AN EVALUATION OF SULPHUR TOPDRESSING STRATEGIES IN EASTLAND PASTURES

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ABSTRACT

Two sampling surveys for soil and herbage, one in autumn and the second in the following spring, were carried out to assess the pasture sulphur status in the Eastland area of the North Island.

A preliminary glasshouse experiment using ryegrass as an indicator plant was also conducted to determine which soil test method best estimated the plant available sulphur pool in the soils covered by the survey. In comparison with calcium chloride extractable sulphur, soil sulphur extracted with calcium phosphate solution was shown to relate well to the yield response of ryegrass. Thus a calcium phosphate extractant was used as the criterion of soil sulphur status in the survey.

In most of the soils surveyed, the levels of phosphate-extractable sulphur tended to decrease with depth down to 30 cm and were not constant throughout the year. Levels were lower in spring than in autumn, possibly due to the leaching loss of sulphate and the slow mineralisation rate of soil organic sulphur during winter. The decrease in soil sulphate levels during winter was observed even at sites with low annual rainfall (900 - 1000 mm) and in soils with anion retention capacities as high as 70% as measured by the phosphate retention test. Although the levels of Olsen extractable soil phosphorus also tended to decrease over winter, this decrease in available phosphorus was not nearly as great as for sulphate, suggesting that sulphate, being the more weakly adsorbed anion, had been leached more readily.

Soil sulphur levels in autumn also reflected the sulphur fertiliser history more markedly than those in spring, thus providing further evidence of sulphate leaching during winter.

The results obtained from the herbage survey were consistent with those derived from the glasshouse study and soil survey in showing that the sulphur status of pasture herbage, whether expressed in terms of total sulphur, sulphate or N:S ratios was generally lower in spring than in autumn. The lower sulphur status of soil and herbage in spring suggests that if sulphur deficiencies do occur in the Eastland pastures, they may be most apparent in early spring.

To confirm the suspected spring sulphur deficiency observed in the survey, five field trials were laid down in the spring of the following year on soils belonging to three New Zealand soil groups: a yellow-grey earth, an intergrade between yellow-grey and yellow-brown earths and a yellow-brown pumice soil. Significant yield responses to spring application of sulphur were recorded at three out of the five sites. These sulphur-responsive sites included both those where there had been no recent application of sulphate-containing fertiliser and also those which had received regular autumn applications of sulphate at rates of 25 to 33 kg S ha^{-1} $annum^{-1}$.

Spring application of sulphur-free nitrogen fertiliser greatly increased dry matter yield but did not appear to aggravate the effect of sulphur deficiency on pasture growth at the sulphur-deficient sites, as evidenced by the fact that yield responses to sulphur application in the presence of nitrogen fertiliser were of similar or lower magnitude than those obtained with sulphur in the absence of nitrogen fertiliser. However, spring application of sulphur-free nitrogen led to very wide N:S ratios (18:1 to 23:1) in mixed herbage at two sulphur-deficient sites. In such situations, there may be a decrease in the nutritive value of the extra feed produced by a tactical application of nitrogen fertiliser.

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CHAPTER 1

INTRODUCTION

More than 80 percent of the phosphatic fertiliser used in New Zealand is applied as superphosphate (MacKay et al., 1980). The cost of this superphosphate to the farmer has increased substantially during the last two years and further price increases are likely in the near future. As a result of this trend, many farmers are already being forced to consider a reduction in the use of superphosphate or to seek alternatives.

Since superphosphate is formed by acidulating phosphate rock with sulphuric acid, about 11 percent of the bulk of superphosphate is sulphur (During, 1972). Over the years, as superphosphate has been applied to satisfy the phosphorus requirements of pasture, the soil has received sulphur, often incidentally.

Any move towards reducing applications of superphosphate or substituting it with high analysis phosphatic fertiliser containing little or no sulphur, will result in lower sulphur additions to soils. Consequently, a sulphur deficiency is likely to occur in areas where sulphur inputs to the plant available soil sulphur pool from other sources, are insufficient to offset losses occurring from this pool. In order to identify these potentially sulphur deficient areas so that steps can be taken to avoid or minimize such a deficiency, a sound knowledge of the sulphur cycle in the soil-plant-animal system is necessary.

The aim of this project is to assess the relative importance of the factors affecting soil and herbage sulphur status in Eastland pastures. Those factors primarily responsible for inducing or aggravating sulphur deficiency may then be established and fertiliser topdressing programmes can be planned and put into effect to minimize such deficiency.

CHAPTER 2

REVIEW OF LITERATURE

2.1 THE SULPHUR CYCLE IN GRAZED PASTURE

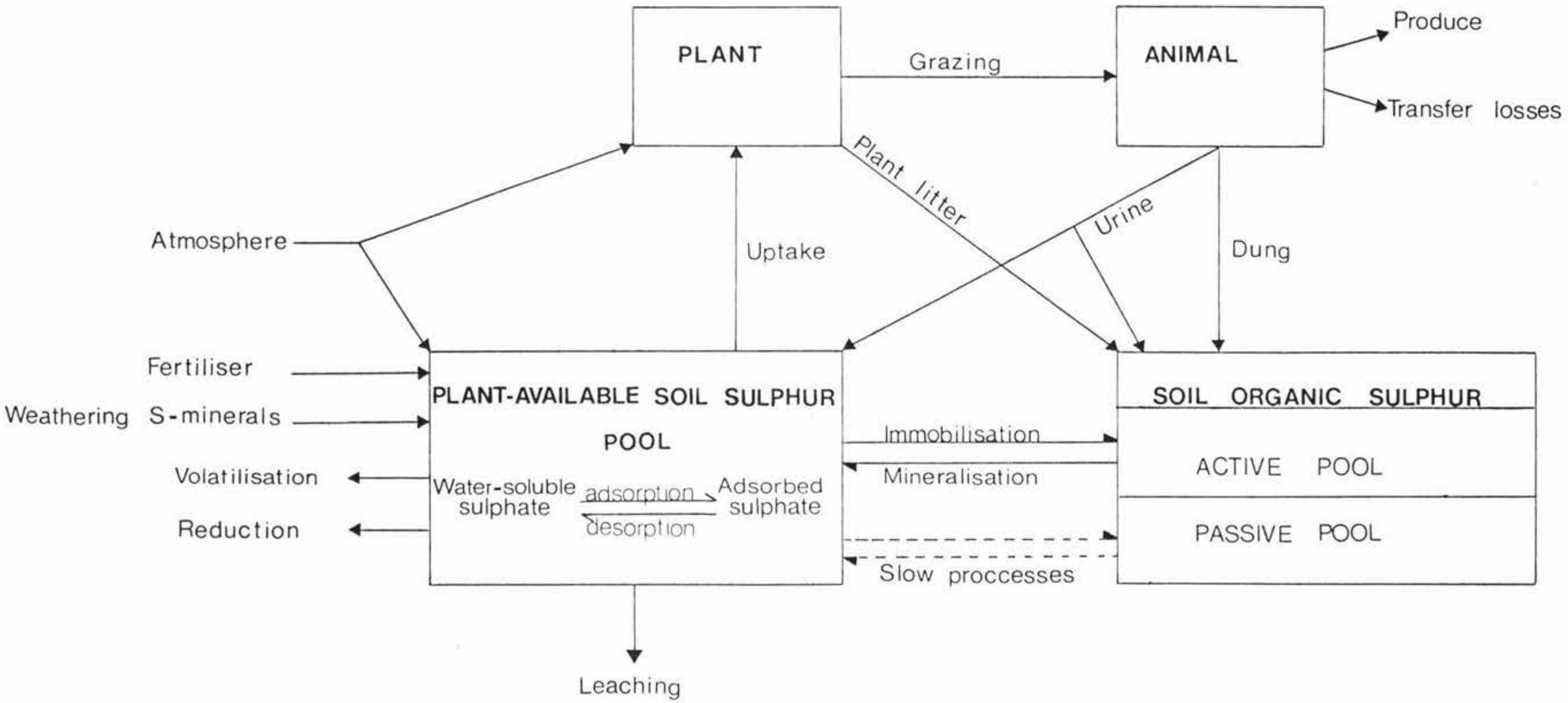
2.1.a THE SULPHUR CYCLE

Sulphur is an essential element in plant and animal nutrition (Anderson, 1978). It is of particular importance in grass-clover associations where grasses depend on clover for the transfer of the atmospheric nitrogen which has been symbiotically fixed by the Rhizobium bacteria that nodulate clover roots (Metson, 1973). When the supply of plant available sulphur is limited, nitrogen fixation decreases. This decrease is brought about by (a) the supression of clover growth due to the inability of clover to compete with grass for available sulphur (Conrad, 1950) and (b) the lack of sulphur for the formation of the nitrogenase enzyme which is involved in nitrogen fixation (Blair, 1979).

The sulphur cycle in grazed pasture is an interactive system comprised of soil, plants and animals (figure 2.1). The soil sulphur pool is the most important source of sulphur for plant growth. Direct absorption of atmospheric sulphur dioxide through plant leaves, as a substitute for sulphur absorbed by roots (Olsen, 1957), is unimportant in agricultural areas which are far from industrial sources (Coleman, 1966). In grazed pastures, sulphur taken up by plants can be returned to the soil directly as plant residues or indirectly via the grazing animal.

Knowledge of the nature of the plant available soil sulphur pool and the processes whereby sulphur is added to or lost from this pool is necessary in assessing the most important factors affecting the size of the pool. If the relative importance of these factors can be determined,

Figure 2.1 The sulphur cycle in a grazed pasture



processes responsible for inducing sulphur deficiency can be identified and management methods planned to avoid or minimise such deficiency.

2.1.b THE PLANT AVAILABLE SOIL SULPHUR POOL

2.1.b.1 COMPOSITION

Soil sulphur is taken up by plant roots almost exclusively as the sulphate (SO_4^{--}) ion (Metson, 1979a). Dissolved sulphate in soil solution is in kinetic equilibrium with sulphate ions adsorbed on soil colloids (Williams and Steinbergs, 1964). In most well-drained soils in New Zealand, this plant available soil sulphur accounts for less than 10 percent of the total sulphur in the upper horizon (0-20cm) but it can represent a larger proportion of total sulphur in some subsoils of red and brown loams, brown granular loams and clays, yellow-brown loams and yellow-brown earths (Blakemore et al., 1968; Metson, 1979b and c).

2.1.b.1 (i) Sulphate in soil solution

Only small amounts of soluble sulphate are normally found in New Zealand soils (Blakemore et al., 1968). The relative absence of soluble sulphate ions in these soils may be explained by various reactions (Metson, 1979a) as follows: (a) soluble sulphate ions are readily utilised for the sulphur nutrition of plants or soil microorganisms, (b) they may be leached downwards, or laterally, out of the profile in soils lacking anion-retaining ability and (c) they may be retained on soil colloids as adsorbed sulphate in anion-retentive soils.

Accumulation of soluble sulphate may occur in soils where the above reactions are inadequate to dispose of the influx of sulphate from the atmosphere, fertilisers, irrigation water, sulphur oxidation and mineralisation. Such conditions can be found in (a) areas such as Central Otago where the rainfall is insufficient to cause leaching and plant growth is limited by a lack of soil moisture (Metson, 1969), and

(b) in soils recently reclaimed from marine sediments and waterlogged lands. These sites are initially anaerobic and contain large amounts of sulphides typically as iron sulphide. Upon drainage and exposure to oxygen, the sulphides are oxidized by Thiobacillus genus to sulphate (Bloomfield and Coulter, 1973; Alexander, 1977).

2.1.b.1 (ii) Adsorbed sulphate:

Nature and distribution. Sulphate anions are specifically adsorbed on hydrous oxides of aluminium and iron, the silica-alumina mineral allophane and crystalline clay minerals, by ligand exchange with the aquo ($-OH_2$) and hydroxyl (-OH) groups on the surface of these soil colloids (Parfitt, 1978; Rajan, 1979). Hydrous metal oxides are more important in sulphate sorption than other crystalline clay minerals, especially if they are present as amorphous (short-range order) components (Parfitt, 1978).

Soils vary widely in their capacity to adsorb sulphate. Conditions favouring the adsorption of sulphate include low pH, low percentage base saturation and high contents of 1:1 clay minerals, and the presence of allophane and hydrous metal oxides (Metson, 1979a,b,c). It appears from the studies conducted by Barrow (1969), Metson and Blakemore (1978) and Couto et al. (1979) that where a soil has a low level of native adsorbed sulphate, it also has negligible capacity to retain added sulphate and hence presumably an inability to build up a reserve from sulphate application. However soils with an appreciable content of native adsorbed sulphate tend to have a capacity to adsorb further sulphate if it is applied.

Survey studies conducted by Blakemore et al. (1968) and Metson (1979b,c) have shown that the levels of adsorbed sulphate are generally low ($< 10\ \mu gSg^{-1}$) in New Zealand topsoils (0-20cm) and often increase with increasing soil depths. The presence of more adsorbed sulphate in subsoils than in topsoil has been attributed by Metson (1979a) to several factors including: (a) the greater contents of 1:1 clay minerals, hydrated metal oxides or allophanes in the subsoils, (b) the commonly lower pH of subsoils and (c) the greater competition from more strongly adsorbed anions such as phosphate, or from soil organic matter, for the sorption sites in topsoils.

Plant availability. The adsorbed sulphate pool in soil is readily available to plants (Freney and Spencer, 1960; Fox et al., 1964; Williams and Steinbergs, 1964; Barrow, 1967; Hasan et al., 1970) but the rate at which it is taken up by plants is influenced by the capacity of the soil to adsorb sulphate (Barrow, 1969, 1970). The results obtained from a glasshouse experiment conducted by Barrow (1969) indicate that soils, with a low ability to adsorb sulphate, release sulphate into soil solution more rapidly than do high sulphate-adsorbing soils. Since only a portion of adsorbed sulphate in high adsorbing soils is desorbed at any one time, these soils may have a greater ability to: (a)minimize the luxury uptake of sulphate (Barrow, 1975) and (b) reduce the loss from sulphate leaching (Barrow, 1975; Williams, 1975).

In addition to the adsorbed sulphate in the surface horizons, the agronomic value of the subsoil sulphate pool to pasture and deep-rooting crops such as lucerne has been recognised by various workers (Ensminger, 1958; Blakemore et al.,1969; Hoeft et al., 1973; Bailey, 1974; Gregg et al., 1977). Toxopeus (1970) demonstrated in field experiments on yellow-brown pumice soils, that pasture yield responses to sulphur application could not be reliably predicted from the available sulphur in the topsoil (0-7.5cm) alone. For a more accurate prediction, it was necessary to take account of the sulphur status of the subsoil to a depth of 60cm. Similar conclusions have been made by During and Cooper (1974) and Probert and Jones (1977).

In contrast, other researchers have reported no improvement in the prediction of sulphur response for pasture (Walker and Doornenbal, 1972) or for deep-rooted crops such as lucerne (Hoeft et al., 1973; Westerman, 1974) with the inclusion of samples below a 30cm depth. This does not necessarily imply that subsoil sulphur is an unimportant source for plant nutrition. It may be due to the high degree of correlation between extractable sulphur levels in the subsoil and those in the topsoil (Probert and Jones, 1977).

In New Zealand, pasture sulphur responses were observed by During (1972) on a highly sulphate retentive yellow-brown loam with a considerable amount of sulphate (80 μgSg^{-1}) present in the 30-45cm depth. He therefore concluded, that this subsoil sulphur pool was not available to plants at a sufficient rate to prevent sulphur deficiency. In field studies on a wide range of New Zealand soils where sulphate retention in the subsoil (30-45cm) was reported to be higher than that in the topsoil (0-7.5cm) (Saunders and Cooper, 1975), there was no advantage in using samples from 0-15cm depth as against those from 0-7.5cm to predict pasture sulphur responses.

To summarize, it would appear that although the subsoil sulphate pool can provide sulphur to plants, the size of its contribution depends upon soil physical and chemical factors (Gregg et al., 1977; Metson, 1979a). In strongly weathered soils of low pH, where adsorbed sulphate is not easily desorbed by soil colloids, or where plant root development may be limited by aluminium toxicity, this sulphate pool may not be available to plants (Metson, 1979a). Isotopic studies on the uptake of sulphur by pasture plants (Gregg et al., 1977) have also indicated that soil physical factors such as the availability of moisture within the profile and soil porosity can affect the penetration of plant roots and consequently influence the magnitude of sulphur uptake from subsoils.

2.1.b.2 INPUTS TO THE PLANT AVAILABLE SOIL SULPHUR POOL

Inputs to the plant available soil sulphur pool include:

(i) The weathering of primary minerals.

(ii) Atmospheric sulphur

(iii) Irrigation water and ground water.

(iv) Fertiliser sulphur additions.

(v) Mineralisation of soil organic sulphur.

2.1.b.2 (i) The weathering of primary minerals

Most of the sulphur in primary minerals is in sulphide form and during the weathering process it is oxidised to sulphate which may then be leached (Walker and Gregg, 1975). Thus, in the early stages of soil development, weathering can be a source of supply. This supply rapidly diminishes with time however and may be considered insignificant in most soils (Metson, 1979a).

2.1.b.2 (ii) Atmospheric sulphur

Sulphur compounds in the atmosphere include hydrogen sulphide (H_2S), sulphur dioxide (SO_2) and sulphate (SO_4^{--}) (Kellog et al., 1972). Atmospheric sulphur comes from the burning of fossil fuels, the anaerobic decomposition of organic matter, volcanic eruption and sea spray (Granat et al., 1976). The pathways by which these sulphur compounds leave the atmosphere include rainfall (wet deposition), dry deposition of sulphate particles and the gaseous uptake of sulphur dioxide by both plants and soil (Granat et al., 1976).

Atmospheric sulphur may be an important source of sulphur to soils and plants in coastal areas, thermally active regions and sites close to swamps and large industrial centres (Terman, 1978). For instance, in coastal areas, where sea spray can contribute sulphate aerosols to the atmosphere, the amount of sulphate collected in precipitation can be up to 9.7 kg S $ha^{-1}year^{-1}$ (Walker and Gregg, 1975). At sites close to industrial areas, major centres of population, and tidal flats where atmospheric accessions of sulphur from the burning of fossil fuels and bacterial emission of reduced sulphur compounds (Granat et al., 1976) can be substantial, high levels of sulphate in rain water have been observed. For example, a range of 7.7 to 10 kg S $ha^{-1}year^{-1}$ in rainfall has been recorded at Taita, near Wellington (Miller, 1968; Blakemore, 1973) and an average input of 13.2 kg S $ha^{-1}year^{-1}$ in rainwater has been measured at Otara, near Auckland (Muller, 1975).

In contrast to the above-mentioned situations, atmospheric accessions of sulphur from sea spray and from the burning of fossil fuels are considered to be insignificant in inland regions, remote from major centres of population or industry. In many inland South Island areas, inputs of as low as 0.6 to 1.0 kg S $ha^{-1}year^{-1}$ have been suggested (Walker et al., 1956; Anon., 1960).

Direct absorption of atmospheric sulphur dioxide (SO_2) by plants and soils can contribute to the sulphur nutrition of plants (Terman, 1978). Although no evaluation of the significance of direct plant and soil absorption of SO_2 has been reported in New Zealand, the amount of sulphur entering the sulphur cycle in this manner is likely to be related to returns in rainfall and therefore to be generally low, and less in inland regions than on the coast (Walker and Gregg, 1975).

2.1.b.2 (iii) Irrigation water and ground water

Irrigation water containing sulphur can be a source of sulphur for plants (Terman, 1978) but there appear to be no reports in the literature on the concentrations of sulphate in irrigation waters in New Zealand.

Fluctuating ground water levels can also contribute sulphur to the plant available pool provided the water table is in the vicinity of plant roots. In several soils in Central Otago, ground water sulphate has been reported to be available to deep rooting lucerne but was at too great a depth for clover sulphur uptake (Blakemore et al., 1969).

2.1.b.2 (iv) Fertiliser sulphur additions

Various forms of sulphur-containing fertilisers are used in New Zealand (During, 1972). Their agronomic values will be reviewed in detail in section 2.2.b.

The main fertiliser source of sulphur in New Zealand is single superphosphate which usually contains 11 percent sulphur (During, 1972). Sulphur in superphosphate is in the form of anhydrite calcium sulphate ($CaSO_4$) which is sparingly soluble (Barton and Wilde, 1971).

Other sulphur fertilisers such as elemental sulphur, elemental sulphur-enriched superphosphate (sulphur-fortified superphosphate) and ammonium sulphate are less frequently used (During, 1972). Common proportions in a sulphur-fortified superphosphate mixture are (a) 90% superphosphate with 10% elemental sulphur and (b) 82% superphosphate with 18% elemental sulphur.

The sulphur in ammonium sulphate is water soluble but elemental sulphur must be oxidized by soil microorganisms to the sulphate form before being taken up by plants (Bixby and Beaton, 1970). As this oxidation process takes place slowly, it tends to reduce sulphate leaching (During, 1972).

Both ammonium sulphate and elemental sulphur can lower soil pH unless the soil contains free calcium carbonate (During, 1972).

2.1.b.2 (v) Mineralisation of soil organic sulphur

Apart from the sulphur sources already mentioned above, plants are dependent upon the mineralisation of organic sulphur to replenish the plant available soil sulphur pool. Since the mineralisation of soil organic sulphur and the opposing immobilisation process occur concurrently in the soil system (Probert, 1976; Tsuji and Goh, 1979), the change in the level of plant available soil sulphur at any one time represents the net effect.

In the early stage of pasture development, there is a net immobilisation of sulphur into the soil organic fraction by microbial incorporation of soil sulphate together with the return of organically bound sulphur in plant residues and animal faeces. However, in well-developed situations where sulphur fertiliser has been applied regularly, the rate of sulphur immobilisation decreases and mineralisation becomes a more significant source of plant available sulphur (Jackman, 1964; Till, 1975; Walker and Gregg, 1975; Sorn-Srivichai, 1980).

Attempts to determine the amount and rate of sulphur mineralisation have been made by many workers using a variety of techniques including: laboratory incubation (Freney et al., 1971 and 1975; Haque and Walmsley, 1972; Kowalenko and Lowe, 1975), glasshouse experiments (Freney and Spencer, 1960; Cowling and Jones, 1970; Nicolson, 1970; Bettany et al., 1974; Goh and Tsuji, 1979; Tsuji and Goh, 1979) and field trials (Williams, 1968; McLaren and Swift, 1977; Swift, 1977). While the determination of sulphur mineralisation in most of these studies was based on the measurement of the accumulation of inorganic sulphate, which is the net balance between the mineralisation and immobilisation over a given time period, the use of the tracer ^{35}S has enabled some workers

(Freney et al., 1971; Bettany et al., 1974; Probert, 1976; Goh and Tsuji, 1979; Tsuji and Goh, 1979) to determine the amount and rate of these processes individually.

Although laboratory studies and glasshouse experiments are of value, their extrapolation to grazed pasture is difficult because they are carried out under artifical conditions and in the absence of competing processes such as plant uptake and grazing (Till, 1975). Evidence from relatively few field experiments (Williams, 1968; Till and May, 1970a,b; Gregg, 1976; McLaren and Swift, 1977) suggests that the mineralisation of soil organic sulphur is inadequate to meet the requirements of high-producing crops or even pasture. In studies assessing the importance of organic sulphur as a sulphur reserve for pasture production in grazed systems, May et al. (1968), Till and May (1970a,b) and Gregg (1976) have indicated that only a portion of soil organic sulphur (the active pool) is significantly involved in the cycling of sulphur and the mineralisation rate of this portion is the key factor in determining production. The pool of organic sulphur which does not make a significant contribution to the plant available soil sulphur pool because of its negligible turn-over rate has been termed the inert or passive pool.

The size of the inert pool of soil organic sulphur varies between soils. In an Australian study (Till and May, 1970a,b, 1971),50% of the soil organic sulphur was held in the inert pool while this pool accounted for 88% of the organic sulphur in the New Zealand soils studied by Gregg (1976). Although the active pool of 55 kg S ha^{-1} in the topsoil (0-25cm) was shown by Till and May (1970) to turn over rapidly enough to replenish the plant available soil sulphur pool at times when pasture production was low because of dry conditions (annual rainfall of 750-800mm), the authors concluded that under favourable climatic conditions, where pasture sulphur requirements and sulphate leaching losses may be considerably higher, the sulphur mineralisation rate may limit pasture production. In fact, Gregg (1976) was able to show that in a high rainfall situation (1000mm per annum), a pasture sulphur deficiency occurred even though about 70 kg S ha^{-1} was present in the active pool at any one time.

Since the mineralisation of soil organic sulphur is a microbial process, it is sensitive to environmental factors including soil temperature, moisture, aeration, pH and the effects of plants.

(i) Soil temperature The influence of soil temperature on the mineralisation of soil organic sulphur has been investigated largely under controlled conditions in glasshouse and incubation studies (Burns, 1968).

Little or no mineralisation of soil organic sulphur occurs at low soil temperatures (10^{0}C or below) (Chaudhry and Cornfield, 1967b; Williams, 1967; Nicolson, 1970), and it has been suggested by Biederbeck (1978) that this strong inhibition of sulphur mineralisation at low soil temperatures would tend to decrease leaching losses of sulphate during seasons that are both wet and cool.

