Fig. 3.4). Nevertheless, less than 50% of the Na salts

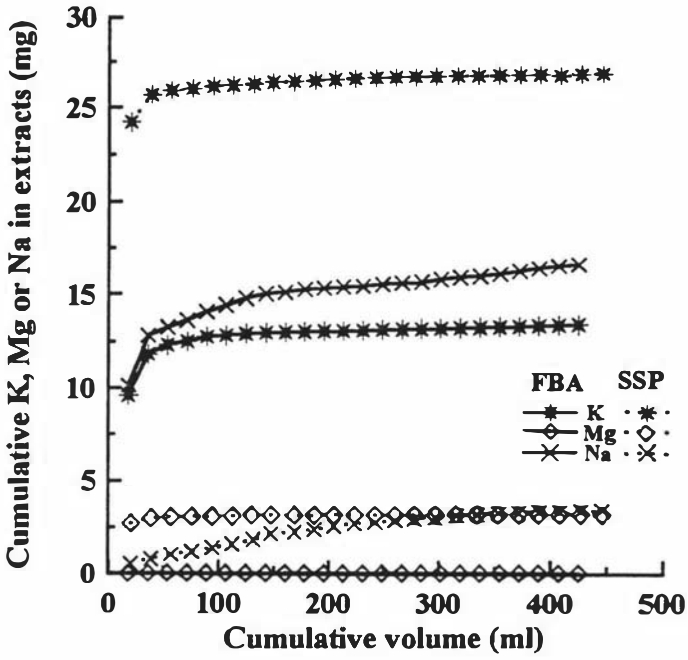


Fig. 3.4 Cumulative K, Mg and Na in sequential water extracts of FBA and SSP.

in FBA were water extractable, and most of them were extracted by first several extractions (Fig. 3.4). The Mg concentration in FBA extracts was so low that there was negligible Mg dissolving after 24 extractions, despite its relatively high total content (Table 3.3), indicating that the small amount of Mg in FBA is in a water insoluble compound (Fig. 3.4).

3.4 CONCLUSIONS

As a low cost technology to control SO_2 emission during the burning of high S fossil fuel, limestone chip fluidised-bed combustion may become prominent, consequently, large quantities of waste FBA could be expected in the future. FBA has potential to be used as a liming material and a S fertiliser, due to high levels of CaO or $Ca(OH)_2$, residual calcite and gypsum.

Approximately 50% of the sulphur in the slaked FBA material was in a water soluble, fast release form, with the remainder showing slow solubility in water. The soluble fraction had release characteristics similar to the gypsum in single superphosphate. This slow release S in FBA has potential to reduce the leaching of sulphate that is considered to be a major problem in some New Zealand soils.

In addition, trace amounts of K and Mg are present in FBA, with K being almost totally water soluble whereas all the Mg is water insoluble. On initial dissolution, FBA forms a very caustic solution with water, therefore care should be taken to avoid skin contact with FBA in wet conditions. Similarly ingestion by grazing animals should be avoided.

Chapter 4

Measurement of water repellency in a peat soil and its amelioration with fluidised bed boiler ash

4.1 INTRODUCTION

Once dried, peat soils are often exceedingly difficult to rewet despite their relatively high water holding capacities (Hupkens van der Elst 1958). Therefore, pasture growth in autumn following a dry summer is generally much slower for peat than mineral soils. Slow recovery of plant growth following a dry period is a major problem for farmers on peat soil, in the Waikato region, New Zealand (Hupkens van der Elst 1971).

Fluidised bed boiler ash (FBA) is a source of both electrolytes and alkalinity (refer Chapter 3). Surface-applied FBA have been successfully utilised to increase water infiltration and control erosion of high-clay content soils (Reichert et al. 1994; Reichert & Norton 1994; 1996). Application of FBA to acidic organic soils may affect repellency via removal or reconfiguration of some fractions of the hydrophobic and hydrophilic compounds adhering to the surface of the soil matrix. These organic compounds may be changed by chemical reactions and/or as a result of increased biological activity associated with an increase in pH (Roper 1994). Therefore, it is hypothesised that the addition of liming materials to a water repellent, acidic peat will decrease repellency. The availability of FBA, in close proximity to Waikato peat soils provided further impetus to this investigation of the effect of liming reagents on water repellency in peat soil.

The literature suggests that the majority of soils affected by water repellency are coarse-textured (Savage 1975). Numerous studies have been conducted to measure the magnitude of repellency in sandy soils, to elucidate the process or mechanisms by which repellency develops in these soils and to find ways to ameliorate this repellency (Schreiner & Shorey 1910; Jamison 1945; Wallis & Horne 1992). A range of techniques have been used to measure repellency including: capillary rise (Letey et al. 1962), infiltration (Sawada et al. 1989), intrinsic diffusivity and sorptivity (Philip 1957), repellency index (RI) (Tillman et al. 1989), water drop penetration time (WDPT) (Letey 1969), ninety degree surface tension (NDST) (Watson & Letey 1970), molarity of an ethanol droplet (MED) (King 1981) and thermal analysis (Hammond & Yuan 1969; Lishtvan & Zuyev 1983). For measurements of hydrophobicity in more repellent soils, the MED test has been widely adopted by researchers because of its simplicity. However, it has been found that in some situations the MED value is affected by the field moisture content at sampling and the drying temperature prior to MED evaluation (Carter et al. 1994; Franco et al. 1995).

Numerous strategies for ameliorating water repellency in sandy soils have been developed, including claying (Blackwell et al. 1994b; Hendrichx et al. 1988; McGhie 1987; Ward & Oades 1994), furrow sorrowing (Blackwell et al. 1994a), application of wetting agents (Wallis et al. 1990; Watson et al. 1969), cultivation during rain, deep cultivation/subsoiling, bioremediation (Mechelsin & Franco 1994) and irrigation (DeBano 1971; Wallis et al. 1990).

In comparison with sandy soils, only a few attempts to measure or ameliorate water repellency of organic soils have been reported. It has been suggested that water table management or irrigation could be used to prevent excessive drying of the surface peat layers (Hupkens van der Elst 1958). Van't Woudt (1969) claims that repellent surface peat layers must be removed so as to expose a moist layer. However, he pointed out that such management was unsustainable since the peat surface is gradually lowered and productivity decreased. Lishtvan and Zuyev (1983) reported on the use of wetting agents to improve peat wettability. While wetting agents have been demonstrated to be effective in ameliorating repellency in the short term (Wallis et al 1990), their regular use in broad scale agriculture is prohibitively expensive. Therefore, practical and low cost techniques are required to ameliorate water repellency in organic soils.

The aims of this study were to investigate the severity of repellency of a New Zealand peat, seasonal changes in the MED values of this soil, the effect of drying temperature on the MED values of this soil, and the feasibility of using FBA as a ameliorant of water repellency in a peat soil.

4.2 MATERIALS AND METHODS

4.2.1 Field trial and soil sample collection

The soil used in this investigation was a medium developed, deep, acid peat and is classified as oligotrophic high moor (Davoren 1978), or 'Hemic Sphagnofibrist' (USDA 1994). The surface layer (0 - 150 mm) is composed of mineralised peat, overlaying a layer (150 - 300 mm) which is predominantly partly-decomposed wood. The soil has a very low permeability (Davoren 1978). Some measured values for selected properties of the soil are given in Table 4.1. Soil sampling and a field trial were conducted on a dairy farm on the Moanatuatua Swamp, 15.5 km south-east of Hamilton, New Zealand. Mean annual rainfall is 1252 mm which is evenly distributed. Mean temperatures are 18.0°C and 8.0°C for January and July, respectively (Davoren 1978).

In March, July and September 1992 and January 1993, samples of Moanatuatua peat (0 - 75 mm, 75 - 150 mm and 150 - 300 mm in depth) were collected to study the effect of drying temperature on the MED value, and to monitor the seasonal variation of water repellency as measured by the MED test.

A field trial was carried out between July 1992 and March 1993. The trial was a complete factorial experimental design with all treatments replicated six times in a RCB layout. In addition to a control (no amendment), treatments included; FBA at three different rates (1000, 6616 and 26462 kg FBA ha^{-1}) and three rates of lime addition (401, 2656 and 10625 kg lime ha^{-1}). The low, medium and high rates of FBA had the same $CaCO_3$ equivalence as the corresponding rates of lime, respectively. The plots measured 3 m × 4 m.

Table 4.1 Selected properties of Moanatuatua peat soil.

Depth (mm)	pH	Organic C (%)	CEC (cmol$_{(+)}$ kg^{-1})	Bulk density (g cm^{-3})	Field moisture content[2] (%)
0 - 75	5.1	44.0	97	0.33	230
75 - 150	4.4	n.d[1]	n.d.	0.27	290
150 - 300	3.9	n.d.	n.d.	0.12	779

[1] Not determined.

[2] Sampled in September 1992.

All the amendments were broadcast on the pasture on July 14, 1992. Other details of the trial design are described in Chapter 5 (refer Sections 5.2.4 & 5.2.5).

Slaked FBA was employed in this experiment as an ameliorant for soil water repellency. The sample of slaked FBA was 27.1% moisture and had a pH_{water} of 12.4 and a $CaCO_3$ equivalent of 37.8%. Detailed chemical and physical properties of the FBA are described in Chapter 3 (refer Section 3.3).

In September 1992, all the plots were sampled from 0 - 75 mm and 75 - 150 mm depth intervals. In January 1993, samples with intervals of 0 - 25 mm, 25 - 50 mm and 50 - 75 mm were taken from all plots. In October 1992, only three treatments (control, high FBA and high lime treatments) were sampled at depths of 0 - 25 mm, 25 - 50 mm and 50 - 75 mm. At each sampling, six cores per plot were taken with a 25 mm diameter soil corer and bulked. The MED values (refer Section 4.2.4) of these samples were measured following sieving (2 mm mesh) and drying; in the air, in an oven at 40^0C for 7 days, and at 105^0C for 24 hours (refer Section 4.2.4). The repellency index (RI) (refer Section 4.2.5) was measured for the control, medium FBA and high FBA treatments in March 1993, eight months after FBA application.

4.2.2 Laboratory studies

To further examine the influence of rewetting and liming materials on the peat soil water repellency, an incubation experiment was conducted in the laboratory. Moanatuatua peat soil (20 -75 mm depth) was taken for this study in January 1993 from an area adjacent to the field trial site. This study comprised three replicates of three treatments including; control (no amendment), FBA (26.5 g kg^{-1} of soil) and lime (10 g kg^{-1} of soil). Lime and FBA mixed with soil in these proportions gives addition rates which are most similar to the 'medium' of the 3 rates applied in the field trial. Air dried soil (100 g) was placed into a plastic bag (150 mm × 200 mm). The soil was mixed with FBA or lime and then wetted with 112 ml of distilled water. Incubation was carried out at a temperature of 20. The bag tops were left open to allow air entry and the moisture content was adjusted once a week. Sub-samples of soil were removed from all bags on the first day, after four weeks and at completion of the 26 week incubation period. pH (soil:water = 1:2.5) and the MED values of these sub-samples were measured.

In another laboratory experiment, the RI of cores (internal diameter 75 mm, 50 mm long) of air dried repacked Moanatuatua peat were measured and compared with the RI of cores of repacked air dried Moanatuatua peat to which FBA had been surface applied at a rate of 2.93 g core^{-1} (equivalent to 6616 kg ha^{-1}, i.e. the medium rate used in the field trial). There were 5 replicates of each treatment.

4.2.3 Extraction experiments

An FBA-water solution was prepared by dissolving 15 g of FBA in 300 ml of water. This extractant (150 ml) was then mixed with 100 g of peat soil. The mixture was left to stand for 15 hours with only occasional shaking by hand. The extracted solution was poured off and the extraction was repeated. The compounds removed in the 300 ml of extractant were weighed. MED measurements were made on the extracted peat soil after it had been air dried.

Peat soil (40 g) was extracted in a Soxhlet apparatus using an iso-propanol:ammonia mixture (7:3) in a manner similar to that described by Ma'shum et al. (1988). The materials extracted were characterised by elution from a florisil column according to a modified version of the technique described by Ambeles et al. (1994).

4.2.4 The Molarity of Ethanol Droplet (MED) test

The Molarity of Ethanol Droplet (MED) test, as first proposed by Watson & Letey (1970) and developed by King (1981), measures the molarity of an aqueous ethanol droplet required for infiltration into an air dried soil sample within 10 seconds. The most important advantages of the MED test are the relative ease and speed with which measurements can be made, especially for severely repellent soils (Wallis et al. 1991). King (1981) provided the following guideline for interpretation of MED values: MED = 0, non-repellent; MED < 1.0, low repellency; MED 1.0 - 2.2, moderate repellency; MED > 2.2, severe repellency. Recently, concern has been expressed at the tendency of the MED test performed on air dried samples to underestimate the repellent nature of some soils, particularly soil sampled during moist or wet conditions (Carter et al. 1994). Accordingly, numerous researchers now measure the MED values of soil samples after drying at elevated temperatures. In this study, the MED tests of the peat soil were determined on air dried samples, as described above, and on samples which have been heated at 40°C for seven days, and on samples which have been heated at 105°C for 48 hours. Soil samples which had been heated were allowed to cool to room temperature before the MED test was performed.

4.2.5 Repellency index measurements (RI).

The RI was measured *in situ* on plots at the field trial using a modified version of the procedure described by Wallis et al. (1991). Sites for measurements on each plot (treatment) were selected randomly. Any vegetation on the sites was trimmed to < 5 mm height with scissors. Pairs of 75 mm (internal diameter) × 50 mm (height) PVC pipes were placed on the site and driven into the soil, until almost flush with the surface, using a block of wood and hammer. A measured quantity of non-repellent sand (Muffle-furnaced Himatangi sand) was spread on the soil surface within each pipe, to provide a contact medium of approximately 5 mm deep. A disk permeameter (Wallis & Horne 1992) was used to measure the infiltration rate of water into one core of each pair, and of 95% ethanol into the other. The disk permeameter was clamped to a laboratory retort stand to prevent it from falling.

In order to calculate RI, cumulative infiltration (I) was plotted against the square root of time ($t^{1/2}$), and sorptivity (S) of water and ethanol measured as the slope of the curve over short time when I was proportional to $t^{1/2}$. The intrinsic sorptivity repellency index (RI) was calculated using the equation given by Tillman et al. (1989):

$$RI = 1.95\,(S_E/S_W),$$

where S_E and S_W are determinations of sorptivity of ethanol and water, respectively. Water repellent soils will have RI values greater than 1.95 (Tillman et al. 1989). A similar procedure was used to determine the RI of repacked cores in the laboratory.

Analysis of variance of measurements of water repellency was carried out using the SAS software package.

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of heat on MED value

For almost all soil samples, the MED value measured after heating the sample at 105°C for 48 hours was significantly ($P < 0.05$) greater than the values measured for either air dried soil or samples heated at 40°C for 7 days (Table 4.2 & Fig. 4.1). There was no significant difference between MED values measured for air dried samples and those measured on soil samples heated at 40°C for 7 days (Table 4.2).

Nakaya et al. (1977) found a Japanese peat soil to be most repellent after heating at 150°C, but it became non-repellent when this peat was heated to temperatures above 250°C. They suggested that the samples heated to 150°C or less were dominant in organic matter while those heated to 250°C or more were dominant in inorganic matter. Franco et al. (1995) suggested that particulate organic matter in Australian sandy soils acted as a reservoir of hydrophobic materials which diffused onto the surfaces of sand grains during heating and that heating to 105°C obtained maximum diffusion of these materials. Heating peat soil may also result in diffusion of hydrophobic materials (e.g. long chain fatty acids) to the surface of soil particles (Franco et al. 1995). Heating may produce some hydrophobic materials on the particle surfaces as well.

Table 4.2 Effect of heating on the MED values of soils sampled from field trial site.

Sample Date	Soil Depth (mm)	Treatment	Soil drying prior to MED test		
			Air dry	40°C for 7 days	105°C for 48 hours
9/92	0 - 75	Control	1.1	1.4	3.7
9/92	0 - 75	high FBA	0.9	0.9	3.5
9/92	0 - 75	high Lime	1.0	1.3	3.5
		$LSD_{0.05}$	0.5	0.8	0.5
10/92	0 - 25	Control	1.7	1.9	3.7
10/92	0 - 25	high FBA	1.2	1.4	3.1
10/92	0 - 25	high Lime	1.4	1.7	3.4
		$LSD_{0.05}$	0.4	0.6	0.4
1/93	0 - 25	Control	2.9	3.0	3.7
1/93	0 - 25	high FBA	2.2	2.3	3.2
1/93	0 - 25	high Lime	2.7	2.9	3.6
		$LSD_{0.05}$	0.3	1.1	0.4

4.3.2 Seasonal variation of peat soil water repellency

Seasonal climate patterns have a major influence on the moisture content of the peat soil and consequently on the expression of peat soil water repellency as measured by the MED test on air dried soil. Other workers have noted the influence of soil water content at the time of sampling on the MED value measured for air dried samples. Carter et al. 1994 reported that the sandy soils sampled from 'wet patches' had a lower MED value than those from 'drier patches' even if sampled at the same time. In this study, the MED value measured for air dried peat soil from the surface, i.e. top 150 mm layer, and especially the surface 75 mm, varied greatly depending on the time of sampling (Fig. 4.1 & Table 4.2). In the wet winter season, when the surface soil was sampled at or near saturation, the MED value of the air dry surface soil (MED 0.8) was significantly ($P < 0.05$) smaller than the MED values of air dried soil sampled in summer (MED 2.5) and autumn (MED 1.9). MED values measured for air dried surface soil sampled in spring (MED 1.0) were similar to the winter values and significantly smaller than corresponding values for summer and autumn sampling. In summer, the topsoil was very dry and the water repellency increased markedly (MED of air dried sample 2.5). Occasional rainfall is unable to infiltrate into the repellent soil during the dry season (Wallis & Horne 1992). After summer, autumn rains begin to rewet the surface soil and this is reflected in a lower ($P < 0.05$) MED value (1.9) for the air dried sample of soil from the 0 -75 mm depth removed in autumn.

Similar trends were observed for MED values measured following heating at 105^0C (Fig. 4.1), i.e. MED values measured for heated soil sampled in summer and autumn were significantly greater than values measured for samples removed in winter and spring. However, the range of MED values measured for the heated samples (e.g. 3.9 to 4.8 for the 0 - 75 mm depth) was much smaller than the range measured for air dried samples (e.g. 0.8 - 2.5 for the 0-75 mm depth). The MED test performed on soil samples following heating at 105^0C is much less sensitive to the season of sampling than is the MED test performed on air dried soil.

MED values measured on samples which had been heated to 105^0C were invariably greater than the corresponding MED value measured for air dried samples (Fig. 4.1). MED measurements made on air dried samples of peat soil collected in winter may underestimate

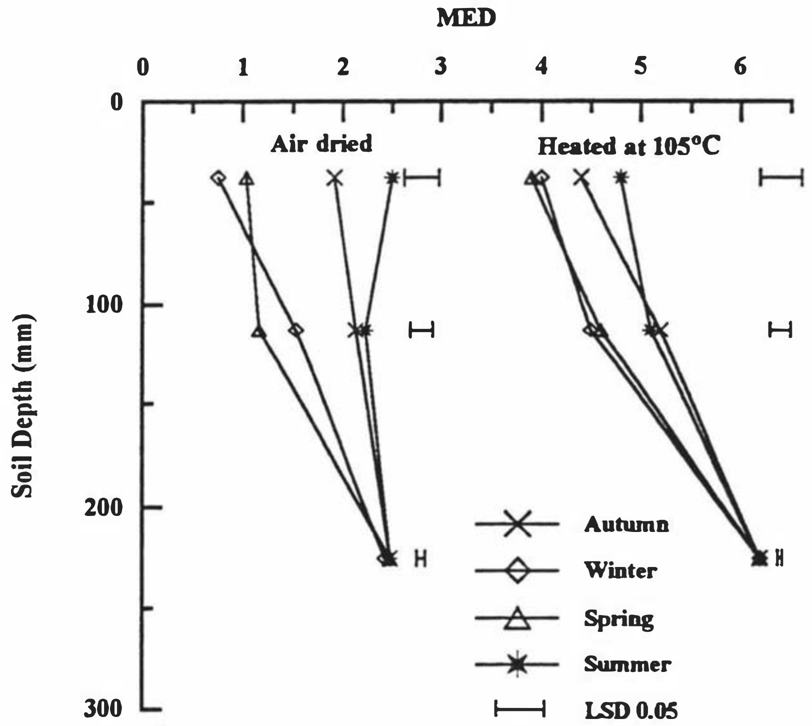


Fig. 4.1 Seasonal variation of water repellency (MED test) of Moanatuatua peat soil.

the degree of repellency that may develop in dry summer months. In this situation, MED measurements made following heating to 105^{0}C may be a more reliable indicator of a soil's propensity or potential to develop repellency in the driest season. However, there is the concern that heating to 105^{0}C may induce repellency and that MED measurements made after heating at 105^{0}C may be criticised for overestimating the severity of repellency of a soil. For soil samples such as those of Moanatuatua peat, there is probably merit to making MED measures on both air dried samples and samples heated to 105^{0}C (or some other elevated temperature, e.g. 70^{0}C): the MED value of the air dried sample might be said to be an indicator of repellency 'expression' at the time of sampling while the MED value measured following heating may be an index of the risk of severe repellency developing in dry conditions.

At a depth of 150 mm a constant MED value (2.4) was obtained for air dried soil regardless of the season in which sampling occurred. The consistent, severely repellent MED value measured for this depth suggests that this zone is the most repellent part of the profile which is consistent with the very high MED value (6.2) measured for soil from this depth after heating at 105°C. This may be due to the relatively small changes in moisture content of the subsurface soil between seasons. Furthermore, unlike the top layer which contains mineral material, the subsurface layer is predominantly semi-decomposed wood material (Davoren 1978) with little microbial activity due to a highly acidic ($pH_{water} < 4$) and anoxic environment.

4.3.3 Effect of FBA on amelioration of peat soil water repellency

4.3.3.1 MED measurement - incubation study

Incubation with only water for a period as short as one day is sufficient for initially repellent peat soil to become wettable (MED = 0) as measured by the MED tests made on air dried soil samples or samples heated to 40^{0}C (Table 4.3). Likewise, incubation of moist peat soil for four and 26 weeks resulted in wettable soil (MED = 0) as measured by the MED tests following air drying and heating at 40°C. That MED values of zero were not measured for soil sampled from the trial site in the wet part of the year may be a reflection of the relative

Table 4.3 Effect of incubation on peat soil MED value.

Incubation time	Treatment	pH_{water}	Air dry	40°C for 7 days	105°C for 48 hours
One day	Control	5.05	0	0	4.1
One day	FBA	5.29	0	0	4.0
One day	Lime	5.36	0	0	4.1
	$LSD_{0.05}$	0.04			0.3
Four weeks	Control	4.76	0	0	4.1
Four weeks	FBA	5.23	0	0	4.0
Four weeks	Lime	5.16	0	0	4.1
	$LSD_{0.05}$	0.03			0.3
Six months	Control	4.47	0	0	4.1
Six months	FBA	5.13	0	0	3.9
Six months	Lime	5.01	0	0	4.0
	$LSD_{0.05}$	0.03			0.3

efficiencies with which chemical reactions and microbial activity occur in incubation studies compared with the field situation. This notwithstanding, keeping the surface of a peat soil moist by irrigation may be a strategy to ameliorate repellency.

In contrast, soil incubated with 'water only' was found to be severely repellent (MED = 4.1) if samples were heated at 105°C (Table 4.3). This may suggest that upon prolonged drying of the incubated soil, repellency is likely to re-develop. For any particular MED test (e.g. on air dried samples), there was no significant difference between the 'water only', FBA or lime treatments for any of the three incubation periods (Table 4.3). Despite the significant increase in pH values ($P < 0.05$) for the FBA and lime treatments over the control (water only), neither of the amendments lowered the MED value measured after heating at 105°C.

4.3.3.2 MED measurement - field trial

Compared with the control, the high rate of FBA applied to the peat significantly ($P < 0.05$) decreased the water repellency of surface soil (0 - 25 mm) in the field trial as measured by the MED test on air dried soil (10/92 & 1/93, Table 4.4) and samples heated at 105°C (10/92 & 1/93, Table 4.2). No significant differences were measured between the other treatments. Soil amended with the high rate of FBA had consistently lower MED values than the control treatment, as measured on both air dried soil samples and those heated at 105°C. This suggests that FBA had a profound effect on the repellent characteristics of the peat, that is, reducing both repellency expression and its ability or potential to develop hydrophobicity. FBA had no effect on MED values of soils sampled from 25 -50 or 50 - 75 mm depths.

Agricultural lime had no significant effect on peat soil repellency. Similar results for lime addition have been reported on sandy soils (Blackwell et al. 1994b).

It is interesting to speculate on the reasons why the addition of FBA to peat soil significantly reduced MED values in the field trial but not in the incubation experiment (Section 4.3.3.1). As discussed above, the fact that soil samples were incubated moist had the overriding effect on MED measurements of air dried samples. In addition, the quantity of FBA added to the bags in the incubation experiment corresponded more closely to the medium rate used in the field and therefore a lack of response to FBA addition in the incubation experiment may not be surprising.

Table 4.4 Effect of FBA and lime on MED values of the peat soil from field trial site as measured on air dried soil.

Treatment	0 - 75 mm	0 - 25 mm		25 - 50 mm		50 - 75 mm	
	9/92	10/92	1/93	10/92	1/93	10/92	1/93
Control	1.1	1.7	2.9	0.7	2.6	0.7	2.2
low FBA	1.0	n.d[1]	2.8	n.d.	2.6	n.d.	2.2
medium FBA	1.1	n.d.	2.8	n.d.	2.7	n.d.	2.2
high FBA	0.9	1.2	2.2	0.6	2.5	0.7	2.1
low Lime	1.0	n.d.	3.0	n.d.	2.7	n.d.	2.2
medium Lime	0.9	n.d.	2.8	n.d.	2.6	n.d.	2.2
high Lime	1.0	1.4	2.7	0.9	2.6	0.9	2.0
$LSD_{(0.05)}$	0.5	0.4	0.3	0.4	0.4	0.4	0.3

[1] Not determined.

4.3.3.3 Water infiltration and Repellency index (RI) measurement

Compared with the control plots, FBA applied at the high rate increased ($P < 0.05$) water infiltration into the peat soil at the field trial site (Fig. 4.2). The mean water infiltration rate of plots which received FBA at the medium rate was not significantly greater than the mean rate measured for control plots. In the laboratory, the infiltration rate into repacked cores top-dressed with FBA (at a rate similar to the medium rate used in the field trial) was significantly greater ($P < 0.05$) than the rate of water entry into the control cores. The mean infiltration rate of the FBA treatment in the first minute reached 84 mm hr^{-1}, compared with 5 mm hr^{-1} for the control treatment.

Addition of the high rate of FBA at the field trial site and to the repacked soil cores reduced water repellency, as measured by the RI technique. The mean RI of the repacked control cores was 236 while that of the FBA amended cores was 79. At the field trial site, the RI of the control, medium FBA and high FBA treatments were 22, 14 and 8, respectively. The high FBA treatment was significantly different from the control plots ($P < 0.05$), but there was no significant difference between the medium FBA rate and the control plots.

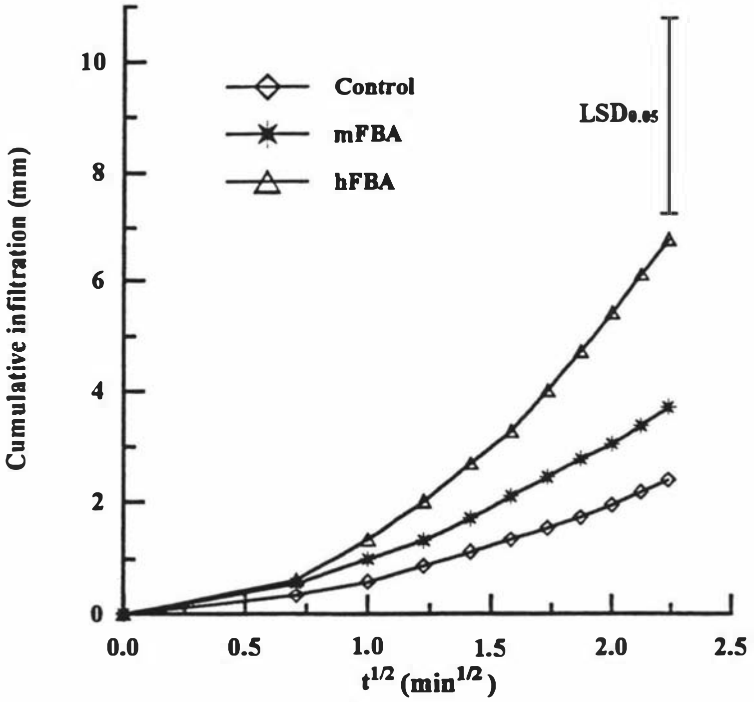


Fig. 4.2 Effect of FBA on water infiltration into soil measured using a disk permeameter at field trial site.

4.3.3.4 Extraction of peat soil using Soxhlet apparatus and an FBA solution

Chemical analysis of the compounds extracted by the Soxhlet apparatus identified fatty acids as the fraction most responsible for the repellent character of the peat soil. Other workers have also found fatty acids to be the cause of hydrophobicity (Franco et al. 1995; Ma'shum et al. 1988).

Fifteen hours after mixing with the peat soil, the FBA-water solution (pH 12.4) had extracted 3.4 g of material from 100 g of soil. After air drying, the MED test indicated that the FBA solution had reduced the MED value from 2.9 to 1.8. Presumably, the high alkalinity of the FBA solution (refer Chapter 3) insured some fatty acids were extracted. Siddaramappa et al. (1994) suggested that caustic $Ca(OH)_2$ in FBA could chemically degrade some types of soil organic matter.

4.3.3.5 Possible mechanisms of amelioration of water repellency by FBA

Horne & McIntosh (1994) proposed that repellent soil particles are coated by alternating 'layers' of hydrophobic and non-repellent material. If the compounds at the surface of the soil particles are hydrophobic then the soil has a high MED; if the outer layer is composed of polar material then the soil is non-repellent. They found that repellency could be removed using 'gentle' extraction techniques (e.g. mixing and shaking by hand) but the extractant must contain a base, such as $NH_3.H_2O$. As FBA is a much more caustic material than either limestone or $NH_3.H_2O$, the high rate of FBA may have removed a pool of labile hydrophobic materials that formed the outer coat of the soil particles, leaving the non-repellent compounds as the 'new' surface. Alternatively, the hydrophobic fatty acids could have been transformed into hydrophilic materials, the inorganic salts of fatty acids.

As FBA is a source of electrolytes as well as alkalinity, another possible mechanism for the amelioration of peat hydrophobicity by FBA is the increase in infiltration rate caused by the presence of high concentrations of dissolved salts (refer Chapter 3). Ghildyal and Tripathi (1987) reported that moderate application of ammonium sulphate has been found to increase the infiltration rate more than urea which forms a neutral organic molecule when it is dissolved in water. This 'salt effect' of FBA treatment may have been a more important factor in the measurement of water infiltration rate and RI, particularly the experiment involving the application of FBA to repacked cores.

4.4 SUMMARY AND CONCLUSIONS

Severe water repellency is a condition which develops in Moanatuatua peatland in dry summer and autumn periods and repellency results in reduced and uneven infiltration of water into the soil.

MED values of air dried soil samples are a measure of the expression of repellency of peat soil at the time of sampling. The MED test made on peat soil samples heated to 105°C may over-estimate the severity of water repellency in the field. However, these values provide an index of the potential repellency or the risk that severe repellency will develop upon drying of the soil. This will be an important consideration for samples collected during a wet period (e.g. winter) or for a prognosis of the likely long-term effect of a treatment imposed to ameliorate repellency (e.g. addition of FBA).

Simply wetting the peat soil reduced repellency as measured by the MED test on air dried soil samples. However, the large MED values measured for incubated samples heated at 105^{0}C and common-place experience suggest that this solution is short-term and that repellency will re-develop once the soil dries.

Higher rates of surface dressed FBA reduced the water repellency of surface peat soil and increased the rate of water infiltration. The decrease in MED values measured for FBA treated soil following air drying, and heating at 105°C suggests that FBA affected a significant change in the repellent character of the peat. Unfortunately, although FBA may reduce soil water repellency, this improvement will only be gradual even at very high application rates. At best, the high rate of FBA applied in the field trial reduced repellency by approximately 0.7 of an MED unit. Therefore, FBA will be of limited effectiveness as an amendment for water repellency in peat soils.

It would appear that FBA modifies the hydrophobic nature of the peat soil by removing fatty acids. This effect may be attributed to the high alkalinity of applied FBA.

Chapter 5

Effect of fluidised bed boiler ash on peat soil acidity and pasture growth

5.1 INTRODUCTION

There are ten large peat swamps in the Waikato region of New Zealand and peatland covers about 5% of the land area there (Anonymous 1982). Undeveloped New Zealand deep peats are very acidic ($pH_{water} < 4.5$) and in the oligotrophic phase (Steering Committee on Peatlands Policy Management 1982). Despite high acidity and low nutrient availability, most of the Waikato peatlands are being developed for dairy pasture. Unlike acidic mineral soils in which aluminium (Al) toxicity is the most important growth-limiting factor for plants (Foy 1974), Al may not impose much negative effect on plant root growth in peat soil because peat lacks Al-containing minerals and the high organic matter content helps to alleviate Al toxicity problems (Hargrove & Thomas 1981; Schnitzer & Rautham 1981). H^+ toxicity and Ca deficiency may be the main causes of root growth reduction in peat soil. However, lime applied to the surface of peat soil stays where it is put. Base (OH^- and HCO_3^-) generated by the lime is extremely slow to move downward (Feyter et al. 1986). This is because the pH buffer power and CEC of the organic soil are extremely high and H^+ consumed results in a net increase in negative surface charge. The increased negative charge increases CEC and the Ca^{2+} distribution coefficient in favour of surface exchangeable Ca^{2+} thus restricting the concentration of Ca^{2+} capable of movement in percolating soil solution.