(ii) Soil moisture and aeration Sulphur mineralisation is sharply reduced at moisture contents appreciably above or below field capacity (Williams, 1967). A moisture content of 60% of the field capacity has been reported to be optimum for the mineralisation process (Chaudhry and Cornfield, 1967a).

Moisture fluctuations caused by wetting and drying are known to produce a flush in the release of sulphate from soil organic sulphur (Williams, 1967). Sulphate may be released both abiologically from soil organic sulphate by the physical effects of drying and heating on the ester (C - O - S and C - N - S) linkages (Barrow, 1961; Kowalenko and Lowe, 1975a) and biologically through increased microbial activity after the remoistening of dry soil (Birch and Friend, 1956; Birch, 1959).

(iii) Soil pH The amount of sulphate released from soil organic matter is increased by liming (Freney and Stevenson, 1966; Williams, 1967; Probert, 1976). This increase may be due to two factors: (i) chemical hydrolysis of sulphate esters caused by the increased alkalinity (Barrow, 1960; Williams, 1967) and (ii) an increased mineralisation rate resulting from the effect of a favourable pH environment on microbial activity (Williams, 1967).

(iv) Effect of plants The mineralisation of soil organic sulphur is found to be greater in the presence of plants than in bare soil (Freney and Spencer, 1960; Cowling and Jones, 1970; Nicolson, 1970; Freney et al., 1975), presumably because of the greater microbial activity in the rhizosphere of the plants and the excretion, by plant roots, of enzymes which catalyse the decomposition of soil organic matter (Freney, 1967).

In addition to these environmental factors, the amount and sulphur content of the organic matter present influences the rate of turnover of soil organic sulphur since it is the source for the mineralisation process (Biederbeck, 1978). It is probable that larger amounts of sulphur are mineralised from soils with relatively high organic matter contents and in particular from soils with low C:S or N:S ratios (Barrow, 1960; Haque and Walmsley, 1972; Bettany et al., 1974; Kowalenko and Lowe, 1975b).

2.1.b.3 OUTPUTS FROM THE PLANT AVAILABLE SOIL SULPHUR POOL

Outputs from the plant available soil sulphur pool include:

(i) Volatilisation losses.

(ii) Leaching losses

(iii) Immobilisation losses.

(iv) Plant uptake.

(v) Losses associated with grazing animals.

2.1.b.3 (i) Volatilisation losses

Hydrogen sulphide (H_2S) and other volatile compounds such as methane thiol (CH_3SH) and ethane thiol (CH_3CH_2SH) can be produced as a result of the anaerobic decomposition of organic sulphur compounds by soil microorganisms (Alexander, 1977). Hydrogen sulphide can also be formed by the reduction of sulphate (dissimilatory sulphate reduction) by sulphate-reducing bacteria (Alexander, 1977).

Evidence obtained from studies conducted by Sachdev and Chhabra (1974) and Banwart and Bremner (1976) suggests that sulphur losses due to volatilisation under the aerobic conditions normally encountered in grazing systems are likely to be minimal. Loss of volatile sulphur compounds from animals and excreta represents a negligible proportion of the sulphur in the cycle (Till, 1975).

2.1.b.3 (ii) Leaching losses

Sulphate losses from the plant available soil sulphur pool can occur in water either moving over the soil surface (surface runoff) or through the soil profile (subsurface drainage).

Sulphate losses in surface runoff are often negligible, but where soil infiltration is low, vegetation cover sparse and rainfall intense, these losses can be significant (Ward, 1967). This is especially the case on steeply, sloping land (Hamvray and Laften, 1971; Kilmer et al., 1974).

Sulphate losses in subsurface drainage water (leaching) are influenced by: (i) climatic factors (ii) soil properties such as water holding capacity, sulphate retention capacity and soil texture (iii) vegetation cover and (iv) fertiliser factors, such as the physical and chemical nature of the sulphur fertiliser and the rate and time of application.

(i) Climatic factors The amount of sulphate leaching depends on the extent and rate of water movement through the soil profile. Such water movement occurs whenever rainfall exceeds evapotranspiration (During and Cooper, 1974).

The effects of rainfall on sulphate leaching have been measured in various studies. Gregg (1976) found that 90 days after the application of ^{35}S labelled gypsum fertiliser, almost all of the added sulphate remained within the upper 15cm of a soil which had received 106mm of rainfall during that period. In a similarly-textured soil which received a higher rainfall (384mm over the same period of 90 days), labelled $^{35}SO_4$ was distributed evenly to a depth of 60cm. Similarly, Rhue and Kamprath (1973) showed that 56mm of rainfall after an autumn application of gypsum fertiliser caused sulphate to penetrate to a depth of 30-45cm in a soil of loamy sand texture. After 180 days, a further 344mm of rainfall over the winter months had caused the complete removal of fertiliser sulphur from the 0-45cm depth. In contrast, under dryer conditions (260mm over 215 days), leaching losses appeared to be negligible as $^{35}SO_4$ remained in the top 10cm over the entire experimental period (May et al., 1968; Till and May, 1970a,b; 1971).

(ii) Soil water holding capacity The pattern of sulphur movement is influenced by the water holding capacity of a soil (Gregg and Goh, 1978). Although two soils in their study received similar amounts of rainfall and had similar sulphate retention capacities, the penetration of $^{35}SO_4$ was greater in a soil with a low water holding capacity (a steepland yellow-brown earth) than in a soil with a much higher capacity (a recent soil from aeolian loess).

(iii) Sulphate retention capacity Greater leaching of sulphate has been observed in low sulphate retaining soils than in soils with higher sulphate retention capacities (Hogg, 1965; Hogg and Toxopeus, 1966). Similar findings have been obtained from a field study using $^{35}SO_4$ as a tracer (Gregg and Goh, 1978; 1979). On a recent soil with low sulphate retention (5%) within the 0-60cm zone, labelled sulphate was lost from the top 60cm of soil in the winter following a spring application. In contrast, on a yellow-brown earth soil with a medium sulphate retention (50%) in the subsoil (30-60cm), labelled sulphate did not penetrate beyond 60cm. In another field trial conducted on a highly sulphate retentive yellow-brown loam, sulphate appeared to remain in the top 45cm soil depth even after five years had elapsed since its application and in spite of 3000mm of excess rainfall over evapotranspiration during this period (During and Cooper, 1974).

The capacity of the soil to retain sulphate against leaching is reduced by the application of lime and phosphate-containing fertilisers (Metson, 1979a). Liming reduces the sulphate adsorbing ability of soils by decreasing the surface charge of hydrous metal oxides, allophane and 1:1 clay minerals (Metson, 1979a).

Sulphate is adsorbed by soils less strongly than phosphate (Metson and Balkemore, 1978). Thus, additions of phosphate to the soil surface can displace sulphate from anion adsorbing sites on soil colloids. The displaced sulphate ions are then free in the soil solution and can be leached down the soil profile and either lost in percolating water where sulphate adsorption is low or readsorbed at a lower depth in a subsoil with a higher sulphate retention capacity (Metson, 1979a).

(iv) <u>Soil texture</u> Leaching losses are higher in coarse-textured than in fine-textured soils because of the greater rate of water movement (Gregg and Goh, 1978) and lower sulphate retention capacity (Beaton et al., 1974) in the former. Gregg and Goh (1978) found that 48 days after the application of ^{35}S-labelled gypsum, sulphate derived from the fertiliser had moved further than 60cm in a sandy loam. Under a similar rainfall regime, fertiliser sulphur remained in the upper 30cm of a heavy silt loam.

(v) <u>Vegetation cover</u> Sulphate leaching losses from bare soils tend to be higher than those from pastures (Harward and Reisenauer, 1966).Pasture plants not only remove sulphate from soil solution thus reducing the quantity of sulphate liable to leaching, but also utilise soil water thus influencing water movement. The more active the plant growth is, the greater will be the tendency for plants to reduce the extent and rate of sulphate movement through the soil profile.

The botanical composition of a pasture may also influence the amount of sulphate leaching from the plant available soil sulphur pool. Since grass is able to recover a higher proportion of applied sulphur than clover (Walker and Adams, 1958; Metson, 1972) it is probable that leaching losses would be less in a grass-dominant sward.

The distribution of roots with depth will affect the significance of sulphate leaching as deep-rooting crops can retrieve leached sulphate from the subsoil more effectively than shallow-rooting crops (Blakemore et al., 1969).

(vi) <u>Fertiliser</u> The form, rate and time of application of sulphur fertilisers are significant factors influencing the movement of fertiliser-derived sulphate in soils.

Elemental sulphur is less susceptible to leaching than calcium sulphate, in either the anhydrite form in superphosphate or the dihydrate form, gypsum (Hogg and Cooper, 1964; Muller and McSweeney, 1974).

Increased particle size (granulation) reduces sulphur leaching losses from superphosphate and gypsum through a reduction in surface area (Cooper and Hogg, 1966; Williams, 1970) and from elemental sulphur through a reduction in the rate at which elemental sulphur can be oxidised to sulphate (Burns, 1968).

A reduction in the rate of fertiliser sulphur application has been shown to result in a similar proportional decrease in the amount of sulphur lost by leaching (McKell and Williams, 1960; Chao et al., 1965). Similarly,the use of ^{35}S-labelled gypsum has enabled Gregg and Goh (1978) to show that although halving the rate of fertiliser sulphur application did not affect the depth of fertiliser sulphur movement it did result in 50% less fertiliser sulphur in any one of the soil depths investigated.

The timing of fertiliser application can also affect the degree of sulphate leaching. On low sulphate retaining soils, application of gypsum or superphosphate in autumn can result in severe sulphate leaching losses during the winter months (Hogg and Cooper, 1964; Toxopeus, 1965; Van der Elst, 1968; Toxopeus, 1970). This is due to the considerable excess of rainfall over evapotranspiration during this period (Toxopeus 1965) and also possibly the low rate of both plant uptake and incorporation of sulphate into soil organic matter over the winter , resulting in a higher potential for the downward movement of sulphate (Clarke and Lewis, 1974; Gregg and Goh, 1978).

2.1.b.3 (iii) Organic immobilisation

Soil sulphate, after being absorbed by plants from soil solution, is returned to the soil as plant litter and animal excreta to become part of the soil organic matter (Till, 1975). Sulphate is also incorporated directly into the soil organic fraction by microorganisms (Freney and Stevenson, 1966).

Up to 15 kg S $ha^{-1}year^{-1}$ has been estimated by Walker et al. (1959) to be incorporated into the organic sulphur fraction of the top 20cm of soil. This estimation was based upon the differences in the total sulphur contents in the top soils taken from virgin and developed pastures. Total sulphur was reported to increase from 290 kg ha^{-1} in the virgin soils to 670 kg ha^{-1} in the developed situations after 25 years of development (Walker et al., 1959). Using a similar approach, Jackman (1964) found that over 30 years, organic sulphur levels increased by 7.2 - 18.5 kg S $ha^{-1}year^{-1}$ in a range of New Zealand soils.

The results obtained from incubation studies (Freney et al., 1971; 1975) and field trials (Till and May, 1970a,b; Gregg, 1976) suggest that substantial immobilisation of applied sulphate can occur in the short term. For instance, in a laboratory incubation study using ^{35}S as a tracer to follow the transformation of applied sulphate, Freney et al. (1971) observed that over 50 percent of added $^{35}SO_4^{--}$ was incorporated into the organic pool over 160 days. The majority of this incorporation occurred within the first two weeks. Studies on grazed pasture following the application of ^{35}S-labelled gypsum (Till and May, 1970a, b; 1971) have shown that, of the radioactivity from ^{35}S-labelled gypsum remaining in the top 7.5cm of soil after 151 days, 82% was in the organic sulphur fraction. Similarly, Gregg (1976) noted a substantial incorporation (36%) of ^{35}S fertiliser into soil organic sulphur in the upper 15cm in one year.

In another field study conducted by During and Cooper (1974) on a highly sulphate retentive soil where no sulphate leaching beyond 45cm depth had been observed, 39-55 kg ha^{-1} (23-33%) of fertiliser S applied over a period of five years was apparently immobilised in the organic form in the upper 45cm of soil.

2.1.b.3 (iv) Plant removal

In cropping situations or in systems of pastoral farming where pasture herbage is cut for conservation, the plant available soil sulphur pool can be depleted by the removal of sulphur in plant tissues. The amount of sulphur removed depends on the crop type and yield (Martin and Walker, 1966; Bixby and Beaton, 1970; Blair, 1979). For instance, in a high producing grass-clover sward with an annual production of 10,000 kg ha^{-1} of dry matter (During, 1972; Wilkinson and Lowrey, 1973) and with an adequate sulphur concentration of 0.3 percent (Metson, 1973) the total amount of sulphur incorporated in the plant tops is 30 kg S $ha^{-1}year^{-1}$.

Although the amount of sulphur in root residues has not been investigated under New Zealand pastoral conditions, it was estimated to be about 10 to 12 kg S $ha^{-1}year^{-1}$ (Goh and Gregg, 1980). This estimation was based on two assumptions: (a) the annual addition of root residues may be in the range 5500-6000 kg ha^{-1} of dry matter (Goedewaagon and Schuurman, 1950; Shamoot et al., 1968) and (b) the sulphur concentration in roots is about 0.2%.

Thus altogether, a high producing pasture may incorporate about 40 to 42 kg S $ha^{-1}year^{-1}$. If all or a large fraction of the above-ground herbage is removed from the area, it can represent a substantial annual sulphur loss from the system. Under grazing, much of this plant sulphur will be returned as plant litter, root residues and animal excreta.

The extent to which sulphur in plant residues can contribute to the plant available soil sulphur pool depends primarily on the rate of decomposition and the net result of mineralisation and immobilisation processes in the soil. According to Stewart et al. (1966), about 0.15% sulphur in plant residues is sufficient to ensure a maximum decomposition rate. The mineralisation of sulphur from decomposing residues added to soil depends upon the C:S ratios of these materials (Barrow, 1960). The C:S ratios of 200 and 420 are the lower and upper limits respectively, of the range within which, either mineralisation or immobilisation of residue sulphur would occur. Net mineralisation takes place at C:S ratios of 200 or less, while net immobilisation occurs when the C:S ratio is greater than or equal to 420 (Barrow, 1960).

The rate at which fertiliser sulphur incorporated in plant residues can be released through mineralisation to the plant available pool, has been investigated by Goh and Gregg (1980). In a growth chamber study, carried out over a period of 23 weeks, where conditions for plant growth and plant residue decomposition were optimum, these workers observed that perennial ryegrass only recovered between 7 and 20% of labelled sulphur which had been incorporated in plant residues. Based on this finding, they suggested that less than 10% of fertiliser sulphur in decomposing residues would be made available to plants within one year under field conditions. This estimated recovery of labelled fertiliser sulphur is not, however, conclusive evidence of the extent to which sulphur in decomposing materials may be released to the plant available pool, since the plant residues used in Goh and Gregg's study were not evenly labelled with radioactive sulphur (Goh and Gregg, 1980).

2.1.b.3 (v) Sulphur losses associated with grazing animals

Sulphur is lost from the sulphur cycle in animal products and animal excreta deposited on unproductive sites outside the grazing area. This aspect is reviewed in more detail in the following section.

2.1.b.4 THE IMPACT OF GRAZING ANIMALS ON THE SULPHUR CYCLE

In grazed systems, sulphur moves from the soil to the plant and back to the soil, either directly in plant residues, or indirectly via the grazing animal. The amount of sulphur returned in plant litter varies depending on the level of pasture utilisation by grazing animals. With good grazing management ensuring high pasture utilisation, more sulphur in the above-ground herbage will be returned in excreta (During, 1972; Wilkinson and Lowrey, 1973).

The amount of sulphur excreted in faeces is relatively constant, but urinary excretion depends on the sulphur content of herbage (Walker, 1957a; Barrow and Lambourne, 1962). In other words, the effect of increasing dietary sulphur is to increase the levels of sulphur excreted in urine (Wilkinson and Lowrey, 1973). According to During (1972) and Till (1975), animals grazing pasture adequately supplied with sulphur excrete 50-60% of their total sulphur output in urine. Approximately 90% of the urinary and some of the faecal sulphur is inorganic sulphate which is water-soluble and liable to leaching (Walker, 1957a; During, 1972). Faecal organic sulphur consists of undigested protein, microbial protein sulphur and compounds such as indican which are water-insoluble and somewhat resistant to bacterial breakdown (Walker, 1957a; During and Weeda, 1973).

Grazing animals can influence the losses from the plant available soil sulphur pool in several ways:

(i) Losses in animal products Only a small proportion (less than 10%) of ingested sulphur (During, 1972; Wilkinson and Lowrey, 1973; Till, 1975) is used by animals in the production of body tissues, milk and wool and the remainder (90%) is returned to the soil in the animals' excreta.

(ii) The cycling of sulphur in soil-plant-animal systems. Sulphur cycling via grazing animals is considered to avoid the slow process of the decomposition of plant residues and effectively increase the turnover rate of the sulphur cycle (Wilkinson and Lowrey, 1973; Till, 1975). This increase in the rate of cycling occurs because:

(a) A large proportion (50-60%) of the sulphur in the excreta is in the immediately plant available form (Till, 1975).

(b) Although faecal sulphur is mineralised more slowly than plant sulphur (Barrow, 1961), the trampling of dung by grazing animals, especially at high stocking rate, encourages the decomposition process (Wolton, 1963; Bromfield and Jones, 1970).

Although the presence of grazing animals can increase the turnover rate of sulphur within the pasture system, grazing animals can cause sulphur losses from the cycle through the uneven distribution of dung and urine and the transfer of sulphur from the main grazing areas to the much smaller areas of stock camps. Losses by these means will depend on the type of grazing animals, the stocking rate and the contour of the land (During, 1972; Gillingham, 1980; Gillingham et al., 1980).

Sulphate from urine patches can be lost from the cycle through volatilisation and leaching. Leaching losses of sulphur from urine patches can be extremely high on soils with a high rainfall, low water-holding capacity and low sulphate retaining capacity (section 2.1.b.3). Sulphate adsorption by soil colloids can be reduced by dung deposition because dung raises soil pH levels and also supplies phosphate and organic anions which can block adsorption sites for sulphate (During and Weeda, 1973).

Grazing can influence both the botanical composition and the rate of growth of pasture by affecting its leaf area index so as to influence the plant's ability to intercept radiation and the efficiency of photosynthesis (Clarke and Lewis, 1974). These in turn will influence the plant's sulphur requirement and consequently the amount of sulphate leaching (Clarke and Lewis, 1974; Till, 1975).

2.1.c CONCLUSIONS

The size of the plant available soil sulphur pool at any one time is the net balance of various inputs and outflows. If their relative contributions to the gains and losses of sulphur from this pool can be determined, it may be possible to identify the major factors responsible for the onset of sulphur deficiency in a certain agricultural system. For instance, sulphur deficiency may occur in many inland regions of New Zealand where atmospheric accessions of sulphur from sea spray and from anthropogenic emissions are insufficient to offset sulphur losses occurring from the plant available soil sulphur pool.

Sulphur deficiency is more likely to occur in undeveloped pastures than in those which have been topdressed over the years with fertiliser sulphur, since the process of sulphur immobilisation may be a major factor in depleting the plant available soil sulphur in the initial stages of pasture development.

In areas with a high annual rainfall, sulphate leaching may constitute a major problem in well drained, coarse-textured, low sulphate retaining soils. Under these conditions, pasture sulphur deficiency may be induced when the additions of sulphur to the plant available soil sulphur pool are insufficient to offset the losses occurring from this pool. The degree of such deficiency depends on the rate at which sulphur-containing fertiliser can augment the plant available pool. This rate is influenced by the physical and chemical nature of the fertiliser sulphur, the amount and the time of application. The application of lime or high analysis phosphatic fertiliser containing little or no sulphur may even aggravate sulphur deficiency by reducing the size of plant available soil sulphur pool. This arises from the decrease in the capacity of the soil to retain sulphate against leaching.

2.2 OCCURRENCE AND CORRECTION OF SULPHUR DEFICIENCIES IN NEW ZEALAND PASTURES

2.2.a OCCURRENCE

Sulphur deficiency can occur in both unimproved and improved pastures (section 2.1). In unimproved situations, net sulphur immobilisation and leaching losses will be the major processes depleting the plant available soil sulphur pool. With increasing development, the loss to the soil organic pool will gradually decrease, but leaching will still occur and may even be increased by changes in soil pH (liming) and phosphate status (phosphate application).

The following review reports the occurrence of sulphur deficiency in both unimproved and improved New Zealand pastures.

2.2.a.1 UNIMPROVED PASTURES

In the South Island, field trials by Walker et al. (1956), Walker (1957b), Walker and Adams (1958), Lobb (1962), Ludecke (1962, 1965), O'Connor (1962) and Vartha (1963) have established the existence of widespread sulphur deficiencies in unimproved pastures on the brown-grey earth, yellow-grey earth and yellow-brown earth soil groups, together with the steepland soils of the hilly inland regions of Marlborough, Canterbury and Otago. Sulphur responses have also been observed on an undeveloped soil sequence derived from loess on Bank's Peninsula, Canterbury (Walker and Gregg, 1975), the gley podzols of the West Coast (During et al., 1964; During and Martin, 1968; McNaught and During, 1970) and in Nelson districts (Chittenden and Dodson, 1963; Chittenden, 1964, 1965; Goodall, 1964; Metson et al., 1971).

In the North Island, sulphur deficiencies in unimproved pastures have been observed on (i) yellow-brown pumice soils (Hogg, 1965; Toxopeus, 1965; Cooper and Hogg, 1966; Hogg and Toxopeus, 1966), (ii) steepland soils derived from sandstone (central yellow-brown earths and intergrades between yellow-grey and yellow-brown earths) in both Wanganui and Rangitikei districts (Blackmore et al., 1969), (iii) peat soils of the Waikato (Van der Elst, 1968) and (iv) northern podzols (Hogg and Cooper, 1964; During, 1967; Ludecke, 1970).

In seeking factors common to these sulphur deficient soils of both islands, it would appear that the size of the plant available sulphur pool is limited by sulphate leaching at certain critical times (section 2.1.b.3) because of the soil's low capacity to adsorb sulphate (Hogg and Cooper, 1964; Hogg, 1965; Cooper and Hogg, 1966; Hogg and Toxopeus, 1966; Metson, 1979a,b,c). This low sulphate retention capacity is due to either the coarser texture of the upper horizons (gley podzols and yellow-brown pumice soils) or to a predominance of 2:1 layer type clays which exhibit low anion retention capacities (brown-grey earths, yellow-grey earths, high country yellow-brown earths and recent soils from greywacke, loess or alluvium) (Metson, 1969). In addition to leaching losses, substantial amounts of sulphate from the plant available soil sulphur pool are likely to be incorporated into soil organic sulphur during the early stages of pasture establishment (Walker and Gregg, 1975).

Although many unimproved pastures in New Zealand are sulphur deficient (Walker and Gregg, 1975), exceptions can occur on:

(i) highly sulphate retentive soils which contain considerable amounts of adsorbed sulphate (more than 15 g S g^{-1}) in the top soil (During, 1972; During and Cooper, 1974). In some cases, this adequate sulphur status appeared to to be only temporary as sulphur responses in the second year of field trials have been reported by During and Cooper (1974).

(ii) soils where there are large accumulations of adsorbed sulphate in the subsoil and where chemical and physical conditions in the subsoil allow plant roots to tap this source (Gregg et al., 1977).

(iii) soils of coastal areas in South Canterbury where atmospheric contributions of sulphur through sea spray, rainfall and sea fog were sufficient to meet the pasture's requirements for sulphur (Walker and Gregg, 1975).

(iv) soils where fluctuating ground water contains appreciable sulphate (Blakemore et al., 1969; Bailey, 1974).

2.2.a.2 IMPROVED PASTURES

After many years of intensive farming, the rate of accumulation of organic sulphur decreases and the mineralisation process becomes a more significant source of plant available sulphur. In these improved pastures, there is still a continual need for sulphur fertiliser (unless sulphur inputs from other sources are substantial) to offset losses, but the requirement may be less than during unimproved stages (During, 1972; Walker and Gregg, 1975).

The occurrence and magnitude of sulphur deficiencies in improved pastures seem to be mainly dependent upon the extent of sulphate leaching. For example, on soils with low sulphate retention, such as the yellow-brown pumice soils of the central North Island, sulphur deficiencies have been observed in spring on pastures where superphosphate had been applied regularly in autumn, at an average rate of 375 kg ha^{-1} (Toxopeus, 1965, 1970). Toxopeus (1970) concluded that the effectiveness of applied sulphate was short-lived because of rapid leaching losses during winter. Although the immobilisation process was not considered by this worker as another factor which may influence the level of plant available soil sulphur pool, it is likely that only a small fraction of the soil sulphate can be incorporated into soil organic matter by microorganisms during the winter months because of low soil temperature and high soil moisture (Barrow, 1960; Williams, 1967). Indirect evidence of sulphate leaching was obtained by comparing the levels of phosphate extractable sulphur in top soils (0-7.5cm) one month (40 to 70 μg S g^{-1}) and four months (1 to 12 μg S g^{-1}) after the application of superphosphate (22.5 - 45 kg S ha^{-1}) (Toxopeus, 1970). In another pasture mowing experiment conducted in eastern Bay of Plenty on sites with a long history of superphosphate application, sulphur responses were recorded only in soils with low sulphate retention capacities (Cottier and Hewitt, 1975).

Trials conducted on soils with higher sulphate retention capacities have shown variable results. Saunders and Cooper (1975) indicated that in the first year after cessation of sulphur application, no sulphur response can be expected in regularly topdressed pastures on soils with either a high sulphate retention, or a low sulphate retention and low annual rainfall ($<$ 900mm per annum).

In contrast, Ludecke (1970) has reported that sulphate was required to maintain maximum pasture production at a site on Takapau sandy loam which had received regular applications of superphosphate. The Takapau sandy loam (a yellow-brown loam yellow-brown earth intergrade) has a low to medium sulphate retention capacity in the topsoil and is highly retentive in the subsoil. Significant sulphur responses were also obtained at a site on highly sulphate retentive Waihou sandy loam (a yellow-brown loam) where sulphate had been withheld for two years

(Ludecke, 1970). This author suggested that leaching losses can occur even on high sulphate retaining soils where the rainfall is above 1200mm per annum.

To summarize, the above review suggests that the occurrence of sulphur deficiency in developed or undeveloped pastures depends on two main factors:

(i) the balance of mineralisation and immobilisation processes. A slow mineralisation rate may limit pasture production in areas where sulphur inputs from external sources such as the atmosphere and fertiliser are low.

(ii) the extent of sulphate leaching, which is influenced mainly by the amount of rainfall and the sulphate retention capacity of the soil.

2.2.b CORRECTION OF SULPHUR DEFICIENCIES

2.2.b.1 SULPHUR FERTILISERS AND THEIR AGRONOMIC EFFECTIVENESS

In New Zealand, the need for sulphur, recognised or otherwise, is often met by the application of superphosphate (During, 1972; Metson, 1979a). The sulphur in superphosphate is in the form of anhydrite calcium sulphate (dehydrated gypsum : $CaSO_4$) which is readily available to plants and can be leached through the soil by moving water (Barton and Wilde, 1971). In soils where there is a sulphur deficiency but the phosphate status is adequate or where sulphur requirements are not adequately met by a normal autumn application of superphosphate (Chittenden and Dodson, 1963; During and Martin, 1968; Toxopeus, 1970), elemental sulphur, usually in sulphur-fortified superphosphate (section 2.1.b.2) can be used (Metson, 1969; McIntosh and Sinclair, 1981). Elemental sulphur alone has not been considered to present a commercial alternative to sulphur-fortified superphosphate on soils primarily deficient in sulphur because of the risk of explosion in the hopper of the aeroplane (During, 1972). Recently however, it has been reported (McIntosh and Sinclair, 1981) that elemental sulphur can be safely spread from a hopper slung below a helicopter so the possibility of using it in aerial topdressing has become more practicable.

In low rainfall areas, calcium sulphate as gypsum ($CaSO_4.2H_2O$) has been found to give a greater initial response than elemental sulphur when applied at equivalent rates (Lobb and Reynolds, 1956; Walker, 1957b; Lobb, 1958; Lobb and Bennetts, 1958; Jones and Ruckman, 1966; Martin and Walker, 1966; McIntosh and Sinclair, 1981). The greater initial response is due to the fact that the sulphate in gypsum is immediately plant available, while elemental sulphur must first be oxidized to sulphate by soil microorganisms before it becomes available to plants (Burns, 1968; McLachlan, 1975). In field trials conducted by Walker (1957b) and Ludecke (1965) on brown-grey earths and dry subhydrous yellow-grey earths, gypsum was found to be more effective than elemental sulphur even up to four years after application. On these soils, sulphate leaching is not a problem because of a low annual rainfall (500mm), and the oxidation rate of elemental sulphur is restricted because of semi-arid conditions (Ludecke, 1965; Burns, 1968).

In high annual rainfall areas where substantial amounts of sulphate can be lost from low sulphate retaining soils (Chittenden, 1964; Goodall, 1964; Hogg and Toxopeus, 1966; During and Martin, 1968; McNaught and During, 1970; Wright and Morton, 1976), elemental sulphur is superior to gypsum in providing sulphur for plant growth. For instance, on the "pakihi" soils of the West Coast of the South Island, elemental sulphur at the rate of 21 kg ha^{-1} in the first year and again at the same rate in the third year was sufficient to produce relatively higher dry matter yields over a four-year experimental period than gypsum applied at a similar rate (McNaught and During, 1970). Similarly, on low sulphate retentive yellow-brown pumice soils of the central North Island, the residual value of gypsum has been reported by Hogg (1965), Hogg and Toxopeus, (1966) and Toxopeus (1965, 1970) to be short-lived (3 months) presumably due to rapid leaching losses during winter. In these strong leaching conditions (Toxopeus, 1970), autumn application of elemental sulphur is preferred to gypsum (Hogg and Toxopeus, 1966). Further evidence can be obtained from overseas studies conducted in similar leaching conditions. For example, results obtained from the study of Jones et al. (1970a) in northern California indicated that elemental sulphur was just as effective as gypsum in providing sulphur for plant growth in the first year after application but that it provided a greater residual effect in the following year. Similar findings have been observed on the Northern Tablelands of New South Wales (Weir, 1970).

2.2.b.2 RATE OF APPLICATION

(i) Unimproved pastures Information on the exact amounts of sulphur required to overcome initial sulphur deficiencies in New Zealand pastures is lacking. In a summary of his earlier work, Lobb (1958) reported that average levels of 34 to 45 kg sulphur ha^{-1}year^{-1} (sulphur in a 2:1 ratio of elemental sulphur and gypsum) were needed to give initial economic improvement on soils of Canterbury and Otago and a review of other trials (Walker, 1957b; Ludecke, 1962; Chittenden and Dodson, 1963; Goodall, 1964; Ludecke, 1965; Ludecke and Leamy, 1972; McLeod, 1974; Douglas and Risk, 1981) has revealed that maximum sulphur responses were obtained at rates of gypsum or elemental sulphur ranging from 14 to 60 kg sulphur per hectare. For instance, field trials on the tussock grassland of the South Island (McLeod, 1974; Douglas and Risk, 1981) indicate that sulphur-fortified superphosphate applied in late winter at the rates of 48 to 56 kg sulphur per hectare (25 to 33 kg ha^{-1} as elemental sulphur and 17 to 23 kg ha^{-1} as gypsum) is sufficient for the initial establishment of clover.

In low sulphate-retentive soils such as the yellow-brown pumice soils of the central North Island and the "pakihi" (gley podzols) of the South Island, where sulphate leaching can be substantial, heavier rates of sulphur are required for the initial establishment of clover (Chittenden, 1964, 1965; Toxopeus, 1965; McNaught and During, 1970; Metson et al., 1971; Toxopeus, 1971; During, 1972). For instance, field trials on the gley podzols of the Golden Bay area in Nelson district (Chittenden, 1964, 1965) showed that sulphur applied at a rate of up to 112 kg sulphur $ha^{-1}year^{-1}$ (62 kg as gypsum and 50 kg as elemental sulphur) was required for vigorous clover growth, and once pasture was established, maximum pasture production was maintained at an annual rate of 80 kg sulphur per hectare (28 kg in autumn and 52 kg in spring).

(ii) Improved pastures As with unimproved pastures, few field trials critically assessing sulphur requirements have been conducted on improved pastures. Published evidence to support a contention that the sulphur requirements of improved pastures are less than in unimproved situations (Walker and Gregg, 1975) is lacking.

Based on the results of their studies, Toxopeus (1964, 1970) and Toxopeus and Gordon (1971) considered that an annual rate of 380 kg ha^{-1} superphosphate (42 kg ha^{-1} sulphur), applied in early spring, should be adequate to maintain a high level of dry matter production ($>$ 10,000 kg ha^{-1}) on the low sulphate retentive yellow-brown pumice soils of the central North Island. In another study conducted in eastern Bay of Plenty on soils developed from volcanic ash, Cottier and Hewitt (1975) reported that a spring application of 25 kg per hectare per annum of sulphur as gypsum in superphosphate would provide adequate sulphur for pasture requirements. Indirect evidence obtained from field trials conducted by Bircham and Crouchley (1976) and fertiliser rates recommended by During (1970, 1972), During and McNeur (1975) and During and O'Connor (1975) suggest that an annual application of superphosphate resulting in the addition of sulphur at a rate of 14 - 28kg ha^{-1} sulphur is generally required for maintaining near maximum (85%) production on North Island pastures. The time of application has been considered unimportant except in areas where soils have a low ability to retain sulphate against leaching and rainfall exceeds 1000mm per annum (During and O'Connor, 1975).

The results from trials on irrigated pastures of Lismore stony silt loam (a yellow-grey earth) by Quin (1981) and Quin and Rickard (1981) suggested that sulphur requirements of improved pastures can be met by spring applications of superphosphate at the rate of 14 to 21.5 kg ha^{-1} of sulphur. A review of field trials conducted by McLeod (1974) revealed that maximum pasture production can be maintained by a late winter application of 50 kg ha^{-1} sulphur (17 kg as gypsum and 33 kg as elemental sulphur) every second year on high country yellow-grey earths and every third year on lowland yellow-brown earths.

2.2.b.3 TIME OF APPLICATION

In the past, decisions on the timing of superphosphate application have been dictated mainly by the phosphorus rather than the sulphur status of the soil. Since applied phosphate can be readily fixed by soil colloids and made less available to plants (During, 1972; Rajan, 1979), superphosphate is usually applied just prior to rapid pasture growth to ensure that pasture plants can utilise as much phosphate as possible before it is sorbed by soil particles. This is one reason why superphosphate is usually applied in early autumn. Other reasons for autumn application include: (i) the importance of maximum pasture growth in autumn and winter to meet animal demands (ii) the observation that late summer-autumn production is more sensitive to a lack of phosphorus than production at other times of the year (During, 1972) and (iii) the high incidence in spring of strong winds which may hinder aerial application. Wet air-strips in spring can also limit spring application.

This predominant practice of autumn application may not be appropriate for soils with low sulphate retention capacities because a large proportion of the applied sulphate can be leached out from the main rooting zone of pasture by winter rains. For instance, autumn application of superphosphate has been reported to be unable to ensure an adequate supply of sulphur for the following spring and summer growth on yellow-brown pumice soils (Hogg and Cooper, 1964; Toxopeus, 1965; Hogg and Toxopeus, 1966; Toxopeus, 1970), peat soils (Van der Elst, 1968), steepland soils related to yellow-brown earths (Blackmore et al., 1969), and gley podzols (During and Martin, 1968; McNaught and During, 1979). Alternative times of application such as spring application of superphosphate or split applications of superphosphate in the spring and autumn, have been recommended by these workers as a means of minimizing sulphate leaching. According to Hogg and Cooper (1964) and Hogg and Toxopeus (1966), sulphate applied in the spring is likely to be retained in the main rooting zone until the following winter and applications of sulphate in split dressings may maintain soil sulphate levels more evenly throughout the year than a single application in the autumn. However, there is little field evidence available to substantiate these claims, apart from those obtained in trials conducted by Toxopeus (1965) and Toxopeus and Gordon (1971) in which (a) pasture growth was better when superphosphate was applied in spring rather than autumn and (b) split dressings tended to even out pasture growth throughout the year.

2.2.c CONCLUSIONS

The majority of field investigations into sulphur deficiency in New Zealand have been conducted at unimproved sites assessing the nutrient requirements for the establishment of legumes and there is a serious lack of published information on the sulphur requirements of improved pastures.

Widespread sulphur deficiency exists in the initial stages of pasture development. Besides the sulphate losses associated with leaching, animal products and the uneven transfer of dung and urine, there is a net movement of inorganic sulphate into the soil organic matter especially in the early years of pasture establishment.

In more developed situations, sulphur requirements can often be met by the application of superphosphate provided that (i) the annual rate of addition of superphosphate is adequate and (ii) sulphate leaching losses are not substantial. In areas where leaching is significant, there is scope to modify either the form of sulphur fertiliser or the time of application to overcome this problem. For instance, spring application of superphosphate, split applications of superphosphate in the spring and autumn, or the use of slowly-released elemental sulphur with superphosphate (sulphur-fortified superphosphate) in areas where autumn application is unavoidable, are three possible strategies which could be considered as a means of alleviating sulphate losses. More research work is required to determine the most effective strategy in individual situations.

2.3 METHODS OF ASSESSING PASTURE SULPHUR STATUS

2.3.a INTRODUCTION

Methods which have been used to assess the sulphur status of crops and pastures include: (i) sulphur analyses of soil (Beaton et al., 1968) and herbage (Metson, 1973), (ii) glasshouse experiments (Jones and Crack, 1970; Crack, 1971) and (iii) field trials (During and Cooper, 1974; Cottier and Hewitt, 1975; Saunders and Cooper, 1975).

Although there are some advantages associated with glasshouse experiments and particularly field trials (Andrew et al., 1974), inherent limitations such as the amount of time, work and expense involved in conducting these studies make it impractical to apply them to every situation. For routine assessment of nutrient status, soil and herbage analysis are the most common techniques used and these will be discussed in the following review.

2.3.b SOIL ANALYSES

Numerous procedures have been proposed for evaluating the sulphur status of soils. They can be grouped into three main categories: (i) microbiological (Ensminger and Freney, 1966; Tisdale, 1971), (ii) isotopic (McKenzie et al., 1967; Probert, 1976; Arora and Sekhon, 1977; Goh and Tsuji, 1979; Tsuji and Goh, 1979), and (iii) chemical (Beaton et al., 1968; Reisenauer, 1975). Of these, chemical methods are the most practical for routine use because of the time involved in microbiological assays and the problems of working with radioactive isotopes on a large scale. These factors restrict the use of the two latter methods to a research role and they will not be discussed further in this review. Detailed attention will be focussed on chemical methods.

2.3.b.1 LABORATORY PROCEDURES

The usefulness of chemical soil tests in assessing the sulphur status of the area from which the samples were collected, depends upon several factors. These include the methods of sample preparation and soil storage, extraction procedures and analytical techniques.

2.3.b.1 (i) Sample preparation and soil storage

Soil storage (Chaudhry and Cornfield, 1971; Peverill et al., 1974; Spencer, 1974) and the physical treatment of soil samples such as grinding (Freney, 1961, 1967; Spencer, 1974) and drying (Barrow, 1961; Williams, 1967; Kowalenko and Lowe, 1975a; Peverill et al., 1974, 1975), can affect the level of extractable soil sulphur through:

(i) the mineralisation of organic sulphur by soil microorganisms (Chaudhry and Cornfield, 1971; Spencer, 1974).

(ii) the physical breakdown of complex organic sulphur into sulphate and simple organic sulphur compounds (Barrow, 1961; Kowalenko and Lowe, 1975a).

In contrast to the above findings, Probert (1977) indicated that air drying and storage of soil samples did not influence the levels of phosphate-extractable sulphur to any appreciable extent. Searle (1979) in his study with some New Zealand soils also reported that soil storage had no effect on phosphate-extractable sulphur.

These conflicting results indicate that there is further need to study the effects of drying and soil storage on the levels of extractable sulphur. To minimize such effects on the interpretation of analytical results, field moist soils can be frozen and only thawed out in a low temperature environment ($0^{o}C$) prior to the determination of sulphur status (Peverill et al., 1974).

2.3.b.1 (ii) Extraction procedures

Various extractants have been suggested for use in assessing the levels of plant available sulphur in soil but there is no general agreement on which estimate best defines a soil's sulphur supply (Reisenauer, 1975). Most of these extractants can be grouped into two categories depending on the forms of the extracted sulphur:

(i) readily-soluble sulphate.

(ii) readily-soluble and adsorbed sulphate.

(i) Extractants that remove readily soluble sulphate Cold water (Spencer and Freney, 1960; Walker and Doornenbal, 1972) and chloride solutions such as calcium chloride (Barrow, 1961; Kowalenko and Lowe, 1975a), lithium chloride and magnesium chloride (Roberts and Koehler, 1968; Tabatabai and Bremner, 1972) are extractants that have been shown to remove readily-soluble sulphate together with a small fraction of the organic sulphur (Beaton et al., 1968). These extractants are suitable for weakly-weathered soils in low rainfall areas where sulphate adsorption is negligible and little, if any adsorbed sulphate is present (Metson, 1979a).

The use of cold water has two disadvantages: (a) water usually deflocculates the soil particles, and makes the extract difficult to filter and (b) a water extract may overestimate the available soil sulphur levels because the additional organic sulphur extracted by cold water has been shown to be unavailable to either plants or soil micro-organisms (Barrow, 1961, 1967; Ensminger and Freney, 1966). To overcome these problems, the 0.15% calcium chloride solution of Williams and Steinbergs (1959) has been recommended by Barrow (1961, 1967) and Scott (1976). This solution, containing the divalent calcium cation (Ca^{++}), flocculates the soil colloids and as a result, the soil suspensions can be filtered easily (Barrow, 1961; Scott, 1976). Also, the extraction of non-available sulphur which occurs with cold water extracts, is prevented (Barrow, 1961).

(ii) Extractants that remove readily soluble and adsorbed sulphate In soils with the capacity to adsorb sulphate, water and chloride extractants generally underestimate the plant available soil sulphur (Fox et al., 1964; Barrow, 1967, 1969; Cooper, 1968; Tabatabai and Bremner, 1972; Saunders and Cooper, 1975; Goh and Tsuji, 1979). This is because the adsorbed sulphate, although plant available (Williams and Steinbergs, 1964), can only be displaced by an anion which is more strongly bound to the sorption sites of soil colloids. Phosphate is such an anion (Parfitt, 1978) and Ensminger (1954) proposed a potassium dihydrogen phosphate solution (KH_2PO_4 at pH 6.5) containing 500 μg ml^{-1} of phosphorus as an extractant for soil sulphur. However, the use of this solution renders centrifuging and filtering of the soil extract very difficult, as the clay in the sample becomes dispersed in the presence of the monovalent potassium cation (K^+) and the relatively high pH (6.5) (Fox et al., 1964; Ensminger and Freney, 1966). As a result, Barrow (1967) suggested a calcium phosphate solution (0.01 M $Ca(H_2PO_4)_2$ at pH 4) which overcame the problem of clay deflocculation. This extractant has been widely used (Bromfield, 1972; Probert, 1976; Probert and Jones, 1977) and tracer experiments (Probert, 1976; Goh and Tsuji, 1979; Tsuji and Goh, 1979) have shown that the extracted sulphur appears to come from the same pool of soil sulphur as that used by plants. In field studies using ^{35}S-labelled gypsum, Till and May (1971) and Gregg (1976) observed a close similarity between the specific activity of soil sulphate extracted by the calcium phosphate solution and that of the sulphur in plant material. This suggested that calcium phosphate-extractable sulphur is the precursor of plant sulphur.

Ensminger and Freney (1966) and Beaton et al. (1968) have suggested that the calcium ion in the calcium phosphate extractant not only prevents the deflocculation of the clay particles but also depresses the extraction of soil organic matter. However, Peverill and Briner (1974) and Peverill et al. (1974, 1975) have indicated that besides adsorbed and water-soluble sulphates, some organic forms of sulphur are also extracted by the use of a calcium phosphate solution. The Johnson and Nishita (1952) reduction procedure which is normally used for the final sulphur determination in the extracts, measures not only sulphate but also some of the soil organic sulphur compounds which are extracted by the calcium phosphate reagent (Beaton et al., 1968; Blakemore, 1979). This lack of specificity for sulphate means that the resultant estimates of extractable sulphur will include some soil organic sulphur. To remove organic sulphur, charcoal can be added to the extract (Peverill et al., 1975; Blakemore, 1979).

Blakemore (1979) and Searle (1979) have suggested that on highly anion retentive soils, 0.04 M calcium phosphate should be used in preference to the original 0.01 M solution in order to supply sufficient phosphate to displace all the adsorbed sulphur.

Besides the calcium phosphate extractant, phosphate solutions containing acetic acid have been employed by New Zealand workers (Cooper, 1968; Hogg et al., 1970; Saunders and Cooper, 1975) as extractants of the plant available soil sulphur. These acetic acid-phosphate solutions remove the readily soluble and adsorbed sulphate plus a fraction of organic sulphur (Reisenauer, 1975).

A sodium phosphate/acetic acid solution (0.03 M $NaH_2PO_4.2H_2O$ in 2 M HOAc at pH 2) has been reported by Cooper (1968) and Hogg et al. (1970) to be more sucessful than extractants such as potassium dihydrogen phosphate solution containing 500 $\mu g\ ml^{-1}$ of phosphorus (Ensminger, 1954) and 0.15% calcium chloride reagent (Williams and Steinbergs, 1959), in differentiating sulphur-responsive and non-responsive sites on soils of newly-developed pastures, but it has not proved to be a suitable method of soil testing on improved, well-developed pastures. The problems associated with the well-developed soils were assumed by these workers to be due to (a) changes in types of vegetation and the nature of soil sulphur with pasture development, (b) the lack of an understanding of the soil depth from which plants take up sulphate ions and (c) the association of sulphate with soil colloids. On the highly sulphate retentive soils, the sodium phosphate/acetic acid solution is unable to extract enough adsorbed sulphate to indicate fully the sulphur status of these soils.

In an attempt to rectify these problems, the original sodium phosphate/acetic acid solution was modified by Saunders and Cooper (1975). The new reagent (0.03 M $NaH_2PO_4.2H_2O$ in 0.35 M HOAc at pH 3) was shown by these authors to be suitable under New Zealand conditions for a range of unimproved and developed soils. In the low range of soil test values (less than 5 $\mu g\ S\ g^{-1}$) it was superior to the original extractant in predicting sulphur response, however both methods were unreliable in differentiating between sulphur responsive and non-responsive sites in soils where sulphur values between 6-9 $\mu g\ g^{-1}$ were recorded. To assist in assessing pasture sulphur status, these workers suggested that the sulphate retention capacity of soils should be measured in conjunction with a soil sulphur test because it indicates the potential for a soil to maintain sulphate in the plant available soil sulphur pool against leaching.

A calcium phosphate/acetic acid solution ($Ca(H_2PO_4)_2\ H_2O$ containing 500 $\mu g\ ml^{-1}$ of phosphorus in 2 M HOAc) has been shown by Hoeft et al. (1973) to be (i) superior to the Cooper's (1968) sodium phosphate/acetic acid extractant (0.03 M $NaH_2PO_4.2H_2O$ in 2M HOAc at pH 2) and (ii) as reliable as the calcium phosphate solution as proposed by Fox et al. (1964) and Barrow (1967) in predicting plant response. In contrast to these findings, Goh and Tsuji (1979) and Tsuji and Goh (1979) have reported that soil sulphur extracted by calcium phosphate solution or by Saunders and Cooper's modified sodium phosphate/acetic acid reagent (0.03 M $NaH_2PO_4.2H_2O$ in 0.35 M HOA at pH 3) was more strongly correlated with the isotopically exchangeable soil sulphur (E value) and plant sulphur uptake than the sulphur fraction removed by a calcium phosphate/acetic acid solution.

These conflicting results suggest that further research is necessary before phosphate/acetic acid solutions are widely used.

2.3.b.1 (iii) Analytical problems

The unavailability of an accurate, rapid and simple method for sulphate analysis is a major factor contributing to the relative lack of interest in sulphur research (Blair, 1979; Metson, 1979a). The amounts of sulphate in soil extracts can be measured by one of two main methods:

(i) the turbidimetric determination of sulphate as barium sulphate.

(ii) the reduction procedure of Johnson and Nishita (1952).

(i) Turbidimetric determination as barium sulphate This procedure has been widely used for the determination of sulphate in soil extracts (Beaton et al., 1968; Reisenauer et al., 1973). However, interferences in the formation of the barium sulphate precipitate can cause gross errors in the quantity of sulphate measured (Reisenauer et al., 1973). For instance, the presence of colloidal organic matter can lead to two types of errors. Firstly, it acts as a protective colloid causing an underestimation in extracts containing small amounts of sulphate ($< 10\ \mu g\ ml^{-1}$ of sulphur), and secondly, at higher concentrations of sulphate, the organic matter is coprecipitated with the barium sulphate resulting in abnormally high sulphur values.

In spite of these problems, the turbidimetric method can be automated (Sinclair, 1973), thereby offering the great advantage of increased speed over the more tedious reduction procedure devised by Johnson and Nishita (1952) and described in the next section. The possible interference of colloidal organic matter in the precipitation of sulphate as barium sulphate must still be removed before analysis on the Autoanalyser and this is achieved by the addition of charcoal to the soil extracts (Sinclair, 1973).

(ii) Reduction to hydrogen sulphide This procedure involves reduction of the sulphur in soil extracts to hydrogen sulphide, collection of this hydrogen sulphide in zinc acetate solution and the colourimetric determination of the resulting methylene blue solution (Johnson and Nishita, 1952).

This reduction procedure circumvents the problem of interference in the precipitation of barium sulphate but is time consuming (Sinclair, 1973). Furthermore, the technique is not specific for sulphate, as other inorganic sulphur compounds such as sulphides, sulphites and possibly some very labile fractions of organic sulphur such as sulphate esters, can also be reduced to hydrogen sulphide (Beaton et al., 1968). This problem can be partly overcome by the addition of activated charcoal to soil extracts to remove organic sulphur compounds (Peverill and Briner, 1974; Peverill et al., 1974, 1975; Blakemore, 1979).