The restricted rooting zone that results from excessive H^+ or insufficient Ca^{2+} in peat soil becomes particularly acute during dry periods because the moisture in the subsoil is beyond the reach of roots (Hupkens van der Elst 1980). The shallow rooted ryegrass and white clover may wilt, die or be seriously weakened requiring early pasture renewal. To alleviate this problem, lime must be mechanically incorporated as deep as possible, using a rotary hoe or a chisel plough or both implements (Feyter et al. 1986). The depth of soil affected by liming constantly decreases because of the oxidation and shrinkage of the aerobic top organic layer of peat soil. Deep cultivation and liming, therefore, must be repeated periodically (Feyter et al. 1986), which increases the cost of pasture production greatly. An alternative strategy , based on the hypothesis that H^+ toxicity may be reduced by the presence of Ca^{2+} (Foy 1992), is to use soil amendments which can promote Ca^{2+} movement down the profile, e.g. gypsum, to overcome H^+ toxicity in subsurface layers of peat soils.

In addition to soil acidity, nutrient deficiency is another major problem in peat soil (Hupkens van der Elst 1958; 1971). Among the nutrients which are deficient in peat soil, sulphur (S) deficiency is one of the most difficult to overcome. This is because sulphate is readily leached (Hupkens van der Elst 1958) from peat soils that lack clay minerals containing Fe and Al hydrous oxides and other variably charged minerals which are responsible for sulphate sorption (Parfitt 1978). Therefore, slow-release forms of S fertiliser are likely to be beneficial for pasture production on peat soil.

The slaked fluidised bed boiler ash (FBA), as described in Chapter 3, mainly contains calcium hydroxide, gypsum and low solubility ettringite which should make it highly suited to ameliorate the problems of deep acid peat soil associated with subsoil Ca deficiency, H^+ toxicity and SO_4^{2-} leaching. A number of studies have been conducted in the United States to examine the potential of using FBA as a liming material and plant nutrient source on mineral soils. The studies have shown that FBA is useful for both purposes (Korcak 1984; Stehouwer et al. 1995a; b; Stout et al. 1979, 1988; Terman et al. 1978). However, there is no published work on the amelioration of acidity in organic soils by application of FBA, nor any reports about using slaked FBA as nutrient source in pasture production.

The objective of this study was to evaluate the agronomic effectiveness of surface applied FBA as a liming material and fertiliser on pasture growth under field conditions in undisturbed acid peat soil. The effect of surface applied FBA and lime on peat soil solute movement in repacked soil columns will be reported in Chapter 6.

5.2 MATERIALS AND METHODS

5.2.1 Field trial site and soil description

The field trial site was located on a dairy farm on the Moanatuatua Swamp in the Waikato region, New Zealand. The site has been used for pasture production for at least three decades. The soil and its physical properties have been described in Section 4.2.1. The field trial was conducted between July 1992 and March 1993. During the experimental period the rainfall in that region was 845 mm and 2/3 of this rainfall fell between July and October 1992 (NIWA 1992, 1993). The pasture predominantly consisted of perennial ryegrass and white clover. The chemical properties of the peat soil (0 - 75 mm) are shown in Table 5.1. Despite continuous use of lime, the soil is still highly acidic, especially the subsurface soil (Table 5.2).

5.2.2 Fluidised bed boiler ash (FBA)

The detailed chemical and mineralogical properties of the slaked FBA used in this experiment have been described in Chapter 3. In summary, the FBA is an alkaline material (pH_{water}= 12.4, 37.8% $CaCO_3$ equivalence on a wet weight basis) and commonly

Table 5.1 Selected properties of Moanatuatua peat topsoil (0-75 mm).

Organic C (%)	pH_{water}	Olsen-P ($\mu g\ g^{-1}$)	SO_4-S^1 ($\mu g\ g^{-1}$)	Exchangeable Cations (cmol $_{(+)}$ kg^{-1}) K	Ca	Mg	Na	CEC^2
44.0	5.08	29	21	0.68	57.4	3.64	0.10	106

[1] 0.01 M $Ca(H_2PO_4)_2$ extractable sulphate.

[2] Cation exchangeable capacity, determined by the ammonium acetate method.

Table 5.2 The soil pH in water of samples taken from different depths in the peat profile.

Soil depth (mm)	0 - 75	20 - 75	75 - 150	150 - 300	300 - 450	450 - 600
pH_{water}	5.08	4.85	4.38	3.90	3.79	3.86

contains 27% moisture. This sample had 27.1% moisture, 4.9% S, 19.3% Ca and 0.99 g kg^{-1} B on a wet weight basis. Approximately 50% of the sulphur in the slaked FBA is soluble gypsum ($CaSO_4 \cdot 2H_2O$) with the remainder being low solubility ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$). For other elemental analysis refer Table 3.3 in Chapter 3. The agricultural lime applied in the trial contains 94.1% $CaCO_3$ analysed using HCl titration (refer Section 3.2.3).

5.2.3 Determination of lime requirement of peat soil

Samples (100.8 g) of air-dried peat soil (20 - 75 mm layer in field, $pH_{water} = 4.85$, < 2 mm and equivalent to 80 g oven-dry) were weighed into 150 mm × 200 mm plastic bags. The soil was mixed with the amendment then wetted with 112 ml distilled water. The amendment treatments included:

(1). No amendment, (Control),
(2). FBA 0.529 g bag^{-1} (equivalent to 50 mmol $[OH^-]$ kg^{-1}),
(3). FBA 1.058 g bag^{-1} (equivalent to 100 mmol $[OH^-]$ kg^{-1}),
(4). FBA 1.587 g bag^{-1} (equivalent to 150 mmol $[OH^-]$ kg^{-1}),
(5). FBA 2.116 g bag^{-1} (equivalent to 200 mmol $[OH^-]$ kg^{-1}),
(6). FBA 2.645 g bag^{-1} (equivalent to 250 mmol $[OH^-]$ kg^{-1}),
(7). lime 0.213 g bag^{-1} (equivalent to 50 mmol $[OH^-]$ kg^{-1}),
(8). lime 0.426 g bag^{-1} (equivalent to 100 mmol $[OH^-]$ kg^{-1}),
(9). lime 0.638 g bag^{-1} (equivalent to 150 mmol $[OH^-]$ kg^{-1}),
(10). lime 0.851 g bag^{-1} (equivalent to 200 mmol $[OH^-]$ kg^{-1}),
(11). lime 1.064 g bag^{-1} (equivalent to 250 mmol $[OH^-]$ kg^{-1}),

The trial was a complete factorial design, with three replications of each treatment. Amended soil was incubated at 20°C for six months. During incubation the plastic bag was fastened lightly with a rubber band to allow air exchange and the bags were weighed weekly and water added to replace that lost via evaporation. Samples were taken from all the treatments after one day incubation and then weekly during the first seven weeks of incubation and the last sampling was after six months incubation. The samples taken weekly were oven-dried at 30°C and sieved to < 2 mm. pH in water (pH_{water}) and pH in 0.01 M $CaCl_2$ were measured.

5.2.4 Field trial design

The trial was a complete factorial experimental design with all treatments replicated six times and arranged in a randomised complete block (plot size: 3 m × 4 m). The treatments included:

(1). No amendment (Control);
(2). Low FBA (lF) = 1000 kg ha^{-1} FBA;
(3). Medium FBA (mF) = 6616 kg ha^{-1} FBA;
(4). High FBA (hF) = 26462 kg ha^{-1} FBA;
(5). Low lime (lL) = 401.5 kg ha^{-1} lime;
(6). Medium lime (mL) = 2656 kg ha^{-1} lime;
(7). High lime (hL) = 10625 kg ha^{-1} lime.

The three rates were based on similar $CaCO_3$ equivalence between the FBA and lime treatments. All plots received a basal dressing of 187.5 kg ha^{-1} $Ca(H_2PO_4)_2.H_2O$, 126.2 kg ha^{-1} KCl, 10 kg ha^{-1} $CuSO_4.5H_2O$ and 150 g ha^{-1} $Na_2MoO_4.2H_2O$. After the fourth and sixth harvests, 69 kg ha^{-1} urea and 32 kg ha^{-1} KCl was applied to all plots to replace losses by herbage removal (based on weights of dry matter removed from the highest yielding plots).

5.2.5 Field experimental procedure

An area with uniform sward components, including ryegrass (*Lolium perenne*), white clover (*Trifolium repens*), Yorkshire fog (*Holcus lanatus* L.), was selected for the trial. The area was fenced to prevent access by stock. On July 14, 1992, pasture on the plots was mown to about 50 mm in height above ground level and discarded. Soil samples were taken from each plot (0 - 75 mm and 75 mm - 150 mm soil depths using a 25 mm diameter soil corer, six cores per plot, bulked before analysis). Lime, FBA and basal fertilisers were applied to individual plots by hand and the required amounts of $CuSO_4.5H_2O$ and $Na_2MoO_4.2H_2O$ were thoroughly mixed with a bulking of river sand before spreading.

Soil samples for soil pH analysis were taken from each plot after the first, second and fifth harvests with various depth increments. On September 22, 1992, all the plots were sampled for soil pH measurement. On October 20, 1992, soil samples were taken from no amendment, high FBA and high lime treatments with depth intervals of 0 - 25, 25 - 50 and 50 - 75 mm. On January 8, 1993, all the plots were sampled at the same depth increments as on October 20, 1992. Soil pH in water and in 0.01 M $CaCl_2$ was determined with a 1:5 soil:solution ratio.

The first harvest was conducted on September 22, 1992 after low pasture growth rates during the winter season. The other harvests were carried out at four to six weeks' intervals depending on pasture height. The final harvest was on March 17, 1993. At each harvest, three cuts were taken within the plot using a lawn mower. Each cut covered an area of 3.1 m × 0.47 m. The fresh weight of herbage was measured using an electronic scale. Subsamples of herbage were taken and dried at 65°C for 24 hours and weighed to constant weight for dry matter determinations. A small sample of dried herbage from each plot was ground and stored in sealed plastic bags awaiting chemical analyses. After sampling, the remaining herbage was cut and removed from the plots. During the experimental period, seven harvests were carried out with no grazing influence.

On 8 December 1992, a herbage sample from each plot was taken for botanical analysis using a clipper. Samples were sorted into grass, clover and weeds. Each component was oven dried and the dry matter was recorded for calculation of botanical composition.

5.2.6 Herbage sulphur analysis

Finely ground dried herbage samples were digested with hypobromite (NaOBr) solution (Tabatabai & Chae 1982) and the SO_4^{2-} concentration in the digest solution was determined using the same method as described in Section 3.2.4 of Chapter 3.

The statistical data analysis was conducted using the SAS software package.

5.3 RESULTS AND DISCUSSION

5.3.1 Determination of lime requirement of peat soil with FBA and lime

To determine the lime requirement of the peat soil, soil pHs were measured after various periods of incubation with FBA and lime. The pH was measured both in water (pH_{water}) and 0.01 M $CaCl_2$ to evaluate the effect that ionic strength would play in the variation in readings. For example, it was expected that Ca^{2+}, K^+ and Na^+ ions released from the more soluble components in FBA may displace H^+ ions from soil exchange sites into solution and this would result in lower pH in water of FBA treatments than expected for a particular addition of OH^- equivalent. This was indeed the case, except for high rates of OH^- (> 150 mmol kg^{-1}) incubated for six weeks or longer (Table 5.3). The measurement of pH in 0.01 M $CaCl_2$, which supplied an equivalent ionic strength to eliminate the "salt effect", allowed a better comparison of the extent of neutralisation of acidity by the lime and FBA materials. Sumner (1994) reported similar results. Regression analysis indicated that increasing soil pH in the incubated peat samples was linearly related to the application rates of FBA and lime ($R^2 > 0.9$, Fig. 5.1). The soil pH measurements in this incubation experiment indicated that FBA was as efficient as lime as a soil acidity ameliorant (Table 5.3 & Fig. 5.1).

It had also been noticed that the overall soil pH decreased with time during incubation (Table 5.3). This may be caused by nitrification and build up of organic acids by decomposition of the peat. These mechanisms will be discussed in Section 6.3.1. Edmeades et al. (1984a) reported that to achieve optimum pasture production, the pH_{water} of the mineral soils should be limed to maintain pH above 5.8 - 6.1, whereas the pH of a peat soil needs to be maintained above 5.0. After six months incubation, 2.116 g FBA bag^{-1} (equivalent to 200 mmol (OH^-) kg^{-1}, or 10000 kg $CaCO_3$ ha^{-1}) provided sufficient base to maintain the soil pH_{water} of the major rooting zone (0 - 75 mm) above 5.0. Therefore, the rates of FBA and lime used in the field trial were chosen to give a liming value up to 10000 kg $CaCO_3$ ha^{-1}.

Table 5.3 Effect of incubation with FBA and lime on peat soil pH change[1].

	OH^-	pH in water			pH in $CaCl_2$		
Amendment	(mmol kg^{-1})	One day	Six weeks	Six months	One day	Six weeks	Six months
Control	0	5.05	4.71	4.47	4.47	4.39	4.33
FBA	50	4.99	4.75	4.58	4.60	4.50	4.48
FBA	100	5.02	4.85	4.73	4.70	4.64	4.64
FBA	150	5.12	4.99	4.86	4.86	4.80	4.79
FBA	200	5.18	5.10	5.01	4.96	4.92	4.96
FBA	250	5.29	5.22	5.13	5.10	5.06	5.09
Lime	50	5.09	4.81	4.61	4.54	4.49	4.48
Lime	100	5.17	4.88	4.72	4.63	4.58	4.59
Lime	150	5.24	4.96	4.81	4.69	4.65	4.70
Lime	200	5.31	5.04	4.90	4.76	4.73	4.79
Lime	250	5.37	5.14	5.01	4.84	4.83	4.91
$LSD_{0.05}$			0.03			0.03	

[1] Soil pH in water and in 0.01 M $CaCl_2$, soil:solution = 1:5.

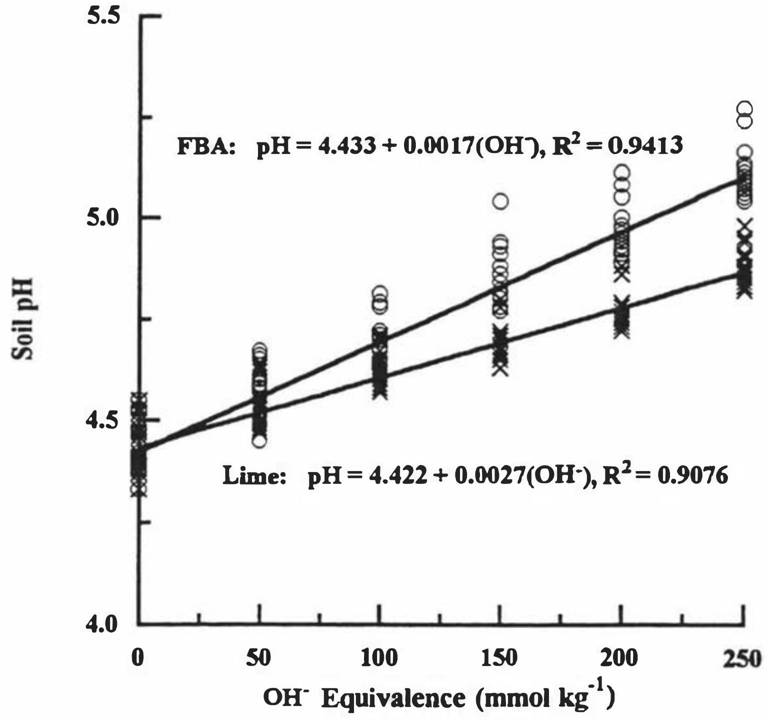


Fig. 5.1 Soil pH in 0.01 M $CaCl_2$ of the FBA (O) and lime (x) treatments (incubation experiment).

5.3.2 Effect of FBA and lime on peat soil acidity - field experiment

Most of the undeveloped peat has a pH of about 4.0. The topsoil (0 - 75 mm) of the field trial site had an initial pH_{water} of 5.08 (Table 5.1) due to the continuous application of lime after the peatland was developed as a dairy farm, but pH was markedly stratified within this depth (Table 5.4). Rather surprisingly, the top 25 mm consistently had pH_{water} values above 6, however, the soil pH was significantly lower in the 25 - 50 mm and decreased markedly with depth (Tables 5.2 & 5.4).

The surface applied FBA, containing gypsum, was expected to ameliorate the subsurface acidity in this peat soil, because a number of researchers have demonstrated gypsiferous materials are effective at amending the subsurface acidity of some mineral soils (Ritchey et al. 1995a; Shainberg et al. 1989; Sumner 1994). In this trial, however, even the high rates of FBA (hF) and lime (hL) treatments (equivalence of 10000 kg ha^{-1} $CaCO_3$) significantly increased the soil pH_{water} of only the 0 - 25 mm layer ($P < 0.01$) and pH in 0.01 M $CaCl_2$ at 25 - 50 mm layer, but they had no effect on soil pH below 50 mm (Table 5.4). Similar results were obtained from the samples taken on September 22 and October 20, 1992 (data not shown). This indicates that there was a negligible movement of the bases generated from the surface application of FBA and lime. The movement of solutes added through FBA and lime was examined in a separate chapter (refer Chapter 6).

Therefore, the results indicated that although surface applied FBA was not able to increase the subsurface soil pH in acid peat, it had a similar liming value to lime. The amounts of FBA products needed to increase soil pH to a certain level, however, will vary from one FBA material to another, as FBA materials vary considerably in their neutralisation potential (refer Table 2.1 in Chapter 2) (Fowler et al. 1992; Stout et al. 1988). The sample of FBA used in this study was as efficient as lime in neutralising peat soil acidity when applied at the same $CaCO_3$ equivalent. Therefore, FBAs with similar characteristics would be good alternatives to agricultural lime for pasture production in acid peat soils.

Table 5.4 Effect of FBA and lime on soil pH (Field trial)[1].

Amendment	Rate ($CaCO_3$ kg ha^{-1})	Soil pH[2]					
		pH in water			pH in $CaCl_2$		
		0-25 mm	25-50 mm	50-75 mm	0-25 mm	25-50 mm	50-75 mm
No amendment	0	6.14	5.28	4.84	5.98	4.83	4.45
FBA	380	6.17	5.29	4.97	5.98	4.81	4.44
FBA	2500	6.56	5.51	5.19	6.52	5.15	4.69
FBA	10000	6.97	5.53	4.92	6.85	5.18	4.47
Lime	380	6.22	5.26	4.93	6.05	4.75	4.36
Lime	2500	6.43	5.59	5.13	6.30	5.16	4.66
Lime	10000	6.84	5.64	5.15	6.67	5.30	4.67
$LSD_{0.05}$			0.36			0.34	

[1] Soil sampled on January 8, 1993.

[2] Soil pH in water and in 0.01 M $CaCl_2$, soil:solution = 1:5.

5.3.3 Effect of FBA and lime on pasture yield and botanical composition

Fertiliser and soil amendment applications to pasture soil are aimed at maintaining or increasing the quality and quantity of forage available for animal feed. During the whole field experimental period (eight months), the total yields from the FBA treatments were significantly higher than the lime treatments ($P < 0.05$). This was due to differences in the third, fourth and fifth harvests yields, where the FBA treatments yielded significantly greater than the lime treatments ($P < 0.05$, Table 5.5). Although more clover appeared in the FBA treatments than in the lime treatments at the field trial site, botanical composition changes were not significant (Table 5.6) due to the high amount of experimental variability (coefficients of variation ranged 24 - 60%).

Although the subsurface of this peat soil is very acidic and it may limit pasture root growth (Edmeades et al. 1984b), the lack of change of subsurface soil pH in the FBA treatment indicated that the positive response of pasture yield to FBA application was probably not caused by the liming value of FBA but due to the gypsum and other sulphate components in FBA which may have ameliorated S deficiency in the peat soil and/or enabled Ca^{2+} ions to move into the subsurface layers.

Table 5.5 Effect of FBA and lime on pasture dry matter production.

Amendment	Rate $CaCO_3$ (kg ha^{-1})	Dry matter (kg ha^{-1}) H1[1]	H2	H3	H4	H5	H6	H7
Control	0	566	1157	1235	1414	1452	477	1095
FBA	380	792	1403	1449	1483	1620	486	1130
FBA	2500	444	1248	1401	1583	1768	548	1262
FBA	10000	603	1148	1420	1506	1665	558	1215
Lime	380	719	1206	1190	1367	1277	449	1065
Lime	2500	386	1064	1183	1315	1446	508	1206
Lime	10000	489	1078	1246	1442	1526	492	1144
$LSD_{0.05}$		309	290	169	182	201	126	192

[1] H: harvest number.

Table 5.6 Effect of FBA and lime on botanical composition of pasture in Moanatuatua peatland.

Amendment	Rate $CaCO_3$ (kg ha^{-1})	% Grass	Clover	Weeds
Control	0	54.4	40.6	5.0
FBA	380	53.7	42.2	4.2
FBA	2500	62.5	34.0	3.5
FBA	10000	56.3	36.5	7.2
Lime	380	56.8	38.0	5.2
Lime	2500	58.2	34.0	7.8
Lime	10000	56.4	38.5	5.1
$LSD_{0.05}$		16.3	16.9	3.6

5.3.4 FBA - A combined fast- and slow-release S fertiliser?

Despite the phosphate extractable soil SO_4^{2-}-S in the trial site being high (21 mg S kg^{-1}, weight basis), if calculated on a volume basis, the concentration is very low (Brady 1984), that is, the SO_4^{2-}-S in this peat soil (bulk density 0.33 g cm^{-3}) is equal to 7 mg S kg^{-1} of a mineral soil with a bulk density of 1 g cm^{-3}. Furthermore, peat soil is not only low in S but has weak sulphate adsorption, which results in high leaching losses of SO_4^{2-} from the topsoil (Hupkens van der Elst 1958). Therefore, pasture growth responses to FBA as a S source in this field experiment were expected.

Herbage analysis indicated that FBA treatments significantly increased herbage S concentration at the third harvest (Fig. 5.2), and the corresponding dry matter yields of these treatments were greater than the control and lime treatments (Table 5.5). The concentration of S in herbage from the FBA treatments increased with increasing application rate from 0.27 to 0.40% S, which is in the optimum (0.27 - 0.32% S) to high (> 0.32% S) range for white clover growth, whereas the herbage S from the control and lime treatments were in the deficient range (< 0.25% S) (Cornforth 1984b).

S is required by plants mainly for the synthesis of certain essential amino acids and proteins, and a component of enzymes involved in photosynthesis and production of vitamins (Marschner 1986). Sulphide is a component of nitrogenase enzymes which catalyse nitrogen fixation of rhizobium species (Lehninger 1982) which is particularly important for legume based pasture production. Furthermore, only with sufficient S supply is the pasture is able to maximise the response to P and K application. For example, S deficiency may have significantly limited pasture responses to P and K fertilisers applied as basal nutrients in the control and lime treatments and resulted in the lower yield on the control and lime plots in this trial (Table 5.5). Eight months after application in the field trial site, herbage S concentrations of the medium (mF) and high (hF) FBA treatments were still significantly higher than the control and lime treatments (Fig. 5.3). Due to its long-term effect, FBA may be useful as a basal S dressing in soils prone to severe leaching, which are common in some high rainfall areas of New Zealand and in soils with low anion retention capacities.

Herbage S concentrations raised by FBA application at harvests 3 and 7 (Fig. 5.2 & 5.3) were associated with higher yielding treatments (Table 5.5). The cumulative yield for the first three harvests of the low rate FBA (lF) treatment (1000 kg ha^{-1}, containing 49 kg S) was the highest amongst the treatments and was significantly higher than the control and medium and high lime treatments ($P < 0.05$, Fig. 5.4). From the fourth harvest, medium rate FBA (mF) treatment (6616 kg ha^{-1}) produced the highest yield, followed by the high rate FBA (hF) treatment (26462 kg ha^{-1}) (Fig. 5.5). This implied that after the wet winter and spring, the residual S in soil at lF treatment was not sufficient to support optimum pasture production because of high leaching losses of sulphate. This was supported by herbage S analysis after the seventh harvest where herbage S contents of the mF and hF treatments were significantly higher than the other treatments, whereas herbage S content of the lF treatment was at the same level as the control treatment (Fig. 5.3). This agrees with the observation by Hupkens van der Elst (1968) who reported that pasture top-dressed with superphosphate (containing P and S) in autumn may be yellow and near death in spring because the sulphate in superphosphate has been leached out during the wet winter. Hupkens van der Elst (1971) suggested that a single spring application of superphosphate as S fertiliser has the effect of giving maximum responses in spring and summer and small responses in autumn and winter. A good fertiliser strategy would, therefore, be to apply S fertiliser, e.g. FBA, in the spring when actively growing plants can take up most the S before the soluble SO_4^{2-} is leached. Approximately, 50% of the S in slaked FBA is in the slow-release form of ettringite (refer Section 3.3.1) and this S may be less affected by leaching loss and therefore longer term pasture yield responses to mF and hF treatments would be expected in this experiment.

Despite its relatively high alkalinity, high boron content (refer Chapter 3) and high rate of application (up to 26462 kg ha^{-1}), no negative yield responses to FBA nor boron toxicity symptoms were observed in this field experiment. It was also observed that application of small amounts of KCl to the plots after the fourth harvest boosted the yields of the fifth harvest, particularly in the FBA treatments (Table 5.5). This was probably because peat soil was not only deficient in K but had little ability to retain potassium (Hupkens van der Elst 1971), particularly the presence of high concentrations of Ca^{2+} released from dissolution of FBA may accelerate K^+ leaching. This aspect is one issue investigated in the following Chapter.

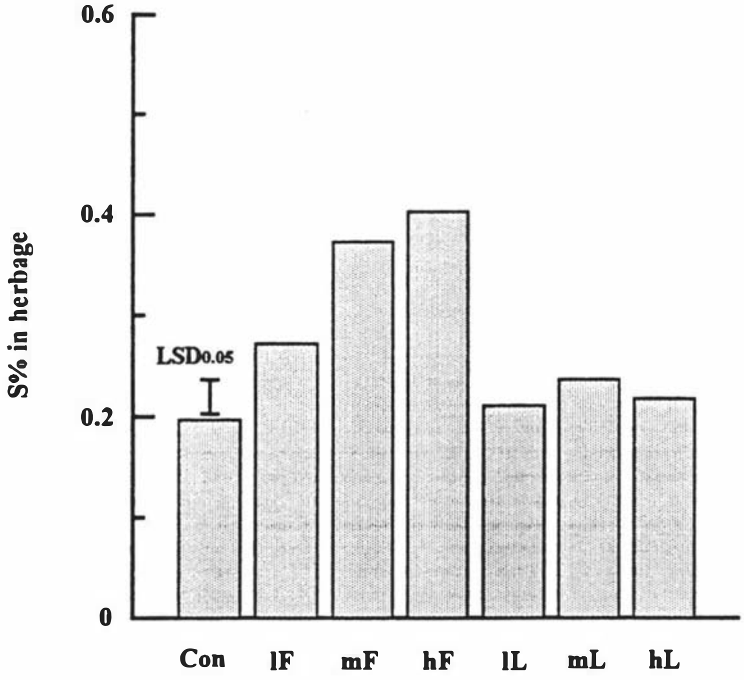


Fig. 5.2 Effect of the FBA and lime treatments on herbage sulphur concentration of the third harvest (Con: no amendment; lF, mF and hF: low, medium and high FBA treatment; lL, mL and hL: low, medium and high lime treatment).

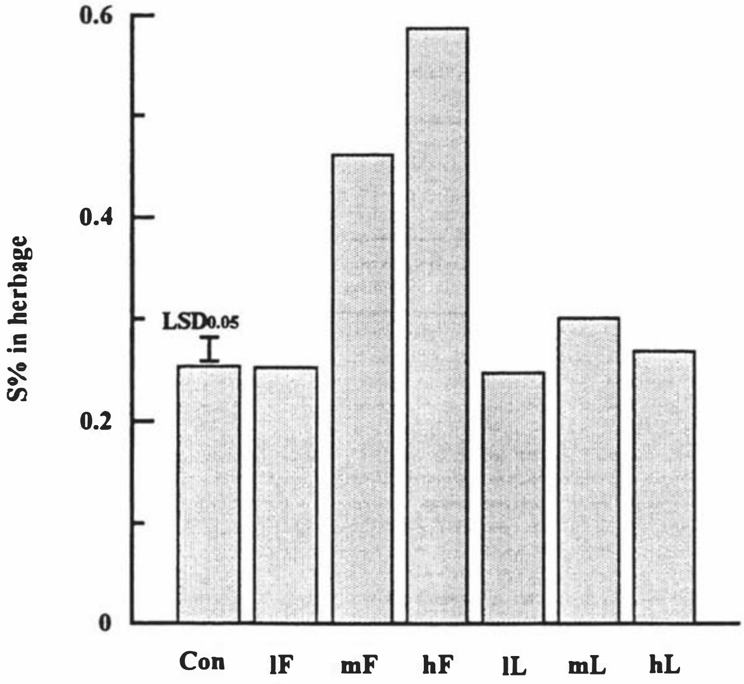


Fig. 5.3 Effect of the FBA and lime treatments on herbage sulphur concentration of the seventh harvest (Con: no amendment; lF, mF and hF: low, medium and high FBA treatment; lL, mL and hL: low, medium and high lime treatment).

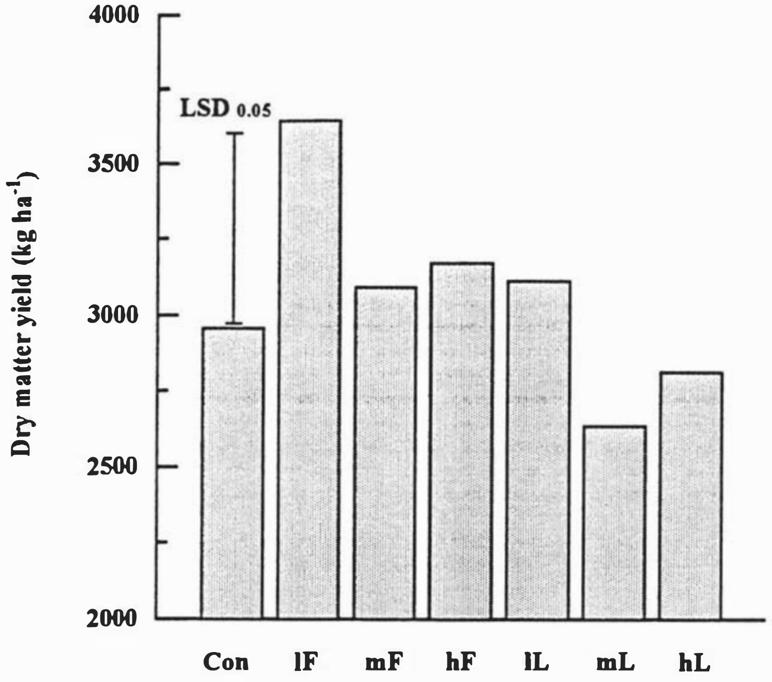


Fig. 5.4 Effect of the FBA and lime treatments on the cumulative pasture yield of the first to third harvests (Con: no amendment; lF, mF and hF: low, medium and high FBA treatment; lL, mL and hL: low, medium and high lime treatment).

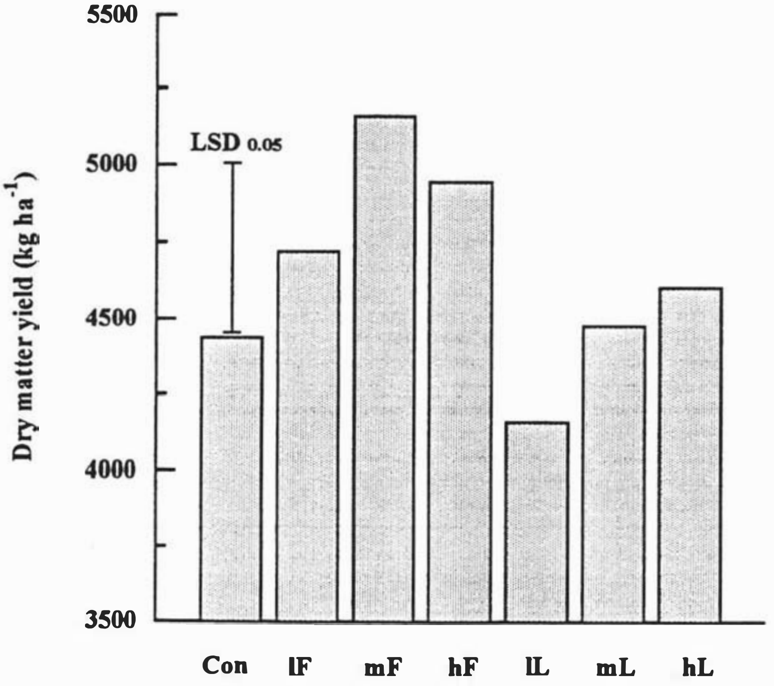


Fig. 5.5 Effect of the FBA and lime treatments on the cumulative pasture yield the fourth to seventh harvests (Con: no amendment; lF, mF and hF: low, medium and high FBA treatment; lL, mL and hL: low, medium and high lime treatment).

5.4 CONCLUSION

The results from the incubation and field experiments indicated that FBA was an effective alternative to agricultural lime to neutralise the acidity of peat soil. By acting as a sulphur fertiliser, FBA contributed significantly to increased pasture yield.