2.3.b.2 CALIBRATION OF SULPHUR SOIL TESTS

There are many inherent limitations in the extrapolation of sulphur soil test results to field situations (Reisenauer, 1975; Saunders and Cooper, 1975). These include:

(i) the unpredictable rates of mineralisation and immobilisation processes which are largely influenced by climatic conditions such as soil temperature and soil moisture.
(ii) the degree of sulphate leaching under field conditions.
(iii) the recycling of sulphur through dung and urine.
(iv) the contribution of sulphur from the atmosphere and irrigation water.
(v) the tendency of adsorbed sulphate to accumulate in the subsoil and its possible contribution to plant uptake.

The latter problem has been discussed by several workers (Cooper, 1968; Hogg et al., 1970; Toxopeus, 1970). It has been suggested that, to fully evaluate the supply of soil sulphur, soil samples should be taken to a depth that encompasses the zone of active root uptake, especially when sulphate levels in the top soil (0-7.5cm) are low yet pasture plants contain a significant amount of sulphur (Goh et al., 1977; Gregg et al., 1977). In practice, it is difficult to define an active zone of sulphur uptake without (i) the use of isotopes to assess the contribution from various soil depths to the total sulphur uptake by plants and (ii) an investigation of the rooting habit of the plant and the effects of soil physical and chemical factors on root activity.

In view of the above discussion, soil test figures for sulphur based on 0-7.5cm samples should not always be considered as the sole criterion for indicating pasture sulphur status. A study of the sulphate distribution within the soil profile at least to a depth of 50cm could well be useful in some situations.

2.3.b.3 CONCLUSIONS

The plant available soil sulphur pool is a dynamic system which is influenced by several factors such as leaching losses, plant uptake, mineralisation and immobilisation. Therefore the amount of sulphur extracted by a soil test at any one time is the result of several processes and it would be desirable that a chemical method for determining soil sulphur status should take into account (a) the readily soluble and adsorbed sulphate anions which are considered to represent plant available soil sulphur (Metson, 1979a) and (b) the portion of labile organic sulphur which is likely to be mineralised over a growing season. Extractants containing phosphate are considered to be most suitable in high sulphate retaining soils because phosphate anions can displace adsorbed sulphate and also extract some organic sulphur. In soils with low sulphate retention, chloride solutions are as effective as phosphate extractants in estimating the plant available soil sulphur pool.

Soil testing for sulphur has, in general, a limited value in predicting plant response because soil tests do not take into account several factors such as sulphur additions from the atmosphere, the rate of mineralisation and immobilisation of organic sulphur and leaching losses which influence the size of plant available soil sulphur pool. Its predictive value can be improved by proper sampling procedures, and by including in the interpretation of soil test data the possible effects of the above-mentioned factors.

Different critical levels for soil sulphur, above which no response to fertiliser sulphur would be expected, have been proposed by various workers and adequately reviewed by Beaton et al., (1968), Reisenauer et al.

(1973), Andrew (1975), Reisenauer (1975), Arora and Sekhon (1977) and Blair (1979). The variability in the critical values obtained, serves to emphasize the need for correlation studies to be conducted in all regions of interest to establish which soil test method best predicts the plant availability of soil sulphur in those individual localities.

2.3.c PLANT ANALYSES

Plant analysis relies on the concept that the concentration of a nutrient within the plant is an integral of all the factors that have influenced the nutrient concentration up to the time of sampling (Ulrich and Hills, 1967). As such, the sulphur content in the tissue of a specified plant part may indicate whether or not the plant represented by the herbage sample is receiving adequate amounts of sulphur at the time the sample is taken (Ulrich and Hills, 1967). This judgement is made by comparing the analytical results with a predetermined critical value derived from a curve showing the relationship between yield and nutrient concentration (Ulrich and Hills, 1967). Various ways of defining the term "critical value" have been outlined by Metson (1973). In the folloiwng review, it is referred to as the minimum nutrient concentration required in plant tissue for a near maximum production (McNaught and Christoffels, 1961; McNaught, 1970).

2.3.c.1 FACTORS AFFECTING CRITICAL SULPHUR CONCENTRATIONS

Several factors have been reported to affect the relationship between plant yield and sulphur content (Jones, 1975; Spencer et al., 1977a,b). These include:

(i) Environmental conditions and the supply of nutrients other than sulphur.

(ii) Plant age.

(iii) Plant part.

(iv) Plant species.

(v) Sample decomposition prior to sulphur analysis.

(i) Environmental conditions and the supply of other nutrients. The inadequacy of any other essential nutrient can influence the magnitude of the critical values of plant sulphur indices. For instance, the correction of phosphorus or nitrogen deficiency has been shown to lower the critical values of total sulphur and sulphate in clover plants (Bouma et al., 1969; Jones et al., 1970b; Spencer et al., 1977a,b). When nitrogen is deficient for grass growth or molybdenum is insufficient for efficient legume-Rhizobium symbiosis (Kerridge et al., 1972), a medium to high level of sulphate in grass and clover plants does not necessarily indicate an adequate sulphur supply but rather the limiting of protein formation by a lack of nitrogen relative to sulphur (Ensminger and Freney, 1966; O'Connor and Vartha, 1969).

In the same way as the inadequacy of supply of other nutrients, any environmental factor that limits plant growth, be it light, temperature or moisture stress, can cause the accumulation of sulphur in plant tissues and invalidate any conclusions drawn from plant analyses (Jones, 1975).

(ii) Plant age. The stage of plant growth can markedly influence sulphur concentrations in plant tissue. As the plant ages, there is an appreciable decrease in sulphur levels (McNaught and Christoffels, 1961; McNaught, 1970; Spencer et al., 1977a,b). Such effects can make it difficult to interpret analytical data unless the approximate age of the plant is known. To overcome this problem, established procedures for the foliar analysis of trees and crops generally require that leaf samples be taken at a certain stage of plant growth. This can be achieved by sampling at a particular time interval from sowing, or at some easily recognisable growth stage, such as the commencement of flowering (McNaught, 1970). For pastures where a reliable estimation of plant age is difficult because plants are subjected to grazing, McNaught (1970) has suggested that the sampling of grass and clover species should be standardised at a grazing height (4 to 8cm for sheep and 8 to 15cm for dairy farms).

(iii) Plant part. Sulphur content can vary within the plant (Ensminger and Freney, 1966; Spencer et al., 1977a,b). For instance, the stems of clover have lower sulphur concentrations than the laminae and the petioles (McNaught and Christoffels, 1961). Thus it is necessary to standardise the part of the plant to be analysed. In New Zealand, it is the practice for white clover leaves (laminae and petioles) and grass leaves to be sampled for pasture sulphur analyses (McNaught, 1970).

(iv) Plant species. There are inherent differences between grass and clover in their sulphur requirement and ability to absorb sulphur from the soil (Walker and Adams, 1958; McNaught and Christoffels, 1961; McNaught, 1970; Metson, 1973). Furthermore, different species or strains of grasses and clover can vary in their sulphur requirements and therefore their critical sulphur concentrations (Saalbach, 1970; Metson, 1973; Andrew, 1975). Thus, it is difficult to accurately predict from the sulphur values of a mixed sward, what the sulphur levels in clovers and their associated grasses would be, even when the exact botanical composition is known (McNaught, 1970; Briner et al., 1974). There are also other reasons for analysing grasses and clovers separately:

(a) Since grasses in New Zealand pastures depend almost entirely on associated clovers for their nitrogen supply (During, 1972) and sulphur deficiency has been shown to limit nitrogen fixation by affecting the metabolism of symbiotically nitrogen fixing nodule bacteria (Anderson and

and Spencer, 1950; Walker, 1957a; Walker and Adams, 1958), an accurate estimation of the sulphur status of clover is very important.

(b) In a mixed sward where nitrogen deficiency occurs in grasses while their associated clovers are nitrogen-adequate (McNaught, 1970; Jones, 1975), diagnosis of pasture sulphur status can be complicated by such deficiency. The nitrogen deficient grasses tend to accumulate sulphate in their tissues and this accumulation can give an erroneous picture of plant sulphur status (Jones, 1975). Thus the sulphur status of the mixed sward is best revealed by analysis of the clover component.

(v) Sample decomposition prior to sulphur analysis. After cutting, herbage samples should be dried as rapidly as possible to minimize chemical and biological changes. If drying is unduly delayed, considerable loss in dry weight may occur due to respiration, and this loss can have the effect of changing the apparent nutrient analyses to a point where serious errors occur (Jones and Steyn, 1973; Jones, 1978). For instance, Lockman (1970) observed that the average level of total sulphur (0.34%) in decayed samples in which 36 percent of the dry weight had been lost by a rotting process, was about 189% of that in non-rotted samples (0.18% sulphur).

Overall, the above review indicates that there are many factors which can affect the critical values of plant sulphur indices. It is therefore difficult to extrapolate the critical concentrations which are appropriate in one situation and apply these to other situations. Any published information on the critical concentrations for plant sulphur must be treated as a tentative guide in the interpretation of plant analyses and should not be applied uncritically to all situations.

2.3.c.2 INDICES FOR ASSESSING PLANT SULPHUR STATUS

Plant analyses which have been used as indices for assessing the sulphur status of plants include:

(i) total sulphur content (S).

(ii) sulphate content (SO_4-S), alternatively termed reducible sulphur (Jones, 1975).

(iii) sulphate as a percentage of total sulphur (SO_4-S:S).

(iv) the ratio of total nitrogen to total sulphur (N:S).

(v) the ratio of total phosphorus to total sulphur (P:S).

(vi) amide nitrogen.

Of these, the commonly used indices in New Zealand and overseas are: total sulphur, sulphate, sulphate as a percentage of total sulphur and the ratio of total nitrogen to total sulphur (Metson, 1973; Spencer et al., 1977a,b) and attention will be focussed on these. The less common indicators such as the ratio of total phosphorus to total sulphur (Beaton et al., 1969; Aulakh and Dev, 1977; Martel and Ziska, 1977) and amide nitrogen (Metson and Collie, 1972; Bolton et al., 1976; Rendig et al., 1976; Freney et al., 1978) will not be discussed further.

(i) Total sulphur. The total sulphur concentration in plant tissues has been used as an index of plant sulphur status because it is thought to be directly related to the sulphur supply (Jones, 1962; Ensminger and Freney, 1966; Spencer et al., 1977a,b).

Total sulphur in grass. The critical sulphur levels for the grass component of mixed swards are in the range 0.23 to 0.30% on a dry matter basis (McNaught and Christoffels, 1961). These levels appear to be related to the nitrogen concentration in the grass. The higher the nitrogen content, the higher the sulphur requirement (McNaught and Christoffels, 1961; O'Connor and Vartha, 1969).

Total sulphur in clover. A narrow range of critical levels has been recommended for clovers. A critical sulphur concentration of

0.26% (with a range of 0.25% to 0.29%) for white clover containing a mean nitrogen content of 4.8% has been proposed by McNaught and Christoffels (1961), while in another review, McNaught (1970) has suggested the critical sulphur level in white clover with high total nitrogen (4.5 to 5.5%) is approximately 0.28% (0.25% to 0.30%).

Observing that very few reported sulphur analyses for white clover ever exceeded the critical ranges mentioned above, Metson (1973) suggested that because of competition from grasses for sulphur, white clover may only ever attain a marginal sufficiency in sulphur, even in well-developed pastures.

(ii) Sulphate. Herbage sulphate concentration can be used as an indicator of plant sulphur status because it is related to sulphur supply and tends to accumulate in plant tissues when the soil sulphur supply is in excess of the plant's requirement for protein synthesis (Dijkshoorn et al., 1960; Jones, 1962, 1963; Smith and Dolby, 1977; Spencer et al., 1977a,b). Although sulphate has been considered by these workers to be a more sensitive index than total sulphur because of the greater difference in sulphate concentrations between sulphur deficient and non-deficient plants, it has several shortcomings which preclude its use as a reliable criterion in assessing plant sulphur status. For instance, any deficiency affecting protein synthesis, such as a molybdenum or nitrogen deficiency, can also cause sulphate to accumulate in the plant (Ensminger and Freney, 1966). Furthermore, although the work of Smith and Dolby (1977) suggested sulphate to be more useful than total sulphur as an indicator of green panic grass (Panicum maximum) sulphur status because of its reduced dependence on plant age, the results obtained by Spencer et al., (1977a,b) with subterranean clover (Trifolium subterraneum) indicate that the critical sulphate concentrations are markedly affected by the stage of plant growth.

Critical sulphate levels for grasses and their associated clovers have not been determined by New Zealand workers. A wide range of sulphate levels in white clover plants (Trifolium repens) has been reported in a trial conducted by Metson (1972), ranging from 0.009% to 0.049% in the control and 0.010% to 0.239% in the sulphur-treated plots. However, the data did not enable this worker to define a critical value because it was not certain that the maximum yield was obtained. Using the critical sulphate level (0.032%) suggested by Dutch scientists (Dijkshoorn et al., 1960), Metson (1972) was able to show that the corresponding critical level of total sulphur, derived from a graph showing a close relationship ($r = 0.97$) between total sulphur and sulphate in grass, was less than 0.20%. This concentration was well below the critical sulphur levels proposed by McNaught and Christoffels (1961) and McNaught (1970). Thus he concluded that while the critical level of sulphate proposed by Dijkshoorn et al. (1960) may be useful as an index of acute physiological deficiency (as gauged by the presence of chlorotic symptoms and reduced utilisation of nitrogen in protein formation), it does not necessarily indicate the critical level required for near maximum (90 to 95%) dry matter production.

Since the accumulation of sulphate in grasses could be due to nitrogen or molybdenum deficiency, the sulphate status of a mixed sward is best indicated by the sulphate content of associated clovers (Ensminger and Freney, 1966; Jones, 1975). Critical sulphate values for clovers in the range of 0.017% to 0.030% have been proposed by overseas workers (Jones, 1962; Jones and Martin, 1964; Bouma et al., 1969; Jones et al., 1972).

(iii) Sulphate as a percentage of total sulphur. The proportion of total plant sulphur occurring as sulphate has been suggested recently as a measure of plant sulphur status (Smith and Dolby, 1977; Freney et al., 1978). It is claimed that this parameter has great potential, as it is related to plant yield and is unaffected by plant age or nitrogen supply. Smith and Dolby (1977) reported that green panic grass (Panicum maximum) had adequate sulphur when more than 12% of its total sulphur was in the sulphate form. Similarly, the results by Freney et al. (1978) suggest that wheat plants (Triticum aestivum) containing more than 10% of their sulphur in sulphate form, are adequately supplied with sulphur. For subterranean clover (Trifolium subterraneum) the critical value of this index, 3.5%, was much lower than that for the non-legumes (Spencer et al., 1978).

In a field trial conducted by Metson (1972) to investigate the solubility of various sulphur fertilisers, the results obtained from the sulphur-treated plots showed that the highest proportion of total sulphur as sulphate in grass was about 55%, but the proportion in clover seldom exceeded 20%. This suggests that grass is a stronger accumulator of sulphate than clover. Since it was not certain that the maximum yield was obtained in this study, no critical value was proposed.

(iv) The ratio of total nitrogen to total sulphur. The ratio of total nitrogen to total sulphur (N:S) in plant tissues has been advocated as a useful means of assessing the sulphur status of plants (Pumphrey and Moore, 1965; Dijkshoorn and Van Wijk, 1967). This index is based on a relatively constant nitrogen:sulphur ratio in the protein fraction in plant tissues for a particular species. As a result, any major change in the supply of nitrogen or sulphur which leads to an accumulation of non-protein nitrogen or of non-protein sulphur, will cause a corresponding change in the ratio of total nitrogen to total sulphur (N:S). Thus when the sulphur supply is in excess of the plant's current requirement for protein synthesis or when a nitrogen deficiency is pronounced, the accumulation of non-protein sulphur such as sulphate, is reflected in a low N:S ratio. In contrast, when protein formation is restricted by a sulphur deficiency, simpler nitrogen compounds accumulate and a high N:S ratio results (Metson, 1973).

Although the N:S ratio is claimed to be a more reliable index of plant sulphur status than sulphate or total sulphur in overcoming the effects of plant age and plant part (Pumphrey and Moore, 1965; Spencer et al., 1977a,b), it should be treated with caution, as it is greatly influenced by the supply of nitrogen (Smith and Dolby, 1977). For instance, a high N:S ratio may be misinterpreted as indicative of sulphur deficiency when in fact it is caused by the liberal input of nitrogen to the soil-plant system. Similarly, a low N:S value may be a reflection of nitrogen deficiency rather than a surplus of sulphur. Thus, the N:S ratios should not be used alone as a parameter of plant sulphur without taking into consideration any environmental factor which may seriously affect plant nitrogen status. For example, the level of soil pH and the adequacy of soil phosphorus, molybdenum or calcium can influence the capacity of Rhizobium to fix nitrogen (Andrew, 1977) and hence the N:S ratios in the clover plants. In the case of the associated grasses, their nitrogen status can also be governed by factors other than the indirect effect of sulphur deficiency on biological nitrogen fixation (Walker, 1957a; Walker and Adams, 1958; Metson, 1973). Grazing management and climatic conditions can seriously affect the efficiency of pathways in which the nitrogen fixed symbiotically by Rhizobium bacteria in clover nodules, is transferred to associated grasses (Ball, 1977).

N:S ratios in grass. A wide range of critical N:S ratios have been reported by various workers. The review of Dijkshoorn and Van Wijk (1967) suggests that a N:S ratio in excess of 14 may be indicative of sulphur deficiency in grasses. From the study conducted by

McNaught and Christoffels (1961) in which different critical sulphur concentrations for grasses were proposed for various levels of nitrogen, the corresponding critical N:S ratios can be calculated and are approximately 9 - 11 for low nitrogen status (2 to 2.5%); 10 - 12 for medium nitrogen (2.5 to 3%) and 12 - 14 for high nitrogen concentrations (3.5 to 4%). In contrast to these findings, McNaught (1970) and McNaught and During (1970) have proposed a critical N:S range of 15 - 17 without stating the significance of nitrogen status in influencing N:S ratios.

Based on the results obtained from fertiliser trials of McNaught and During (1970), in which the clovers showed evidence of marginal sulphur deficiency with low levels of total sulphur ($< 0.24\%$) and N:S ratios exceeding 18:1, while the associated grasses were adequately supplied with sulphur as judged by their high sulphur concentrations ($> 0.26\%$) and low N:S ratios (4 to 8), Metson (1973) has suggested that a N:S ratio of not more than 8 in the grass may be required to ensure adequate clover nutrition and maximum production of mixed pastures. This interpretation is open to criticism because the poor nitrogen status of the ryegrass in the trial of McNaught and During (1970) may have seriously affected its N:S ratios.

N:S ratio in clover. A critical N:S ratio of 17 to 19 for white clover in a mixed sward at grazing height has been proposed by McNaught (1970) and McNaught and During (1970). The mean value of 18:1 corresponds to a total nitrogen level of 5% at a total sulphur concentration of 0.28% (McNaught, 1970). This value for the N:S ratio is similar to that derived from McNaught and Christoffels' review (1961).

2.3.c.3 CONCLUSION

All plant sulphur indices have certain shortcomings which preclude their use as completely satisfactory indicators of plant sulphur status. To overcome the drawbacks inherent in each index, multiple criteria should be employed in assessing the sulphur status of grass and clover in grazed pastures.

CHAPTER 3

A SURVEY OF THE SULPHUR STATUS OF EASTLAND PASTURES

3.1 INTRODUCTION

It is generally accepted that plants take up sulphur from soil almost exclusively in the sulphate form and that the plant available soil sulphur pool consists of the readily soluble sulphate and adsorbed sulphate fractions (Metson, 1979a).

Sulphur, as sulphate, is only weakly adsorbed by soil colloids. As a result, it can be removed from the plant available soil sulphur pool by the movement of water over the soil surface or down through the soil profile.

Soil sulphate status is dependent upon several factors including soil properties, rainfall patterns and the history of sulphur fertiliser application. For instance, the loss of sulphate through leaching would be expected to be significant in areas with both a high rainfall and soils of low sulphate retention capacity.

When attempting to identify areas that may be sulphur deficient or to indicate areas where problems may arise from the omission of sulphur fertiliser, it is necessary to establish associations between soil sulphur status and factors such as the anion retention capacity of soils, rainfall patterns, and sulphur fertiliser histories (including rates, forms and times of application). In this study a survey has been carried out with the object of assessing the importance of the above-mentioned factors in affecting the soil sulphur status in the Eastland area. The survey involved the collection and laboratory analysis of soil and herbage samples.

A pre-requisite of the study was that a suitable chemical extractant exist for the measurement of the plant available pool of sulphur in the soil samples collected. Although a wide range of chemical extractants have been used to determine the levels of plant available sulphur in soils (Beaton et al., 1968), there has been little or no agreement about which extractant best estimates this soil sulphur pool (Reisenauer, 1975). It was therefore decided that a preliminary glasshouse experiment should be conducted to establish which soil test method best predicted the plant availability of soil sulphur in the Eastland soils covered by the survey.

3.2 METHODS AND MATERIALS

Two sampling surveys for soil and herbage were conducted; one in autumn 1979 and the second in the following spring 1979. The survey was concentrated in two areas; one in the Gisborne district and the other in Central Hawke's Bay.

The total number of sites sampled in autumn and spring was 14 and 17 respectively. Of these, three sites were sampled in both autumn and spring for purposes of direct comparison of the levels of soil sulphate before and after winter. Overall, samples from 31 sites were taken for sulphur evaluation. Sites were chosen to cover a wide range of probable soil sulphur retention capacities as indicated by a phosphate retention test, rainfall patterns and fertiliser topdressing histories. Descriptions of these sites are given in appendices I and IV.

In autumn, sites which had received a sulphur application in the previous spring were sampled to assess whether spring topdressing was able to maintain an adequate level of soil sulphur for pasture growth over the following summer and autumn. Areas where there had been a very recent application of a sulphur-containing fertiliser were avoided in the selection of sites because of the likely variable inputs of sulphur fertiliser into the plant available soil sulphur pool at this stage. An exception to this general approach was made for the three sites to be sampled in both autumn and spring (sites 3, 5 and 6). These sites were topdressed just prior to the autumn sampling (appendix I).

To enable an assessment to be made of the ability of autumn applications to maintain soil and pasture sulphur status in the following spring, several sites sampled in spring were chosen where there had been an application of sulphur-containing fertilisers in the previous autumn (appendices III and IV). These sites were compared with others on the same or similar soil types which had received little or no sulphur fertiliser in the past.

At each site, twenty soil cores (25mm diameter) were taken from different depths (0-7.5, 7.5-15 and 15-30cm) and where possible, herbage samples were also taken for laboratory analysis. Attempts were made to avoid collecting samples from recognisable dung and urine patches, stock camps and tracks.

At nine out of the fourteen sites (sites 1, 2, 3, 4, 6, 7, 8, 11 and 12) sampled during the autumn, larger quantities of soil were also taken from a depth of 0-7.5cm for use in a glasshouse trial to determine the most suitable extractant for measuring the plant available sulphur in these soils.

3.2.a GLASSHOUSE PROCEDURE

3.2.a.1 PREPARATION OF POTS

Soil samples used in the glasshouse study were passed through a 5 mm sieve, air-dried, and placed firmly into 10 x 10 x 10 cm^3 plastic pots. Perennial ryegrass seeds (Lolium perenne L.) were sown on 4th August, 1979. Prior to sowing, soils were watered with deionised water to 75% of field capacity.

3.2.a.2 EXPERIMENTAL DESIGN

A subtractive glasshouse technique based on that of Middleton and Toxopeus (1973) was used. This method involves growing a large number of indicator plants per pot (100 ryegrass seeds were sown per pot and no thinning took place) with a balanced nutrient solution added regularly. Control plants received all macro and micro-nutrients. Minus sulphur plants were treated identically except for the omission of sulphur from the nutrient solution. Thus, growth was solely dependent on the soil as a source of sulphur. Similarly, minus phosphorus plants received nutrient solution containing all essential nutrients except for phosphorus. These three treatments were replicated four times for each soil to give a total of 108 pots, which were arranged in a randomised block design.

Pots in each block were randomly moved about weekly to minimise the effect of uneven light intensity in the glasshouse.

Nutrient additions were commenced approximately 20 days after sowing. The frequency of nutrient solution application varied, depending upon the growth rate for the various soils and treatments.

3.2.a.3 HARVESTING TECHNIQUE

Two harvests were taken. The first cut was made 45 days after sowing and the second cut 27 days later. At each harvest, the plants were cut at a height of 3cm above the soil surface and then dried in a fan-oven at $60^{0}C$ for 48 hours before weighing for dry matter yield.

The degree of deficiency due to the ommission of an element was expressed as follows:

$$\begin{array}{c}\text{Degree of deficiency}\\ \text{or}\\ \text{plant response}\end{array} = \frac{\begin{array}{c}\text{D.M. yield in}\\ \text{control pots (g/pot)}\end{array} - \begin{array}{c}\text{D.M. yield in}\\ \text{treated pots (g/pot)}\end{array}}{\text{D.M. yield in control pots (g/pot)}} \times 100$$

3.2.b SOIL ANALYSIS

All soil samples were sieved through a 2mm sieve prior to laboratory analysis.

3.2.b.1 EXTRACTION OF SOIL SULPHATE

Since it is probable that physical breakdown and mineralisation of organic sulphur can occur during air-drying and storage of soil sample prior to the determination of sulphur status (Peverill et al., 1974), soil samples collected in the survey were frozen at $-5^{0}C$ and then thawed in a cool room ($0^{0}C$) immediately prior to analysis.

Subsamples of air-dried soils, used in the glasshouse experiment, were also analysed.

The following extraction procedures were used:

(i) Calcium chloride extractable sulphur:

A 5g sample of air-dried soil, or the equivalent weight of moist soil, (based on measured moisture content) was shaken for 16 hours at room temperature with 25ml of 0.01M $CaCl_2$ (Williams and Steinbergs, 1959).

After centrifuging (3000 r.p.m. for 5 minutes) and filtering through a number 1 Whatman filter paper, 5 ml of filtrate was evaporated to dryness in a digestion flask prior to determination of the sulphur content using a reduction procedure (Johnson and Nishita, 1952). The absorbance of the resulting methylene blue solution, was measured using a Unicam SP 1800 spectrophotometer at a wavelength of 670 nm.

(ii) Phosphate extractable sulphur:

A 5g sample of air-dried soil, or the equivalent weight of moist soil, was shaken for 16 hours with 25ml of 0.01M $Ca(H_2PO_4)_2$ solution at pH 4 (Barrow, 1967).

As with the $CaCl_2$ extracts, the phosphate extracts were centrifuged, filtered and analysed for sulphur.

3.2.b.2 AVAILABLE SOIL PHOSPHORUS

A 1g sample of air-dried soil or a calculated equivalent weight of moist soil was shaken for 30 minutes with 20ml of 0.5M $NaHCO_3$ solution at pH 8.5 (Olsen et al., 1954). After centrifuging (10,000 r.p.m. for 2 minutes) and filtering through a number 5 filter paper, a 4ml aliquot was taken for phosphorus determination using the method of Murphy and Riley (1962). The absorbance of the resulting solution was measured using a Unicam SP 1800 spectrophotometer at a wavelength of 712 nm.

3.2.b.3 PHOSPHATE RETENTION CAPACITY

A 5g sample of air-dried soil or a calculated equivalent weight of moist soil was shaken for 16 hours with 25ml of 0.2M sodium acetate solution at pH 4.65 containing 1000 μg P ml^{-1} (Saunders, 1965).

The amounts of phosphorus left in the soil extracts were determined by the method of Murphy and Riley (1962).

3.2.b.4 SOIL pH

Subsamples (10g) of the air-dried soils used in the glasshouse study were mixed with 25ml of distilled water and left to equilibrate overnight. The pH was measured with a combination electrode.

3.2.c HERBAGE ANALYSIS

All herbage samples were oven-dried at $60^{0}C$ and finely ground prior to analysis for sulphate, total sulphur and total nitrogen.

3.2.c.1 SULPHATE:

A weighed sample of less than 0.025g was placed in a digestion flask and analysed directly for sulphate using the 'Johnson-Nishita' reducing mixture (Beaton et al., 1968).

3.2.c.2 TOTAL SULPHUR :

A weighed sample of less than 0.01g was oxidised with 0.25g of a mixture of sodium bicarbonate and silver oxide at $550^{0}C$ for 3 hours (Steinbergs et al., 1962). After cooling, the mixture was transferred to a digestion flask and the sulphur content determined by a reduction procedure (Johnson and Nishita, 1952).

3.2.c.3 TOTAL NITROGEN:

A weighed sample of less than 0.15g was digested with 5ml of a digestion mixture (containing 1g of selenium, 100g of potassium sulphate, and 1000ml of concentrated sulphuric acid) at $360^{0}C$ for 3.5 hours. Nitrogen was then determined colourimetrically (M.A. Turner, pers. comm. 1979). Details of the technique are listed in appendix V.

3.3 GLASSHOUSE STUDY

3.3.1 RESULTS AND DISCUSSION

There were significant reductions in dry matter yield in the first harvest due to the omission of sulphur on six of the nine soils tested in the glasshouse investigation (table 3.1, appendix VI). The magnitude of the sulphur deficiencies obtained from the glasshouse trial appeared to reflect the sulphur fertiliser history of each site. For instance, at site 11, which had not been frequently topdressed with superphosphate (appendix II), omission of sulphur induced a reduction in dry matter yield of up to 46% in the first harvest (table 3.1). Similarly, sulphur deficiencies of over 20% existed at sites 1 and 4 where superphosphate had not been applied for several years prior to soil sampling.

In contrast, where the sites had received regular applications of superphosphate over the years, or it had been applied just prior to soil collection, depressions in yield in the first cut caused by the withdrawal of sulphur in the pot trial were either nil (sites 2, 3 and 8), or less than 20% (sites 6, 7, and 12).

In the second harvest, there was a highly significant reduction in yield due to the omission of sulphur at eight of the nine sites (table 3.1). The exception was site 3, where the soil had a high ability to adsorb sulphate (table 3.2) and superphosphate had been applied in both spring 1978 and autumn 1979 prior to soil collection (appendix I).

In extrapolating the results obtained from this glasshouse study to the field situation, several aspects must be taken into consideration. For instance, the contributions of atmospheric sulphur (Terman, 1978) and subsoil sulphate (Gregg et al., 1977) to the plant available soil sulphur

Table 3.1 Percentage reduction in dry matter yield for minus sulphur and minus phosphorus treatments on nine soils in a glasshouse trial.

	HARVEST ONE % Yield reduction		HARVEST TWO % Yield reduction	
Site	- S	- P	- S	- P
1	21**	61**	68**	83**
2	Nil	19**	59**	26**
3	Nil	39**	Nil	11**
4	26**	26**	77**	36**
6	14*	24**	69**	36**
7	18**	47**	66**	57**
8	Nil	Nil	53**	Nil
11	46**	80**	75**	85**
12	10**	18**	60**	35**

* significant at 5% level of probability.

** significant at 1% level of probability.

Table 3.2 Some chemical properties of air-dried soils used in the glasshouse study.

Site	Calcium chloride extractable sulphur $\mu g\ S\ g^{-1}$	Calcium phosphate extractable sulphur $\mu g\ S\ g^{-1}$	Adsorbed sulphur † $\mu g\ S\ g^{-1}$	Olsen extractable phosphorus $\mu g\ P\ g^{-1}$	Phosphate retention %	pH
1	6.5	15.7	9.2	7	76	5.8
2	9.4	19.4	10.0	18	57	5.7
3	20.1	53.4	33.3	20	82	6.1
4	8.5	11.2	2.7	17	29	5.7
6	12.7	15.4	2.7	16	27	5.7
7	12.0	15.4	3.4	18	50	5.7
8	17.4	18.8	1.4	38	24	5.6
11	8.4	9.4	1.0	10	33	5.5
12	9.4	17.1	7.7	19	54	5.5

† Adsorbed sulphur is the difference between calcium phosphate extractable sulphur and calcium chloride extractable sulphur.

pool were absent from the pot experiment in which only a top soil (0-7.5cm) was used as the medium for plant growth. Furthermore, the limitation of soil volume in the pot trial could result in a more rapid depletion of available soil sulphur than would occur in a field situation (Andrew et al., 1974). Thus, this exhaustive glasshouse technique may overestimate the extent of sulphur deficiency in the field. Allowing for some overestimation by this technique, the magnitude of sulphur responses obtained in this study (table 3.1) still suggests that any long term omission of fertiliser sulphur on many of these soils would lead eventually to sulphur deficiencies.

According to Middleton and Toxopeus (1973), each harvest period of approximately one month, in this type of glasshouse trial, represents one year's growth in the field. Thus, sulphur deficiency showing up in the first harvest may occur in the field within a year if not rectified. On this basis, pastures on sites 2, 3 and 8 (table 3.1) are unlikely to be sulphur deficient if sulphur is not applied for one year, whereas the widespread sulphur deficiencies at the second harvest suggest that pasture at eight of the nine sites, may exhibit responses to applied sulphur if sulphur-containing fertiliser is omitted from the topdressing programme for two years.

The plant responses to sulphur application, obtained from this glasshouse study, relate well to the amounts of sulphur extracted from the soil by a calcium phosphate solution (figure 3.1). A much poorer relationship exists between plant response and calcium chloride-extractable sulphur (figure 3.2).

The probable reason for the superiority of the phosphate extractant in evaluating plant response is that some of the Eastland soils have considerable amounts of adsorbed sulphur (table 3.2) which can become available to plants. Thus some sites (1, 2 and 12) with low or medium

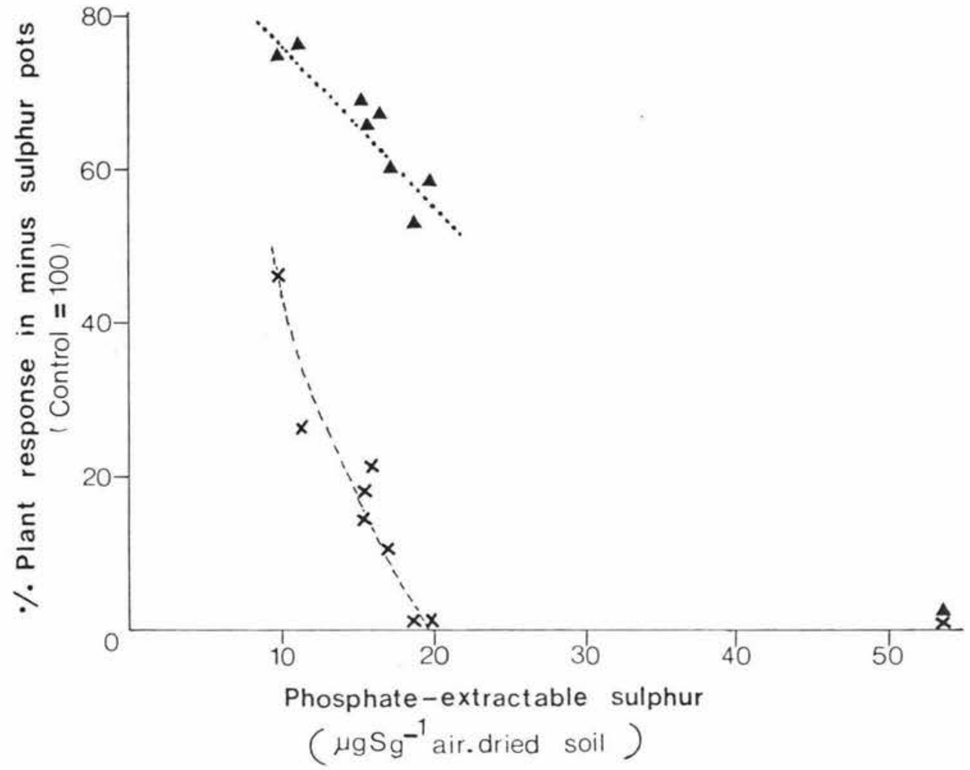


Figure 3.1 Relationships between plant response and phosphate extractable soil sulphur

Key: x----x First harvest
▲....▲ Second harvest

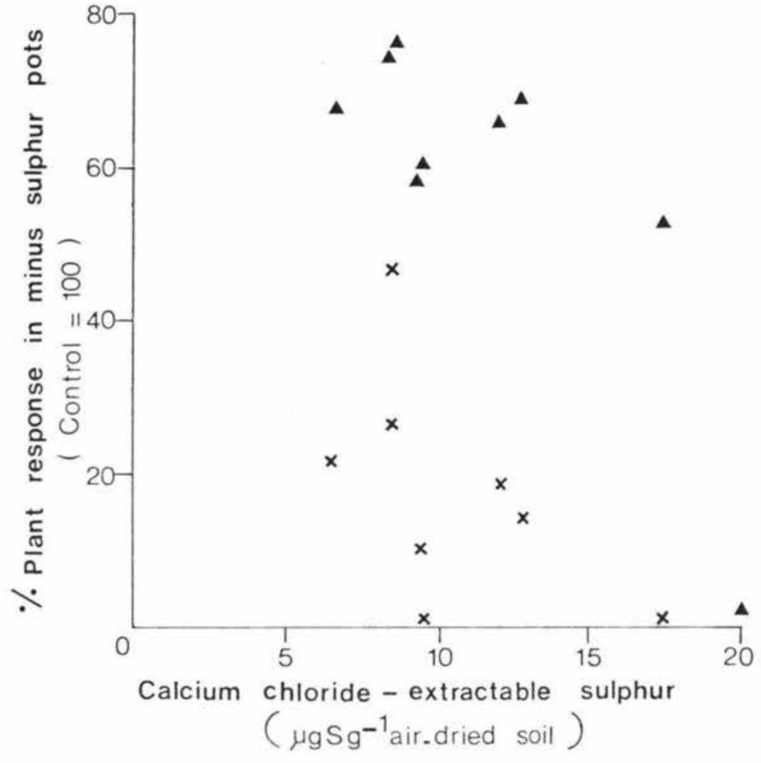


Figure 3.2 Relationships between plant response and calcium chloride extractable soil sulphur

Key:
x First harvest
▲ Second harvest

calcium chloride extractable sulphur values showed a much lower response than expected because of high levels of adsorbed sulphur (tables 3.1 and 3.2). The importance of adsorbed sulphur, as a source of sulphur for plant growth, particularly when soil sulphur reserves become depleted can be seen in the good relationship (figure 3.3) between adsorbed sulphur and plant response obtained in the later stages of plant growth (second harvest).

The results of this study suggest that a phosphate extractable sulphur level of 14 μg S g^{-1} was about the critical value (figure 3.1) below which, there was a sufficiently large yield reduction (over 20%) in the first harvest in the glasshouse to suggest that a sulphur deficiency might also be expected in the field. In contrast to other extraction procedures, there appears to be very few critical calcium phosphate-extractable values in the literature. The level of 14 μg S g^{-1} obtained in this study compares favourably to those (11 - 13 μg S g^{-1}) reported by overseas workers (Anderson and Webster, 1968; Andrew et al., 1974; Andrew, 1975) using the same extractant. New Zealand workers (Cooper, 1968; Hogg et al., 1970) using a similar potassium phosphate extractant or else sodium phosphate in 2M acetic acid solution have recorded lower critical values (8 μg S g^{-1} and 10 μg S g^{-1} respectively), but these were from soils under undeveloped pastures. In well-developed situations Hogg et al. (1970) have reported that the potassium phosphate solution was unable to differentiate between sulphur-responsive and non-responsive sites and that all trial sites had phosphate extractable sulphur values above 8 μg S g^{-1}. Sulphur responses were observed even at sites with potassium phosphate-extractable sulphur levels of between 10 - 15 μg S g^{-1} (Saunders and Cooper, 1975).

Thus although the critical level of phosphate extractable sulphur derived from this study may be an overestimate because of the exhaustive

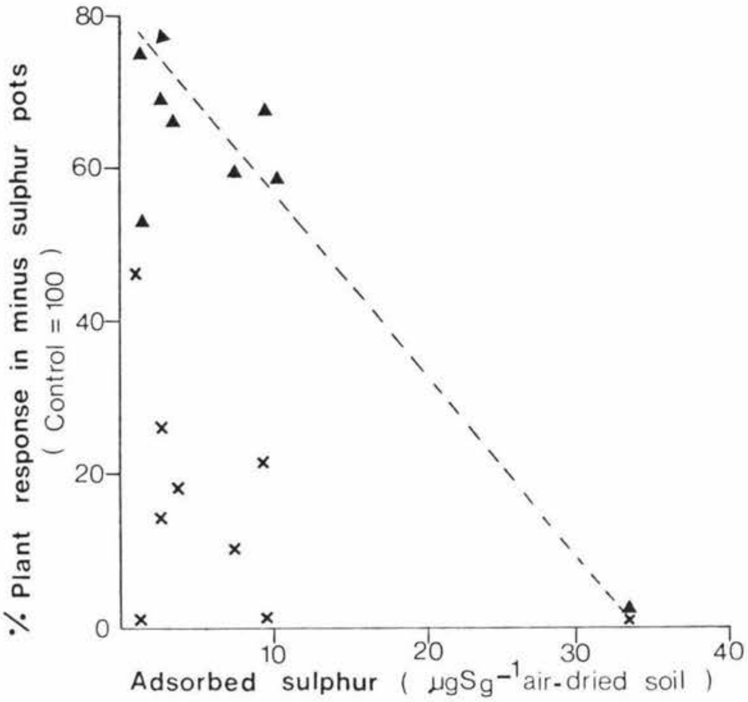


Figure 3.3 Relationships between plant response and adsorbed sulphur

Key: × First harvest
▲ Second harvest

technique employed in this glasshouse experiment, it compares favourably with the limited number of critical values reported in the literature.

When soils were collected for the glasshouse trial, the herbage growing at the site was also sampled as part of the survey (tables 3.3 and 3.4). The sulphur status (sulphate, total sulphur and nitrogen: sulphur ratio) of the herbage related well to the degree of plant response obtained in the glasshouse study (figures 3.4 and 3.5). The levels of total sulphur and the nitrogen:sulphur ratios in grass and clover at sites with a substantial yield response (> 20%) to sulphur application were well below the critical values proposed by McNaught and Christoffels (1961) and McNaught (1970) for maximum dry matter production (section 2.3.c). This supports the suggestion that sites with a reduction of over 20% in dry matter yield in the glasshouse due to the omission of sulphur may be considered to be sulphur deficient.

The results from the glasshouse experiment also indicated that phosphate deficiency usually occurred together with a sulphur deficiency (table 3.1). The percentage reductions in yield due to the omission of phosphorus from the nutrient solution were related to the amounts of soil available phosphate as measured by the Olsen test (figure 3.6).

3.3.2 CONCLUSIONS

On the basis of this study, it is concluded that calcium phosphate-extractable sulphur is superior to calcium chloride extractable sulphur in estimating the sulphur status of Eastland soils under glasshouse conditions. This is due to the ability of the phosphate solution to extract the plant available pool of adsorbed sulphate. In view of these findings, calcium phosphate extractable sulphur will be used as the main criterion of soil sulphur status in the survey.

Although the technique employed in this glasshouse study is likely to overestimate the degree of sulphur deficiency found in the field, the

Table 3.3 Chemical composition of grass and clover collected in the autumn survey.

	GRASS					CLOVER				
Site	SO_4 - S (% D.M.)	SO_4 - S (% Total S)	Total S (% D.M.)	Total N (% D.M.)	N:S Ratio	SO_4 - S (% D.M)	SO_4 - S (% Total S)	Total S (% D.M.)	Total N (% D.M.)	N:S Ratio
1	.067	24	0.278	4.40	15.8	0.032	13	0.251	4.90	19.5
2	.112	35	0.318	4.20	13.2	0.061	22	0.280	5.14	18.4
3	.117	34	0.345	3.94	11.4	0.058	21	0.276	5.03	18.2
4	.055	23	0.240	3.77	15.7	0.028	14	0.202	4.41	21.8
5	.199	59	0.340	4.30	12.7	0.062	23	0.267	4.86	18.2
6	.096	32	0.302	4.40	14.6	0.040	15	0.261	5.09	19.5
7	.071	25	0.282	4.27	15.1	0.035	14	0.254	4.84	19.1
8	.125	40	0.312	4.06	13.1	0.065	24	0.269	4.89	18.2
9	.090	32	0.282	3.07	10.9	0.038	15	0.262	4.80	18.3
10			*					*		
11	.027	19	0.142	3.46	23.7	0.010	7	0.137	3.74	27.4
12	.082	29	0.285	3.97	13.9	0.037	15	0.251	5.02	19.8
13			*					*		
14			*					*		

* Inadequate pasture growth for herbage sampling.

Table 3.4 Chemical composition of grass and clover collected in the spring survey.

	GRASS					CLOVER				
Site	SO_4 - S (% D.M.)	SO_4 - S (% Total S)	Total S (% D.M.)	Total N (% D.M.)	N:S Ratio	SO_4 - S (% D.M.)	SO_4 - S (% Total S)	Total S (% D.M.)	Total N (% D.M.)	N:S Ratio
15	0.065	22	0.291	3.53	12.1	0.035	13	0.266	5.08	19.1
16	0.060	22	0.279	3.42	12.2	0.030	12	0.257	5.03	19.2
17	0.020	14	0.146	2.07	14.2	0.007	6	0.122	4.02	32.9
18	0.034	18	0.185	2.41	13.1	0.020	11	0.188	4.01	21.4
19	0.088	31	0.280	2.62	9.4	0.041	16	0.256	4.50	17.5
20	0.060	22	0.268	2.94	11.0	0.030	12	0.252	4.85	19.3
21	0.038	20	0.190	2.41	12.7	0.020	11	0.190	4.10	21.6
22	0.045	25	0.182	2.42	13.3	0.026	15	0.168	4.58	27.3
23	0.083	30	0.280	2.31	8.3	0.031	12	0.255	4.51	17.6
24	0.045	18	0.248	2.83	11.4	0.028	14	0.205	4.23	20.6
25	0.042	18	0.230	2.42	10.5	0.027	13	0.203	4.45	21.9
26	0.046	21	0.220	2.53	10.1	0.025	13	0.197	4.13	21.0
27	0.043	18	0.245	2.67	10.9	0.027	13	0.201	4.67	23.2
28	0.048	21	0.231	2.96	12.8	0.028	13	0.211	4.53	21.4
29	0.033	16	0.212	3.23	15.2	0.012	9	0.129	4.39	34.1
30	0.035	20	0.176	3.69	20.9	0.015	8	0.186	4.45	23.9
31	0.035	18	0.198	3.46	17.3	0.018	11	0.166	4.52	27.3

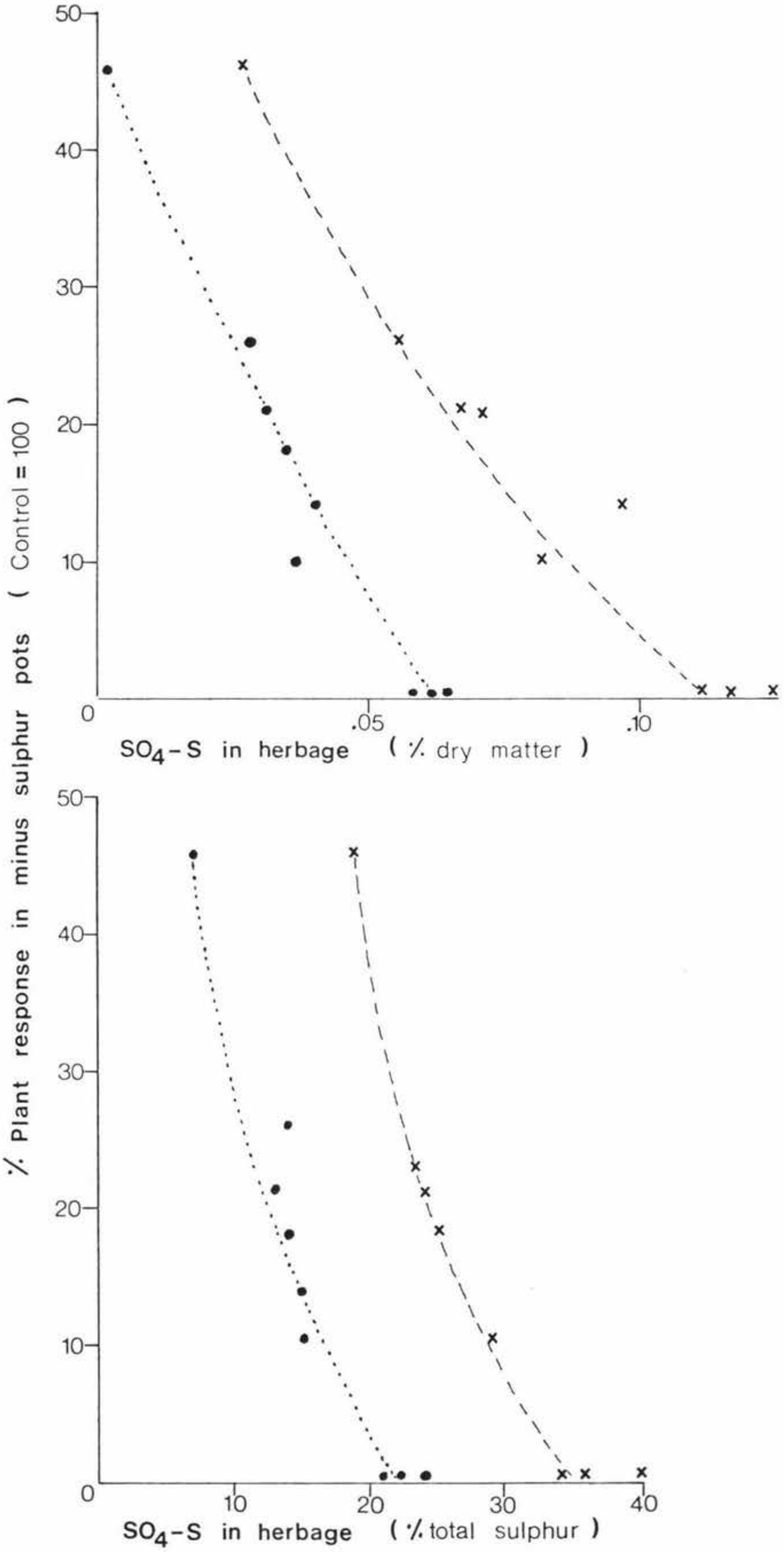


Figure 3.4 Relationship of plant response in the first harvest to sulphate as a percentage of dry matter (a) and to sulphate as a percentage of total sulphur (b)