The ettringite-sulphate in FBA acted as a slow-release S fertiliser. The high application rate of FBA not only had no adverse effect on pasture growth but increased the longevity of raised S concentrations in the herbage. Therefore, slaked FBA shows potential to be used as a basal S fertiliser, as it appears to be able to reduce leaching loss, a common problem in many New Zealand soil types.

Adequate application of K fertiliser will enhance the beneficial effect of FBA. Although FBA had little effect on subsurface acidity of the peat soil, it may improve the downward movement of Ca^{2+} as a companion cation of SO_4^{2-}, which may ameliorate the H^+ phytotoxicity in the subsurface and consequently improve deep rooting of the pasture.

The movement and distribution of the Ca^{2+}, SO_4^{2-}, base and other solutes, and the change in soil acidity after FBA treatment will be further examined in experiments conducted under controlled conditions in Chapter 6.

Chapter 6

Solute movement in a peat soil amended with fluidised bed boiler ash

6.1 INTRODUCTION

The results of the field trial discussed in Chapter 5 have raised a number of issues that require detail examination. It was shown that when FBA was surface applied to pasture on a peat soil it neutralised acidity as effectively as lime. The pH measurements showed that the base generated after surface application of FBA and lime, however, did not move down the soil profile to neutralise subsurface acidity. Increases in pasture yield were observed in the FBA treatments but not the lime treatments suggesting that the pasture was responding to the increased supply of S by FBA. These yield increases may have resulted directly from the alleviation of sulphur deficiency, or partly from Ca^{2+} being carried deeper into the peat profile by the mobile sulphate anion. Increased concentrations of Ca^{2+} in the low pH subsurface peat may encourage root development (Foy 1992).

It has been reported that sulphate fertilisers should be applied twice a year to acid peat soil to achieve good crop and pasture yields, because peat is not only deficient in S but applied sulphate will be leached readily (Feyter et al. 1986; Hupkens van der Elst 1958). In the field trial, the pasture response to higher rates of FBA continued through the whole experimental period, despite the high rainfall after FBA application (refer Section 5.2.1). This suggested that some slow-release ettringite in FBA had remained in the pasture root zone, thus FBA displays a better residual S fertiliser value than could be expected for gypsum alone (e.g. gypsum in superphosphate).

Despite their agronomic value, the addition of gypsiferous materials to mineral soils often increases the leaching loss of some nutrients, such as Mg and K, from the profile, especially from the topsoil layer, because of displacement of these nutrients from the exchange sites on the surface of soil colloids by Ca^{2+} released from dissolution of gypsum

(Korcak & Kemper 1993; Sumner 1994; Wrubel et al. 1982). In peat soils further depletion of exchangeable Mg^{2+} and K^+ from upper layers may create additional agronomic problems. This field experiment also indicated that adequate application of K fertiliser could increase the pasture response to FBA application (refer Section 5.3.3 in Chapter 5).

The objectives of this study were, through controlled incubation and leaching of repacked peat columns, to investigate the base and solute movement in acid peat soil following the surface application of FBA and lime, to help explain the field trial results. In particular the long term effect of FBA as a S source, the lack of subsurface soil pH change, and the fate of native soil exchangeable cations following FBA application, are investigated.

6.2 MATERIALS AND METHODS

6.2.1 Description of peat soil and FBA

The soil material used in this study was taken from 20 - 75 mm layer of the field trial site at Moanatuatua Swamp, Waikato, New Zealand. The site and soil has been described in Section 5.2.1 (Chapter 5). Some properties of the peat are shown in Table 6.1.

Slaked FBA was used in this study, characteristics of the FBA are described in detail in Chapter 3.

Two experiments were undertaken in this study.

Table 6.1 Selected properties of peat soil used (20 -75 mm).

B. D.[1]	Org. C[2]	pH $_{water}$[3]	Olsen-P	SO_4^{2-}-S	Exchangeable Cations (cmol $_{(+)}$ kg^{-1})				
(g cm^{-3})	(%)		(µg g^{-1})	(µg g^{-1})	K	Ca	Mg	Na	CEC[4]
0.33	46.0	4.9	53	21	2.09	45.6	2.62	0.4	97

[1] Bulk density.
[2] Organic carbon.
[3] Soil:Water=1:5.
[4] Cation exchange capacity.

6.2.2 Experiment 1. Effect of FBA and lime on solute movement in the repacked columns of peat soil under leaching

The peat soil columns were packed in PVC pipes (internal diameter 75 mm, 50 mm high). A fine nylon mesh was attached to the bottom of each column to support the soil. Air dried peat (80 g) was repacked in each column to a bulk density of 0.33 g cm^{-3} (oven dry basis), equivalent to field bulk density. Treatments of FBA (2.93 g FBA column^{-1}, equivalent to 6616 kg ha^{-1}) and lime (1.41 g column^{-1}, equivalent Ca to FBA treatment) were applied on the soil surface. One set of repacked columns remained untreated (the control). All the treatments were replicated three times.

The repacked soil columns were wetted slowly with deionised water using disc permeameters (Clothier & White 1981) to ensure water infiltrated into the columns evenly. The surface pressure potential of water was imposed by air entry into the permeameter via a 0.66 mm internal diameter needle. Wetting was stopped as the first drops of effluent left the column.

After wetting, the column was placed on a funnel for the leaching study. A piece of glass-fibre filter paper was put on the column surface to spread the simulated rain. Each column was leached with 50 mm deionised water daily at a rate of 25 mm hour^{-1} using a peristaltic pump. Three samples (approximately 74 ml volume per sample) of leachate were collected daily from each column. The leaching lasted eight days, i.e. each column received around 400 mm water during the experiment. This amount of water is equal to a common winter drainage volume for the peat soil in the field. Electrical conductivity (EC) and pH of all the leachate samples were measured immediately after the leachate was collected and the volume of each leachate was recorded. A subsample of about 25 ml of leachate was acidified to 0.1 M H^+ with concentrated HCl and stored in a sealed plastic bottle until chemical analysis could be completed. The concentrations of Ca^{2+}, Mg^{2+}, K^+ and Na^+ in the leachate were analysed with atomic absorption spectroscopy using appropriate ionisation suppressants. The SO_4^{2-}-S concentrations of leachates were determined using the same method as described in Section 3.2.4.

When the leaching was completed, each soil column was sliced into seven sections: 0 - 5, 5 - 10, 10 - 15, 15 - 20, 20 - 25, 25 - 30 and below 30 mm, respectively, using a piston microtome. The sectioned soil samples were air dried, passed through a 2 mm sieve and kept for chemical analysis.

Soil pH in water and 0.01 M $CaCl_2$ (soil:solution = 1:5) were measured. The cations and anions in each soil section were extracted by shaking 1 g soil with 25 ml of 10% HCl (1 : 3, V/V) overnight in an end-to-end shaker at 30 rpm. The extracts were centrifuged and the supernatant liquids were filtered through a Whatman No. 40 filter paper. The concentrations of Ca^{2+}, Mg^{2+}, K^+, Na^+ and SO_4^{2-}-S in the 10% HCl extracts were analysed using the same methods as for leachate analysis. The concentrations of NH_4^+ and NO_3^- were determined by the methods of Downes (1978) and Technicon (1976) using an autoanalyser.

6.2.3 Experiment 2. Effect of incubation and leaching on solute movement in peat soil columns with surface applied FBA and lime

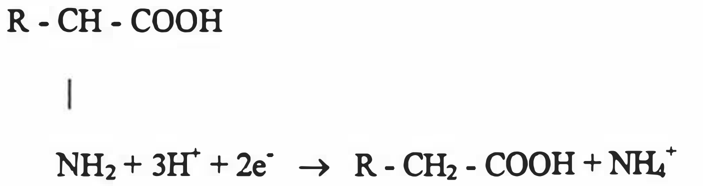
The methodology used in Experiment 2 was the same as in Experiment 1, except that in Experiment 2 the soil columns were incubated prior to leaching. After the column was wetted using a disc permeameter, it was placed in a plastic bag that was fastened lightly with a rubber band to allow air exchange. The columns were incubated at 20 ± 2°C for 17 days. After incubation, the columns were leached and then sliced following the same procedures as in Experiment 1. The incubation was intended to simulate a period of no rainfall post treatment application, when FBA and lime would be allowed to react with the soil and influence processes such as organic matter mineralisation.

6.3 RESULTS AND DISCUSSION

6.3.1 Leachate electrical conductivity and pH

A comparison of the differences in electrical conductivity (EC) of the leachate from the control and treated columns reflects the movement of solutes as affected by the amendments. The FBA treatment resulted in much higher leachate EC than the control and lime treatments (Fig. 6.1) because of the high solubility of gypsum and other soluble components in the FBA treated columns. Leachates from the control and lime treatments had similar EC values (Fig. 6.1) which implied that lime had very low initial solubility and little effect on downward movement of solute. On average, the EC from the incubated columns was slightly higher than that from the non-incubated, indicating that greater dissolution of FBA and lime occurred in the incubated columns and mineralisation of the peat occurred with time.

The pH of leachate from all the columns, regardless of treatments, increased with time (Fig. 6.2) probably as a direct consequence of ammonification (refer Fig. 6.15, Equation 6.1). However, the initial pH in leachate from the columns with incubation was much lower than that from the columns without incubation. This difference can be attributed to additional nitrification of NH_4^+ occurring during incubation (Equation 6.2) (Bolan et al. 1991a).



$$\begin{array}{l} R-CH-COOH \\ \qquad | \\ \qquad NH_2 + 3H^+ + 2e^- \rightarrow R-CH_2-COOH + NH_4^+ \end{array}$$

(Eqn. 6.1)

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

(Eqn. 6.2)

The *zigzag* shape of the leachate pH curve implied that significant amounts of H^+ had been generated every day which made the pH of the first daily leachate the lowest among the three collected each day. The pH in the final leachate (400 mm) of columns treated with the same amendment was similar, regardless of whether they were incubated or not. The lime treatment caused leachate pH to increase while the leachate pH from FBA treated column was the lowest (Fig. 6.2).

Variable-charged organic colloids dominate the CEC of peat soil and their surface negative charge (CEC) would increase with alkaline FBA application. The existing and increased CEC was not sufficient to retain the large amounts of Ca^{2+} released from the dissolution of gypsum and portlandite ($Ca(OH)_2$) during FBA dissolution. Solution Ca^{2+} moved downward with SO_4^{2-} as a companion cation balancing the charge. This mobile Ca^{2+} ion front could account for the low pH of leachates from the FBA treatment because Ca^{2+} displaced exchangeable H^+ from soil colloids into solution so the leachate pH decreased (Fig. 6.2).

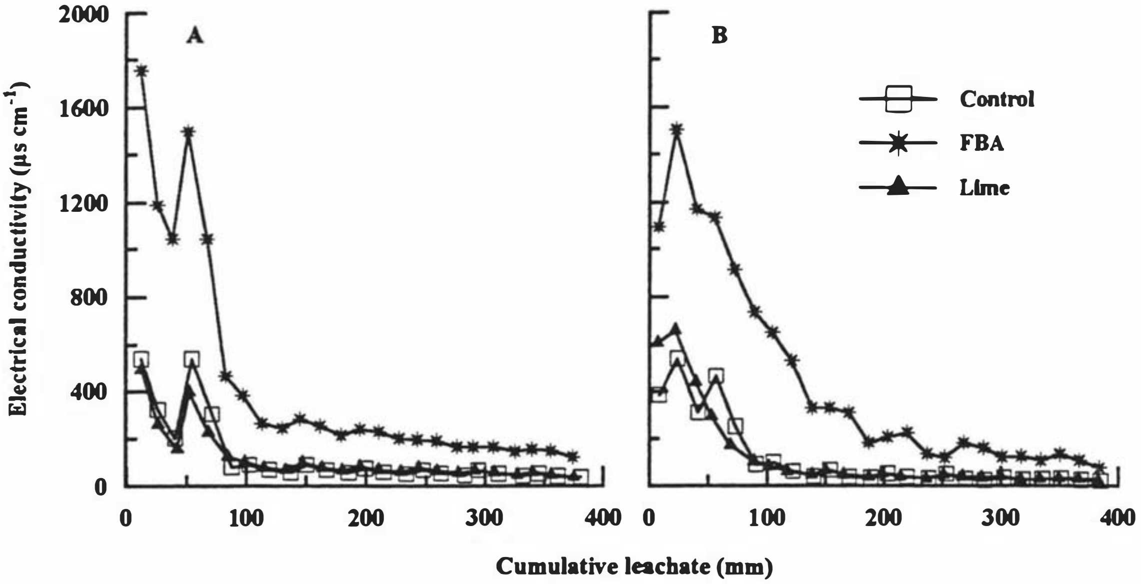


Fig. 6.1 The electrical conductivity of leachates collected (after daily leaching with 50 mm water) from peat soil columns treated with FBA or lime (A, Experiment 1 and B, Experiment 2).

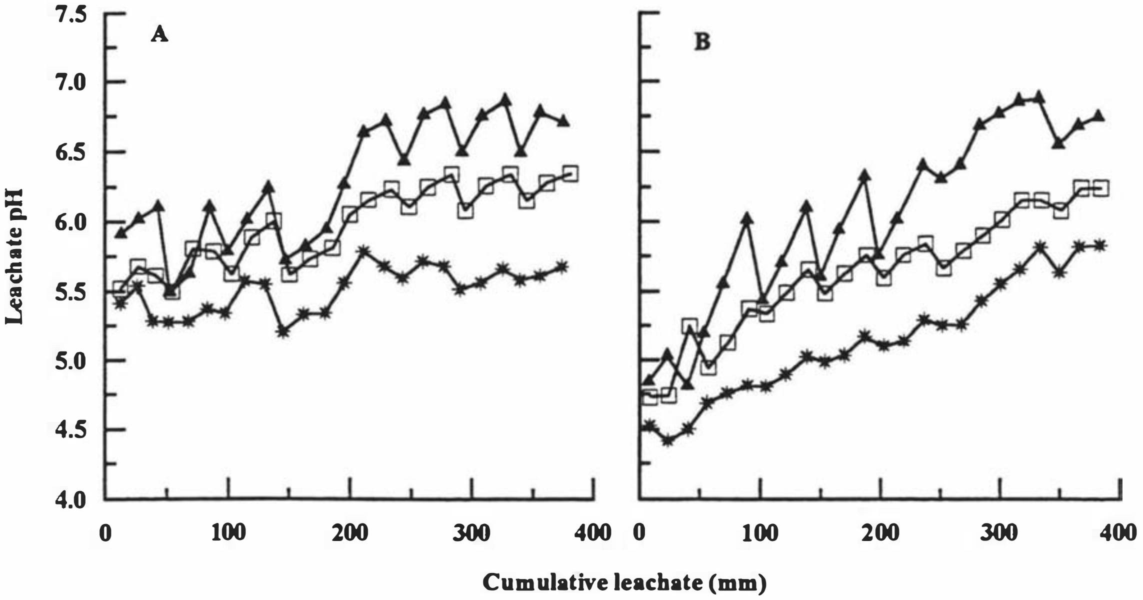


Fig. 6.2 The pH of the leachates collected (after daily leaching with 50 mm water) from peat soil columns treated with FBA or lime (A, Experiment 1 and B, Experiment 2).

It was also noticed from this study that the leachates collected from the columns of FBA treatment were much lighter brown colour than the control and lime treatments and this indicated that less dissolved organic matter appeared in the soil solution of the FBA treatment. This was probably the result of a Ca^{2+} common ion effect on the precipitation of Ca-organic matter complexes. As the pH increased, the soluble organic molecules would approach their net zero point of charge, which may lead to flocculation of soluble organic matter.

6.3.2 Peat soil pH

Surface applied amendments had little effect on increasing pH in the subsurface soil (below 15 mm) (Fig. 6.3). The lime treatment raised the pH_{water} slightly in all slices of the non-incubated soil columns and the pH increase in top two sections was significantly higher than the control. However, the FBA treatment increased pH_{water} in the topmost section but decreased pH_{water} in deeper sections relative to the control. Incubation of the peat had little effect on pH_{water} except that pH_{water} for all three treatments were slightly lower in the incubated peat due to nitrification (Equation 6.2). The soil pH of the lower sections of all treatments were similar when measured in 0.01 M $CaCl_2$. This demonstrated that the decreases in pH_{water} of lower sections of the FBA treated columns (Fig. 6.3) were solely due to H^+ displacement into solution by Ca^{2+} which had moved into these section as Ca^{2+} and SO_4^{2-} leached down the column (refer discussion in Section 6.3.3). There was no evidence for displacement and movement of H^+ from upper peat layers to contribute to increased H^+ in the lower layers (Fig. 6.4). In fact, the trend in leachate pHs (Fig. 6.2B) indicated that the Ca^{2+} from dissolved $CaSO_4$ displaced mobile acidity into the leachate and therefore the pH in lower soil sections slightly decreased relative to the control, particularly in the incubated columns (compare Fig. 6.2B, 6.3B & 6.4B).

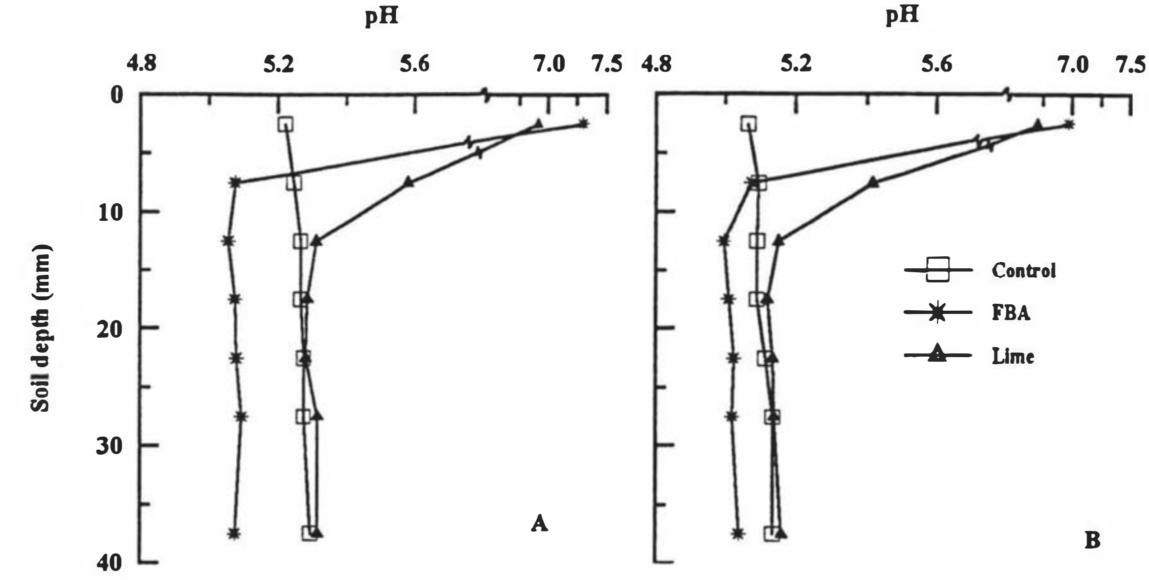


Fig. 6.3 The pH_{water} of sectioned samples of peat from columns , after treatment with FBA or lime (A, Experiment 1, and B, Experiment 2).

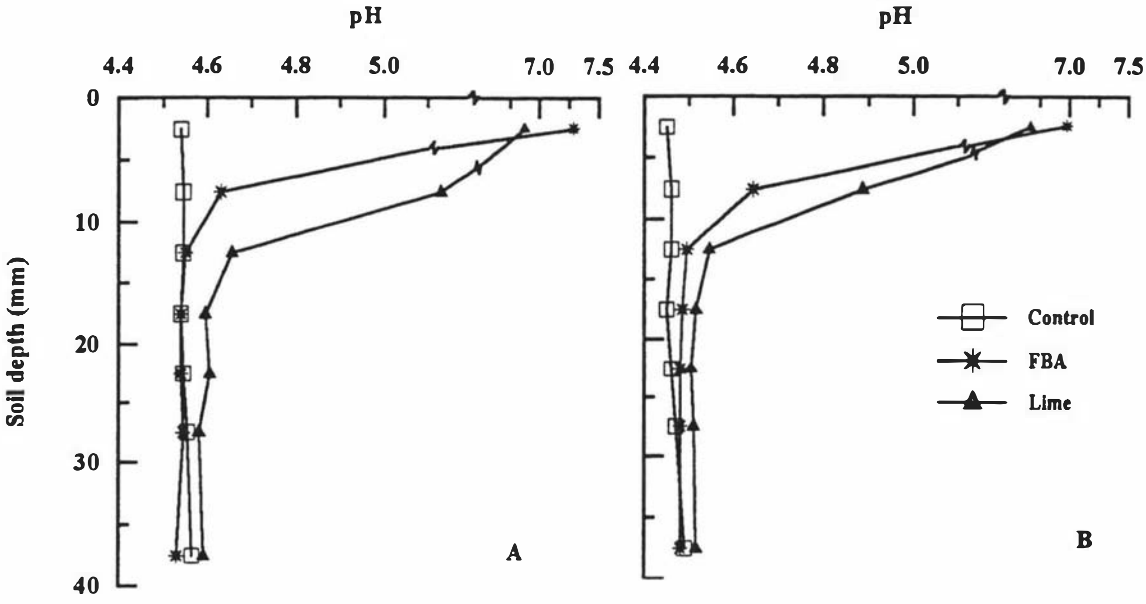


Fig. 6.4 The pH in 0.01 M $CaCl_2$ of sectioned samples of peat from columns , after treatment with FBA or lime (A, Experiment 1, and B, Experiment 2).

6.3.3 Sulphate movement

The cumulative sulphate concentrations in leachates from the control and lime treatments were very low both with and without incubation (less than 0.05 mmol S column^{-1}, Fig. 6.5) indicating that very small amounts of SO_4^{2-} were released from peat mineralisation. The leached SO_4^{2-} from the FBA treatment, however, was significantly higher ($P < 0.05$) than the control and lime treatments.

Furthermore, the total amount of SO_4^{2-}-S leached from the incubated column of the FBA treatment (3.56 mmol S) was significantly higher ($P < 0.05$) than that from the column without incubation (2.56 mmol S, Fig. 6.5). Therefore, incubation of acid peat made SO_4^{2-} in FBA more soluble. Approximately 50% of the SO_4^{2-} in FBA is in the relatively soluble form of gypsum and the rest is in the form of ettringite that has low solubility in water (refer Chapter 3). It was apparent that some of the ettringite-S was solubilised during incubation and leaching. Considering the negligible amount of SO_4^{2-} (< 0.05 mmol S) leached from both the control and incubated control treatments, it has been assumed that essentially all SO_4^{2-} in the leachate of FBA treatments was from applied FBA (4.50 mmol S column^{-1} in total with approximately 2.25 mmol S in ettringite form). Fifty seven and 79% of FBA-SO_4^{2-} was leached in non-incubated and incubated treatments respectively, indicating that if all gypsum derived SO_4^{2-} was leached then 400 mm of drainage water leached only 14% of ettringite-SO_4^{2-} without incubation and 58% after incubation.

Because peat soils lack clay minerals, in particular the Fe- and Al-oxides and allophanes which are responsible for SO_4^{2-} adsorption (Parfitt 1978), it was expected that peat would be weak in holding sulphate. It has been reported that virgin New Zealand deep acid peat is very deficient in S and the applied sulphate leaches readily (Feyter et al. 1986). The experimental results above support these observations.

New pasture developed on peat and top dressed with superphosphate (11% S) in autumn may be yellow and near death in spring because the sulphate in superphosphate has leached out (Feyter et al. 1986). In the current experiment, although FBA had little effect on increasing SO_4^{2-} adsorption and all of the soluble SO_4^{2-} from FBA moved down

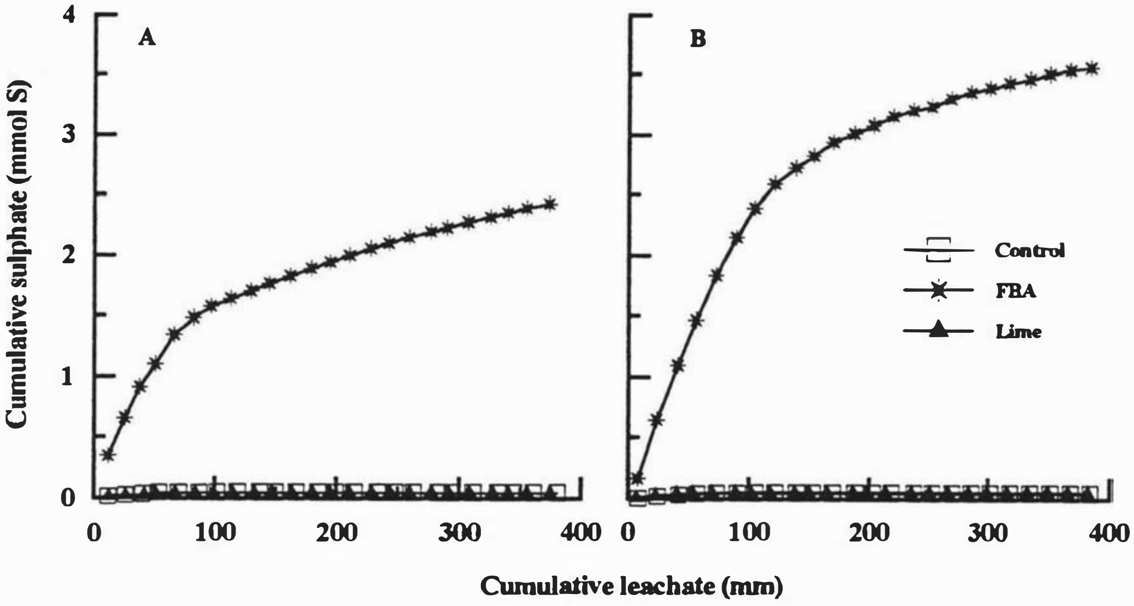


Fig. 6.5 The sulphate concentration in leachates collected (after daily leaching with 50 mm water) from peat soil columns treated with FBA or lime (A, Experiment 1 and B, Experiment 2).

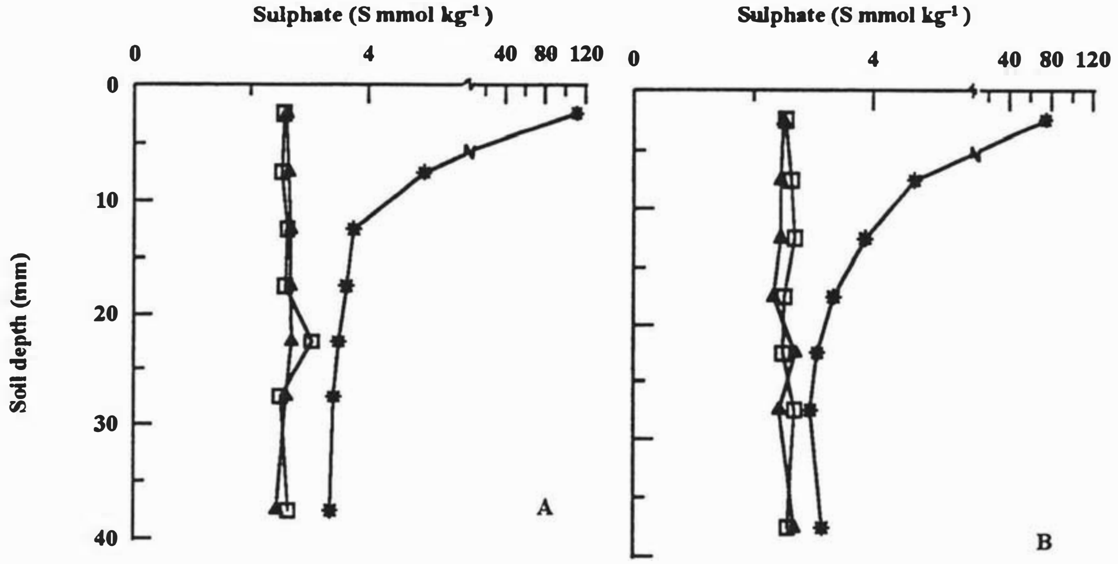


Fig. 6.6 The sulphate concentration in 10% HCl extracts of the sectioned samples from peat soil columns, after treatment with FBA or lime (A, Experiment 1 and B, Experiment 2).

the peat column with the leachate, considerable amounts of the applied SO_4^{2-} (21 - 43%) were retained in peat as insoluble ettringite (Fig. 6.6). This result helps explain the good residual effect of FBA on herbage S in the field trial (Chapter 5) and indicates that FBA could be a good alternative S source in New Zealand, where SO_4^{2-} leaching is the largest single cause of S loss from most agricultural soils, including peat (Saggar et al. 1990; Sinclair & Saunders 1984).

6.3.4 Calcium movement and retention

The cumulative amounts of Ca^{2+} leached from the treated columns (Fig. 6.7) accounted only for a small percentage of the applied Ca. The lime treatment retained virtually all the applied Ca in the column and the cumulative Ca^{2+} concentration in leachate was similar to the untreated control (between 0.44 to 0.51 mmol column^{-1}). This reflected the low solubility of $CaCO_3$ and increased Ca^{2+} retention as CEC increased through liming.

The pattern of Ca^{2+} concentration in leachate of FBA treatment was similar to that of SO_4^{2-} (Fig. 6.5), i.e. incubation made Ca in FBA more soluble and susceptible to leaching. Although the cumulative Ca^{2+} concentration of the leachate of the FBA treatment (2.79 mmol from incubated column and 2.19 mmol from the column without incubation) was much higher than those from the control due to FBA containing soluble Ca in the form of gypsum and portlandite (refer Chapter 3), leached Ca^{2+} accounted for less than 20% of applied Ca even assuming there was no native soil exchangeable Ca^{2+} in leachate, although this peat had a high Ca^{2+} saturation (Table 6.1). These Ca^{2+} ions were leached mainly as companion cations accounting for 80-95% of the SO_4^{2-} charge in leachate.

Sectioned soil sample analysis indicated that majority of the applied Ca in the FBA and lime treatments (66 - 83%) was retained on the surface of peat in the columns. There was little difference in the distribution pattern of Ca in the column between the FBA and lime treatments (Fig. 6.8).

Surface application of FBA did not raise subsurface soil pH (Fig. 6.3, 6.4), but it did provide a higher concentration of Ca^{2+} in subsurface soil (Fig. 6.8) and raise the base saturation in subsurface soil which could overcome Ca^{2+} deficiency, a common problem in acid peat soil. Higher base saturation and Ca^{2+} concentration may also ameliorate H^+ toxicity because of the antagonistic relationship between these two ions (Foy 1992).

6.3.5 Magnesium, potassium and sodium leaching

The leaching of Mg^{2+} followed the same pattern as Ca^{2+}, but Mg^{2+} concentration in leachate was much lower than Ca^{2+} concentration because the amendments are low in Mg. Little Mg^{2+} was leached from the control and lime treatments during the experiment (Fig. 6.9). Although there are small amounts of Mg in FBA, most of it, present in silicates, is insoluble in water but soluble in concentrated HCl (refer Chapter 3). Therefore, the low Mg^{2+} concentrations in leachate could be attributed to the relatively low exchangeable Mg^{2+} in the peat (Table 6.1). High concentrations of Ca^{2+} released by FBA resulted in the native soil exchangeable Mg^{2+} in the upper sections of the peat being displaced by Ca^{2+} and driven down the column (Fig. 6.10). Consequently small amounts of Mg^{2+} were leached out of column. This agreed with reports by Wrubel et al. (1982) that FBA application would induce leaching losses of topsoil exchangeable Mg^{2+}. However, the leached Mg^{2+}, even in the FBA treatment, accounted for only a small part of the available Mg^{2+} in this peat soil (about 17% of exchangeable soil Mg^{2+}) despite the short column used in this experiment. Therefore, considering the conditions in this experiment, (a large leaching volume and very short column length), the leaching loss of plant available Mg^{2+} caused by FBA application would not be a serious problem in acid peat soil. Lime had little effect on Mg^{2+} movement in soil. The high Mg^{2+} concentration in the top-most section of the FBA treatment was due to the FBA-Mg being soluble in the 10% HCl extractant (refer Chapter 3).

In contrast to the little amount of Mg^{2+} leached, relatively large amounts of K^+ were leached from the control treatment (Fig. 6.11). This reflects the weak adsorption of K^+ by peat. Application of FBA increased K^+ leaching and caused a significant depletion of the exchangeable K^+ in the peat column compared to the lime and control treatments. The cumulative amount of K^+ leached from the FBA treated column without incubation was nearly equal to the sum of extractable soil K^+ initially present in the soil column (Table 6.1) and soluble FBA-K (refer Chapter 3). As a result of K^+ movement, 10% HCl

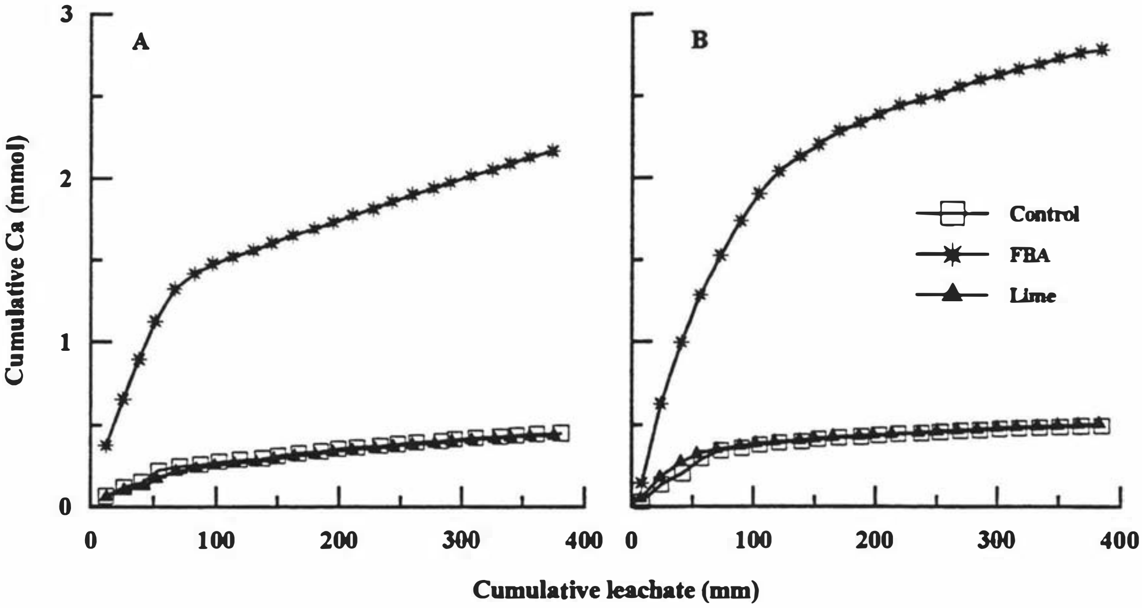


Fig. 6.7 The calcium concentration in leachates collected (after daily leaching with 50 mm water) from peat soil columns treated with FBA or lime (A, Experiment 1 and B, Experiment 2).