Key: x---x Grass

•....• Clover

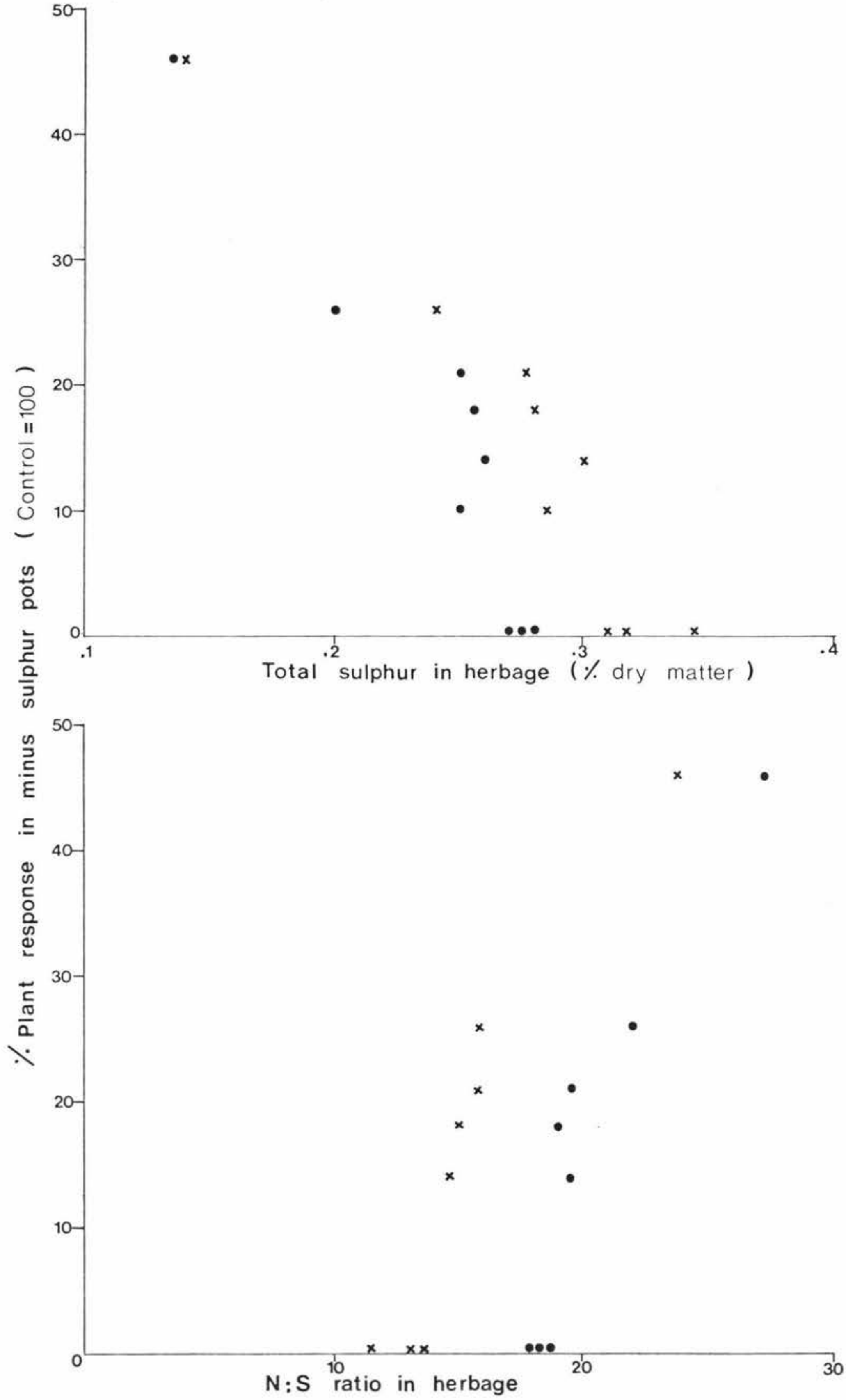


Figure 3.5 Relationship of plant response in the first harvest to total sulphur (a) and N:S ratios in herbage (b)

Key:
- × Grass
- • Clover

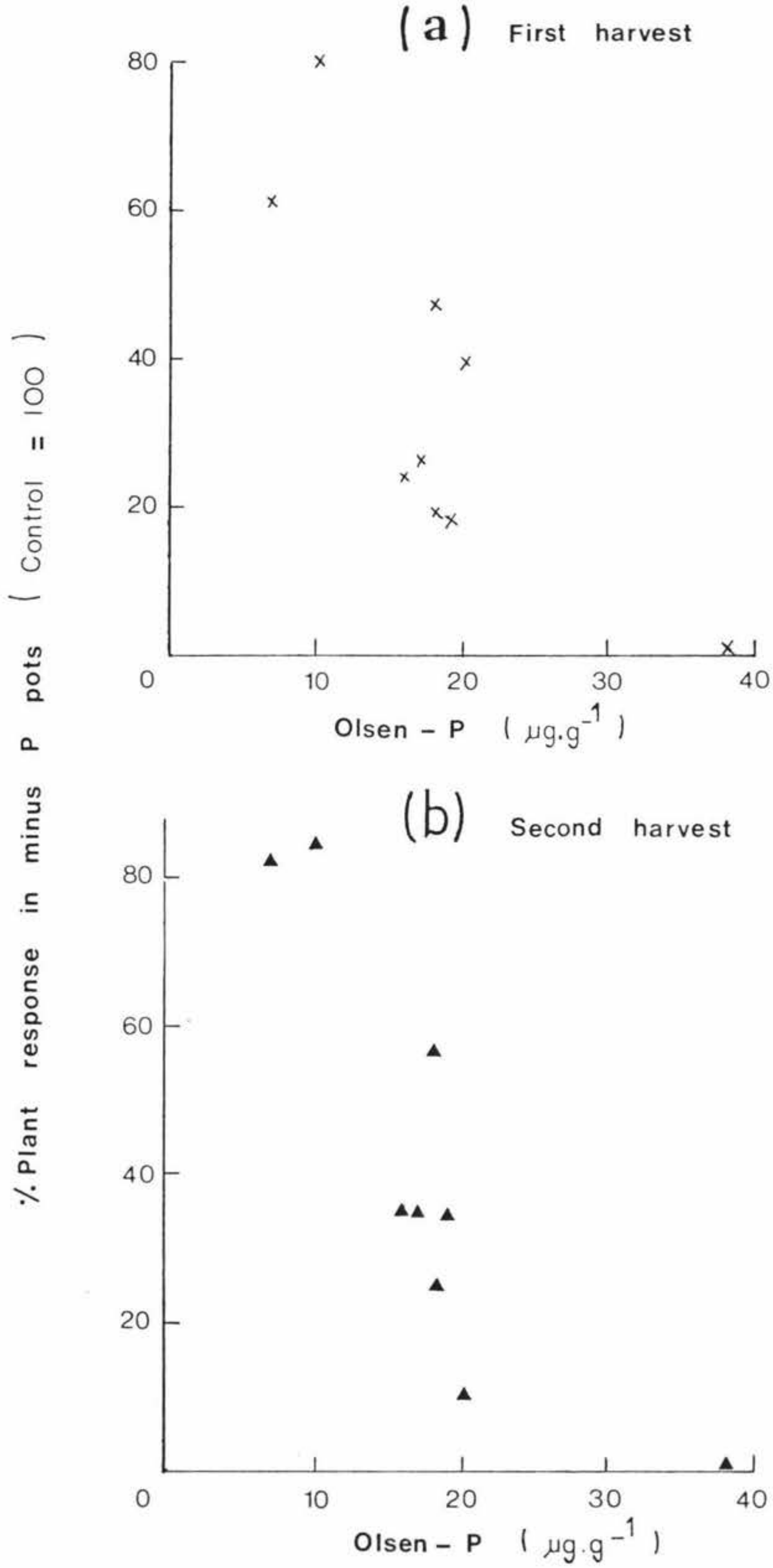


Figure 3.6 Relationship of plant response in minus P pots to Olsen extractable soil phosphorus

Key: × First harvest
▲ Second harvest

levels of sulphur deficiency in the glasshouse trial reflected both the amounts of phosphate extractable sulphur in the soils and the sulphur status of pasture collected from site at the time of soil collection.

Soils which were sulphur deficient were usually also phosphorus deficient.

3.4 SOIL SURVEY

3.4.a RESULTS AND DISCUSSION

(i) Soil sulphur levels in spring and autumn

In general, the levels of phosphate extractable sulphur in surface soils were lower in spring (average = 14 μg S g^{-1}) than in autumn (average = 18 μg S g^{-1}) (figure 3.7, appendices VII and VIII). This trend was well illustrated (figure 3.8) by the three sites sampled in both autumn (sites 3, 5 and 6) and spring (corresponding sites 19, 20 and 21). Although these three soils reflected a wide range of phosphate retention (20% - 82%), there was a marked decrease in phosphate-extractable soil sulphur during winter in each case. The levels of phosphate extractable soil sulphur in spring were less than 50% of those in the previous autumn. It is interesting to note that although the levels of available soil phosphorus also decreased over winter, the drop was not nearly as great (figure 3.8), suggesting that sulphate, being the more weakly adsorbed anion (Metson and Blakemore, 1978), had been leached more readily.

There were however some exceptions to this general trend of low levels of phosphate-extractable sulphur in spring (sites 15, 16, 19 and 23). Of these, sites 15, 16 and 19 had very high anion retention

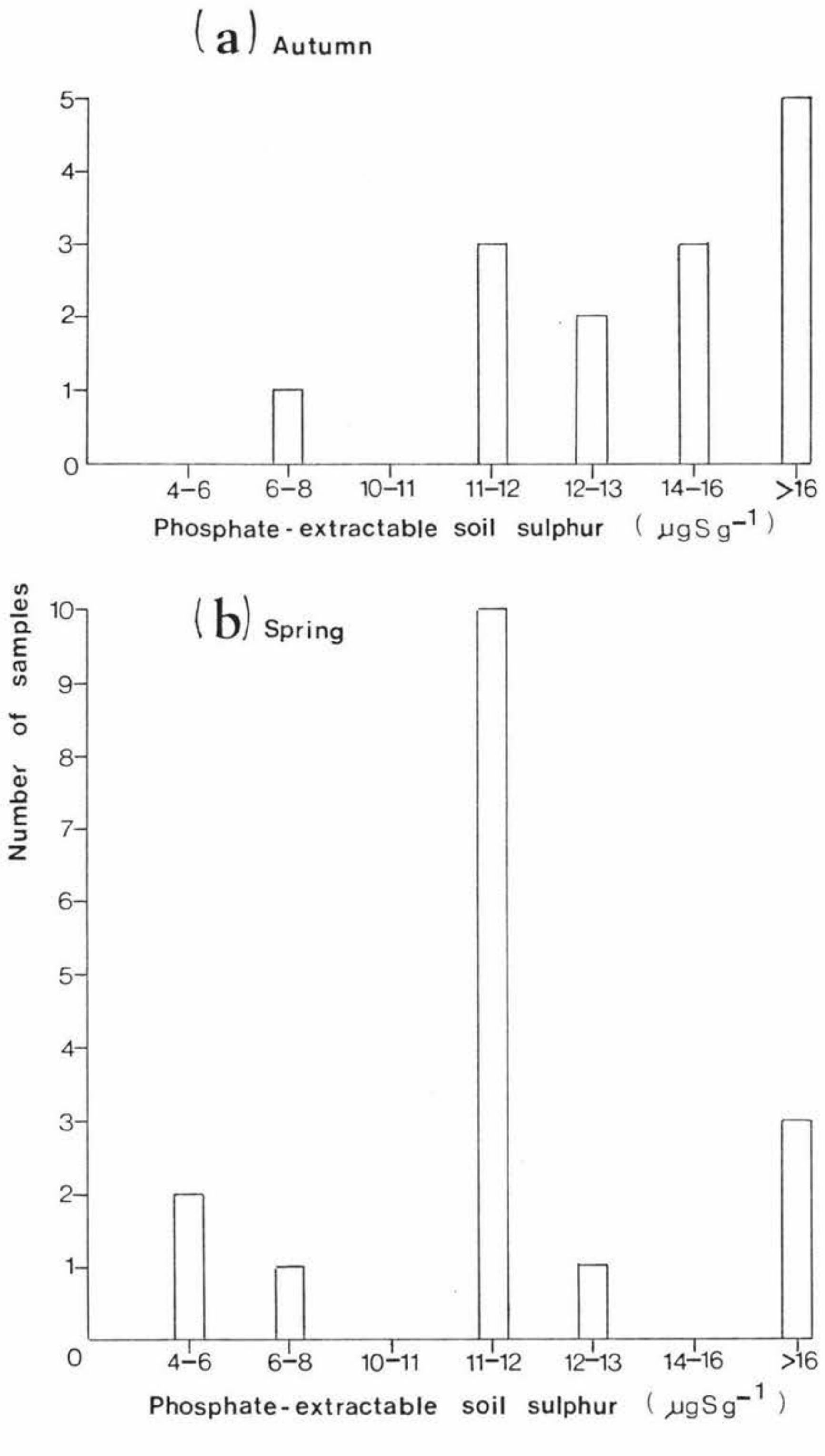


Figure 3.7 Distribution of phosphate extractable sulphur in Eastland top soils (0 - 7.5 cm)

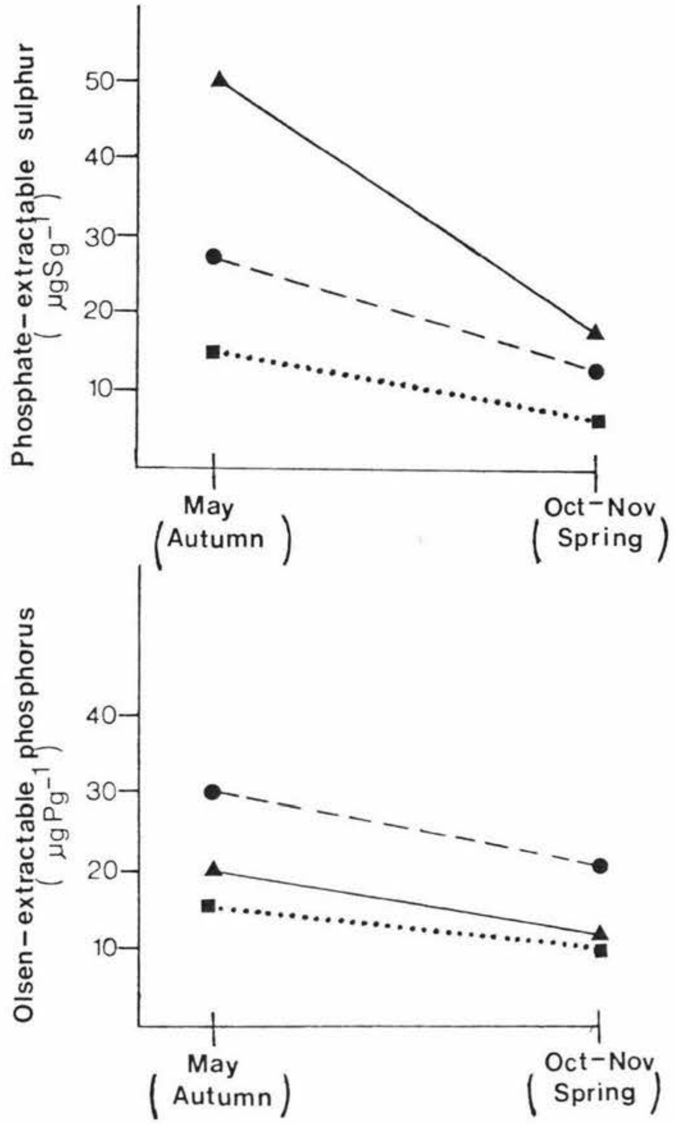


Figure 3.8 Differences in the levels of phosphate extractable soil sulphur and Olsen extractable soil phosphorus between autumn and spring

Key: ▲——▲ sites 3, 19
●---● sites 5, 20
■····■ sites 6, 21

capacities (> 80% phosphate retention) and appeared to be able to accumulate large amounts of sulphate (appendix VIII). No explanation can be given for the fourth site (site 23) since this site had only a medium phosphate retention ability (33%) and superphosphate was last applied in spring 1978 about one year prior to soil collection.

Published information on critical values for calcium phosphate extractable soil sulphur is unavailable in New Zealand. However, overseas work (Fox et al., 1964; Anderson and Webster, 1968; Andrew et al., 1974; Andrew, 1975) suggests that values between 10 and 13 μg $S\ g^{-1}$ are in the critical range below which plant response to sulphur fertilisation is likely to occur. Overall, the average critical values may be assumed to be about 11 to 12 $\mu g\ S\ g^{-1}$. Using these values as an indication of the amount of soil sulphate required for pasture uptake at any one time, it is probable that one out of 14 sites (7%) sampled in the autumn could be sulphur deficient and a further three samples are in a borderline situation (figure 3.7). In contrast, a larger proportion (77%) of samples collected in the spring, that is, 13 out of 17, could be assumed to be either sulphur deficient or marginally so. On the basis of these soil survey results, it is proposed that Eastland pastures are more likely to be sulphur deficient in spring than in autumn.

(ii) Effect of sulphur fertiliser applications on soil sulphur status

The effect of fertiliser history on soil sulphur status differed between autumn and spring. In autumn, the levels of phosphate-extractable sulphur and Olsen-extractable phosphorus were higher in sites with a long history of superphosphate application than they were in sites to which little or no fertiliser had been applied (figure 3.9, appendices I to IV).

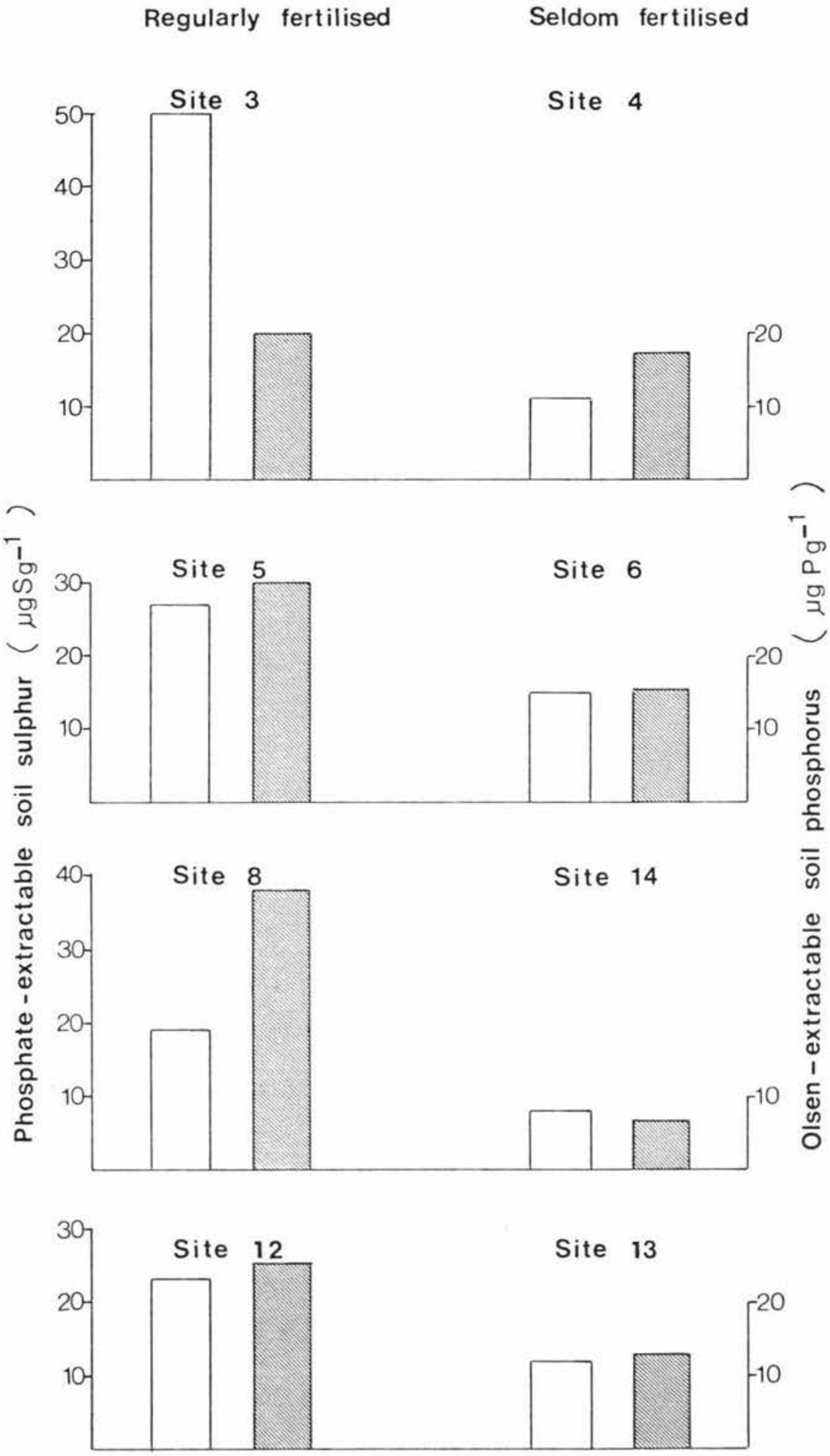


Figure 3.9 Effect of fertiliser history on levels of phosphate extractable soil sulphur and Olsen extractable soil phosphorus to 7.5 cm in autumn

Key ▯ Phosphate extractable soil sulphur
▨ Olsen extractable soil phosphorus

In contrast, there was little difference in spring in the levels of phosphate extractable soil sulphur between sites on the same soil type but with different fertiliser histories (figure 3.10, appendices I to IV). While there was no difference in soil sulphur levels between these sites, the levels of Olsen-extractable phosphorus from sites with a long history of superphosphate application were still higher than those from sites which had received less frequent fertiliser applications (figure 3.10, appendices I to IV).

The high sulphur soil test values in the autumn at sites with a long history of fertiliser application (such as sites 8 and 12) may be due to two factors. Firstly, there may be a direct residual effect of the sulphur applied in superphosphate in the previous spring, and secondly there may be a greater mineralisation of accumulated organic sulphur (Jackman, 1964) during the late summer - early autumn period when the soil temperature and moisture are favourable for microbial activity (Barrow, 1961; Williams, 1968).

The contrasting patterns of phosphate-extractable sulphur and Olsen-extractable phosphorus between sites sampled in the spring are probably due to the different behaviour of phosphate and sulphate anions in soils. Sulphate has been shown in laboratory experiments by several workers (Toxopeus, 1964; Hogg, 1965) to be more readily leached than phosphate, by percolating water. Thus leaching losses during the winter months are more likely to occur with sulphate. In fact, field trials on low sulphate retaining yellow-brown pumice soils from the central North Island (Toxopeus, 1970), have shown that substantial losses of sulphate from autumn application of superphosphate can result in sulphur deficiency in the following spring.

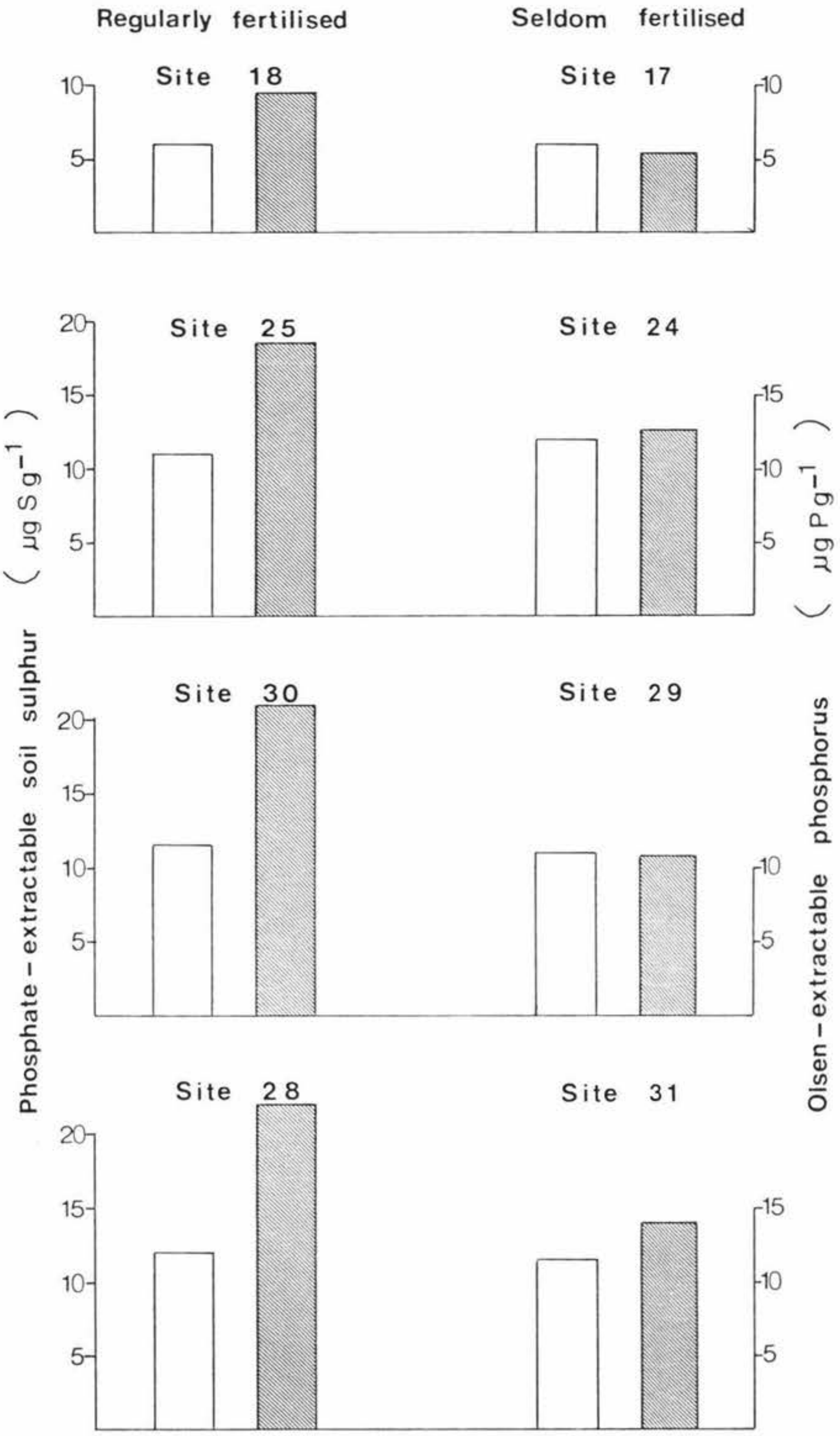


Figure 3.10 Effects of fertiliser history on levels of phosphate extractable soil sulphur and Olsen extractable soil phosphorus to 7.5 cm in spring

Key: ☐ Phosphate extractable soil sulphur
▨ Olsen extractable soil phosphorus

(iii) Effect of phosphate retention capacity on the levels of adsorbed sulphate

Soils with high anion exchange capacities are known to retain both phosphate and sulphate (Metson and Blakemore, 1978). Thus a measurement of phosphate retention may partly reflect the capacity of a soil to adsorb sulphate. Graphs of phosphate retention capacity against the levels of adsorbed sulphate in soil samples collected in autumn and spring (figures 3.11 and 3.12) indicate that there is an association between these two parameters. Soils with strong phosphate retention also have a high ability to accumulate adsorbed sulphate and vice versa. However, this relationship is not linear because the levels of adsorbed sulphate are generally low over a wide range (10 - 70%) of phosphate retention (figures 3.11 and 3.12). This pattern was observed for soil samples collected in both the autumn (figure 3.11) and the spring (figure 3.12). However, the amounts of adsorbed sulphate for any value of phosphate retention less than 70% were less in samples collected in spring than they were in autumn. This low ability of Eastland soils to retain sulphate over a wide range (10 - 70%) of phosphate retention could be due to the competition from the more strongly adsorbed phosphate ion and organic matter for anion adsorption sites (Metson, 1979a).

The above results suggest that soils (0 - 30cm) with phosphate retention capacities between 10 and 70% do not normally contain large amounts (> 10 μg S g^{-1}) of adsorbed sulphate, but those with higher phosphate retention can accumulate significant quantities. Similar findings have also been reported by Hogg et al. (1970) in their studies of the top 7.5cm over a wide range of New Zealand soils.

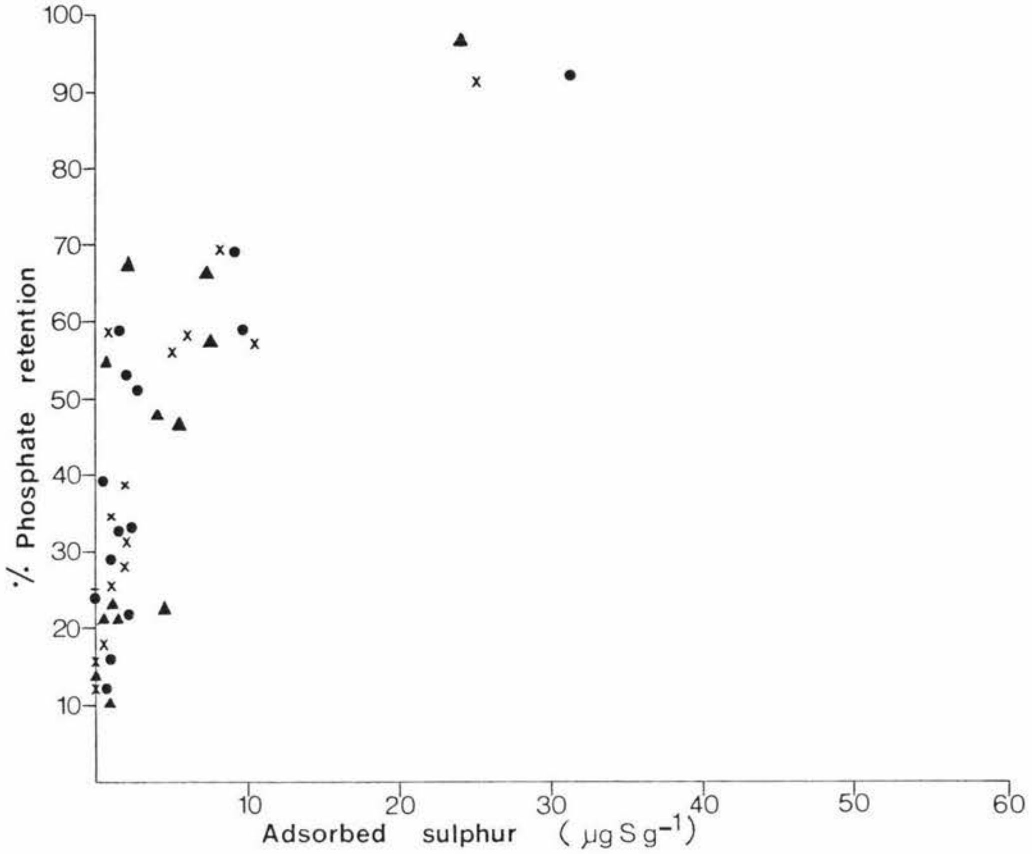


Figure 3.11 Relationship between phosphate retention and adsorbed sulphur at various soil depths for samples collected in autumn

Key:
- ● 0 - 7.5 cm
- × 7.5 - 15 cm
- ▲ 15 - 30 cm

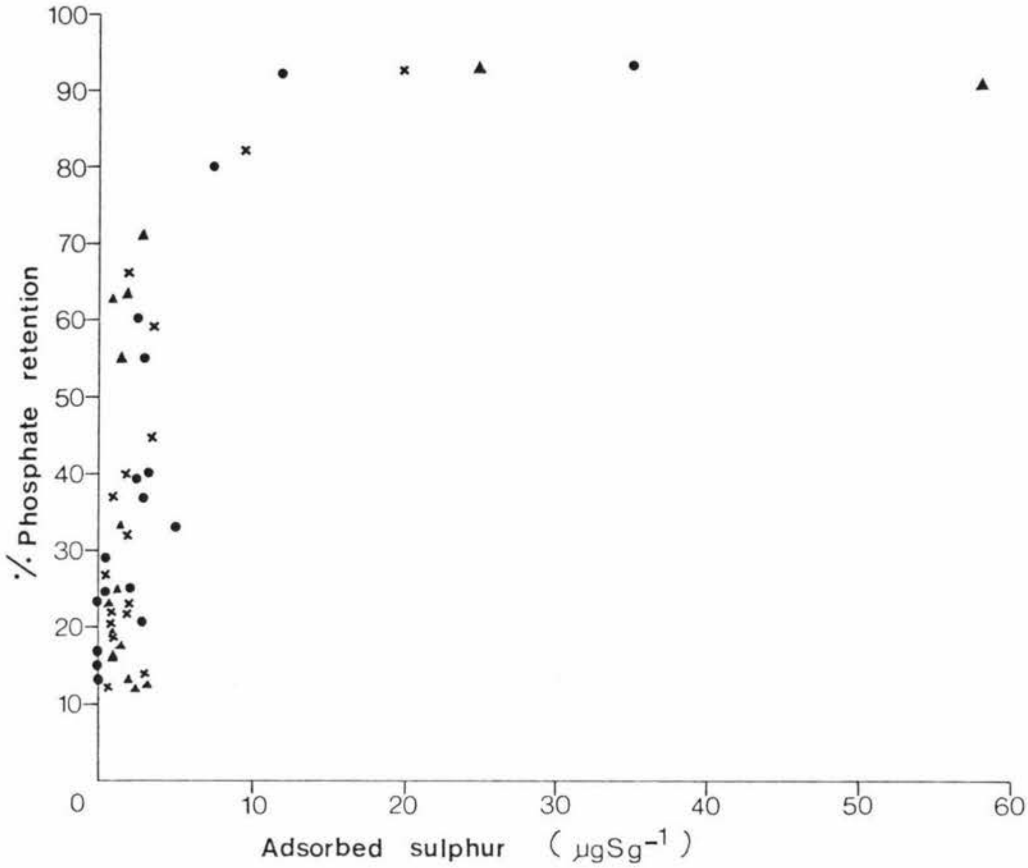


Figure 3.12 Relationship between phosphate retention and adsorbed sulphur at various soil depths for samples collected in spring

Key:
- ● 0 - 7.5 cm
- × 7.5 - 15 cm
- ▲ 15 - 30 cm

(iv) Effect of rainfall on soil sulphur status

In the survey areas it was difficult to find sites with markedly different annual rainfalls but with similar soils and fertiliser histories. Thus a direct evaluation of the effect of rainfall on sulphur availability cannot be made.

There was however indirect evidence of sulphate leaching during winter, even at sites with low annual rainfall (900 - 1000mm per annum). This evidence is provided by the low levels of phosphate extractable soil sulphur in the spring at sites 17 and 18, both of which have moderate sulphur fertiliser topdressing histories (figure 3.14, appendices III and IV) and also by the considerable decreases in phosphate extractable sulphur during winter at sites 5 and 6 (figure 3.8). If leaching can indeed occur under these relatively low rainfalls then spring sulphur deficiencies may potentially occur over most of the Eastland region.

(v) The distribution of phosphate extractable soil sulphur with depth

In contrast to many other areas of New Zealand (Metson, 1979b, c), the levels of phosphate-extractable sulphur in Eastland soils tended to decrease with depth down to 30cm (figures 3.13 and 3.14). Exceptions to this general trend were three sites (sites 15, 16 and 19) sampled in the spring. The very high phosphate retention capacities (over 80%, appendix VIII) in the subsoils of these sites could be the reason for the accumulation of sulphate against the leaching effect of winter rains.

The decrease in the levels of phosphate-extractable sulphur with depth down to 30cm observed in most of these Eastland soils suggests that there may be no advantage in sampling to 30cm, compared with 0-7.5cm, to assess soil sulphur status in Eastland pastures. A similar conclusion has also been reported by Saunders and Cooper (1975).

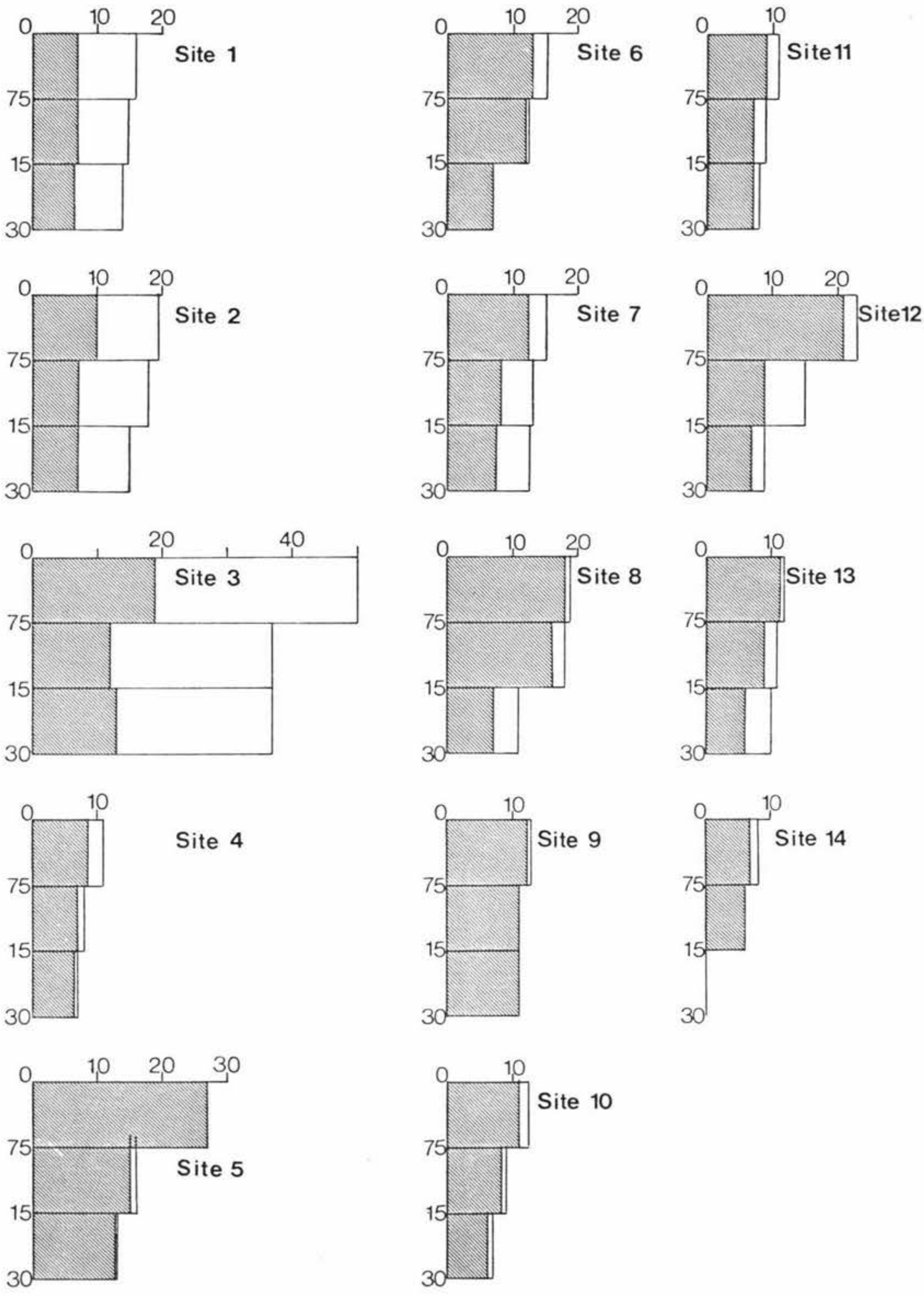


Figure 3.13 The distribution of extractable sulphur with depth in soils in autumn

Key: S ($\mu g\ g^{-1}$ soil)

depth (cm)

▨ Calcium-chloride extractable S

☐ Calcium phosphate-extractable S

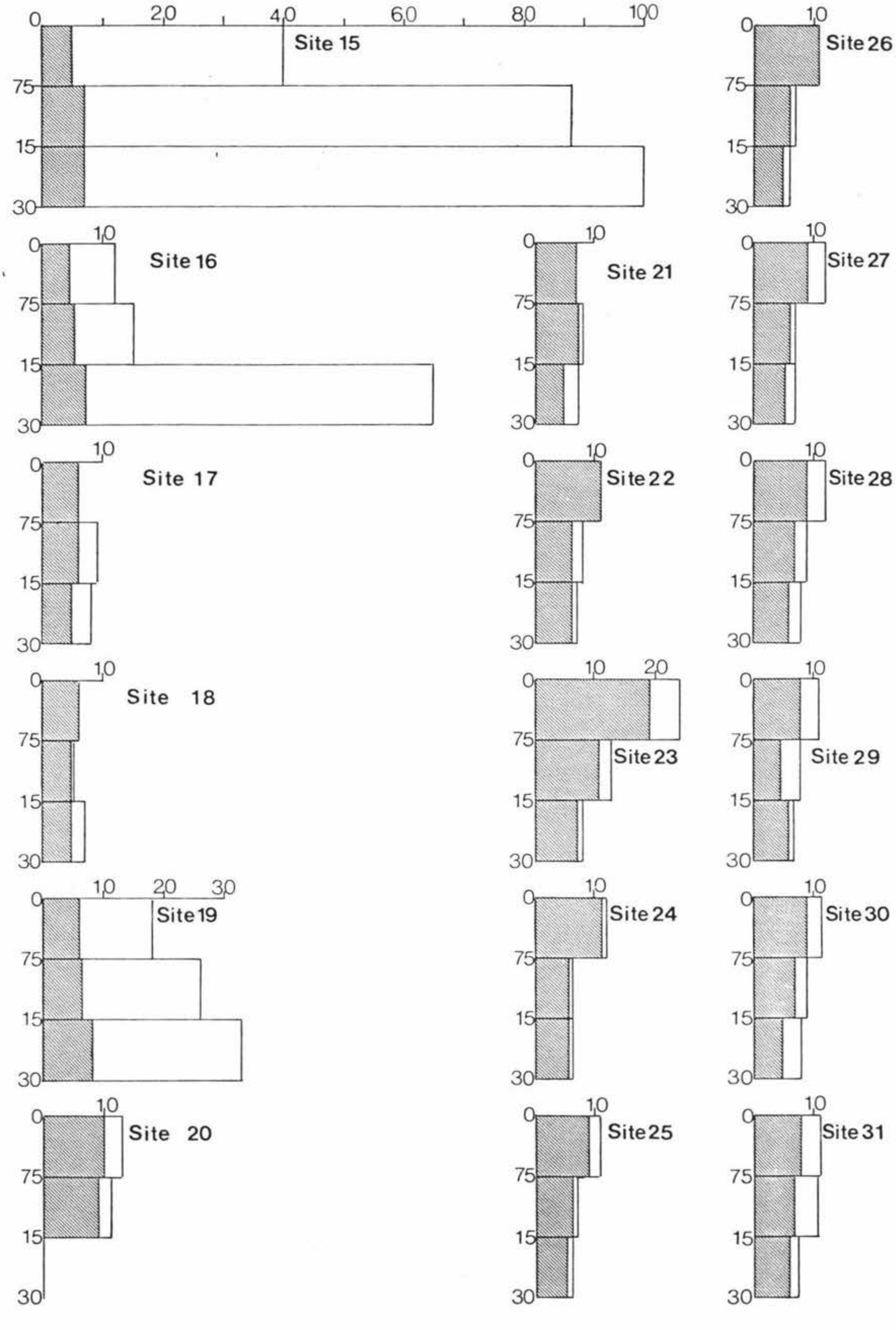


Figure 3.14 The distribution of extractable sulphur with depth in soils in spring

Key: S ($\mu g\ g^{-1}$ soil)

depth (cm)

▨ Calcium chloride extractable S

☐ Calcium phosphate extractable S

3.4.b. CONCLUSIONS

The results obtained from this survey suggest that sulphate can be leached during winter on Eastland soils and that this leaching may occur even at sites with a low annual rainfall (900 - 1000mm per annum) and in soils with phosphate retention capacities as high as 70%. Soils with phosphate retention capacities below this value may be able to accumulate small amounts of sulphate in an adsorbed form during summer and autumn but fail to retain it during winter.

Evidence for these conclusions includes:

(i) The levels of phosphate extractable soil sulphur appear to be lower in spring than in autumn.

(ii) The decrease in the levels of available soil phosphorus over winter is not as great as that in the levels of phosphate extractable soil sulphur.

(iii) The effect of fertiliser history on soil sulphur status differs between autumn and spring. Soil sulphur levels in autumn reflect the pattern of sulphur topdressing histories more markedly than those in spring.

(iv) Low phosphate retention is associated with a low level of adsorbed sulphate. For any given level of phosphate retention below 70%, the greater spread of sulphate values in autumn suggests that soils with phosphate retention capacities below 70% are unable to retain during winter, any adsorbed sulphate which may have accumulated over the summer-autumn period.

3.5 HERBAGE SURVEY

3.5.a RESULTS AND DISCUSSION

The results obtained from the herbage survey indicate that the plant sulphur status at each site, whether expressed in terms of total sulphur, sulphate, or N:S ratios was closely related to the level of phosphate extractable soil sulphur at that site (figures 3.16 to 3.19). This relationship supported the results of the glasshouse study which indicated that phosphate extractable soil sulphur was a good predictor of plant available sulphur.

(i) Total sulphur in pasture herbage

The concentrations of total sulphur in grass and clover at sites with phosphate extractable soil sulphur levels of about 13 $\mu g\ S\ g^{-1}$ or greater (figure 3.16) were within the range (0.25 to 0.30%) proposed by McNaught and Christoffels (1961) and McNaught (1970) for maximum dry matter production. In this situation, the total sulphur concentrations in grass were higher than in clover (figure 3.15). However, when phosphate extractable soil sulphur was below 11 $\mu g\ S\ g^{-1}$, the differences in total sulphur values between grass and clover were reduced (figure 3.15). According to McNaught and Christoffels (1961) a situation where total sulphur in clover exceeds or approximates that in grass, indicates sulphur deficiency.

Critical sulphur levels for grass have been assumed by McNaught and Christoffels (1961) to be dependent upon plant nitrogen status and are about 0.28% to 0.30% for plants with high levels of nitrogen (3.5% to 4%), 0.25% for plants with medium nitrogen status (2.5 to 3%) and about 0.23% for those with low nitrogen status (2 to 2.5%). Based on these proposed critical sulphur levels for grass and an average critical concentration of total sulphur for clover (0.26%) derived from McNaught

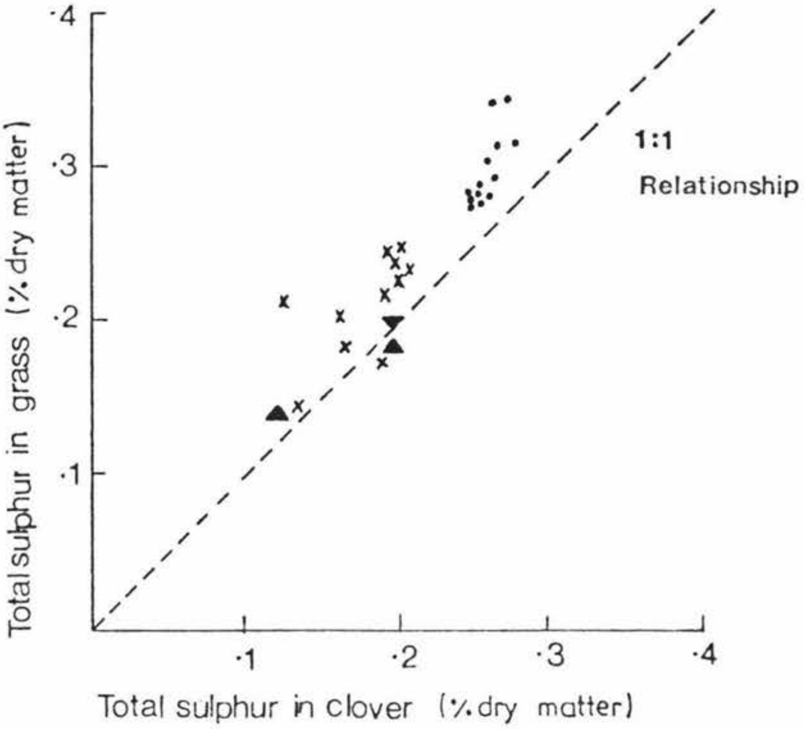


Figure 3.15 Relationship between total sulphur levels in grass and clover at sites with differing sulphur status

Key: Phosphate extractable soil sulphur of

> $13\ \mu g\ S\ g^{-1}$ •
>
> 11 but $< 13\ \mu g\ S\ g^{-1}$ ×
>
< $11\ \mu g\ S\ g^{-1}$ ▲

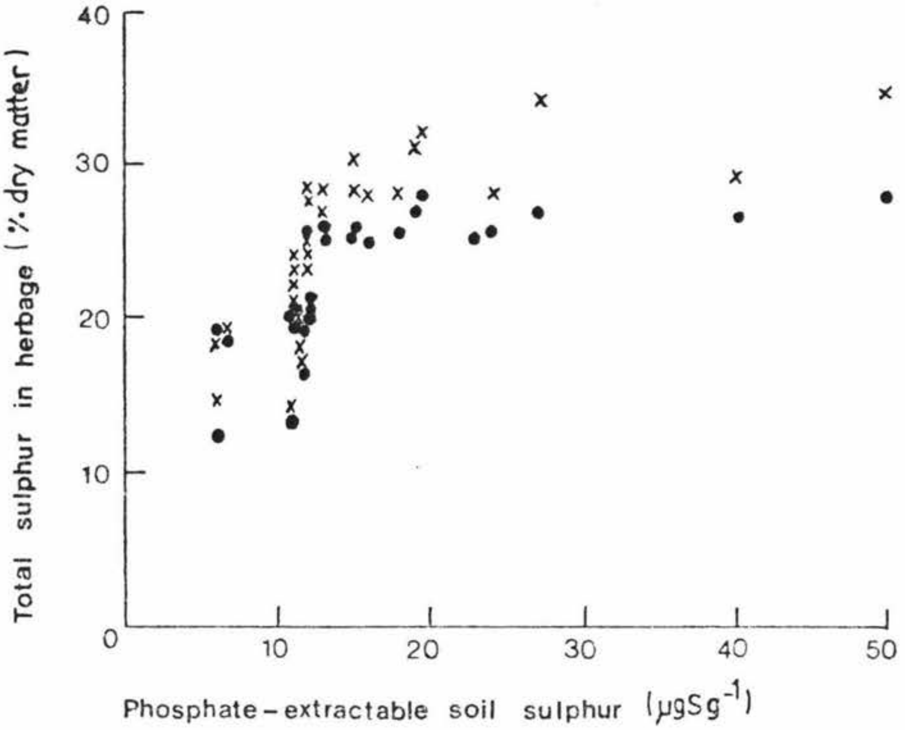


Figure 3.16 Relationship between total sulphur in herbage and phosphate extractable soil sulphur