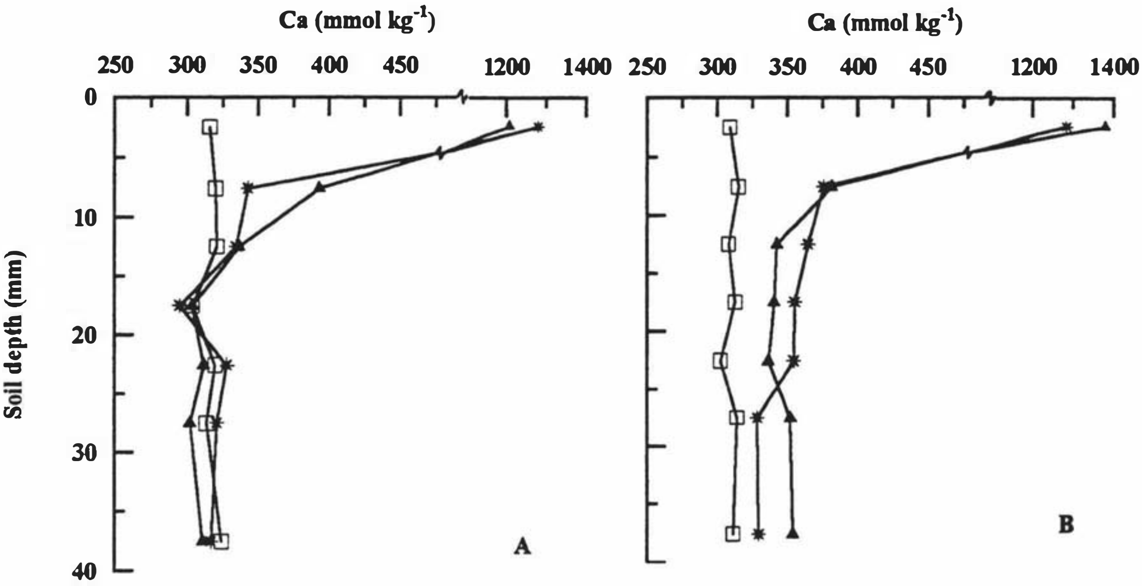


Fig. 6.8 The calcium concentration in 10% HCl extracts of the sectioned samples from peat soil columns, after treatment with FBA or lime (A, Experiment 1 and B, Experiment 2).

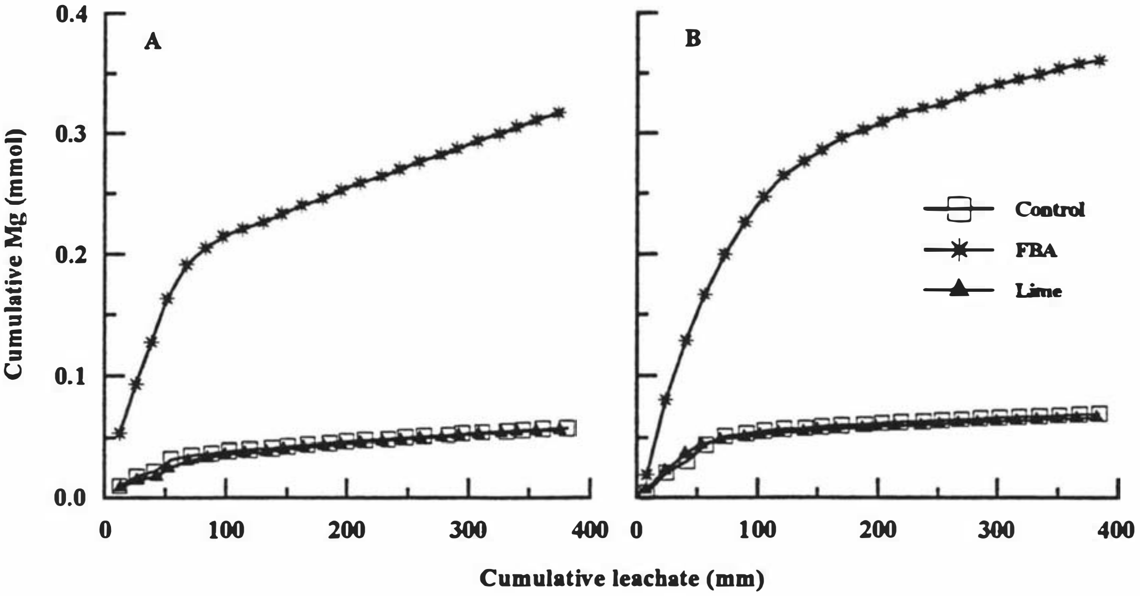


Fig. 6.9 The magnesium concentration in leachates collected (after daily leaching with 50 mm water) from peat soil columns treated with FBA or lime (A, Experiment 1 and B, Experiment 2).

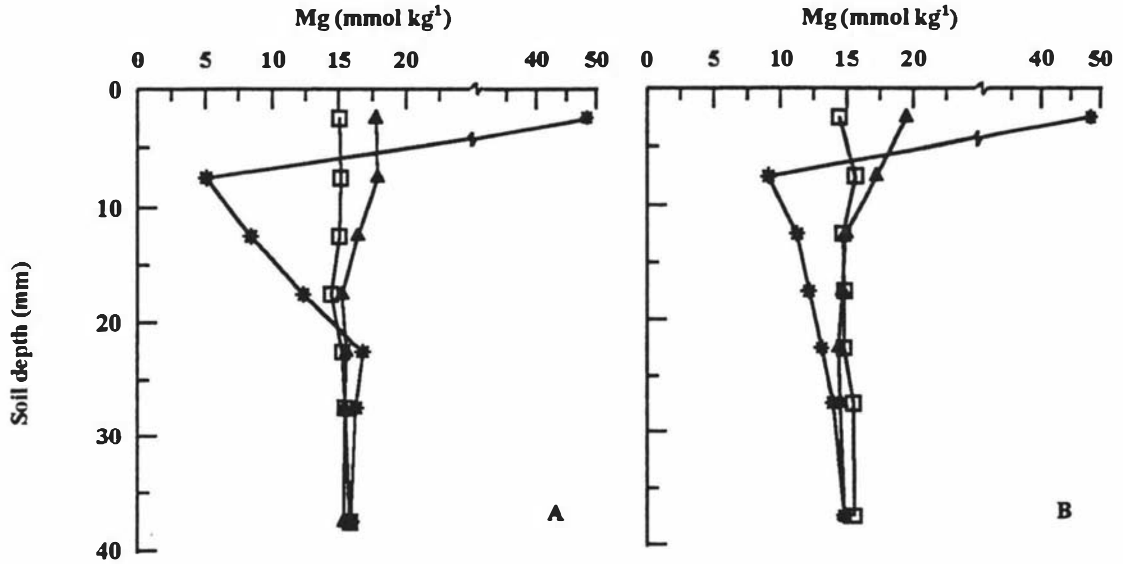


Fig. 6.10 The magnesium concentration in 10% HCl extracts of the sectioned samples from peat soil columns, after treatment with FBA or lime (A, Experiment 1 and B, Experiment 2).

extractable soil K^+ concentrations in all the columns increased with depth except for the FBA treatment, in which some water insoluble K^+ in FBA remained on the soil surface (Fig. 6.12). K^+ movement resulted in significantly lower K^+ concentrations in soil sections of the FBA treatment compared to the control and lime treatments. The lime treatment had little effect on the K^+ concentration of leachate (Fig. 6.12). As a result of the low content of native K in peat (Feyter et al. 1986) and the high leaching loss of K^+ from soil caused by FBA application, K fertiliser would have to be recommended to peat soils treated with FBA.

The concentration of Na^+ in leachate increased after the FBA treatment due to the soluble Na in FBA, but the lime treatment had no effect on leachate Na^+ concentration (Fig. 6.13). Incubation had little effect on Na^+ leaching. Unlike the K^+ concentration in the column, which increased with depth, Na^+ concentrations were relatively evenly distributed throughout the column, and less affected by amendments (Fig. 6.14). This may be attributed to the very low exchangeable Na^+ in this soil (Table 6.1).

6.3.6 Nitrogen transformation and movement

The relative concentrations of ammonium (NH_4^+) and nitrate (NO_3^-) in leachates were highly dependent on the experimental procedure (compare Fig. 6.15A & C; 6.15B & D). Incubation significantly decreased NH_4^+-N concentration in leachate because NH_4^+ oxidised to NO_3^- during the incubation period, and subsequently the NO_3^--N concentration in the leachate from the incubated column increased above that from the non-incubated column (Fig. 6.15). The total extractable N from the incubated column was higher than that from the non-incubated column. It was obvious that organic N was mineralised to inorganic N during incubation, and subsequently the mineralised N transformed from NH_4^+ to NO_3^- through nitrification. Without incubation, most of the N was leached as NH_4^+ before it was oxidised to NO_3^-. The FBA treatment released cations such as Ca^{2+} to displace exchangeable NH_4^+, therefore the FBA treatment significantly ($P < 0.01$) increased NH_4^+ leaching in comparison with the lime and control treatments (Fig. 6.15). FBA treatment significantly ($P < 0.05$) increased total N (sum of

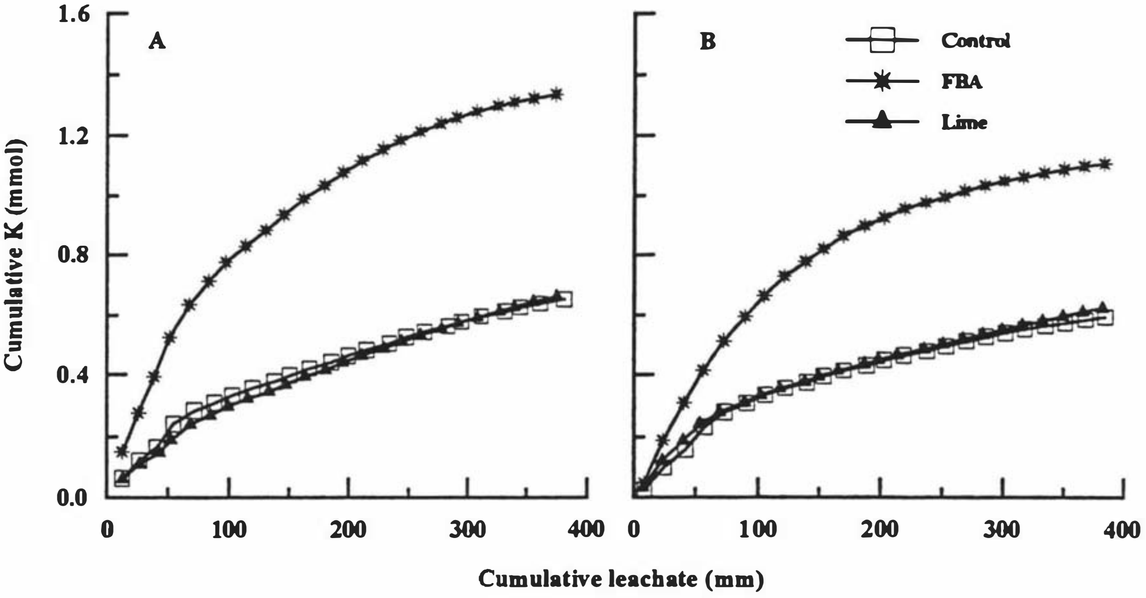


Fig. 6.11 The potassium concentration in leachates collected (after daily leaching with 50 mm water) from peat soil columns treated with FBA or lime (A, Experiment 1 and B, Experiment 2).

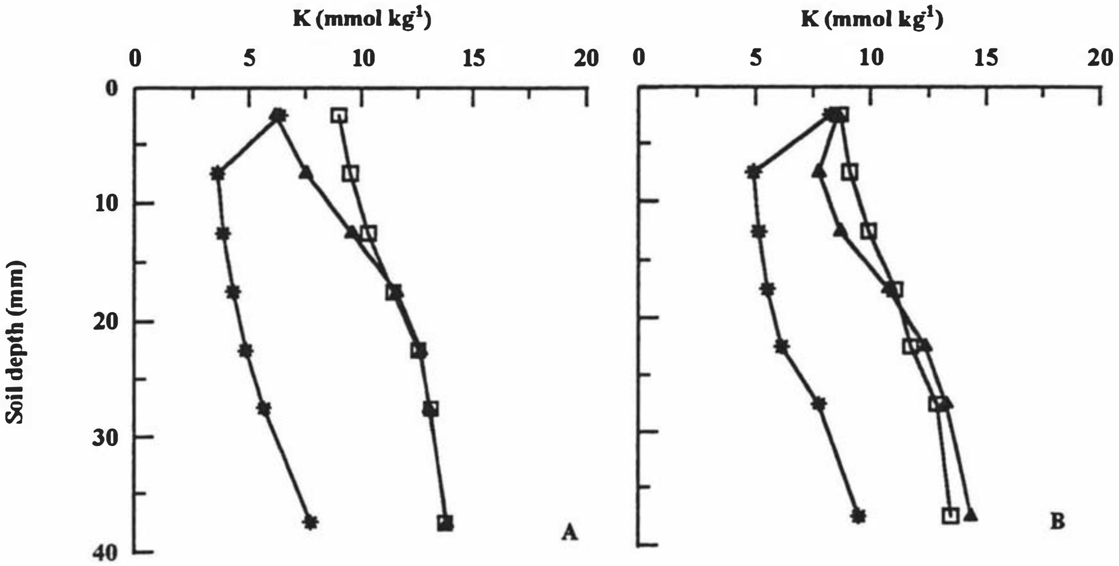


Fig. 6.12 The potassium concentration in 10% HCl extracts of the sectioned samples from peat soil columns, after treatment with FBA or lime (A, Experiment 1 and B, Experiment 2).

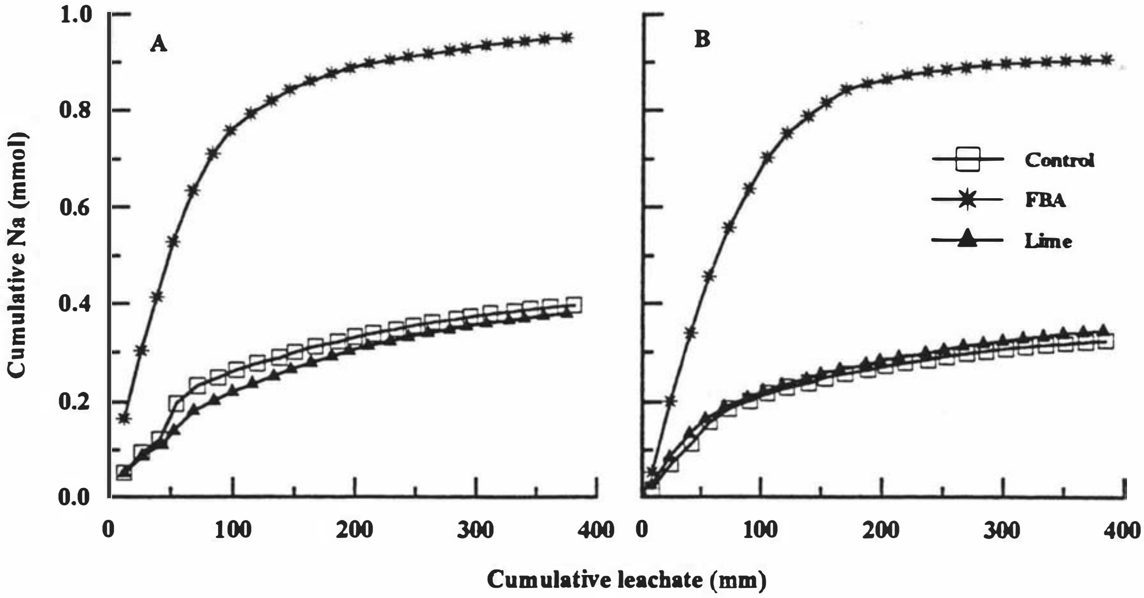


Fig. 6.13 The sodium concentration in leachates collected (after daily leaching with 50 mm water) from peat soil columns treated with FBA or lime (A, Experiment 1 and B, Experiment 2).

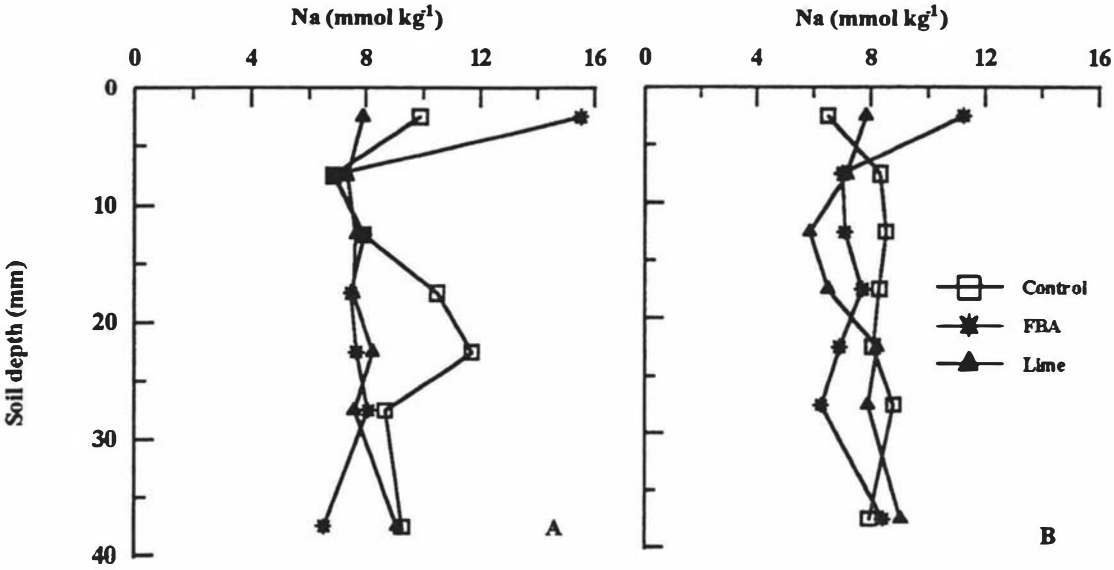


Fig. 6.14 The sodium concentration in 10% HCl extracts of the sectioned samples from peat soil columns, after treatment with FBA or lime (A, Experiment 1 and B, Experiment 2).

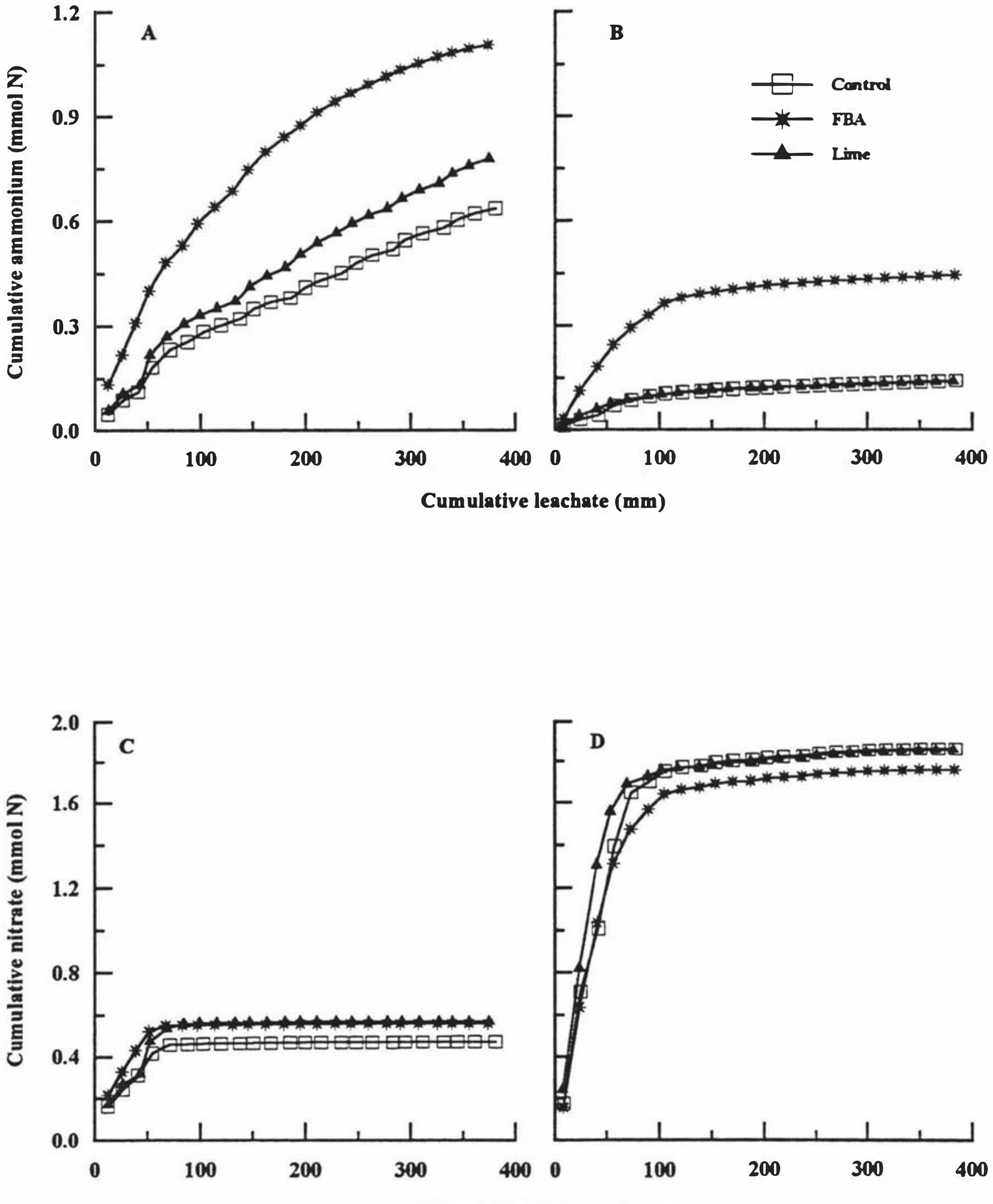


Fig. 6.15 The soluble inorganic nitrogen concentration in leachates collected (after daily leaching with 50 mm water) from peat soil columns treated with FBA or lime (A, ammonium in Experiment 1, B, ammonium Experiment 2, C, nitrate in Experiment 1 and D, nitrate in Experiment 2).

NH_4^+-N and NO_3^--N) leaching from the column, but caused little difference in the amounts of nitrate leached. This implies that FBA application accelerated mineralisation of organic nitrogen.

The leaching loss of NH_4^+-N from the FBA treatment was reflected in the concentration of 10% extractable NH_4^+-N remaining in sectioned peat samples (Fig. 6.16). It was found that FBA significantly ($P < 0.05$) decreased NH_4^+-N and NO_3^--N concentrations in soil extracts from the non-incubated column. The lime treatment had no consistent effect on the transformation of N in the peat soil (Fig. 6.16).

6.4 CONCLUSION

As in the field trial reported in Chapter 5, neither surface applied FBA nor lime has a significant effect on decreasing subsurface soil acidity as measured by pH change in the peat soil.

Most of the Ca applied in FBA and lime was retained in the surface of the peat column. The Ca^{2+} released by FBA dissolution, however, does move down to subsurface soil much faster than that of lime and displaces more acidity from the peat column, although this has little effect on subsurface soil pH. Higher Ca^{2+} concentrations in subsurface soil are likely to remove some soil acidity constraints on pasture root growth through the antagonistic relationship between Ca^{2+} and H^+ ions.

The sulphate from gypsum in FBA is readily dissolved and leached from the column, but the sulphate from ettringite in FBA is able to resist the leaching loss from acid peat soil and remains mostly in the surface of the peat soil. This implies that FBA may provide a method of increasing S fertiliser efficiency in peat soil.

In contrast to the lime treatment, however, FBA caused significant leaching of native soil exchangeable K^+. Therefore, potassium fertiliser application is recommended when acid peat soil is treated with FBA.

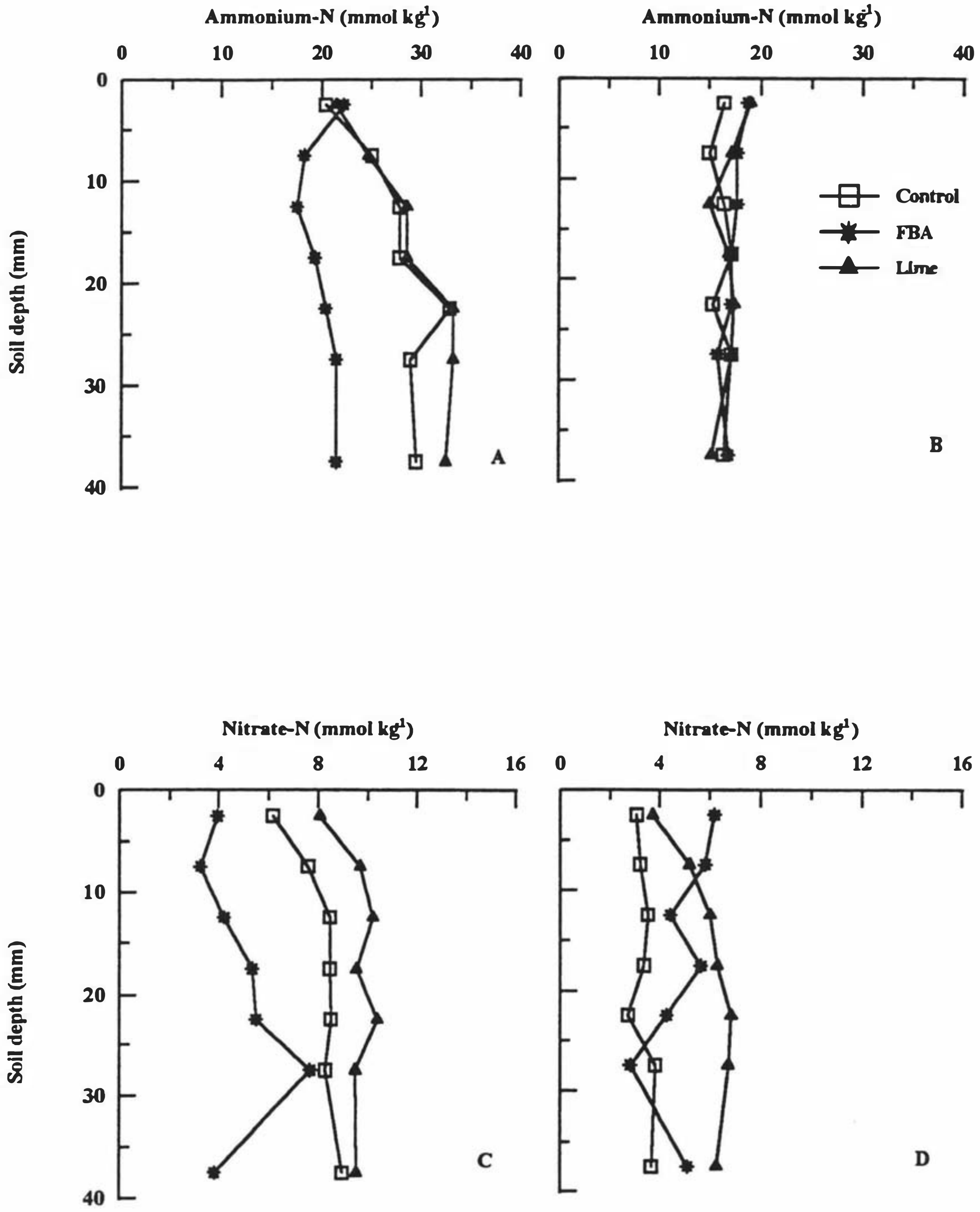


Fig. 6.16 The soluble inorganic nitrogen concentration in 10% HCl extracts of the sectioned samples from peat soil columns, after treatment with FBA or lime (A, ammonium in Experiment 1, B, ammonium Experiment 2, C, nitrate in Experiment 1 and D, nitrate in Experiment 2).

Chapter 7

Amelioration of subsurface soil acidity by surface incorporated gypsiferous by-products. I. Soil solution chemistry

7.1 INTRODUCTION

7.1.1 Subsurface soil acidity

In many parts of the world, acid conditions in subsurface soil horizons are increasingly placing major constraints on successful production of many important crop species (Sumner 1994). Toxic levels of Al^{3+}, or insufficient Ca^{2+}, in the acidic horizons markedly restrict or even entirely prevent root proliferation and subsequent exploitation of water and nutrients in subsurface soil (Foy 1992; McCray & Sumner 1990; Sumner et al. 1991). In New Zealand, Parfitt et al. (1994) found that some pasture soil pH values were lowest at 100 - 200 mm depth and they suggested that this may be the zone where acidification is most likely to occur. Manoharan et al. (1995) and Loganathan & Hedley (1996) reported similar observations.

It is a common practice to surface apply, or incorporate lime into the plough layer, to raise the pH of acid soil and neutralise and precipitate plant-toxic Al. Downward movement of lime ($CaCO_3$) is extremely slow, and therefore subsurface soil acidity in most soils cannot be rectified rapidly by conventional incorporation of lime into the plough layer (Brown & Munsell 1939; Farina & Channon 1988b). This is primarily because, after neutralisation of soil acid by HCO_3^- from $CaCO_3$, no mobile anions remain in soil solution to enable Ca^{2+} transport to subsurface soil horizons with percolating rain water. In addition, in soils with a pH dependent variable charge, liming often increases the negative charge (Bolan et al. 1988) resulting in increased retention of the added Ca^{2+}. Mixing lime into subsurface soil is the most effective procedure, but is commonly not economically feasible (Foy 1992; Sumner 1994). Therefore, practical techniques of amending acid subsurface soil from the surface are needed.

Recently, Sumner (1994) reviewed some potential methods to ameliorate subsurface soil acidity. These procedures include: continued liming of topsoils to near neutrality when using acidifying fertilisers (e.g. ammoniacal nitrogen fertilisers) (Abruna et al. 1964); incorporating lime economically in vertical bands or allowing limed topsoil to fall in slits behind modified subsoilers to create vertical zones of ameliorated soil (Coventry et al. 1987); movement of organic compounds into subsurface soil through natural leaching (Hue et al. 1986; Wright et al. 1985); and surface application or topsoil incorporation of gypsum (Shainberg et al. 1989). In addition, studies have shown that some surface applied Ca-saturated organic materials manufactured from coal (Noble et al. 1995; van der Watt et al. 1991) and some other organic materials (Liu & Hue 1996) are effective in decreasing exchangeable Al and increasing exchangeable Ca^{2+} to depth.

Many laboratory and field experiments have also shown that gypsum, including gypsiferous industrial by-products, are highly efficient in reducing the detrimental effects of subsurface soil acidity on root growth and crop yield (Farina & Channon 1988b; McLay et al. 1994a; Shainberg et al. 1989; Sumner et al. 1986). In Brazil, gypsum is now part of the official recommendation to ameliorate acidity in low-CEC soils (Oxisols) of the Cerrados region (Ritchey et al. 1995a).

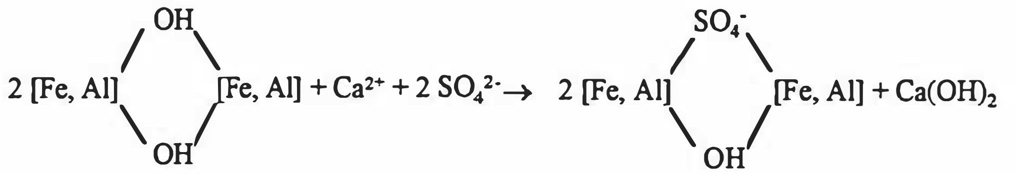
Gypsiferous by-products are increasingly being produced by industry. Increasing concerns about emissions of SO_2 from coal-fuelled plants have promoted the development of flue gas desulphurisation (FGD) technologies (Kalyoncu et al. 1995). The most common scrubbers now in use are wet limestone based, flue gas desulphurisation systems that treat flue gas after fly ash has been removed via electrostatic precipitators of baghouse systems. Wet limestone scrubbers with forced oxidation produce wallboard-quality gypsum (FGD gypsum, or FGDG) (Ritchey et al. 1995a).

Fluidised bed combustion (FBC) is a dry FGD system that is smaller in scale and in engineering requirements than wet FGD processes and requires lower capital investment. FBC is suitable for retrospective installation on existing coal-fired plants to meet the requirement of clean air legislation (Stehouwer et al. 1995a). FBC entails the simultaneous burning of injected coal and limestone (a sorbent for SO_2 absorption). The resultant fluidised bed boiler ash (FBA) contains $CaSO_4$, CaO and conventional coal combustion ash (refer Chapter 3). At present, most of FGD by-products are disposed of in landfills (Bossart & Newman 1995). Utilisation as an amendment for subsurface soil acidity would be a beneficial alternative to disposal (Ritchey et al. 1995a).

Although gypsum does not have the ability to neutralise soil acidity in the same way as limestone, when a $CaSO_4$ front is leached into subsurface soil, the ameliorative effect is due to the increased supply of Ca^{2+} and the decrease in toxic Al^{3+}. Possible mechanisms are: "self-liming effect" (Reeve & Sumner 1972), increased subsurface soil Ca^{2+} (Ritchey et al. 1995a; Shainberg et al. 1989), decreased monomeric Al saturation (Alva et al. 1991; Cronan & Grigal 1995), increasing the ionic strength of the soil solution (McLay et al. 1994b), precipitation of basic aluminium sulphate minerals (Adams & Rawajfih 1977; Hue et al. 1985), $AlSO_4^+$ ion pair formation (Kinraide & Parker 1987; McLay et al. 1994b; Noble et al. 1988) and displacement and leaching of Al^{3+} (Oates & Caldwell 1985; Ritchey et al. 1995c; Singh 1982).

7.1.2 Theory of the "self-liming effect" induced by sulphate sorption

"Self-liming effect" (Reeve & Sumner 1972) is based on the adsorbed SO_4^{2-} displacing OH^- from hydrous oxide surfaces, followed by hydrolysis and precipitation of exchangeable Al as in Equations 7.1 & 7.2 (Sumner 1993).



$$2\,[\mathrm{Fe, Al}]\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\langle\;\rangle}}[\mathrm{Fe, Al}] + \mathrm{Ca}^{2+} + 2\,\mathrm{SO_4}^{2-} \rightarrow 2\,[\mathrm{Fe, Al}]\overset{\mathrm{SO_4}^{-}}{\underset{\mathrm{OH}}{\langle\;\rangle}}[\mathrm{Fe, Al}] + \mathrm{Ca(OH)_2} \qquad \text{(Eqn. 7.1)}$$

$$2\,\mathrm{Al}^{3+} + 3\,\mathrm{Ca(OH)_2} \rightarrow 2\,\mathrm{Al(OH)_3} + 3\,\mathrm{Ca}^{2+} \qquad \text{(Eqn. 7.2)}$$

Sulphate adsorption by soils is associated primarily with Fe- and Al-oxides and allophane (Parfitt 1978). Therefore, the mineralogical composition of a soil will influence the effectiveness of gypsum as an ameliorant for subsurface soil acidity. In soils with high SO_4^{2-} adsorption, solution pH usually increases when soils are equilibrated with a SO_4^{2-} salt solution but not when treated with Cl^- or NO_3^- salt solutions (Mekaru & Uehara 1972). This occurs because SO_4^{2-} displaces OH^- either in a type of ligand exchange reaction (Rajan 1979) or by the non-specific adsorption of SO_4^{2-} causing a release of OH^- (Curtin & Syers 1990), whereas Cl^- and NO_3^- are not significantly adsorbed. The actual magnitude of the pH change, after gypsum is applied, will be dependent on the reactions between gypsum and the soil surfaces, in which Ca^{2+} exchanges with H^+ and Al^{3+} (which hydrolyses to produce H^+) and SO_4^{2-} replaces OH^- by ligand exchange. When gypsum is applied to the topsoil, a leachate saturated with Ca^{2+} and SO_4^{2-} ions will move down the soil profile continuously, resulting in repeated exposure of the subsurface soil to leachate containing high SO_4^{2-} concentrations. In such cases, it is possible to observe an increase in pH as a result of OH^- release in excess of proton dissociation. This will occur particularly when large and sustained applications of gypsum are made to soils which have large quantities of hydroxylated surfaces on sesquioxides available for ligand exchange reactions with SO_4^{2-} (Keng & Uehara 1974; Shainberg et al. 1989). Rajan (1978, 1979), working with allophanic clays, found that SO_4^{2-} adsorption released OH^- ions in a linear relationship. He proposed that on a net positive surface, SO_4^{2-} is adsorbed as a bidentate, forming a six-member ring and displacing either two aquo or OH^- ligands. On a neutral or negative surface, SO_4^{2-} is adsorbed as a monodentate, displacing one aquo or one OH^-, making the surface more negative. A similar bidentate ligand for SO_4^{2-} adsorption in Fe oxides such as goethite and amorphous ferric hydroxide was proposed by Parfitt & Smart (1978). Ritchey et al. (1980) reported increases in pH by as much as 0.8 units following gypsum treatment in a Dark Red Latosol (Typic Haplustox) in soil columns and field studies.

Most experiments evaluating gypsum amelioration of subsurface soil acidity have been conducted on single soil types (Ritchey et al. 1995a; Sumner et al. 1986) or on a number of different soils which have similar chemical properties (McLay et al. 1994a; b). Little work has been carried out to compare the effect of gypsum on soils with different mineralogical properties, though such differences may significantly influence the effectiveness of gypsum use. There is also little published work on evaluating FGDG and FBA materials as amendments for subsurface soil acidity.

The objectives of this study were to examine the influence of topsoil incorporated Ca containing materials (FGDG, FBA and lime) on the subsurface soil acidity and soil solution chemistry of two soils with different mineralogical properties. The effect of the gypsiferous materials on the subsequent plant root growth will be discussed in the next chapter (refer Chapter 8).

7.2 MATERIALS AND METHODS

7.2.1 Selection of soils and preliminary evaluation of their response to gypsiferous material application

7.2.1.1 Leaching test

The objective of this leaching experiment was to select two acid soils with different clay mineralogies such that one was likely to "self-lime" by SO_4^{2-} sorption and the other was not. The soils were to be used in a subsequent leaching and glasshouse experiment.

7.2.1.2 Collection and characterisation of soil materials

In July 1994, samples were collected from the 0-100 mm layers of the following six soils: a yellow-brown earth from Kiwitea, or the Kiwitea silt loam (Typic Orthic Brown soil) (Hewitt 1992), a yellow-brown earth from Mt Bruce, or the Mt Bruce loam (Typic Orthic Brown soil) (Hewitt 1992), a yellow-brown earth from Okaihau, or the Okaihau silt loam (Typic Nodular Oxidic Soil) (Hewitt 1992), a yellow-brown earth from Raglan, or the Kaawa clay loam (Typic Yellow Ultic Soil) (Hewitt 1992), a yellow-grey earth from Tokomaru, or the Tokomaru silt loam (Argillic-fragic Perch-gley Pallic Soil) (Hewitt 1992), and a yellow-brown loam from Patua, or the Patua loam (Acidic Orthic Allophanic Soil) (Hewitt 1992).

The selection was conducted by observing the soil pH, Ca^{2+} and SO_4^{2-} adsorption changes after the soils were leached with diluted $CaSO_4$, $Ca(NO_3)_2$ and $Ca(OH)_2$ solutions. Each soil (15 g) was packed into a glass tube (150 × 20 mm) with small amounts of glass wool in the bottom to support the soil. Replicate soil columns were leached with either diluted (0.02 mol dm^{-3}) $CaSO_4$, $Ca(NO_3)_2$ or $Ca(OH)_2$ solution. After leaching, the soil in each tube was mixed before pH_{water} determination (soil:solution = 1:2.5). An extra set of replicate $CaSO_4$ leached soils were evenly sectioned into three parts for 0.01 M $Ca(H_2PO_4)_2$ extractable SO_4^{2-} measurement. SO_4^{2-}-S concentration was determined by a bismuth sulphide precipitation method on an autoanalyser (CSIRO Division of Forest Research Method, No PS17). Ca^{2+} concentrations in the leachates were analysed using atomic absorption spectroscopy with appropriate ionisation suppressants.

7.2.1.3 Sumner's test

A method for predicting possible responses of soils to gypsum was developed by Sumner in 1994 after we had completed our soil selection and glasshouse experiment. The two selected soils were further tested using Sumner's method, which is based on the capacity of the soil to sorb SO_4^{2-} and raise the pH through displacement of hydroxyl groups. The procedure is: Take 3 × 10 g of soil in three separate centrifuge tubes and add 25 ml of either 0.005 M $CaSO_4$, 0.005 M $CaCl_2$ or distilled water and shake overnight. Centrifuge and measure electrical conductivity (EC) and pH values in the supernatant solution. Calculate ΔpH ($CaSO_4$ - $CaCl_2$) and gypsum sorbed from the EC values. If the pH in $CaSO_4$ is higher than the pH in $CaCl_2$ solution and the EC of 0.005 M $CaSO_4$ is lower than before (indicating sorption of Ca^{2+} and SO_4^{2-}), then this may be a gypsum responsive soil (Sumner 1994).

7.2.2 Effect of topsoil incorporated amendments on subsurface soil acidity and soil solution chemistry - a column leaching experiment

7.2.2.1 Soil and amendment sources

Based on the preliminary soil selection experiments, Kaawa yellow-brown earth (the Kaawa soil) (Typic Hapludult, USDA 1994) and Patua yellow-brown loam (the Patua soil) (Typic Hapludand, USDA 1994) were chosen for this study. Soil materials were collected from depth intervals of 0-10 cm (topsoil) and 20-30 cm (subsurface soil). The air-dry soils were passed through a 3 mm sieve before being packed into sections of PVC pipe. Selected soil properties are shown in Table 7.1.

Table 7.1 Selected properties of soils used.

Soil Name[1]	Texture	pH	Olsen-P ($\mu g\ g^{-1}$)	SO_4-S ($\mu g\ g^{-1}$)	Mineralogy[2]	Exchangeable Cations (cmol $_{(+)}$ kg^{-1}) K	Ca	Mg	Na	CEC[3]
Patua (A)	Sand loam	5.2	7	14	A	0.30	0.18	0.32	0.1	26
Patua (B)	Sand loam	5.4	2	30	A	0.14	0.19	0.05	0.1	16
Kaawa (A)	Clay loam	4.6	20	32	S, K, Q	1.27	7.78	3.52	0.3	45
Kaawa (B)	Clay loam	4.7	3	27	S, K, Q	0.93	4.06	3.58	0.2	34

[1] The Patua soil, Typic Hapludand; the Kaawa soil, Typic Hapludult; A. 0-100 mm; B. 200-300 mm.
[2] Clay mineralogy. A, allophane; S, smectite, K, kandite, Q, quartz.
[3] Exchangeable cation capacity, determined by the ammonium acetate method.

Three Ca containing materials, FBA, FGDG and lime, were used as amendments. The slaked FBA (NZDC FBA) was from the New Zealand Dairy Corporation's Anchor Products Ltd, Te Awamutu Factory. It is an alkaline material (27.1% moisture, pH_{water} 12.4, 19.3% Ca, 4.9% S and 37.8% $CaCO_3$ equivalence). Detailed chemical and physical properties of NZDC FBA are described in Chapter 3 and by Wang et al. (1995). FGDG was from the Florida Phosphate Industry, USA. The FGDG contains 99.7% gypsum, 23.2% Ca, 18.6% S and < 0.1% $CaCO_3$ with a $pH_{water} = 7.0$ (Bolan et al. 1991). The commercial agricultural lime contains 94.1% $CaCO_3$ (37.6% Ca).

7.2.2.2 Soil column preparation for leaching and glasshouse experiments

A soil profile was reconstructed by packing with 2/3 (volume) of subsurface soil (370 g) followed by 1/3 topsoil (140 g) mixed with the amendments in a cylindrical column composed of three PVC pipes (Fig. 7.1). Acid washed sand (291 g) was mixed into the Kaawa subsurface soil to increase its macropore volume to improve drainage. The column was composed of one 70 mm length section of PVC pipe (top one) joined to two 50 mm length pipe sections (internal diameter 75 mm). Each section of the soil was wetted to 80% of field capacity before the column was assembled. The PVC pipes were joined by brown sticky tape. Top soil was separated from subsurface soil by a polyster

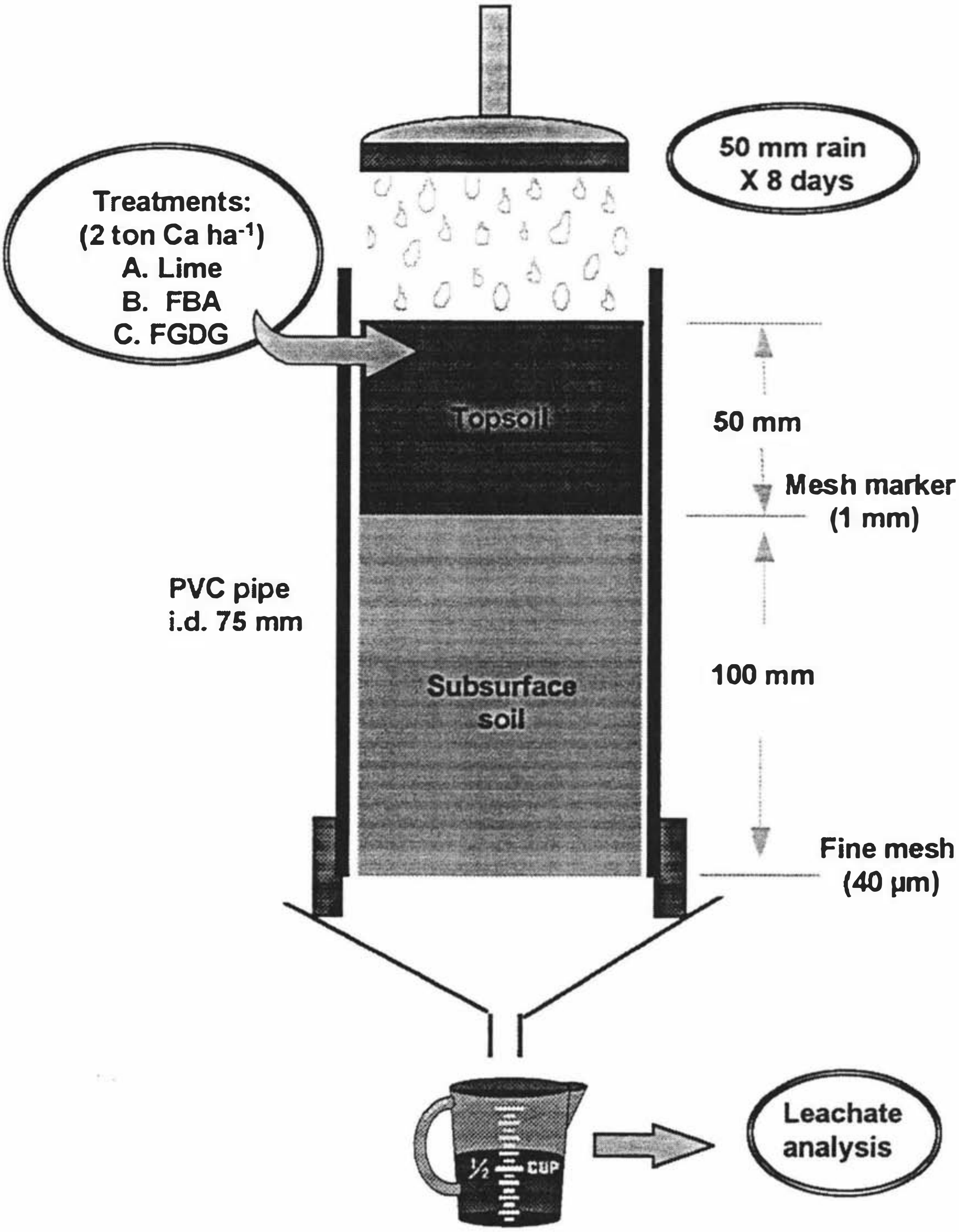


Fig. 7.1 Diagram of reconstructed soil column used for leaching (Chapter 7) and glasshouse (Chapter 8) studies.

mesh marker (1 mm pore-size, Fig. 7.1). The bottom of the soil column was wrapped with a piece of fine nylon mesh (40 µm) and a pipe joint to support the soil. A factorial design comparing the various amendment treatments (three amendments, five treatments, two soils) was applied to the soil columns. The five treatments included:

1. Control treatment: no amendment addition;
2. Lime 1 treatment: incorporation of 2.35 g lime in the topsoil;
3. FBA treatment: incorporation of 4.58 g FBA into the topsoil;
4. FGDG treatment: incorporation of 3.81 g FGDG into the topsoil;
5. Lime 2 treatment: incorporation of lime into both the top and subsurface soil.

The topsoils of all the treated columns received the same Ca equivalent of 5000 kg ha^{-1} $CaCO_3$. In the Lime 2 treatments, the topsoils received 2.35 g lime. According to the measurement of soil pH buffering capacity using NaOH (Bolan et al. 1986a), sufficient lime was incorporated into the subsurface soils to raise the subsurface soil pH to over 6.5, that is, 2.35 g and 6.38 g lime column^{-1} were applied to Patua and Kaawa subsurface soils, respectively. All the treatments were replicated five times and were leached as described below, prior to sowing lucerne seeds.

7.2.2.3 Column leaching and leachate analysis

To simulate the effect of 400 mm of winter rainfall, each treated soil column was leached with 50 mm water (222 ml) daily for eight days. The experiment was completed within a short time mainly to overcome the problems associated with nitrogen mineralisation which may affect leachate analysis. Drainage from each column (leachate) was collected daily: a total leachate volume of 400 mm or 1776 ml was collected. During leaching the temperature was maintained at 20 - 22°C. Electrical conductivity (EC) and pH of all leachate samples were measured immediately after the leachate was collected and the volume of each leachate was recorded. A subsample of about 50 ml leachate was kept in a sealed plastic bottle and put in a fridge. After the measurement of Cl^-, the leachate was acidified to 0.1 M H^+ with concentrated HCl and stored for chemical analysis. Ca^{2+}, Mg^{2+}, K^+ and Na^+ concentrations in leachate were analysed by atomic absorption/emission spectrophotometry. Cl^- concentrations were measured using a

Tecator Flow Injection analyser following the method of Florence and Farrer (1971) and SO_4^{2-}-S concentrations by the same method as in Section 7.2.1.2.

When leaching was completed, the wet and dry weight of each column was recorded to estimate the total soil pore volume. Three of the five replicate columns of each treatment were moved to the glasshouse for growing lucerne. The two remaining replicate columns were sliced into eight sections using a microtome with the intervals (from top) of 0-25, 25-45, 45-50, 50-55, 55-65, 65-85, 85-105 and 105-150 mm. The sectioned soils were kept moist separately in plastics bags and stored in a cool room (< 4°C) for soil solution extraction and chemical analysis.

7.2.2.4 Soil solution analysis

Each moist soil section was wetted to field capacity and the wetted soil was incubated overnight at 20-22°C. Soil solutions were extracted from the incubated soil by centrifugation at 10,000 rpm for 30 minutes (Reynolds 1984). Soil solution pH was measured immediately after extraction and then the solution was filtered through syringes fitted with 0.45 µm membrane filters (Millipore). Soil solution Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^- and SO_4^{2-} concentrations were determined using the same methods as for leachate. The pyrocatechol violet (PCV) method was employed to determine aluminium concentration in soil solution and the labile monomeric Al was determined using a reaction time of 60 seconds (Kerven et al. 1989) and total monomeric Al using a reaction time of 240 seconds (Seip et al. 1984).

All statistical analysis were conducted using the SAS software package.

7.3 RESULTS AND DISCUSSION

7.3.1 Selection of soils and preliminary evaluation of their response to gypsiferous material application

7.3.1.1 Leaching experiment

Leachate analysis showed that for the Patua loam and the Okaihau silt loam, there was no difference between pHs of the $Ca(OH)_2$ and $CaSO_4$ leachates, but the pH of these two leachates was much higher than that obtained from $Ca(NO_3)_2$ (Table 7.2). This indicated that the "self-liming effect" generated by SO_4^{2-} adsorption (Sumner 1993) caused the pH increase of the $CaSO_4$ leachates. However, for the Kaawa, Kiwitea and Mt Bruce soils the pH of the $Ca(OH)_2$ leachate was much higher than that of $CaSO_4$ leachate, and there were relatively small differences between the pHs of the $CaSO_4$ and $Ca(NO_3)_2$ leachates (Table 7.2). Thus "self-liming" (Reeve & Sumner 1972) in these soils had little effect on leachate pH. Further the "salt effect", created by Ca^{2+} exchange with adsorbed H^+ and Al^{3+}, decreased pH and dominated the $CaSO_4$ system's pH reaction. This pH decrease through Ca^{2+} exchange was more marked when the soil was leached with $Ca(NO_3)_2$ solution. The leachate pH of these latter soils was greatly increased by $Ca(OH)_2$, which also indicated that these soils are dominated by permanently charged minerals with low pH buffering capacity (Uehara & Gillman 1981; Sumner 1994). In soils dominated by permanently charged minerals, neutralisation of acid, does not result in an increased cation exchange capacity and thus exchangeable cation movement is less constrained than in a soil dominated by pH dependent charge (Sumner 1994).

Table 7.2 Soil and leachate analysis for selection.

Measurement	Soils[1]					
	Patua (YBL)	Okaihau (YBE)	Kiwitea (YBE)	Mt Bruce (YBE)	Tokomaru (YGE)	Kaawa (YBE)
Original soil pH_{water}	4.40	4.50	5.77	5.66	5.26	4.5
Mean leachate pH						
pH (A) of $CaSO_4$ leachate	4.69	4.41	5.60	4.98	5.54	4.14
pH (B) of $Ca(NO_3)_2$ leachate	4.39	4.03	5.37	4.76	4.97	4.05
pH (C) of $Ca(OH)_2$ leachate	4.78	4.49	6.23	5.93	5.98	5.53
ΔpH (A-B)	0.30	0.38	0.27	0.22	0.57	0.09
ΔpH (C-A)	0.09	0.09	0.63	0.95	0.44	1.39
Cumulative Ca in leachate (mmol Ca)						
Ca_{Total} (A) in $CaSO_4$ leachate	0.71	0.74	0.71	0.67	0.85	0.53
Ca_{Total} (B) in $Ca(NO_3)_2$ leachate	0.92	0.85	0.77	0.83	0.89	0.63
ΔCa_{Total} (B-A)	0.21	0.11	0.07	0.15	0.04	0.10
Sulphur retention in $CaSO_4$ leached soil (μmol S g^{-1})						
Top 1/3 section	91.5	45.4	12.7	21.8	11.4	18.7
Middle 1/3 section	76.9	27.4	13.2	21.8	10.4	18.7
Bottom 1/3 section	41.6	16.9	12.1	21.8	10.4	18.7

[1] YBL, yellow-brown loam; YBE, yellow-brown earth; YGE, yellow-grey earth.

The concentration of Ca^{2+} in the leachate from the $CaSO_4$ treated column was significantly lower than that from the $Ca(NO_3)_2$ treated column of the Patua soil. Differences between the Ca concentrations in the $CaSO_4$ and $Ca(NO_3)_2$ leachates were lower for the other soils (Table 7.2). This implied that in the Patua soil, the specific adsorption of SO_4^{2-} induced higher pH and increased the negative charge on the clay surfaces, which consequently increased the CEC (Chang & Thomas 1963). Unlike the other soils the Patua soil retained nearly all of the added SO_4^{2-}. The distribution of SO_4^{2-} in the sections of the Patua soil decreased with depth, showing strong SO_4^{2-} sorption. This also occurred to a lesser extent in the Okaihau soil. In the other soils, SO_4^{2-}-S sorption was more evenly spread over all depths (Table 7.2). This suggested the adsorption sites of the other soils were near saturation. Due to their similarly low original soil pH and contrasting SO_4^{2-} sorption properties ("self-liming"), the Patua and Kaawa soils were removed from columns for further pH tests.

The tests showed that there were large differences in soil ΔpH between the Patua soil and the Kaawa soil after being leached with $CaSO_4$ and $Ca(NO_3)_2$. ΔpH (pH_{water} difference between $CaSO_4$ leached soil and untreated soil) of the Patua soil was +0.37 pH units whereas the Kaawa soil was -0.58 pH units. This indicated that $CaSO_4$ treatment reduced the acidity in the Patua soil but increased acidity in the Kaawa soil. Furthermore, the difference in pH_{water} between $CaSO_4$ leached soil and $Ca(NO_3)_2$ leached soil of the Patua soil was +0.19 whereas that of the Kaawa soil was +0.12. All these results indicate that the Patua soil may respond to gypsiferous material as an amendment for subsurface soil acidity while the Kaawa soil was less likely to respond to gypsum application. Therefore, the Kaawa soil and the Patua soil were selected for experimental work to evaluate FBA and FGDG.

7.3.1.2 Sumner's test

The soil pH in 0.005 M $CaSO_4$ for both the Patua soil and the Kaawa soil was higher than that in 0.005 M $CaCl_2$. The ΔpH (pH in 0.005 M $CaSO_4$ - pH in 0.005 M $CaCl_2$) of the Patua soil was 0.59 pH units and it was much greater than that of the Kaawa soil (ΔpH 0.12). Instead of calculating the gypsum sorption from the EC values as suggested by Sumner (1994) we used the ΔEC ([EC of soil extract treated with 0.005 M $CaSO_4$ / EC of original 0.005 M $CaSO_4$] × 100%) as an indicator of Ca^{2+} and SO_4^{2-} sorption. The ΔEC of the Patua soil was 46% which was much lower than that of the Kaawa soil (82%). This indicated that considerable amounts of Ca^{2+} and SO_4^{2-} had been adsorbed by the Patua soil. According to the criteria suggested by Sumner (1994), the Patua soil in this study would be expected to respond positively to the application of gypsiferous materials but the Kaawa soil may not. This confirmed our preliminary selection of soils to perform a column leaching experiment.

7.3.2 Effect of topsoil incorporated amendments on subsurface soil acidity chemistry - a column leaching experiment

7.3.2.1 Leachate electrical conductivity (EC) and pH

The solute components and their concentrations in the leachates from the different columns depend on the composition and solubility of the amendments applied to the soil surface and the extent of their reaction with the soil during their passage through the column. The extent of sorption, exchange and neutralisation reactions depends partly on the soil chemical properties and the velocity of the solute through soil pores. Differences in EC and pH of leachates of treated and untreated columns indicate the extent of movement through the column of solute from the surface amendments. In both the Patua and Kaawa soil columns, the topsoil incorporated FGDG and FBA treatments, and the Lime 2 treatment (lime being mixed into soil throughout the column) significantly ($P < 0.05$) increased leachate EC (Fig. 7.2). The FGDG treatment caused the greatest increase whereas the Lime 1 treatment had no effect. The higher leachate EC values from the amended columns were caused not only from the soluble components of the amendments (refer Section 7.2.2.1) but from the exchangeable ions which were displaced from soil particle surfaces. In general, SO_4^{2-} and Ca^{2+} ions accounted for the main electrolytes in leachate from the FGDG treated columns, whereas SO_4^{2-}, Ca^{2+}, Cl^-, K^+, Na^+, etc. contributed to the EC of the FBA treatment (refer later discussion). As FGDG contains only $CaSO_4.2H_2O$ and the Patua soil is low in exchangeable ions, linear regression analysis revealed that the leachate EC from the FGDG treated the Patua soil columns were very well correlated with SO_4^{2-} and Ca^{2+} concentrations (Equations 7.3 & 7.4) in leachates. However, the Kaawa soil contained relatively large amounts of exchangeable cations and anions (Table 7.2) and the leachate EC in the FGDG treatment was not as strongly correlated with SO_4^{2-} and Ca^{2+} concentrations (Equations 7.5 & 7.6).

The Patua soil: $EC = 195.5 + 133.5\,(SO_4^{2-}\text{-}S)$, $R^2 = 0.99$ (Eqn. 7.3)

$EC = 323.5 + 129.9\,(Ca^{2+})$ $R^2 = 0.92$ (Eqn. 7.4)

The Kaawa soil: $EC = 564.5 + 119.3\,(SO_4^{2-}\text{-}S)$ $R^2 = 0.60$ (Eqn. 7.5)

$EC = 135.1 + 328.4\,(Ca^{2+})$ $R^2 = 0.89$ (Eqn. 7.6)

Higher leachate EC values reflect higher soil solution ionic strengths (Gillman & Bell 1978; Sposito 1989). An increase of ionic strength in soil solution caused by gypsum application has been shown to decrease the Al^{3+} activity (Ritchie 1989) and subsequently reduce the Al^{3+} toxicity (McLay et al. 1994b).

As expected, the Lime 2 treatment (thorough mixing of lime through both soil layers) greatly elevated leachate pH whereas the Lime 1 treatment had no effect on pH due to the slow movement of base down the soil column (Fig. 7.3).

After collecting 150 mm (approximately 2 column pore volumes) the leachate pH of the FGDG and FBA treatments of both the Patua and Kaawa soils did not increase as in the control, Lime 1 and Lime 2 treatments. This difference occurred probably because the large amounts of Ca^{2+} ions dissolved from gypsum are highly mobile with companion SO_4^{2-} ions and they would have exchanged with and displaced the H^+ or Al^{3+} from the exchange sites into solution. This would result in a “front” of low pH solution moving with the Ca^{2+} and SO_4^{2-} front and leachate pH is lower than that of the untreated control. Leachate pH of the FGDG treatment from the Kaawa soil column was about 2 units less than that of the control treatment (Fig. 7.3B).

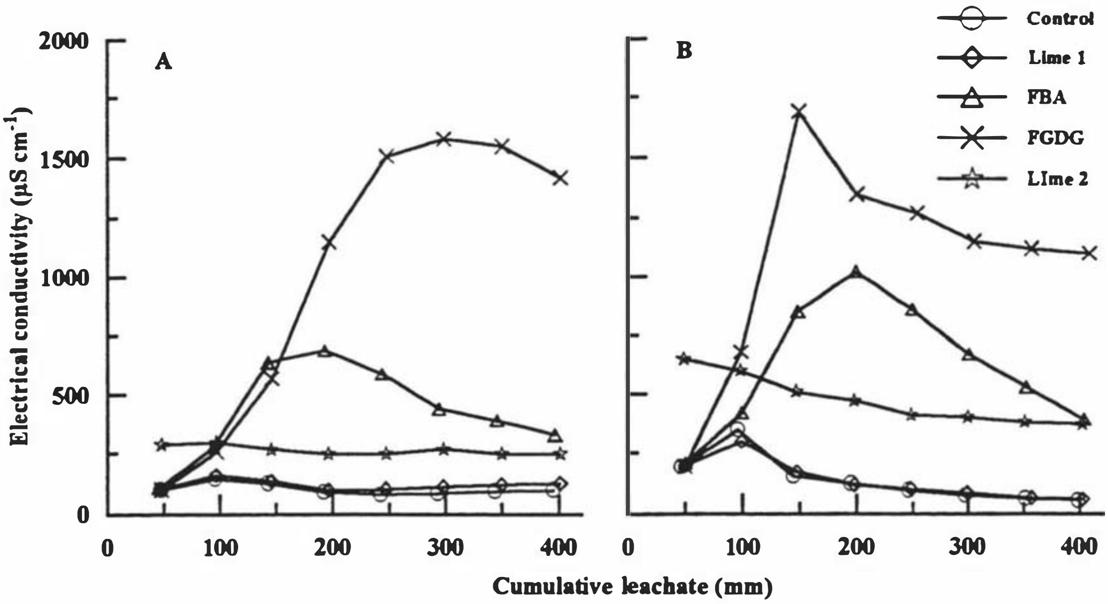


Fig. 7.2 The electrical conductivity of leachates collected (after daily leaching with 50 mm water) from columns of A, the Patua loam and B, the Kaawa clay loam, treated with lime or gypsiferous materials.

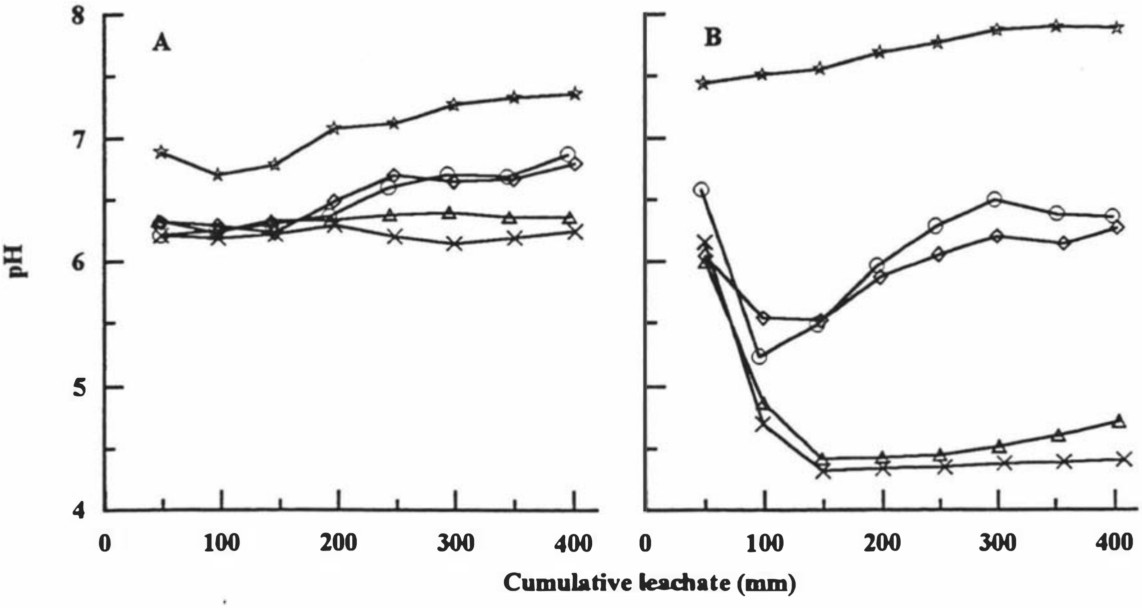


Fig. 7.3 The pH of the leachates collected (after daily leaching with 50 mm water) from columns of A, the Patua loam and B, the Kaawa clay loam, treated with lime or gypsiferous materials.

7.3.2.2 Soil solution pH and monomeric aluminium

Aluminium toxicity is the most important growth-limiting factor for plants in most acidic soils (Foy 1974; Kamprath & Foy 1985). Conventional tests for Al toxicity in soil, such as soil pH and salt extractable Al are not useful in predicting Al toxicity problems in various soils (Adams & Lund 1966; Wright 1989). Soil solution analysis has become a more popular practice, because it provides more accurate information (Bruce et al. 1988). The inorganic monomeric forms of Al (or labile monomeric Al) have been found to be the toxic forms limiting plant growth (Barcelo et al. 1996; Blamey et al. 1983) and the labile monomeric Al usually increases with a decrease in soil pH (Foy 1974, 1992). Measurement of soil solution pH and inorganic monomeric Al represent direct methods for evaluating the effectiveness of soil amendments on amelioration of soil acidity.

FBA significantly increased soil solution pH both in the top and subsurface of the Patua soils ($P < 0.01$). Although FGDG had little effect on the soil solution pH of the top layer, it increased the soil solution pH from the subsurface soil sections significantly ($P < 0.01$), which could be attributed to the "self-liming" effect. Lime increased the soil solution pH only where it was incorporated with the soil, that is, when lime was mixed with the topsoil only (Lime 1), it had little effect on the subsurface soil (Fig. 7.4A). In the Kaawa soil, although topsoil mixed lime and FBA treatments increased topsoil pH they had little effect on the subsurface soil acidity (Fig. 7.4B). FGDG treatment of the Kaawa soil slightly reduced the soil solution pH in both topsoil and subsurface soil relative to the untreated control (Fig. 7.4B). This reflects acid (H^+) displacement through $Al^{3+}(H^+)/Ca^{2+}$ exchange exceeding the acid (H^+) neutralisation. This is similar to the results obtained from a Hororata stony silt loam (Dystrochrept) by Black & Cameron (1984) who found that gypsum treatment increased subsurface soil exchangeable Ca^{2+} but soil pH was decreased.

The labile monomeric Al concentration in soil solution decreased with the increase in soil solution pH. In the Patua soil, the labile monomeric Al concentration was consistently high in the untreated control (8 - 64 μmol Al dm^{-3}, Fig. 7.5) which corresponded to the low soil solution pH ($pH < 5.0$, Fig. 7.4). FGDG treatment slightly raised soil solution Al in the topsoil layer but reduced it significantly in the subsurface sections ($P < 0.01$, Fig. 7.5A) where the pH of the soil solution was raised to > 5.5 (Fig. 7.4A). This pH increase was due to the OH^- release from the clay mineral surface into soil solution induced by SO_4^{2-} adsorption (Equations 7.1 & 7.2). The FBA treatment significantly reduced Al concentration throughout the Patua soil column ($P < 0.01$, Fig. 7.5A), because the topsoil acidity was neutralised by $Ca(OH)_2$ and $CaCO_3$ in FBA, and the subsurface soil acidity in the column was overcome by "self-liming effect" caused by downward movement of gypsum component from FBA. The topsoil incorporated lime (Lime 1) had little influence on subsurface soil Al concentration, which was consistent with its lack of effect on soil solution pH.

In contrast, in the Kaawa soil, the FGDG treatment significantly increased the labile monomeric Al concentration in soil solution of both top and subsurface layers ($P < 0.01$, Fig. 7.5B). Similar to the small response of subsurface soil pH to the treatment, the soil solution Al concentration of the subsurface soil in the Kaawa soil column was little affected by the top incorporated FBA and lime (Fig. 7.5B). Unlike the Patua soil, in which allophane is the dominant clay mineral, the clay in the Kaawa soil is dominated by permanently charged smectite (Table 7.2), and the extent of the ligand exchange between OH^- and SO_4^{2-} in the Kaawa soil will be small since it mainly takes place in soils with hydrous oxides or allophane components as the dominant clay mineral (Parfitt & Smart 1978; Rajan 1978). Therefore, lack of "self-liming effect" in the FGDG and FBA treatments of the Kaawa soil columns was expected. On the other hand, the "salt effect", in which the cations from soluble salts displace exchangeable H^+ and Al^{3+} from soil particle surface into soil solution, appears to dominate the chemical process in the FGDG treated Kaawa soil column, which resulted in the lower soil solution pH (Fig. 7.4B) and much higher labile monomeric Al concentration in soil solution of the FGDG treatment than in other treatments (Fig. 7.5B).

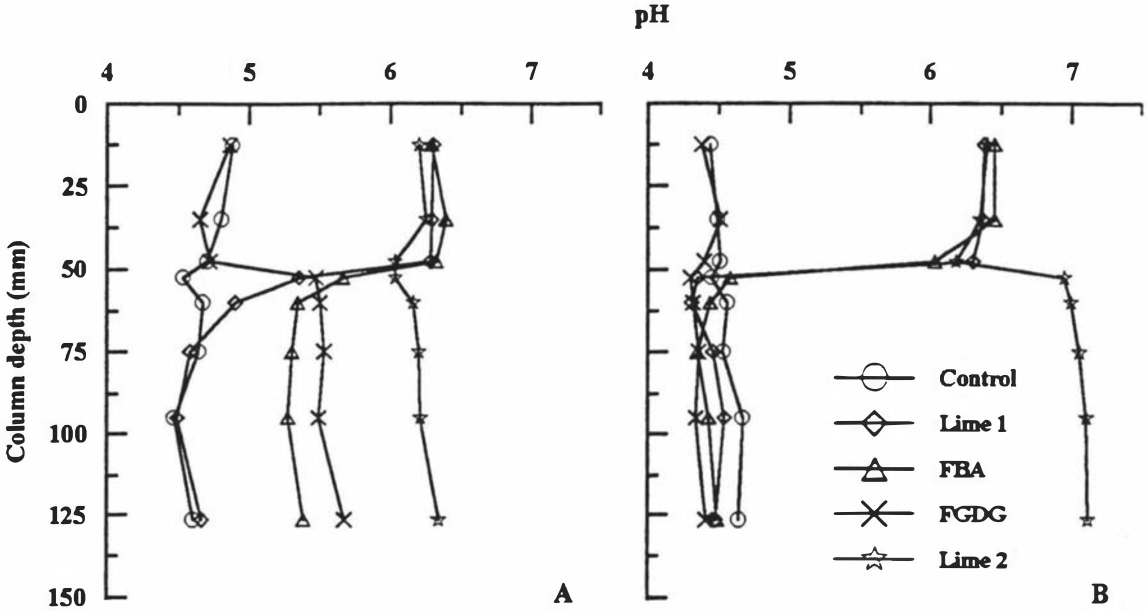


Fig. 7.4 The pH in soil solutions of the sectioned samples from leached columns of A, the Patua loam and B, the Kaawa clay loam, after treatment with lime or gypsiferous materials.

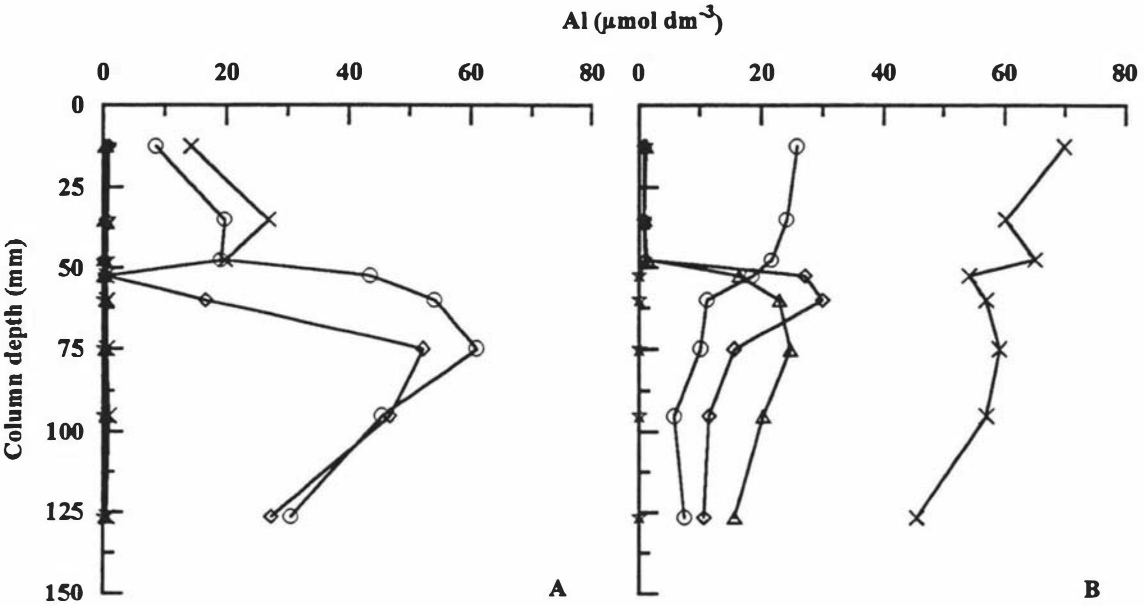


Fig. 7.5 The concentration of labile monomeric Al in soil solutions of the sectioned samples from leached columns of A, the Patua loam and B, the Kaawa clay loam, after treatment with lime or gypsiferous materials.

7.3.2.3. Sulphate

Sulphate in leachate

As discussed in Section 7.1.2, in $CaSO_4$ containing materials (FBA and FGDG), sulphate can play a very important role in amelioration of subsurface soil acidity. Therefore, the effectiveness of using a gypsiferous material as a subsurface soil amendment largely depends on the movement and sorption pattern of SO_4^{2-} in the soil profile. In the FGDG treated columns, the first 150 mm of leachate (approximately 2 column pore volumes) removed small amounts of SO_4^{2-}, whereas 400 mm (five column pore volumes) of continuous leaching removed 39 - 50% of the applied SO_4^{2-} from the Patua soil and 35-45% from the Kaawa soil, respectively (Fig. 7.6). After leaching with about 250 mm water (approximately 3.2 column pore volumes), SO_4^{2-} concentrations in leachate from the Kaawa soil columns decreased markedly while that from the Patua soil columns remained consistently high, which resulted in the large amounts of SO_4^{2-} being removed from the Patua soil columns. Similar results were obtained from the FBA treatment though the SO_4^{2-} concentration in leachate was much lower due to the lower SO_4^{2-} content in FBA and some of the FBA-SO_4^{2-} was present as less soluble ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$, refer Chapter 3).

The distribution of SO_4^{2-} in leachate implied that in the Patua soil, the initial adsorption of SO_4^{2-} was more rapid than in the Kaawa soil. It appeared that the adsorption of SO_4^{2-} to the Patua soil was similar to that observed for the adsorption of SO_4^{2-} on pure hydrous oxides and allophane (Rajan 1978, 1979). In a similar manner the adsorbed SO_4^{2-} in the Patua soil could be readily removed by repeated leaching with water, which agreed with the observations by Sanders & Tinker (1975), Johnson & Henderson (1979). The distribution of soil solution SO_4^{2-} in the FGDG treatment of the Patua soil reflected the leaching of SO_4^{2-} in the column, that is, most of the SO_4^{2-} moved to the lower part of the column (Fig. 7.7A). The significant increase of soil solution pH (Fig. 7.4A) due to initial SO_4^{2-} adsorption may also partly contribute to the higher leaching loss of SO_4^{2-} from the FGDG treatment of the Patua soil because it has been found that liming the Patua soil will significantly reduce its SO_4^{2-} adsorption (Marsh et al. 1987).

In contrast, in the Kaawa soil, SO_4^{2-} concentrations in several initial leachates from the FGDG treatment increased rapidly and then decreased quickly (Fig. 7.6B). Formation of $AlSO_4^+$ (Ajwa & Tabatabai 1995) and consequently its adsorption by the dominant negative charge of the soil colloids, and Ca^{2+} induced SO_4^{2-} adsorption (Bolan et al. 1993) may be a possible mechanism to explain the high retention of SO_4^{2-} in the Kaawa soil (refer later discussion on CEC and Ca^{2+} exchange). That more SO_4^{2-} remained in the FGDG treatment of the Kaawa soil may also be caused by the formation of Al hydroxy sulfate minerals, such as basaluminite and alunite (Adams and Rawajfih, 1977; Hue et al., 1985). Whereas the SO_4^{2-} carrying treatments, FBA and FGDG significantly ($P < 0.05$) increased the SO_4^{2-} concentration in leachates, the lime treatments had little influence on the leachate SO_4^{2-} concentration, although the Lime 2 treatment in the Patua soil slightly increased leachate SO_4^{2-}. This increase may be due to the high pH inducing sulphate desorption (Curtin & Syers 1990; Marsh et al. 1987) and enhanced mineralisation of organic S (Bolan et al. 1988).

Sulphate in soil solution

Besides leachate, SO_4^{2-} concentrations in soil solution of the subsurface section were also significantly raised by FGDG application ($P < 0.01$). The soil solution SO_4^{2-} concentration in the topsoil of the FGDG treatment of the Patua soil was very low (< 0.7 mmol dm^{-3}) and most of the SO_4^{2-} was retained in the subsurface soil where the SO_4^{2-} concentration increased with depth (Fig. 7.7A). The FBA treatment greatly increased soil solution SO_4^{2-} concentrations in the topsoils of both the Patua soil and the Kaawa soil because of the slow release SO_4^{2-}-S from ettringite in FBA (refer Chapter 3). The FBA treatment also increased the SO_4^{2-} concentration in soil solution of subsurface layers in both soils. The Lime 1 treatment had no influence on the SO_4^{2-} concentration in soil solution (Fig. 7.7). The Lime 2 treatment increased the soil solution SO_4^{2-} concentration of the Kaawa soil and it agreed with the results reported by Bolan et al. (1986a) who found that soil adsorption of SO_4^{2-} decreases with liming. Although it has been reported

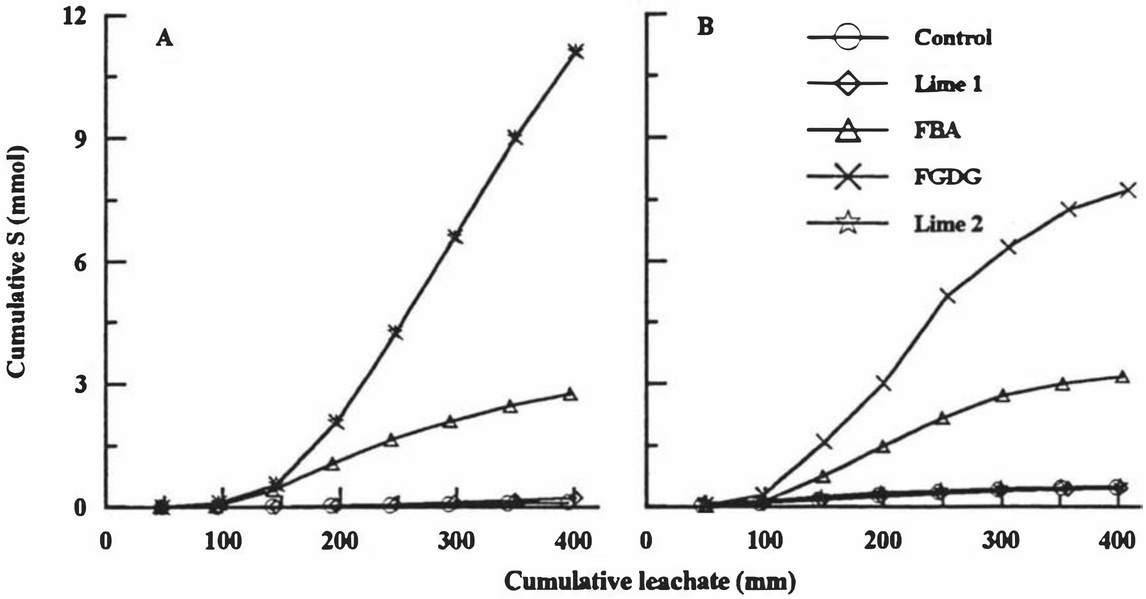


Fig. 7.6 The sulphate concentration in leachates collected (after daily leaching with 50 mm water) from columns of A, the Patua loam and B, the Kaawa clay loam, treated with lime or gypsiferous materials.

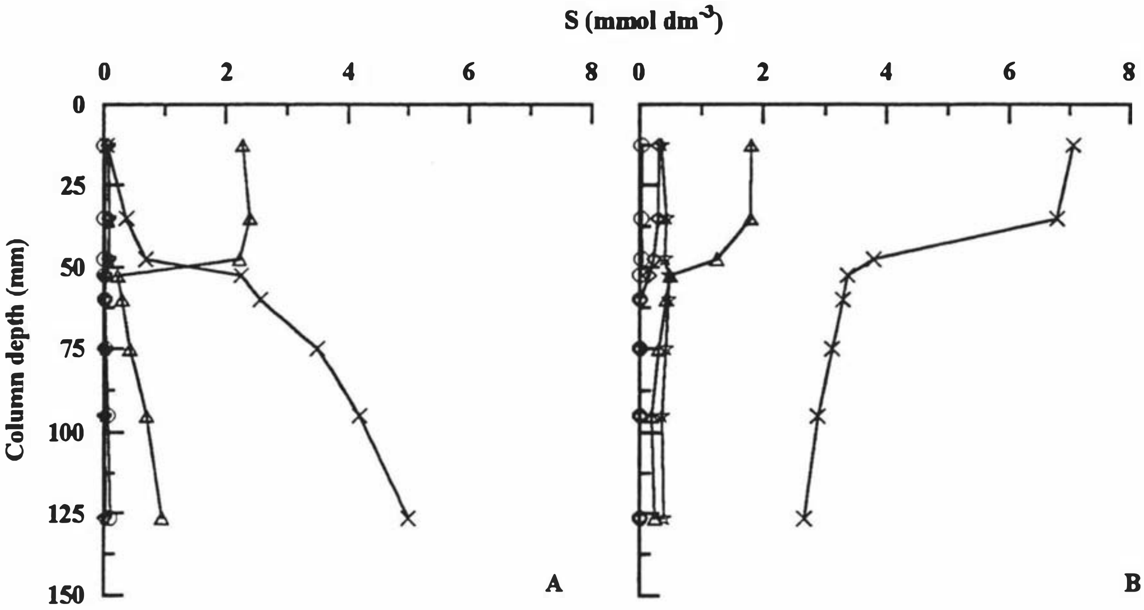


Fig. 7.7 The sulphate concentration in soil solutions of the sectioned samples from leached columns of A, the Patua loam and B, the Kaawa clay loam, after treatment with lime or gypsiferous materials.

that liming the Patua subsurface soil greatly reduced SO_4^{2-} adsorption (Marsh et al. 1987), the Lime 2 treatment had no effect on soil solution SO_4^{2-} in the Patua soil, because most of the native exchangeable SO_4^{2-} in the Patua soil was removed by leaching (Fig. 7.7A).

The lower cumulative concentration of SO_4^{2-} in leachate from the FGDG treatment of the Kaawa soil than that in the Patua soil was also reflected in the soil solution analysis (Fig. 7.6). The soil solution SO_4^{2-} concentrations in the FGDG treatment of the Kaawa soil column were much higher than that in the Patua soil, especially in the topsoil sections (Fig. 7.7). This may be caused partly by the high concentration of exchangeable monomeric Al in the system (Fig. 7.5B). This allows the formation of $AlSO_4^+$ ion pairs, which could be easily adsorbed by the Kaawa soil because of its high CEC (Table 7.2), and is enhanced by the high SO_4^{2-} concentration from FGDG dissolution. According to the results calculated using MINTEQA2 speciation model (USEPA 1991), the extent of $AlSO_4^+$ formation could account for 41-43% of the total SO_4^{2-} in the system due to low soil solution pH (pH 4.3-4.5). This agreed with the results reported by Ajwa & Tabatabai (1995) who found that at low soil pH (pH ≤ 5.0), $AlSO_4^+$ is the dominant component in solution. Therefore, $AlSO_4^+$ adsorption may account for the high retention of SO_4^{2-} in the Kaawa soil column, although it may also be explained by the Ca^{2+} induced SO_4^{2-} adsorption. In this case, SO_4^{2-} adsorption increases as soil surface positive charge increases due to specific adsorption of Ca^{2+} (Bolan et al. 1993), and the formation of an ion pair as $CaSO_4^0$ which adsorbs to mineral surfaces (Bolan et al. 1993; Marcano-Martinez & McBride 1989).

7.3.2.4 Calcium

Calcium in leachate

As a main component of both lime and gypsum, calcium can ameliorate subsurface soil acidity as a nutrient source, or by increasing soil solution ionic strength, or by reducing the Ca:Al ratio in soil solution (Ritchey et al. 1995a). Ca^{2+} is also the main companion ion for SO_4^{2-} movement. The FGDG, FBA and Lime 2 treatments increased Ca^{2+} concentrations in leachate, whereas the Lime 1 treatment had no effect on Ca^{2+} leaching

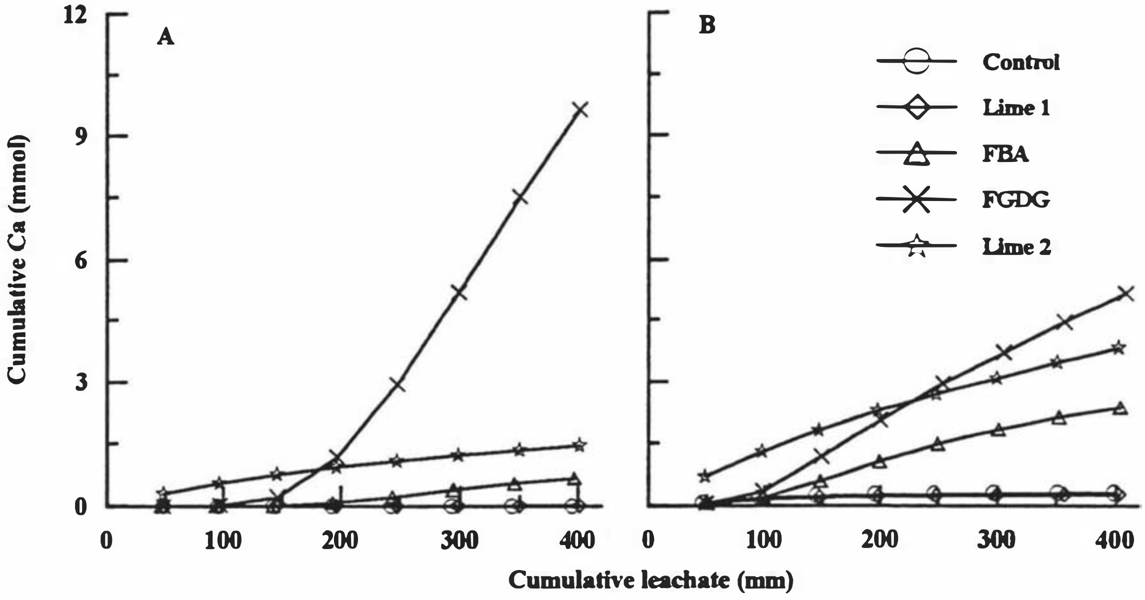


Fig. 7.8 The calcium concentration in leachates collected (after daily leaching with 50 mm water) from columns of A, the Patua loam and B, the Kaawa clay loam, treated with lime or gypsiferous materials.

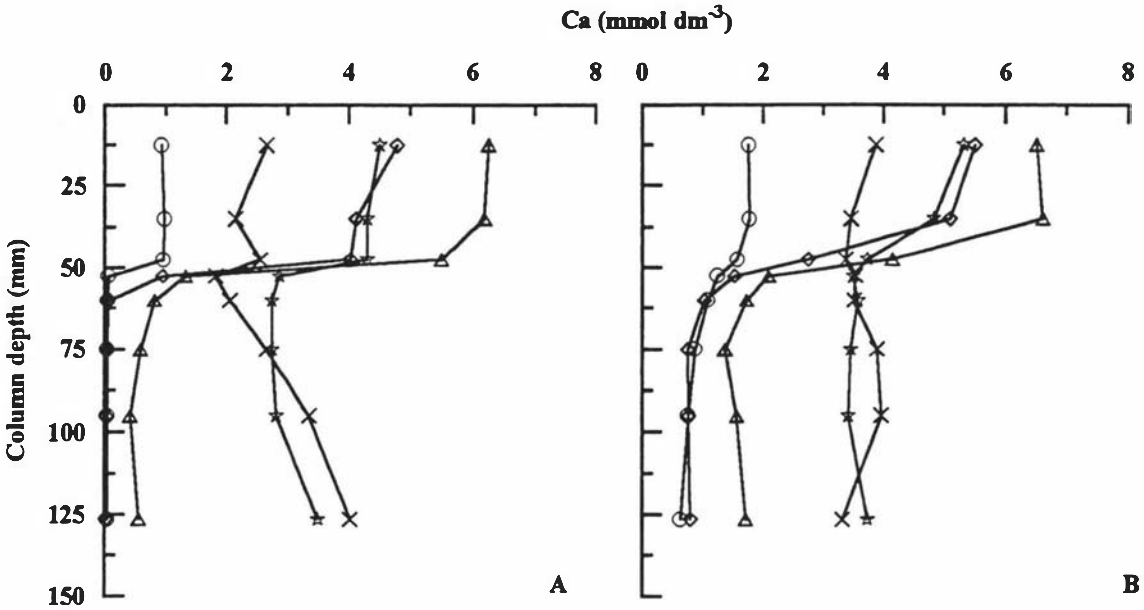


Fig. 7.9 The calcium concentration in soil solutions of the sectioned samples from leached columns of A, the Patua loam and B, the Kaawa clay loam, after treatment with lime or gypsiferous materials.

(Fig. 7.8). The effect of the FGDG and FBA treatments on Ca^{2+} concentration in leachate followed the same trend as the leachate SO_4^{2-} concentration (Fig. 7.6) because Ca^{2+} ions were the dominant cations which balanced the charge of the gypsum-SO_4^{2-} ions leached from the column. On the other hand, the cumulative Ca^{2+} of the leachate from the FGDG treatment of the Kaawa soil column was much lower than that from the Patua soil column, because of the higher CEC of the Kaawa soil (Table 7.2). It was estimated that the Ca^{2+} added through the amendments (e.g. FGDG) was likely to account for 93.6% and 46.6% of the total exchangeable base cations in the Patua and Kaawa soils, respectively. Large amounts of Ca^{2+} adsorption by soil result in increases of positive charge near the soil particle surface. This increase would subsequently increase the adsorption of SO_4^{2-} (Ajwa & Tabatabai 1995; Bolan et al. 1993). Although the FBA and FGDG treatments supplied the same amounts of Ca^{2+} to soil, Ca^{2+} concentration in leachate of the FBA treatment was much lower than that of the FGDG treatment because the composition of FGDG is nearly the same as pure gypsum, whereas FBA contains not only the soluble gypsum and portlandite but also the less soluble calcite and ettringite which greatly limit the solubility and mobility of Ca^{2+} in the FBA treatment (refer Chapter 3).

Calcium in soil solution

All the amendments significantly ($P < 0.05$) increased soil solution Ca^{2+} concentration in the whole column except for the Lime 1 treatment, which raised the Ca^{2+} concentration in the top layer only (Fig. 7.9). That the Lime 1 treatment had no effect on subsurface soil Ca^{2+} concentration agreed with the results reported by other workers (Farina & Channon 1988b; Pearson et al. 1973). Slow downward movement of lime-Ca in the soil profile was caused by the generation of negative charge in variable charge soils (Alva et al. 1990) which retained Ca^{2+} in the topsoil where lime was applied. The relatively high Ca^{2+} concentration in the subsurface soil solutions of the FBA and FGDG treatments would increase the ionic strength and the $Ca^{2+}:Al^{3+}$ ratio in the soil solution, which could reduce Al toxicity to plant roots (Cronan & Grigal 1995; McLay et al. 1994b).

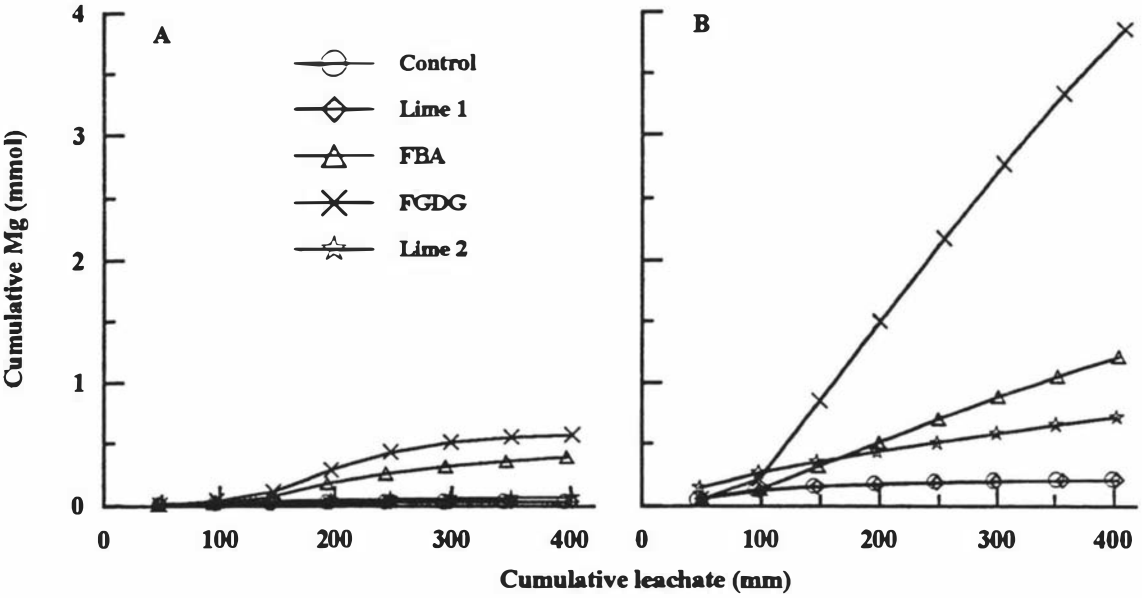


Fig. 7.10 The magnesium concentration in leachates collected (after daily leaching with 50 mm water) from columns of A, the Patua loam and B, the Kaawa clay loam, treated with lime or gypsiferous materials.

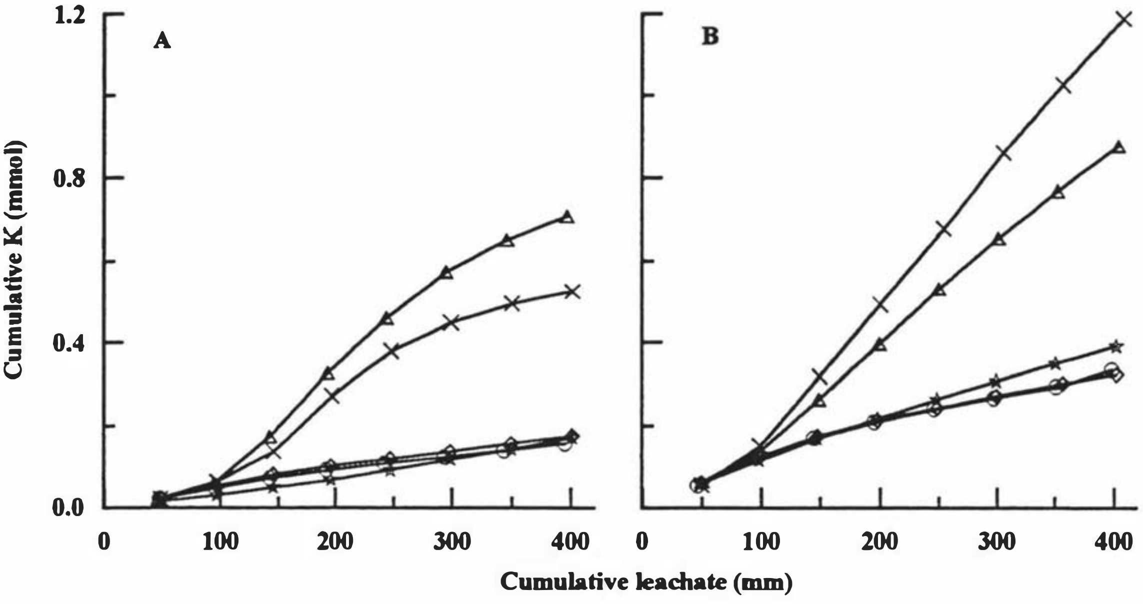


Fig. 7.11 The potassium concentration in leachates collected (after daily leaching with 50 mm water) from columns of A, the Patua loam and B, the Kaawa clay loam, treated with lime or gypsiferous materials.

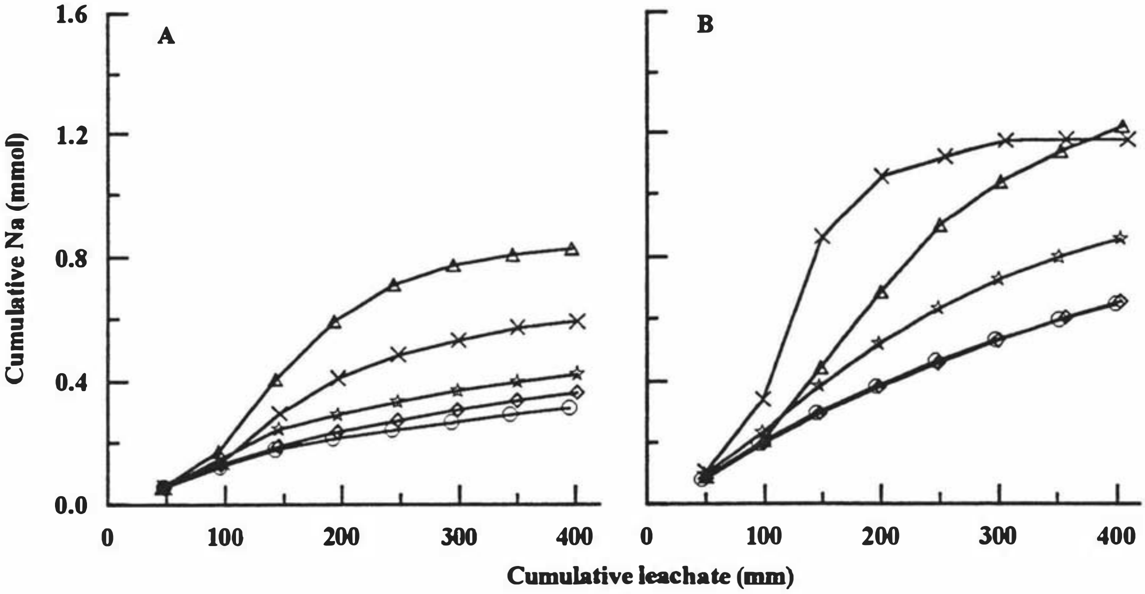


Fig. 7.12 The sodium concentration in leachates collected (after daily leaching with 50 mm water) from columns of A, the Patua loam and B, the Kaawa clay loam, treated with lime or gypsiferous materials.

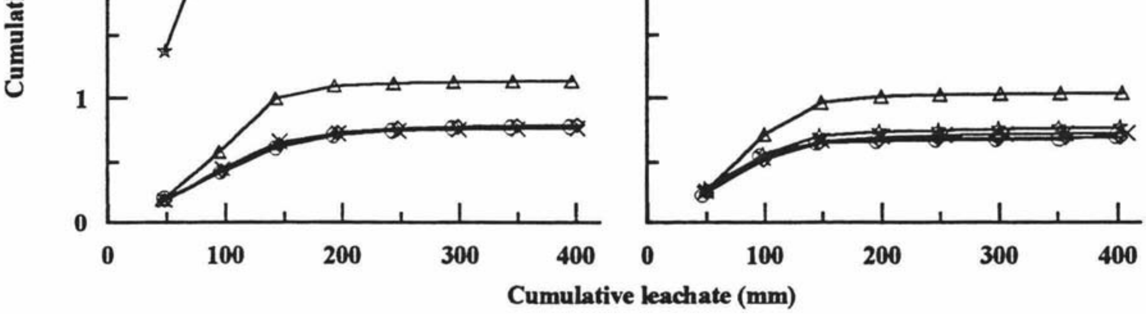


Fig. 7.13 The chlorine concentration in leachates collected (after daily leaching with 50 mm water) from columns of A, the Patua loam and B, the Kaawa clay loam, treated with lime or gypsiferous materials.

7.3.2.5 Magnesium, potassium, sodium and chloride

Leachate analysis

When large amounts of calciferous amendments are applied on to soils, they influence the sorption and movement of the native cations and anions. It was found that the FGDG and the FBA treatments significantly ($P < 0.01$) increased Mg^{2+}, K^+ and Na^+ leaching from the column (Fig. 7.10, 7.11 & 7.12). The Lime 2 treatment significantly increased leaching loss of Mg^{2+} and Na^+ ($P < 0.05$) but had little effect on K^+ leaching. The leached Mg^{2+}, K^+ and Na^+ were mainly from soil because lime and FGDG contained little soluble Mg, K and Na. Small amounts of soluble K and Na in FBA (refer Chapter 3) contributed to their higher concentration in leachate of the FBA treatment, particularly in the leachate of the Patua soil that contained very low exchangeable base cations (Table 7.2). Since the exchangeable Mg^{2+} and K^+ in the Kaawa soil was much higher than found in the Patua soil (Table 7.2), larger amounts of Mg^{2+} and K^+ were leached from the Kaawa soil columns. In comparison with Mg^{2+} and K^+, Na^+ was more mobile under leaching conditions and considerable amounts of Na^+ in the untreated control were leached out of the column (Fig. 7.12).

The effect of soil chemical properties on the composition of the leachate was also reflected in the nature of the cations balancing the SO_4^{2-} charge in the leachate. In the Patua soil, there were low levels of exchangeable cations and the leachate composition was mainly controlled by the components of the amendments, e.g. SO_4^{2-} charge in the leachate of the FGDG treatment was mainly accompanied by Ca^{2+}. However, in the Kaawa soil, the native exchangeable cations played a more important charge balancing role, e.g. SO_4^{2-} in leachate from the column was balanced by considerable amounts of Mg^{2+}, K^+, Na^+ from the soil. The percentage ratio of Ca concentration to the sum of the basic cations $[Ca^{2+}]/([Ca^{2+}]+[Mg^{2+}]+0.5[K^+]+0.5[Na^+])$ in the leachate from the FGDG treatment of the Kaawa soil was only 50% compared with 90% in the Patua soil.

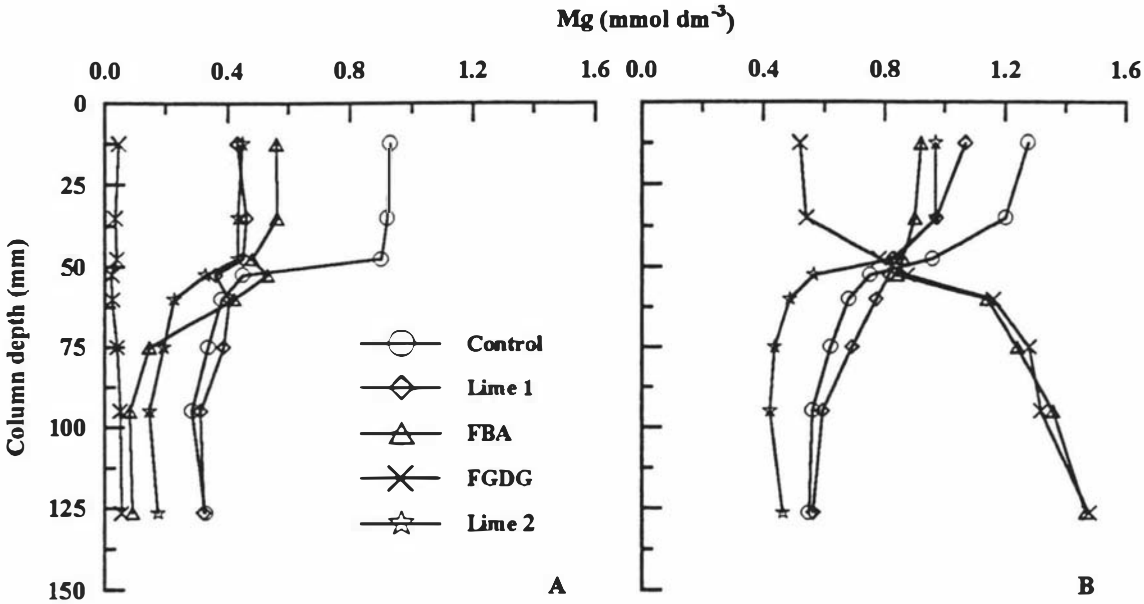


Fig. 7.14 The magnesium concentration in soil solutions of the sectioned samples from leached columns of A, the Patua loam and B, the Kaawa clay loam, after treatment with lime or gypsiferous materials.

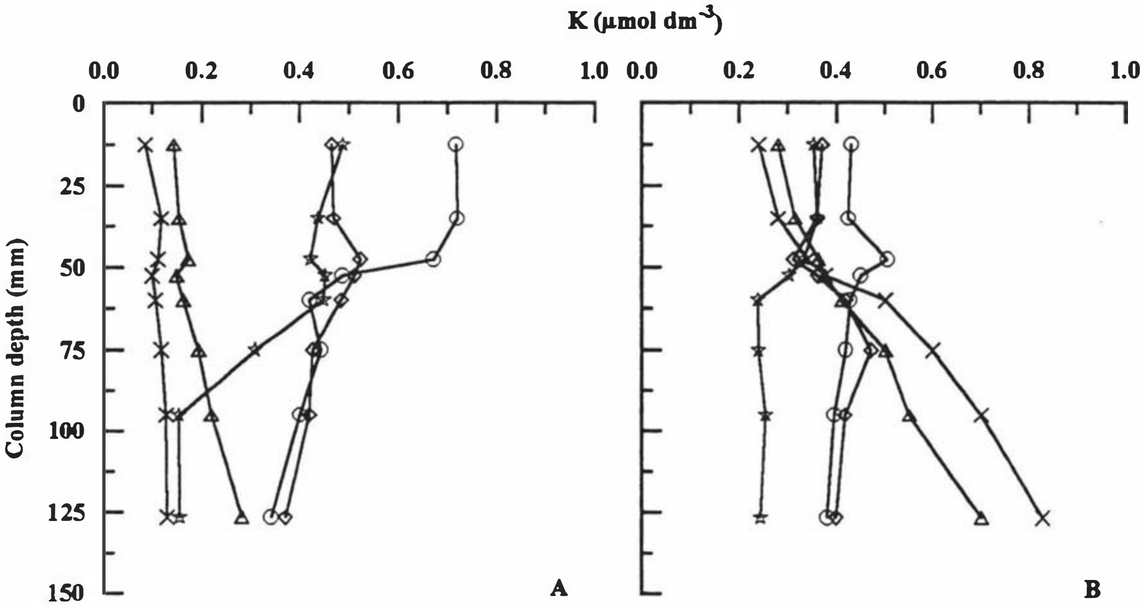


Fig. 7.15 The potassium concentration in soil solutions of the sectioned samples from leached columns of A, the Patua loam and B, the Kaawa clay loam, after treatment with lime or gypsiferous materials.

Most of the solution Cl^- was removed from the soil columns by the first 150 mm leachate (Fig. 7.13), in contrast to SO_4^{2-}, which appeared little in the first 150 mm leachate (approximately 2 column pore volumes). The Cl^- in the leachate of all the columns originated from the soil, except for the FBA treatment which significantly increased Cl^- concentration in leachate ($P < 0.05$) due to the soluble Cl in FBA (refer Chapter 3).

Soil solution analysis

Leaching greatly influenced the movement and redistribution of exchangeable ions and this was reflected in the soil solution composition of sectioned soil samples. The high concentration of Ca^{2+} released from the amendments displaced the other cations from the exchangeable sites into soil solution and these displaced cations were either removed from the column with leachate or redistributed in the lower part of the column (Fig. 7.14, 7.15 & 7.16).

All the amendments significantly ($P < 0.01$) decreased the Mg^{2+} concentration in the soil solution of the top layer sections in the Patua soil columns with the FGDG treatment causing the greatest reduction (Fig. 7.14A). The treatments of FGDG, FBA and Lime 2 also decreased soil solution Mg^{2+} concentration in subsurface soil sections. The reduction of soil solution Mg^{2+} in the FBA and FGDG treatments was caused by leaching loss, whereas the low Mg^{2+} concentration in the Lime 2 treatment was also due to lime induced Mg^{2+} retention through increased CEC (Reeve & Sumner 1970; Sumner 1994). In the Kaawa soil, the FBA and FGDG treatments greatly increased soil solution Mg^{2+} in the subsurface soil sections, whereas the fully limed treatment (the Lime 2 treatment) reduced the Mg^{2+} concentration in the subsurface soil (Fig. 7.14B). Exchange reactions between the Ca^{2+} from the amendments and the soil native Mg^{2+} during leaching drove the downward movement of Mg^{2+} in the FBA and FGDG treatments. The effect of amendments on subsurface soil solution K^+ followed patterns similar to the Mg^{2+} distribution (Fig. 7.15). Compared with the untreated control, all other treatments significantly reduced soil solution Na^+ concentration because of Ca^{2+} displacement, except for the Lime 1 treatment, which had no effect on soil solution Na^+ in subsurface

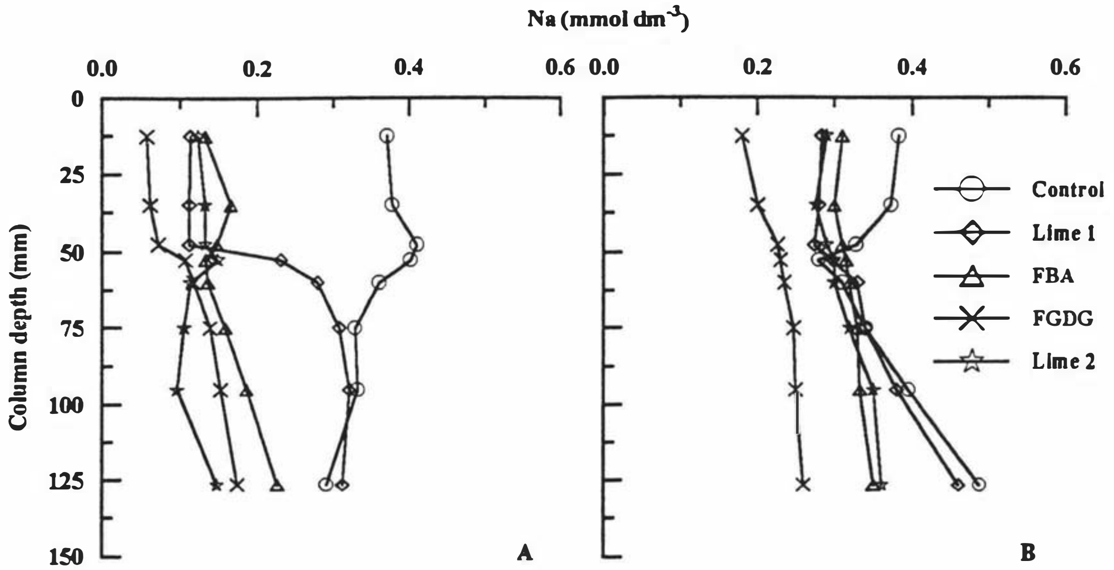


Fig. 7.16 The sodium concentration in soil solutions of the sectioned samples from leached columns of A, the Patua loam and B, the Kaawa clay loam, after treatment with lime or gypsiferous materials.

soil (Fig. 7.16). After leaching the soil solution Cl^- concentrations were very low (none of the treatments exceeding 0.1 mmol dm^{-3}, data not shown) and no significant effects on the soil solution Cl^- concentrations were detected.

The results of this study showed that the leaching loss of Mg and K from the topsoil was an important side-effect of the application of gypsiferous by-products. The leachate analysis indicated that the FGDG treatment removed most of the exchangeable soil Mg (100%) and K (56%) from the Patua soil column. In the Kaawa soil, 42% of the exchangeable Mg and 22% of the exchangeable K were leached after the FGDG treatment and most of the Mg and K was leached from the topsoil to the subsurface soil (Fig. 7.14b & 7.15B) despite the high CEC of this soil (Table 7.2). It was expected that increases in the subsurface soil solution pH of the FBA and FGDG treatments may have increased ECEC and prevented Mg^{2+} and K^+ from leaching loss (Sumner 1994), but it did not happen in the Patua soil. This may be due to the high concentration of Ca^{2+} in the soil solution, which not only displaced exchangeable Mg^{2+} and K^+ into solution but occupied the additional cation exchange sites generated by SO_4^{2-} adsorption. Therefore, in the FGDG treatments, the leaching loss (in both soils) and movement of Mg^{2+} and K^+ into subsurface soils (in the Kaawa soil) implied that application of gypsiferous material may accelerate Mg and K deficiency in soils, particularly in the topsoil. Similar results have been reported by Ritchey et al. (1980). It has been reported that Mg^{2+} can form uncharged ion pairs with SO_4^{2-} and these ion pairs are readily leached downward through the profile (Ritchey et al. 1995a). Syed-Omar & Sumner (1991) also found that when gypsum was applied to a number of Utisols it resulted in the removal of Mg from the soil profile, but no movement of K was found. Sumner (1994) concluded that the preferential movement of Mg was a frequent response to gypsum application and that the movement of K was much more dependent on the type of soil. In soils with low exchangeable Mg^{2+} and K^+, such as the Patua soil in this study, the leaching loss of Mg^{2+} and K^+ may immediately induce Mg and K deficiency in crops. Therefore, to achieve good results from using gypsiferous material as a subsurface soil acidity ameliorant, adequate levels of Mg and K must be maintained and K and Mg fertilisers should be applied when necessary. Syed-Omar & Sumner (1991) found that this can be readily achieved by applying Mg to the surface once most of the gypsum has moved out of the topsoil. The same technique may apply to K supplements.

7.3.3 Summary of mechanisms of subsurface soil acidity amelioration

In the Patua soil, it was the "self-liming effect" that caused the subsurface soil solution pHs of the FBA (pH 5.32) and FGDG (pH 5.53) treatments to be significantly ($P < 0.01$) higher than that of the control treatment (pH 4.58) (Fig. 7.4A). Subsequently the labile monomeric Al in the subsurface soil solution of the FBA and FGDG treatments was repolymerised as $Al_y(OH)_x$, decreasing solution monomer concentrations to a low level (≤ 0.53 μmol Al dm^{-3}), compared with that of the highly toxic level (Foy 1992) in the control (41.2 μmol Al dm^{-3}) and Lime 1 (33.9 μmol Al dm^{-3}) treatments (Fig. 7.5A). The Patua subsurface soil is allophane rich and the adsorption of SO_4^{2-} by allophane plays a key role in amelioration of the subsurface soil acidity through the "self-liming effect" (Rajan 1978, 1979; Sumner 1993). The pH buffering capacity measurement using NaOH (refer Section 7.2.2.2) showed that approximately 70 mmol OH^- kg^{-1} soil were required to raise the pH of the Patua subsurface soil by 1 unit. Linear regression analysis revealed that increases in the Patua subsurface soil pH was well correlated with added OH^- (R^2 = 0.991). The Lime 2 treatment (22.1 mmol $CaCO_3$ column^{-1} or 59.7 mmol $CaCO_3$ kg^{-1} subsurface soil) significantly ($P < 0.01$) increased the subsurface soil solution pH to 6.24, compared with pH 4.58 from the control treatment. Presuming the lime in the subsurface soil to be completely dissolved, it would supply 119.4 mmol OH^- kg^{-1} soil for neutralising acidity. Therefore, raising the pH of the soil solution of 1 kg of subsurface soil by 1 unit consumed 71.9 mmol OH^- from lime (119.4/(6.24-4.58)). This was very close to the calculated value (70 mmol OH^- kg^{-1}) based on the NaOH buffering capacity measurement. It was possible to calculate from the change in the subsurface soil pH that the topsoil incorporated FGDG and FBA treatments generated 66.5 (70×(5.53-4.58)) and 51.8 (70×(5.32-4.58)) mmol OH^- kg^{-1} soil (equivalent to 12.3 and 9.6 mmol $CaCO_3$ column^{-1} in 100 mm deep of subsurface soil), respectively. Considering the large amounts of SO_4^{2-} loss in the leachate (Fig. 7.6A) and the SO_4^{2-} concentration distribution increasing with the depth (Fig. 7.7A), much more OH^- generation may be expected if the subsurface soil depth in the column is increased. On the other hand, the majority of effective pasture roots are in the top 100 mm. Most of the SO_4^{2-} (approximately 50% of total applied 22.1 mmol SO_4^{2-} column^{-1}) in the FGDG treatment was leached out suggesting that the maximum "self-liming effect" (sulphate sorption) had been achieved in the 100 mm column. This may have been achieved with much less FGDG. The FBA treatment contained only 7.0 mmol SO_4^{2-} column^{-1} and whereas considerable amounts of S were either leached or retained in the topsoil (Fig. 7.7A), the treatment significantly increased subsurface soil pH and eliminated the Al toxicity problem in subsurface soil.

By contrast, in the Kaawa soil, which is dominated with permanently charged smectite, the gypsiferous by-products caused little change in the subsurface soil solution pH. For example, the FGDG treatment greatly increased the phytotoxic labile monomeric Al concentration throughout the column of the Kaawa soil (Fig. 7.5B). Instead of the "self-liming effect", the "salt effect" where Ca^{2+} ions displace H^+ and Al^{3+}, was the dominant soil reaction after the application of the gypsiferous materials to the Kaawa soil. The difference of mineralogical composition between the Patua and Kaawa soils accounts for these contrasting responses. According to the literature, so far, nearly all the positive subsurface soil acidity responses to gypsum are from the soils dominated by variable charged clay mineral types, such as Fe- and Al- oxides, allophane, kaolinite and other 1:1 type minerals (McLay et al. 1994a; Ritchey et al. 1995a; Shainberg et al. 1989). After the application of gypsiferous materials to soils dominated by permanently charged clay minerals, the dominant reaction influencing the soil solution pH is Ca^{2+} exchange for H^+ and Al^{3+}. Therefore, it is understandable that there was no positive response of subsurface soil acidity amelioration in the Kaawa soil to FGDG. This may also explain some previous negative responses to gypsum application, such as results reported by Black & Cameron (1984), and Simpson et al. (1979).

7.3.4 Effectiveness of FBA as a subsurface soil acidity ameliorant

Data from the leachate analysis indicated that about 50% of applied SO_4^{2-} in the FGDG treatment of the Patua soil (equivalent to 8.6 t ha^{-1} of gypsum application) was leached out of the columns after leaching with about 400 mm water (approximately 5 column pore volumes). Soil solution analysis also showed that the soil SO_4^{2-} retention increased greatly with depth, so that most of the remaining SO_4^{2-} was in the lower part of the column and little remained in topsoil. This fate of FGDG was supported by the expected solubility of gypsum. The solubility of gypsum is 2.41 g dm^{-3} (CRC 1971). Thus the 400 mm simulated winter drainage volume (1.58 dm^3 $column^{-1}$) for the central North Island, New Zealand was sufficient to dissolve and leach the sulphate, particularly as the dissolution of gypsum would increase considerably in the soil system due to the adsorption of Ca^{2+} and SO_4^{2-} by soil (Bolan et al. 1991b).

On the other hand, FBA significantly increased the subsurface soil solution pH, but due to the low solubility of ettringite, considerable amounts of SO_4^{2-} in the FBA treatment still remained in the topsoil layer after leaching. As discussed above, when using gypsum as a subsurface soil acidity ameliorant it is more effective when combined with lime, to overcome the topsoil acidity. The alkaline materials in FBA, such as $Ca(OH)_2$ and $CaCO_3$, can neutralise the acidity in topsoil. Therefore, the use of FBA, which contains both soluble SO_4^{2-} (gypsum) and slow-release SO_4^{2-} (ettringite), as a subsurface soil acidity ameliorant is a good alternative to lime and gypsum, particularly in the soils with acidity problems both in the top and subsurface, in which adsorbed SO_4^{2-} is readily leached.

7.4 CONCLUSIONS

The results from this study showed that both the simple leaching experiment and Sumner's test were effective at identifying soils that will respond to gypsiferous material treatment.

Top soil incorporated gypsiferous coal combustion by-products, FBA and FGDG significantly increased the subsurface soil pH and reduced the phytotoxic labile monomeric Al of allophane-rich yellow-brown loam soil, through the "self-liming effect". Neither of the above effects occurred to a significant extent on a yellow-brown earth soil, dominated by permanently charged clay minerals.

The more alkaline and slowly soluble FBA was also capable of neutralising the yellow-brown loam topsoil acidity and was a potential long term subsurface soil ameliorant. The results imply that FBA produced at Anchor Products Ltd's Te Awamutu Factory is an ideal by-product for correcting topsoil and subsurface soil acidity in yellow-brown loam soils.

When using gypsiferous materials, however, the soil available Mg and K status should be monitored to avoid a gypsum-Ca induced deficiency of these nutrients.

Chapter 8

Amelioration of subsurface soil acidity by surface incorporated gypsiferous by-products. II. Effects on root growth

8.1 INTRODUCTION

In Part I of this study (Chapter 7), the effect of topsoil incorporated lime and gypsiferous by-products (NZDC FBA and FGDG) on the amelioration of subsurface soil acidity of a yellow-brown loam soil and a yellow-brown earth soil was investigated. The results indicated that gypsiferous materials significantly increased the subsurface soil pH of a yellow-brown loam soil but had no similar effect on a yellow-brown earth soil. Therefore, in yellow-brown loam soils it may be possible to use gypsum to alleviate the constraint placed on root growth by subsurface soil acidity. However, it is difficult to predict whether the action of bases (e.g. OH^- and HCO_3^-) and the "self-liming effect" through sulphate sorption will be successful in removing the chemical constraints to root growth. This is because soil solution pH, monomeric Al, Ca^{2+} concentrations and ratios of Ca:Al as well as the nature of the dominant ion species (e.g. the presence of $AlSO_4^+$ form which is less toxic) all interact to influence root growth (refer Chapters 2 and 7 for review of this area).

Increased yields of crops grown on acid soils with surface incorporated gypsum have been attributed to increased root length density in the subsurface soil (Farina & Channon 1988b). This was due to increased Ca^{2+} levels and decreased Al levels in the subsurface soil, although the soil pH showed little change (Shainberg et al. 1989). However, in a number of cases, there has been no response of root growth in subsurface soil, or of yield, to a gypsum application (Black & Cameron 1984; Keerthisinghe et al. 1991; McLay et al. 1994a; Simpson et al. 1979; Wright et al. 1985) and a relative decrease in root growth has been observed at intermediate depths in the subsurface soil (Farina & Channon 1988b; Sumner & Carter 1988). At present there is no entirely satisfactory explanation for this effect. Ritchey et al. (1995a; b) found that mineralogy of soils and the resulting surface charge characteristics may influence reactions of gypsum and this may, therefore, vary the effectiveness of gypsum in the alleviation of subsurface soil acidity. For example, one hypothesis for an ineffective gypsum application is that, where no significant SO_4^{2-} sorption occurs in the subsurface soil, the "self-liming effect" from subsequent OH^- desorption may be absent, and therefore the gypsum induced increase in ionic strength may decrease soil solution pH and increase the level of toxic elements.

Clear evidence for the successful gypsum treatment of acidic subsurface soils often comes only from root bioassay studies (Ritchey et al. 1980, 1988) or from the success or failure of the crop growth after the gypsum treatment of field soils. Therefore, the objective of Part II of this study was to conduct a root bioassay. This was carried out by growing a low pH sensitive plant, lucerne (*Medicago sativa*. L), in a replicated set of the pretreated and leached columns from the Part I of this study (Chapter 7). Apart from lucerne root growth being pH sensitive, a legume is appropriate for the restoration of acidic soils because legume rotations are required to increase soil organic C, N and S levels which are commonly low in soils which have undergone acidification. The hypothesis was that lucerne root elongation into the treated acidic subsurface layers of two soils with different mineralogical properties would be associated with the changes in soil and solution chemistry observed in Part I (refer Section 7.3 in Chapter 7).

8.2 MATERIALS AND METHODS

8.2.1 Materials and leaching experiment

The details about the soils, soil amendments, column preparation and the leaching study have been described in detail in Section 7.2.2.

8.2.2 Effect of topsoil incorporated amendments on lucerne growth and root elongation in subsurface soil - a glasshouse experiment

After positioning the leached soil columns in the glasshouse, 20 ml of nutrient solution, which contained KH_2PO_4 85 mg, $MgSO_4.7H_2O$ 100 mg, $(NH_4)_6Mo_7O_{24}.4H_2O$ 0.05 mg, $Na_2B_4O_7.10H_2O$, $CuCl_2.2H_2O$ 3 mg and $ZnCl_2$ 3 mg, was applied to all columns.

Lucerne was chosen as the indicator plant in this experiment because it is highly susceptible to aluminium toxicity (Andrew et al. 1973). Its root growth is very sensitive to increasing amounts of exchangeable aluminium in the soil environment (Munns 1965). The cultivar 'Hunter River' has been used as an indicator plant by Simpson et al. (1973) who observed that this cultivar showed poor root penetration into acid subsurface soil (pH 5.0) in the field. On March 29, 1995, eight seeds of lucerne (cv. Hunter River) were sown in the topsoil of each column and were thinned to four plants after establishment. After two weeks the seedlings were inoculated by adding a slurry of rhizobium-peat inoculum onto surface of the column. The column was watered to 80% of field capacity. After seedling establishment (14 - 20 days), water was applied to the column only when the surface soil appeared dry and the water content in the column was about 65% of the field capacity. This was to induce a surface soil drought stress so that the roots were stimulated to penetrate into the moist subsurface soil in order to use the available water there. After eight weeks growing, plant tops were harvested and the mass of dry matter was recorded. The soil in the column was sliced into eight sections using the same technique as for leached but unplanted columns (refer Section 7.2.2.3). Roots in each section were collected manually and the length of washed-roots and dried mass were measured (Tennant 1981) and the root length density (mm cm^{-3}) was calculated. The sectioned soils were kept moist in a cool room for soil solution extraction and other chemical analysis using the same methods described as in Section 7.2.2.4.

All statistical analysis were conducted using the SAS software package.

8.3 RESULTS AND DISCUSSION

8.3.1 Effect of soil type and amendments on lucerne growth and root elongation

Irrespective of soil treatment, shoot dry weights of lucerne were considerably smaller in the lower base saturated (Table 7.2 in Chapter 7) Patua soil (average 59 mg $column^{-1}$) than in the Kaawa soil (average 225 mg $column^{-1}$) (Fig. 8.1 & Table 8.1). However, whereas soil treatment caused significant increases in the shoot dry weights and root dry weights, above those of the untreated control in the Patua soil ($P < 0.05$), there were no

Table 8.1 Effect of amendments on lucerne growth[1].

Treatment	Shoot dry weight ($mg\ pot^{-1}$)	Root dry weight in subsurface soil ($mg\ pot^{-1}$)
	The Patua soil	
Control	27a	1.4a
Lime 1	71bc	8.0a
FBA	76c	48.8b
FGDG	47b	37.8b
Lime 2	74c	10.7a
	The Kaawa soil	
Control	187a	5.9a
Lime 1	225a	8.8a
FBA	244a	17.3a
FGDG	215a	6.2a
Lime 2	255a	102.0b

[1] In a column, means with the same letter are not significantly different ($P<0.05$).

significant increases in shoot dry weights between the treatments in the Kaawa soil (Table 8.1). Only complete liming of the whole column profile (Lime 2) increased root mass in the Kaawa soil. The greatest increase in shoot dry weight in the Patua soil occurred in the FBA treatment, which was 181% higher than untreated control plots. The FGDG treatment increased shoot dry weight by 74%. All the columns received sufficient nutrients, including sulphate, therefore the shoot dry weight increases in the treated Patua soil columns were caused by liming and "self-liming effects" (refer later discussion in Section 8.3.3).

The incorporation of FBA and FGDG with topsoil significantly improved root elongation in the subsurface of the Patua soil ($P < 0.05$). Although the lime treatment significantly ($P < 0.05$) improved root growth in the top layer, it had no significant effect on root elongation in the subsurface layer of the Patua soil (Table 8.1, Fig. 8.1A & 8.2A).

In the Kaawa soil, topsoil incorporated amendments had no significant effect on root penetration into the subsurface soil (Table 8.1, Fig. 8.1B & 8.2B). Mixing lime with both topsoil and subsurface soil (the Lime 2 treatment) greatly increased root proliferation in

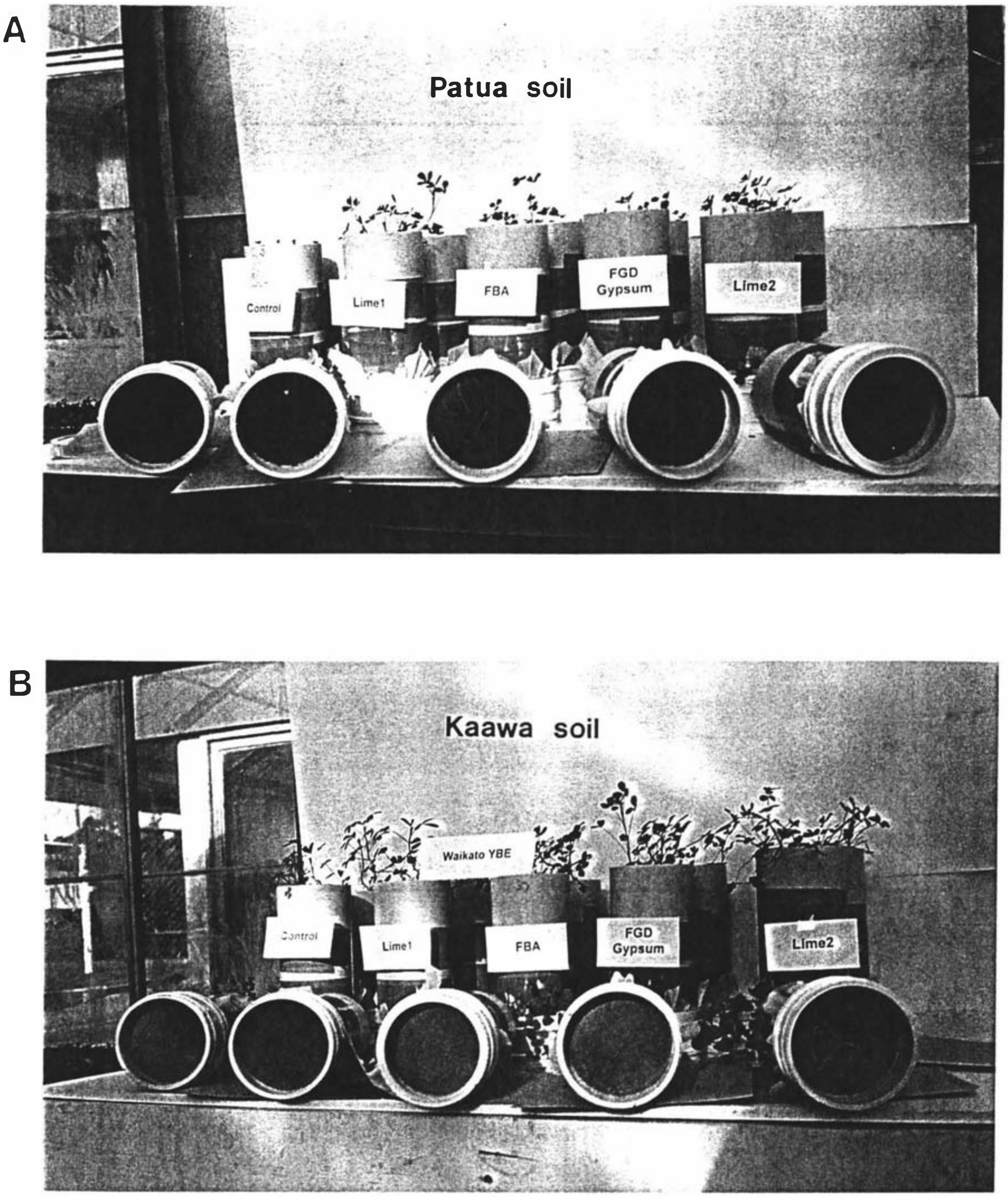


Fig. 8.1 Lucerne growth and root elongation in columns of A, the Patua soil and B, the Kaawa soil, after treatment with lime or gypsiferous materials.

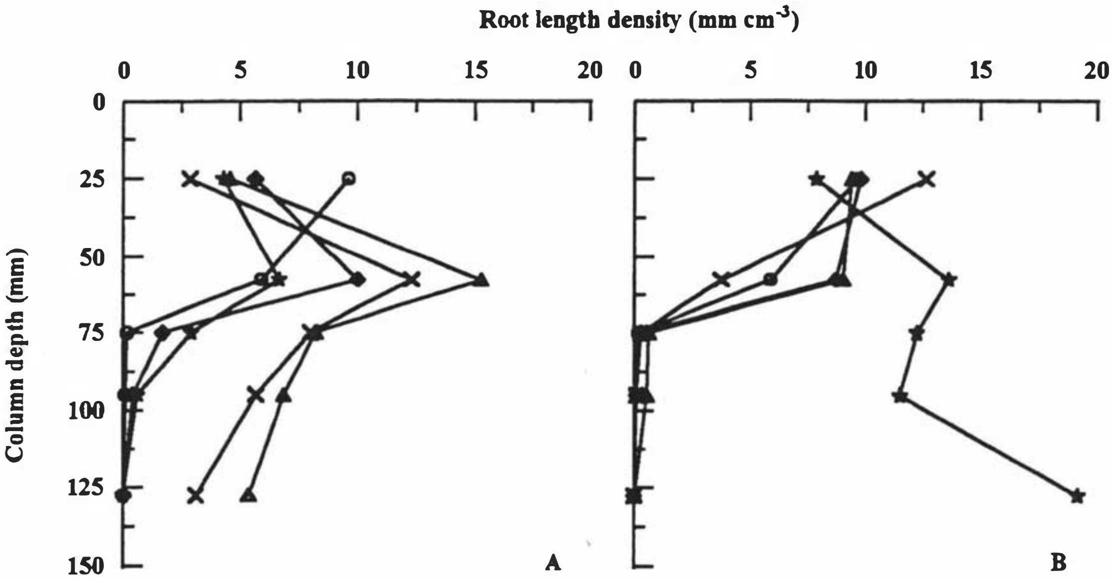


Fig. 8.2 Lucerne root distribution in soil columns of A, the Patua loam and B, the Kaawa clay loam, after treatment with lime or gypsiferous materials.

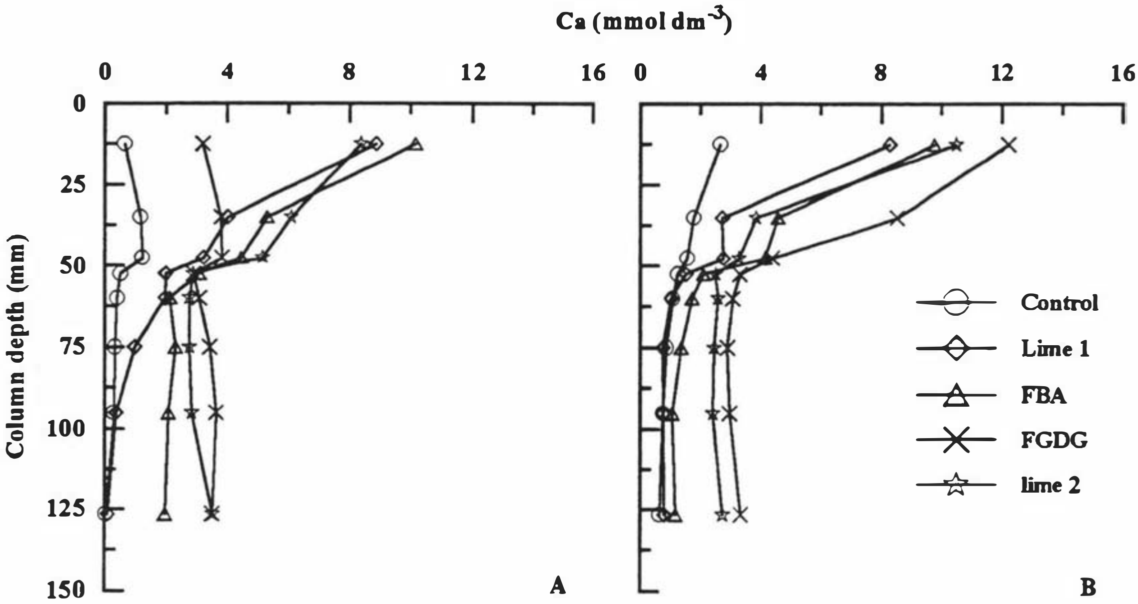


Fig. 8.3 The calcium concentration in soil solutions of the sectioned samples from leached and planted columns of A, the Patua loam and B, the Kaawa clay loam, after treatment with lime or gypsiferous materials.

the Kaawa subsurface soil but no similar response was observed in the Patua soil (Fig. 8.1 & 8.2). The lack of response of root growth to the Lime 2 treatment in the Patua soil was unexpected but may be caused by excessive Ca^{2+} concentrations in soil solution (Fig. 8.3) interfering with the other essential cation uptake by roots, because the concentration of the native soil basic cations in the Patua subsoil was extremely low (refer Table 7.2 in Chapter 7).

8.3.2 Sectioned soil solution analysis

No major differences ($P < 0.05$) in the chemical composition of the soil solutions extracted from sectioned soil were noticed between the samples before (analysed in Chapter 7) and after (this Chapter) growing lucerne, except for the very top 25 mm of topsoil, in which SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^+, Na^+ and other nutrient concentrations were substantially increased by application of nutrient solution onto the planted columns. The soil solution pH and the labile monomeric Al concentrations in all soil sections were little affected by the nutrient solution application and also lucerne growth. Data on the soil solution pH and the labile monomeric Al concentrations in the Kaawa soil, and the SO_4^{2-} and Ca^{2+} concentrations in soil solutions from planted columns of both the Patua and Kaawa soils after growing lucerne are all presented here (Fig. 8.3, 8.4 & 8.5), for comparison with the relevant measurements obtained from the treated and leached columns prior to fertilisation (refer Fig. 7.9, 7.4, 7.5 & 7.7 in Chapter 7).

8.3.3 Soil solution chemistry and plant growth

All the columns received sufficient amounts of nutrients through the nutrient solution to support optimum plant growth for the period of the experiment. Despite this, all amendments significantly increased both the lucerne shoot yield and the root penetration in the Patua soil ($P < 0.05$, Table 8.1) compared to the control treatment. Soil solution pHs in the control treatment (pH 4.5 - 4.9) were well below the level required for good growth of lucerne (Langer 1977). The FBA and FGDG treatments of the Patua soil markedly reduced the toxic labile monomeric Al concentrations in the subsurface soil. This greatly improved root penetration into the subsurface soil, compared with the untreated control. The high Al toxicity in the control treatment (Fig. 8.2A) resulted in a poorly developed root system. This would have limited the uptake of nutrients and water which probably resulted in the low shoot yield (Table 8.1).

Improved root elongation into subsurface of the Patua soil by FBA and FGDG treatments was associated with a less acidic ("self-liming") and higher base saturation environment, created by raised SO_4^{2-} and Ca^{2+} concentrations in the subsurface soil solution (Fig. 8.3 & 8.5). The relationships between the soil solution chemical properties and the lucerne root growth were further investigated by regression analysis. Root length density in the Patua subsurface soil sections is shown as an exponential function of soil solution pH (Fig. 8.6A). The Lime 2 treatment was excluded because lime was incorporated throughout column, in contrast to the other treatments. The root length density was negatively correlated with soil solution pH. When the soil solution pH was greater than 5.2, lucerne root growth in the subsurface soil was markedly enhanced. Few roots appeared in the subsurface soil when the soil solution pH was lower than 4.4. In most acid soils, research has shown (refer Chapter 2) that Al toxicity is probably more important than H^+ ion toxicity *per se* in limiting the growth of plant roots, and much of the poor root development and drought stress in subsurface soil layers may be caused by Al toxicity (Foy 1992). In this study, the concentration of labile monomeric Al in the soil solution was negatively correlated with root length density in the subsurface soil (Fig. 8.6B). As expected, the solution pH in the Patua soil was strongly negatively correlated with the labile monomeric Al concentration (Equation 8.1).

$$\text{Labile monomeric Al} = 264.50 - 48.11\text{pH}, \qquad R^2 = 0.8787 \qquad \text{(Eqn. 8.1)}$$

Although the soil solution Ca^{2+} concentration was not well correlated with root length density (Fig. 8.6C), the molar ratio of Al:Ca in the subsurface soil solution (from all the Patua soil treatments except the Lime 2 treatment), was highly negatively correlated with root growth (R^2 0.9445, Fig. 8.6D). The regression equation, explaining the relationship between the Al:Ca concentration in the subsurface soil solution and root length density, gave the most robust prediction of whether root growth will occur in these treated and untreated columns of the Patua soil. Similar uses of the ratio have been reported by Manoharan et al. (1996).

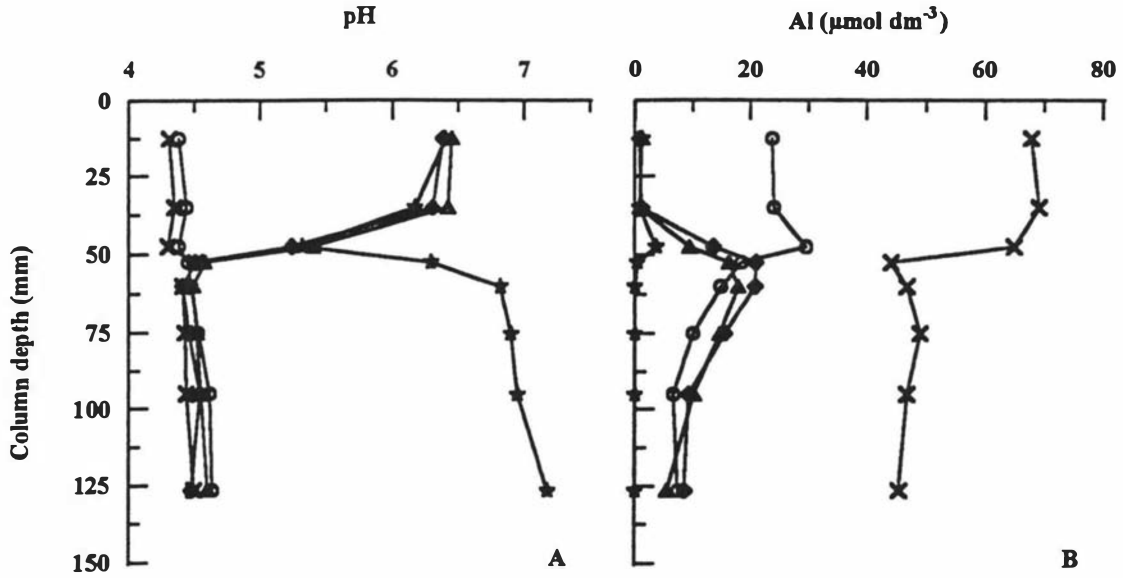


Fig. 8.4 The pH (A) and the concentration of labile monomeric Al (B) in soil solutions of the sectioned samples from leached and planted columns the Kaawa clay loam, after treatment with lime or gypsiferous materials.

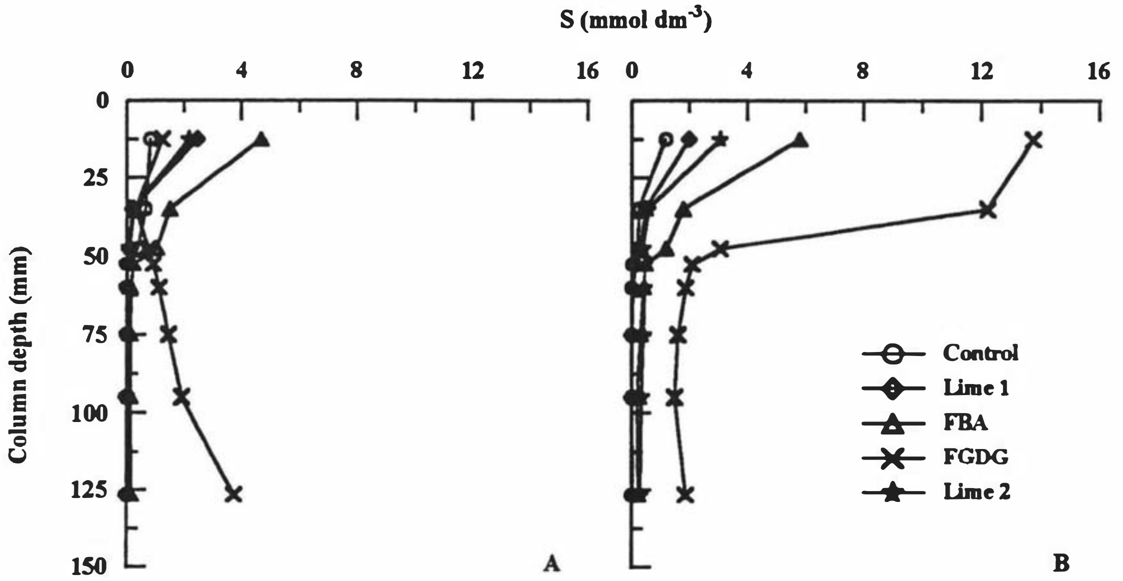


Fig. 8.5 The sulphate concentration in soil solutions of the sectioned samples from leached and planted columns of A, the Patua loam and B, the Kaawa clay loam, after treatment with lime or gypsiferous materials.

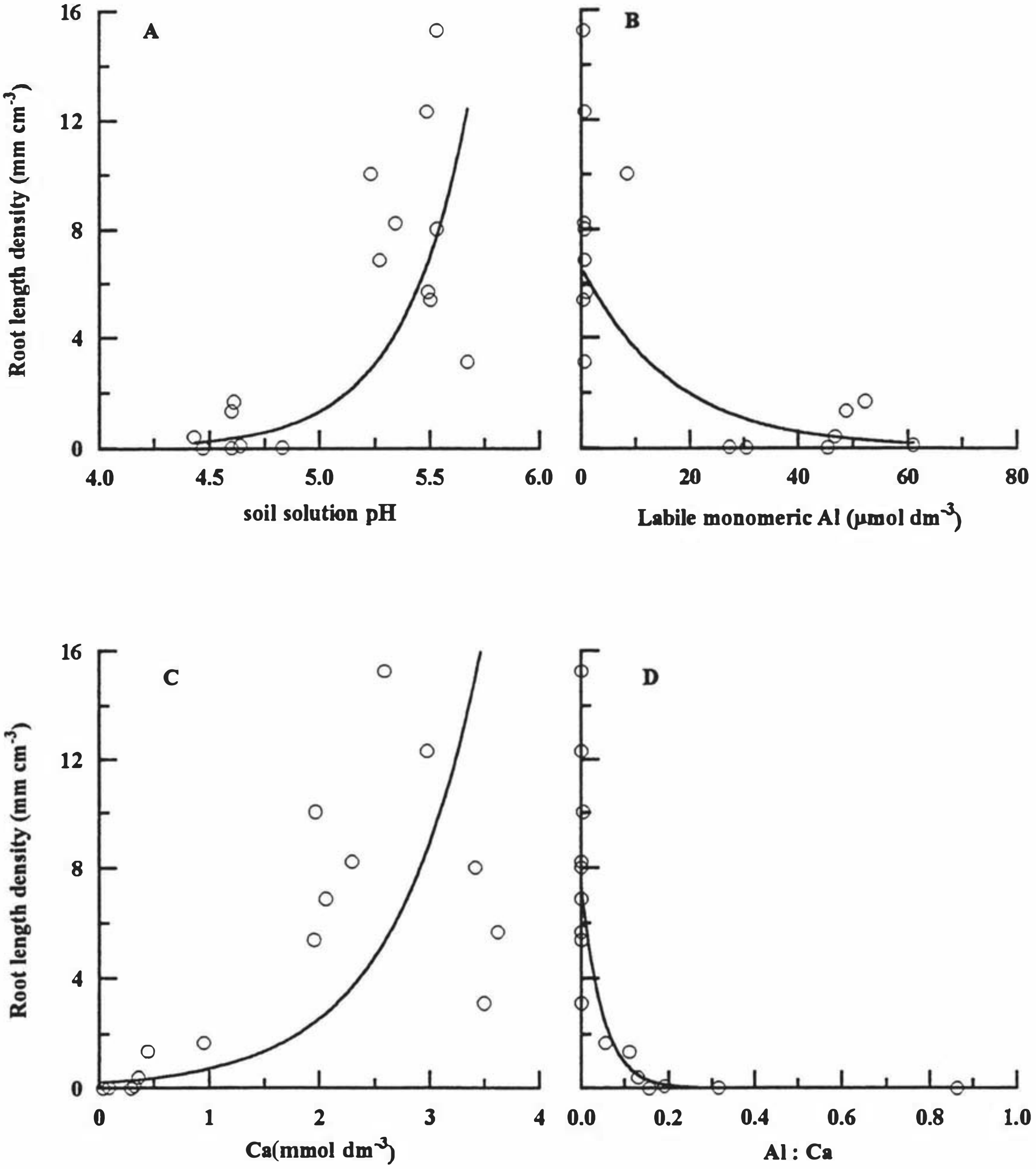


Fig. 8.6 Relationship between lucerne root length density (RLD) and A, the pH, B, the concentration of labile monomeric Al, C, the calcium concentration and D, the Al/Ca molar ratio in soil solutions of the sectioned samples from leached and planted columns of the Patua loam, after treatment with lime or gypsiferous materials. The exponential equations are as follows:

A. $RLD = (9.1750E - 8)\ \exp(3.3023(pH))$, $R^2 = 0.6784$;
B. $RLD = 6.5929\ \exp(-0.06028(Al))$, $R^2 = 0.7649$;
C. $RLD = 0.2127\ \exp(1.2476(Ca))$, $R^2 = 0.6007$;
D. $RLD = 7.3713\ \exp(-20.4763(Al:Ca))$, $R^2 = 0.9445$.

Ca is important in root growth because it stabilises the pectate in the cell wall, bridges phospholipid and proteins in the plasmalemma, serves a crucial role in the function of calmodulin, a multifunctional, Ca-dependent regulatory protein, and is important for the functioning of membrane-bound enzymes and for control of hormones (Bangerth 1979; Tomlinson 1990). Al may bind to the apoplast surface adsorption sites and interfere with the plant uptake or selectivity for nutrient ions such as Ca^{2+}. Al toxicity and stress can potentially affect energy transformations and carbon balance, cell division, membrane transport, nutrient accumulation, and various activities regulated by calmodulin (Cronan & Grigal 1995; Sucoff 1990). Similarly, Hutton (1985) concluded that an unfavourable balance between Ca and Al saturation in Australian subsurface soils prevents deep rooting by perennials such as *Centrosema pubescens* Benth and also of soybean and maize (*Zea mays* L.).

8.3.4 Effect of gypsum on topsoil acidity

8.3.4.1 The Patua soil

Although FGDG treatment greatly reduced subsurface acidity of the Patua soil, it had no influence on the monomeric Al concentration in topsoil where it was incorporated (Fig. 7.4 & 7.5 in Chapter 7). This resulted in less root development in the topsoil (Fig. 8.2) and probably limited the nutrient uptake from the topsoil, even when nutrient solution was added. This was because the dominant reaction in the topsoil horizon after gypsum (in FGDG) application is Ca^{2+} displacing H^+ or Al^{3+} into soil solution. This is expected to be the main cause of low shoot dry weight in FGDG treatment compared with the FBA and lime treatments in the Patua soil. These results confirm the suggestions that treatments which lime the topsoil are required to increase the efficiency of using gypsum as a subsurface soil acidity ameliorant (Shainberg et al. 1989).

There is no published work, however, to explain why gypsum may ameliorate subsurface soil acidity whilst having little effects on topsoil acidity. The possible mechanism for the lack of effect on topsoils may be due to the high organic matter content of topsoils. The high organic matter content in soils dominated by allophane, imogolite, and Al and Fe oxides forms stable humate complexes with these minerals by binding to FeOH and AlOH active sites (Mora & Canales 1995; Parfitt et al. 1977). Mora & Canales (1995) found that humic acid greatly reduced phosphate adsorption capacity of allophanic compounds. Competition between organic matter and inorganic anions for adsorption sites on soils is thought to be due to the chelating ability of hydroxylcarboxyl ligands found in the organic matter, which blocks the reactive surface sites (Sibanda & Young 1986). The forming of such organic matter complexes would prevent "self-liming" through SO_4^{2-} sorption. In practice, researchers usually incorporate lime and gypsum together into topsoil to overcome the topsoil acidity (Shainberg et al. 1989; Sumner 1994).

In this study, the significantly higher yield achieved by the FBA treatment tends to support the explanation given above, because slaked FBA contained not only gypsum but portlandite, calcite and other alkaline components and these compounds were responsible for the significant increase in topsoil pHs recorded prior to seed germination (refer Chapter 7). On the other hand, pH increases in the topsoil and the existing high organic matter content will result in high leaching losses of SO_4^{2-} (Bolan et al. 1986b). It may greatly shorten the longevity of the "self-liming effect" and subsequently raise the cost of application of gypsiferous materials. This is an important consideration when the cost of gypsiferous material and its transportation is a critical factor. FBA, in which 50% of the S is in the low soluble ettringite form (refer Chapter 3), is therefore a preferred material to be used as an amendment for subsurface soil acidity.

8.3.4.2 The Kaawa soil

Although the pH in water of the Kaawa soil (pH 4.6 - 4.7) was much lower than that of the Patua soil (pH 5.2 - 5.4), the Kaawa soil had higher base saturation than the Patua soil (29% vs. 3.5%). This higher base saturation probably reduced the Al toxicity to plant roots (Foy 1992) in spite of its high labile monomeric Al in soil solution (Fig. 8.4). The FGDG treatment significantly increased the labile monomeric Al concentration in the Kaawa topsoil, but it did not reduce the root growth in topsoil probably because most of the labile Al was in the form of non-toxic $AlSO_4^+$ (Kinraide & Parker 1987). The topsoil incorporated lime and gypsiferous by-products did not improve lucerne root penetration into acidic subsurface soil of the Kaawa soil column. This is obviously associated with the lack of "self-liming effect" in the Kaawa soil, as discussed in Section 7.3.2.

8.3.5 Sustainability of using gypsiferous materials as subsurface soil acidity ameliorant

Acidification is an ongoing process in agricultural soils, even in areas that remain unaffected by industrial pollution (acid rain), mainly because farming practices 'uncouple' nitrogen (N) cycling (Bolan et al. 1991a). Bolan et al. (1991a) estimated that a dairy farm with ryegrass and white clover pasture on a yellow-brown loam soil (similar to the Patua soil in properties) in the Waikato region, New Zealand, where the N nutrition was mostly dependent upon biological N_2 fixation, required up to 550 kg $CaCO_3$ ha^{-1} $year^{-1}$ to neutralise the H^+ generated. From the previous leaching study (refer Chapter 7), it can be calculated that the maximum "self-liming effect" through the application of gypsiferous material in the Patua yellow-brown loam soil can generate up to 66.5 mmol OH^- kg^{-1} in the 100 mm depth, that is, equivalent to 3325 kg $CaCO_3$ ha^{-1} (refer Section 7.3.5).

The "self-liming effect" depends on the ligand exchange between SO_4^{2-} and the OH^- on the surface of soil clay minerals, such as Fe- and Al-oxides and allophane (refer Chapter 7). Therefore, the availability of exchangeable OH^- on clay mineral surface determines the maximum potential of "self-liming effect". If the SO_4^{2-} sorption induced "self-liming effect" is the only source of alkali to neutralise the H^+ generated in this system, application of sufficient gypsiferous material may prevent the soil from acidification for six years, that is, after six years, the pH of this soil will start to decrease unless a liming material is also applied. Therefore, in the long-term applying gypsum to neutralise soil acidity through "self-liming" is not sustainable. In practice, neutralising most of the H^+ generated in a soil system through lime application to the topsoil, greatly reduces the acidity input into the subsurface soil and therefore the longevity of the "self-liming effect" in the subsurface soil will be considerably extended. It would be advisable therefore to always undertake a topsoil lime treatment prior to a gypsum application.

On the other hand, FBA contains both $Ca(OH)_2$, $CaCO_3$, and $CaSO_4.2H_2O$ (refer Chapter 3) and can be used as a "one shot" treatment. As discussed previously (Chapter

7), FBA can be used to ameliorate the soil acidity problems both in the top and subsurface. Therefore, application of FBA onto acid soil is a sustainable practice.

Because acidification on pasture soils commonly occurs in the subsurface soil (75 - 150 mm) (Loganathan & Hedley 1996; Parfitt et al. 1994; Williams 1980), broadcasting lime onto the soil surface, which is a common practice in pasture management, usually cannot correct the subsurface acidity. In particular this occurs in the yellow-brown loam soils in the Waikato region, New Zealand, where high stocking rates and additional nitrogen fertiliser inputs accelerate soil acidification (Bolan et al. 1991a). Pasture renewal and lime incorporation to depth will be required. To plough 5000 kg lime ha^{-1} into 150 mm soil and subsequently reseed pasture in the North Island of New Zealand currently costs approximately $NZ 558 ha^{-1} (M. J. Hedley, Personal communications 1996). The establishment of pasture after reseeding will take a period time before it can be available for animal grazing. Instead of recultivating and reseeding, surface applying FBA can ameliorate the subsurface soil acidity. If 5000 kg FBA ha^{-1} is broadcast onto a yellow-brown loam soil pasture with subsurface soil acidity problem, it can solve the acidity problem to at least 150 mm, and supply S as well, and it costs only $NZ 225 ha^{-1} (Terry Beird, Foremost Fertilisers Ltd., Personal communications, 1996). Therefore, on certain soil types, such as yellow-brown loam soils, using FBA is not only a sustainable but an economical practice.

8.4 CONCLUSIONS

Results from this glasshouse experiment show that gypsiferous by-products (FBA and FGDG) mixed in topsoil can significantly increase root elongation into acid subsurface soil of a yellow-brown loam, and subsequently increase shoot yield of lucerne because of an increased ability to take up nutrients and water. This is mainly due to the "self-liming effect" generated from sulphate sorption by the allophane in the yellow-brown loam.

The molecular ratio of labile monomeric Al^{3+} and Ca^{2+} in soil solution (Al:Ca) was a good predictor of the degree of root growth into subsurface soil layers.

The gypsiferous by-products, however, neither increased root elongation into acidic subsurface soil nor improved shoot yield growing in a yellow-brown earth soil because of the lack of a "self-liming effect" in this soil.

The "self-liming effect" caused by sulphate sorption is not a sustainable procedure for long-term neutralisation of subsurface soil acidity. Therefore, lime should be applied to neutralise the topsoil acidity, when using gypsum as subsurface soil acidity ameliorant. NZDC FBA, which contains both lime and gypsum, meets these sustainable liming requirements for decreasing subsurface soil acidity.

Chapter 9

Summary

9.1 BACKGROUND

The quantities of fluidised bed boiler ash (FBA) requiring disposal are likely to increase as incorporating limestone into fluidised bed combustion systems becomes a more popular method of removing sulphur dioxide (SO_2) from flue gases in industrial power and waste incineration plants. The main components in anhydrous FBA are CaO and $CaSO_4$ and therefore FBA has the potential to be used as a liming material and nutrient source. Results reported by a number of US scientists showed that most of that country's FBAs are suitable for agricultural uses, although the chemical compositions of these FBAs vary with the nature of the fuel and limestone.

9.2 RESULTS FROM THIS THESIS

In New Zealand, approximately 1.5×10^7 kg of FBA are produced annually by Anchor Products Ltd., New Zealand Dairy Corporation (NZDC FBA). The sample of slaked NZDC FBA studied is an alkaline material (pH_{water} 12.4, 51.8% $CaCO_3$ equivalent) containing 6.2% S, 25.4% Ca and negligible amounts of P, K and Mg. Approximately 50% of the S in the slaked FBA is gypsum ($CaSO_4.2H_2O$) with the remainder being water insoluble ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$). In addition, the concentrations of heavy metals are low in NZDC FBA making it highly suited to amelioration of soil acidity and S and Ca deficiency.

The agronomic effectiveness of NZDC FBA was evaluated on an acid peat soil, and representative acidic soils of the yellow-brown earth (Ultic soils) and yellow-brown loam

(Allophanic soils) soil groups (orders) because of the proximity of these acidic soils to the FBA source.

In acid peat soils, severe water repellency is a common problem in dry summer and autumn periods. Normal liming and fertiliser rates of FBA application had negligible effect on water repellency and water infiltration into dry peat soils. However, when high rates (up to 26462 kg ha^{-1}, wet weight basis) of surface dressed FBA were applied to Moanatuatua peat under pasture, the water repellency of the surface soil decreased and the rate of water infiltration increased. This may be caused by the high alkalinity of the applied FBA which modified the hydrophobic nature of the peat soil by removing fatty acids from the soil particle surface.

In addition to water repellency, soil acidity and nutrient (e.g. S) deficiency are major problems affecting pasture production in acid peat soil. Both field and laboratory experiments showed that FBA was as effective as agricultural lime in neutralising the peat soil acidity. Although surface-applied FBA had no significant effect on subsurface soil acidity, as measured by pH change in the peat soil, the Ca^{2+} ions released by FBA dissolution moved down to subsurface soil much faster than that of lime, and these Ca^{2+} ions may alleviate the acidity constraints on pasture root growth through the antagonistic relationship between Ca^{2+} and H^+ ions.

The FBA treatments increased pasture yield at the field trial site on Moanatuatua peatland, mainly by overcoming S deficiency and improving herbage S nutrition status. The ettringite-sulphate in FBA acted as a slow-release S fertiliser and high rates of FBA application maintained the high S concentrations in the herbage for a long period. Therefore, slaked FBA has the potential to be used as a source of fast and slow release (50:50) S fertiliser which will reduce S leaching losses, a common problem in many New Zealand soil types.

Overall, the results implied that FBA could be recommended as liming material, S source and ameliorant for Ca deficiency, particularly subsurface soil Ca deficiency for acid peat soils. It is not practical, however, to use FBA as an amendment to minimise water repellency on peat soil.

In glasshouse and laboratory studies on a variable charged, allophanic soil (the Patua soil, a yellow-brown loam), topsoil incorporated NZDC FBA ameliorated top and subsurface soil acidity through the "self-liming effect" induced by sulphate sorption. Consequently, phytotoxic labile monomeric Al concentration was reduced and improved root growth occurred in the initially acidic subsurface soil. Flue gas desulphurisation gypsum (FGDG) had a similar "self-liming effect" on subsurface soils but not the topsoil. No similar effects, however, were observed on a yellow-brown earth soil dominated by permanently charged clay minerals. These results indicate that NZDC FBA is an ideal by-product for correcting topsoil and subsurface soil acidity in yellow-brown loam soils, whereas for permanently charged mineral soils, FBA is recommended as an S fertiliser and to neutralise the topsoil acidity only.

One disadvantage of FBA use was that it caused significant leaching of native soil Mg^{2+} and K^+. These nutrients were displaced from the exchange sites by the relatively high concentration of Ca^{2+} released from dissolution of FBA. Therefore, Mg and K fertiliser application would be recommended when soil is treated with FBA. Alternatively, in the case of Mg deficiency, the use of dolomitic limestone as part of the absorbent during coal combustion would greatly increase the Mg content of FBA and so lessen the potential for a Ca:Mg imbalance.

9.3 FUTURE DIRECTIONS

The potential of using slaked FBA as a long-term basal S dressing appears a promising method to increase S fertiliser efficiency in soils prone to leaching. However, improved data on the dissolution characteristics of FBA in different soils under various climates, is required to achieve this goal. The effectiveness with which topsoil application of FBA alleviated acidity in the yellow-brown loam soil shows that FBA application may provide a sustainable management option for acid soils in this soil group. Based on the "self-liming effect" and sulphate adsorption characteristics, acid soils with high phosphate retention have the potential to respond to gypsum application as a subsurface soil acidity ameliorant. However, confirmation of the laboratory results will need field scale evaluation on different soil types.

In acid peat soil, the value of surface applied FBA for the alleviation of subsurface H^+ toxicity through the Ca^{2+}-H^+ antagonistic reaction should be examined further by root bioassay. Furthermore, FBA also has potential as a micro-nutrient fertiliser, providing elements, e.g. boron and selenium. These further investigations, though beyond the scope of this PhD thesis due to time constraints, are important research aspects if the production of FBA remains a popular way of minimising air pollution, and land application is a preferred method of disposal of FBA.

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