Key: × Grass
● Clover

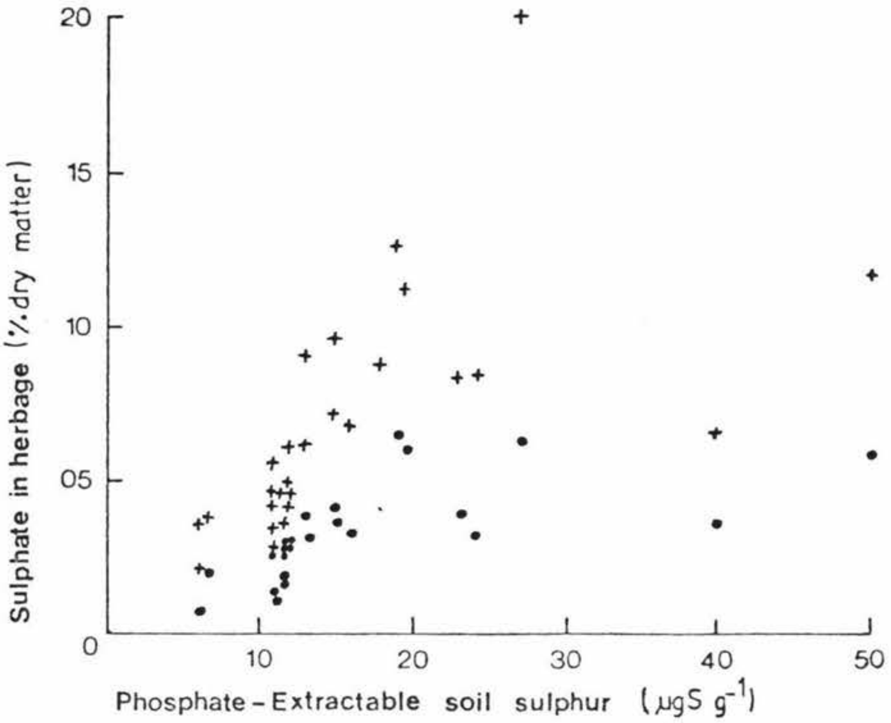


Figure 3.17 Relationship between herbage sulphate (expressed as a percentage of dry matter) and phosphate extractable soil sulphur

Key: + Grass
• Clover

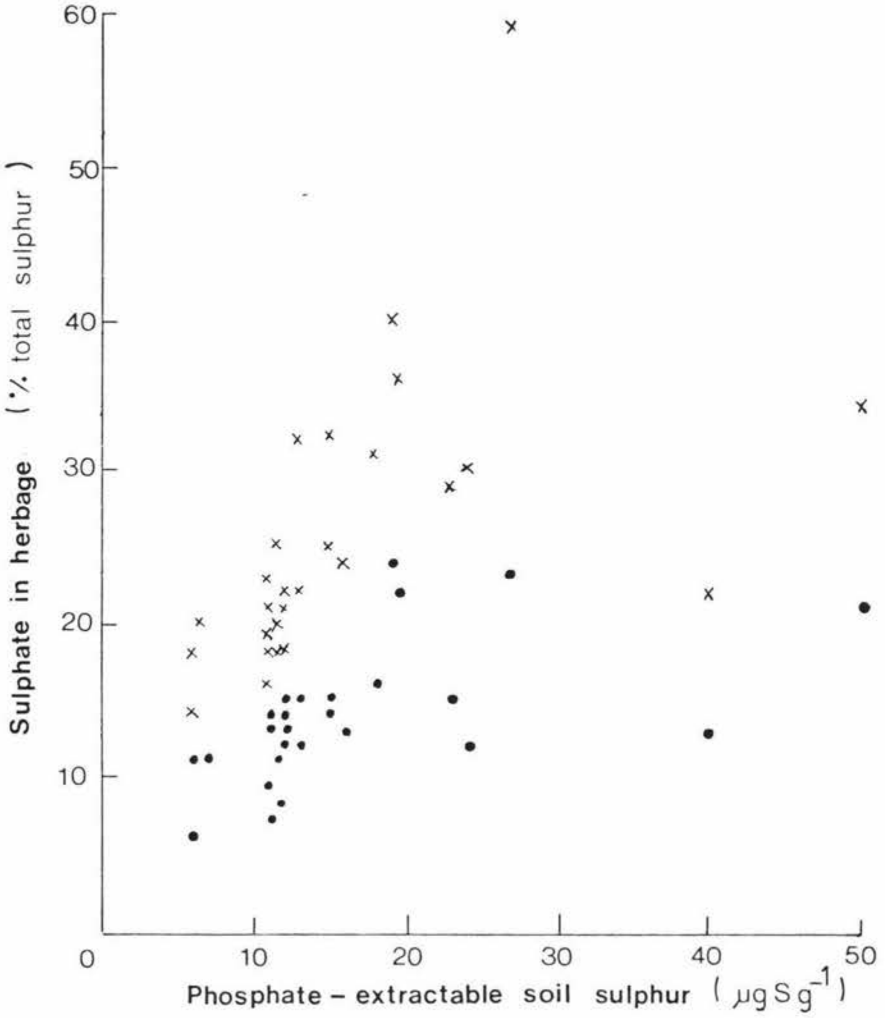


Figure 3.18 Relationship between herbage sulphate (expressed as a percentage of total sulphur) and phosphate extractable soil sulphur

Key: x Grass

• Clover

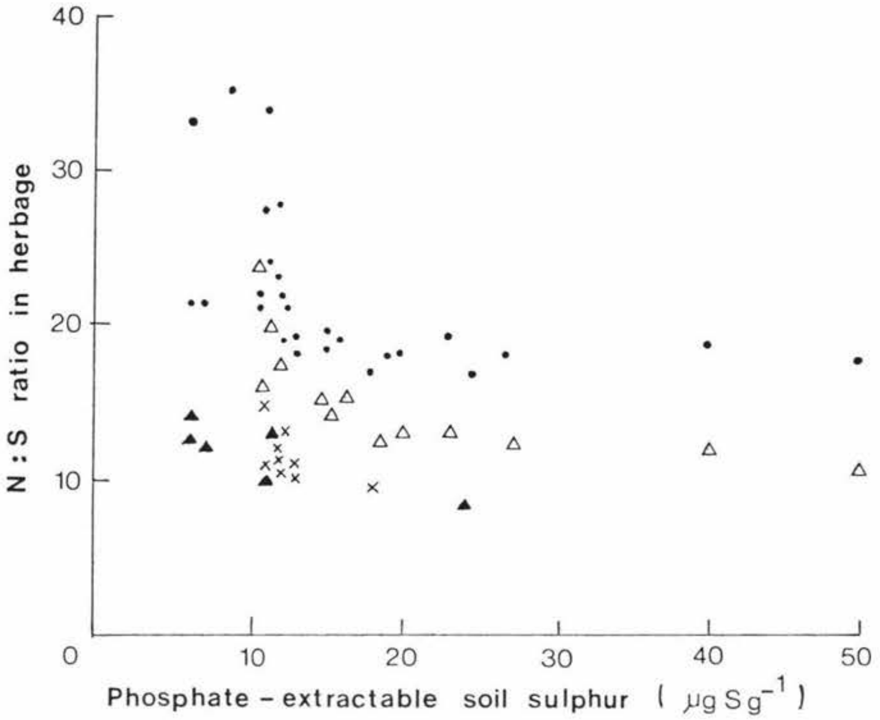


Figure 3.19 Relationship between N:S ratios in herbage and phosphate extractable soil sulphur

Key:			
	Clover	●	
	Grass	△	with high nitrogen status (> 3.5%N)
		x	with medium nitrogen status (2.5 - 3.5%N)
		▲	with low nitrogen status (< 2.5%N)

and Christoffels' review (1961), two out of eleven grass and clover samples collected in the autumn, could be assumed to be sulphur deficient (table 3.3).

Contrasting results were obtained for samples collected in the spring. Nine out of seventeen grass samples (53%) and twelve out of seventeen clover samples (71%) had total sulphur values below the suggested critical levels (table 3.4). More detailed analysis of the spring results revealed that autumn application of superphosphate had often failed to maintain sulphur status in herbage above the critical values. For instance, low levels of total sulphur was observed in both grass and clover taken from sites 18 and 28 (table 3.4) where over 200kg ha^{-1} of superphosphate had been applied in autumn, 1979, about six months prior to the spring soil and herbage collection (appendices III and IV).

Comparison of the levels of total sulphur in herbage taken from three sites in autumn (sites 3, 5 and 6) with those taken from the same sites in the following spring (sites 19, 20 and 21), also indicated that the sulphur status of herbage had been reduced substantially in the six months which had elapsed since the previous autumn topdressing (figure 3.20). This observation together with the results obtained from the soil survey leads to the conclusion that the sulphur status of Eastland pastures is lower in spring than in autumn, possibly due to the leaching loss of sulphate during the winter months.

(ii) Sulphate in pasture herbage

(ii.a) Sulphate as a percentage of dry matter. As the levels of total sulphur increased, the concentrations of sulphate in pasture herbage also increased but the levels of sulphate in clover were always lower than those in grass (figure 3.21). This suggests that

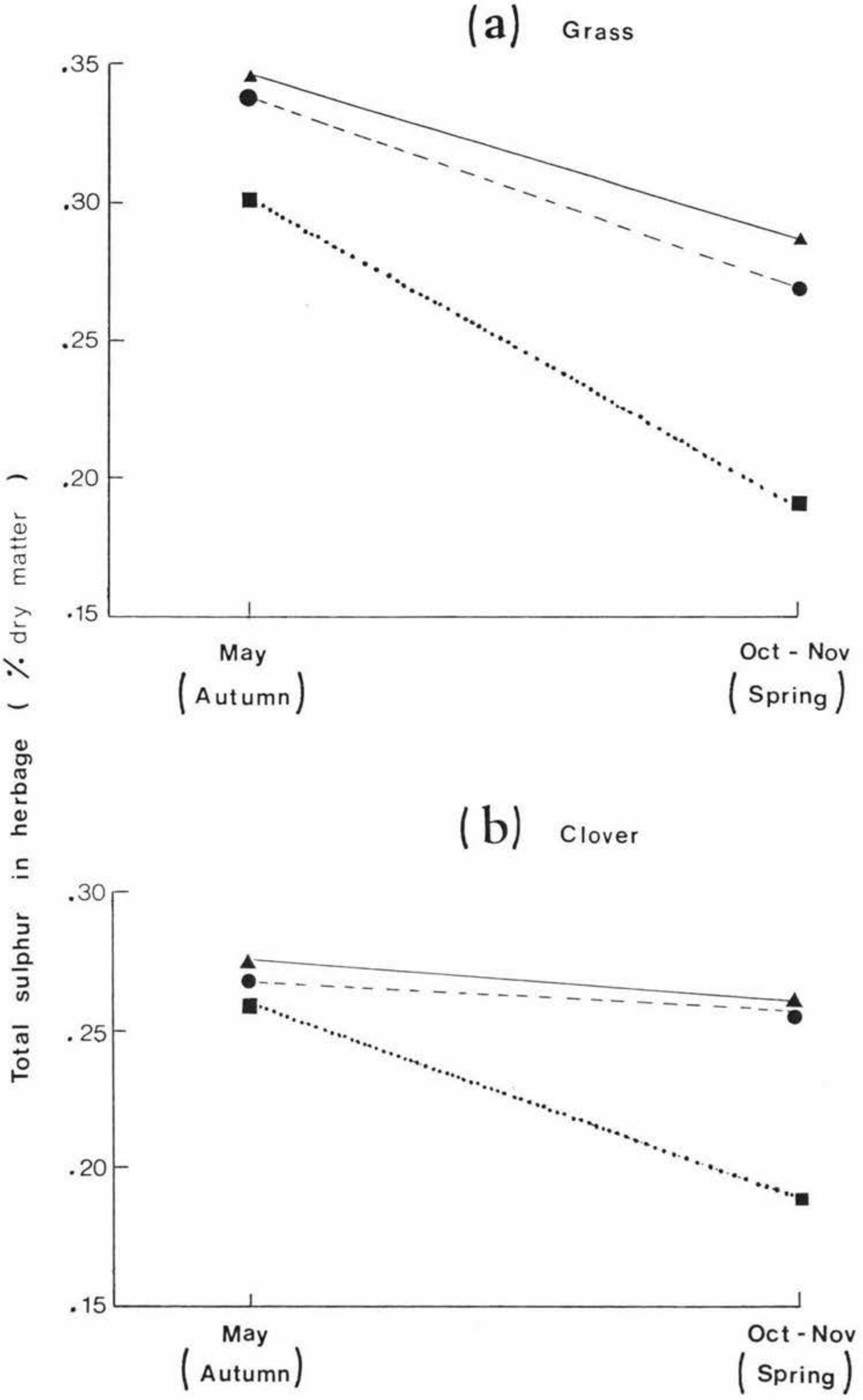


Figure 3.20 Differences in the levels of total sulphur in herbage between autumn and spring

Key: ▲——▲ sites 3, 19
●----● sites 5, 20
■····■ sites 6, 21

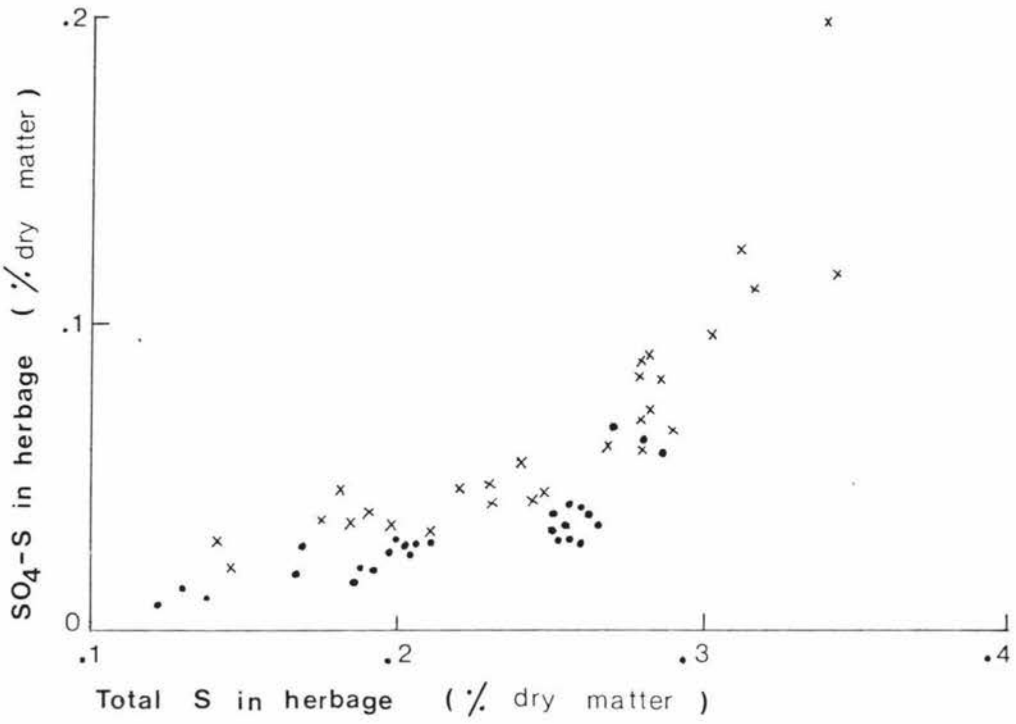


Figure 3.21 Relationship between sulphate sulphur (SO_4-S) and total sulphur (S) in grass and clover

Key: x Grass
• Clover

clover has a lower capacity than grass to accumulate sulphate. Jones et al. (1972) have reported that sulphur in nitrogen-deficient grass tends to accumulate in sulphate form due to a lack of nitrogen for the formation of organic sulphur compounds such as cysteine, cystine and methionine. While this situation could exist in grass samples collected in the spring, where total nitrogen concentrations were below the critical values (4 to 4.5%) proposed by McNaught (1970) for maximum plant growth, the high levels of total nitrogen in grass samples collected in autumn (tables 3.3 and 3.4) suggest that the accumulation of sulphate in grass was due to the luxury uptake of soil sulphate rather than a nitrogen deficiency.

No critical sulphate levels for maximum grass and clover growth under pastoral conditions have been reported by New Zealand workers. Thus, sulphate concentration cannot be used as an index of ranking the herbage samples in terms of sulphur adequacy.

In this study however, the average critical values of total sulphur in grass (0.27%) and clover (0.26%) proposed by McNaught and Christoffels (1961) were used (figure 3.21) to give an estimate of the critical levels of sulphate. In this way, critical sulphate levels of 0.06% and 0.03% were obtained for grass and clover respectively. Similar values for grass (0.06%) and clover (0.03%) can be obtained from figure 3.17 if a phosphate extractable soil sulphur concentration of 13 $\mu g\ S\ g^{-1}$ is chosen as a soil test value below which sulphur deficiency would occur.

Although these estimations of critical levels are only approximate due to the limited data available in the survey, it is interesting to note that the sulphate value obtained for clover (.030%) was similar to that proposed by Australian workers (Bouma et al., 1969). In contrast, the sulphate value for grass (0.060%) was double that (0.032%) suggested by Dijkshoorn et al. (1960).

Dijkshoorn et al. (1960) defined a critical sulphate level of 0.032%, below which chlorotic symptoms and reduced utilisation of nitrogen in protein occurs but it has been suggested by Metson (1973) that while this level may be useful as a measure of acute phsiological deficiency, it does not necessarily indicate the critical level for maximum dry matter production. Thus, the critical sulphate value for grass at which maximum dry matter yield is attained, will be higher than that proposed by Dijkshoorn et al. (1960) and the level (0.060%) obtained in this survey may be more realistic.

(ii.b) Sulphate as a percentage of total sulphur. The percentage of total sulphur that occurred as sulphate, increased with both an increasing soil sulphur supply and total sulphur content in herbage (figures 3.18 and 3.22). The proportion of the total sulphur in sulphate form was always higher in grass than in clover (figure 3.22). The highest ratio of sulphate to total sulphur in grass was 59%, whereas in clover it was 24% (tables 3.3 and 3.4).

Herbage sulphate expressed as a percentage of total sulphur has been suggested as indicator of the sulphur status of wheat (Freney et al., 1978) and subterranean clover (Spencer et al., 1978), but to date, no New Zealand workers have published critical values for pasture plants. Thus this index cannot be used in ranking herbage samples in terms of sulphur deficiency or sufficiency. The proportions of total sulphur in sulphate form, corresponding to the average critical levels of total sulphur in grass (0.27%) and clover (0.26%) as proposed by McNaught and Christoffels (1961), can be derived from figure 3.22. They are in the range of 18 to 22% and 10 to 16% for grass and clover respectively. While the levels (18 to 22%) for grass (ryegrass, Lolium sp.) are slightly higher than that (12%) for green panic grass (Panicum maximum)

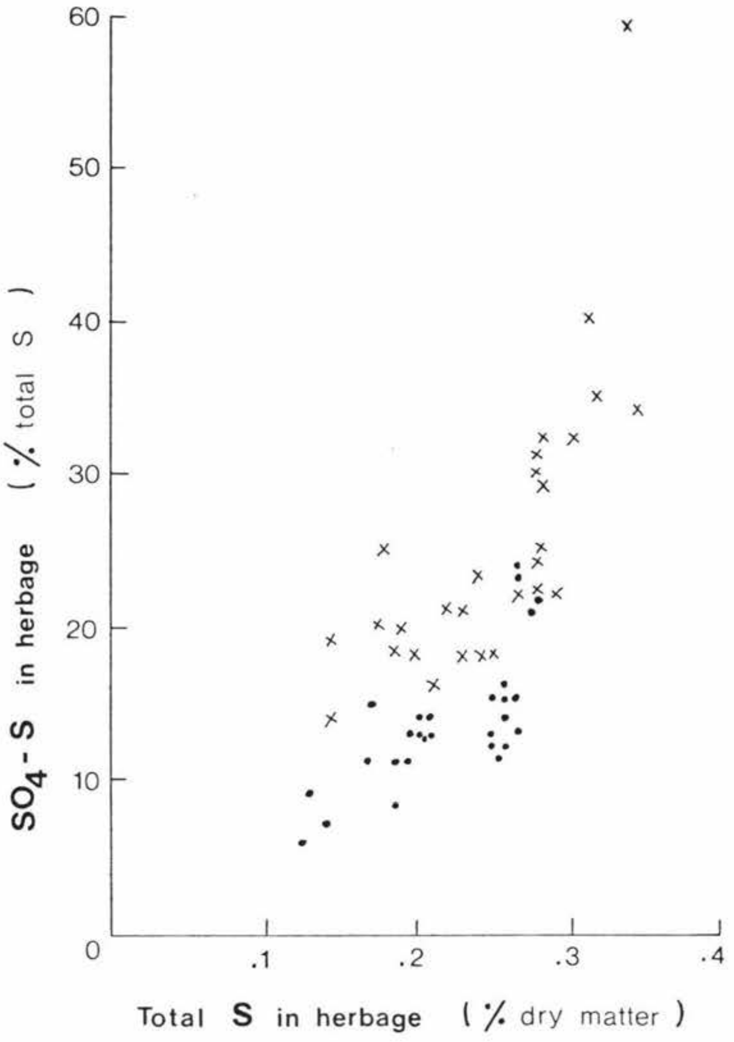


Figure 3.22 Relationship between sulphate sulphur (SO_4-S) expressed as percentage of total sulphur and total sulphur(S) in grass and clover

Key: x Grass
• Clover

proposed by Smith and Dolby (1977), those (10 to 16%) for clover (white clover, Trifolium repens L.) are about 2 to 4 times the level (4%) suggested by Spencer et al. (1978) for subterranean clover (Trifolium subterranean L.) These differences could be attributed to the errors involved in the extrapolation of the data in figure 3.22, the limited number of herbage samples covered in this survey, the inherent differences in sulphur requirements of various species and the effect of environment on plant requirements. For instance, competition for nutrients between species growing in association and the recycling of sulphur through dung and urine are absent from pot experiments involving only a single plant species such as were carried out by Smith and Dolby (1977) and Spencer et al., (1978).

(iii) Total nitrogen (N):total sulphur (S) ratio

(iii.a) Total nitrogen:total sulphur ratios in grass samples.

The N:S ratios in grass were lower than those in clover (figure 3.19). This difference is partly a consequence of the generally greater total sulphur content of the grass and partly of the greater nitrogen content of the clover (tables 3.3 and 3.4).

Using a critical N:S ratio of 16:1 as an indication of sulphur deficiency in grass (McNaught, 1970), almost all grass samples collected during autumn and spring could be considered to have adequate sulphur (tables 3.3 and 3.4). This is not in agreement with the predictions obtained earlier, using critical values for total sulphur. The reason for such a discrepancy might be that the nitrogen levels in the grass samples obtained in this survey were generally lower than those (4 to 4.5%) used by McNaught (1970) to compute his N:S ratios. The importance of nitrogen status in setting the critical sulphur levels and N:S ratios for maximum grass growth has been recognised by McNaught and Christoffels (1961) and these authors have proposed critical N:S ratios of 12 to 14:1

for grasses with high nitrogen status (3.5 to 4%), 10 to 12:1 for those with medium nitrogen status (2.5 to 3%) and 9 to 11:1 for those with low nitrogen status (2 to 2.5%). Further evidence for the dependence of the N:S ratio on nitrogen content can be seen in this study if the N:S ratios in the grass are plotted against available soil sulphur (figure 3.19) or the total sulphur concentrations in grass (figure 3.23). There is a clear differentiation in N:S ratios according to nitrogen status. Although the curves (figures 3.19 and 3.23) were not well-defined, due to the limited number of herbage samples covered in this survey, the N:S ratios in grass associated with the critical levels of phosphate extractable soil sulphur (11 - 13 μg S g^{-1}) and total sulphur concentration in grass (0.27%), were similar to those derived from the study of McNaught and Christoffels (1961).

Based on the critical N:S ratios adjusted for nitrogen content (McNaught and Christoffels, 1961), four out of eleven grass samples collected in autumn and eight out of seventeen grass samples collected in spring (tables 3.3 and 3.4) could be considered sulphur deficient. These observations are in close agreement with those obtained using total sulphur values.

(iii.b) Total nitrogen:total sulphur ratios in clover samples. Using a critical N:S ratio of 17 to 19:1 (McNaught and Christoffels, 1961; McNaught, 1970) as an indicator of a likely sulphur response, twelve out of seventeen (70%) clover samples collected in spring can be classified as sulphur deficient (table 3.4). In contrast only 10% of autumn samples could be assumed to be sulphur deficient (table 3.3).

3.5.b CONCLUSIONS FROM THE HERBAGE SURVEY

The results obtained from this study indicate that the sulphur status of pasture herbage is generally lower in spring than in autumn and a

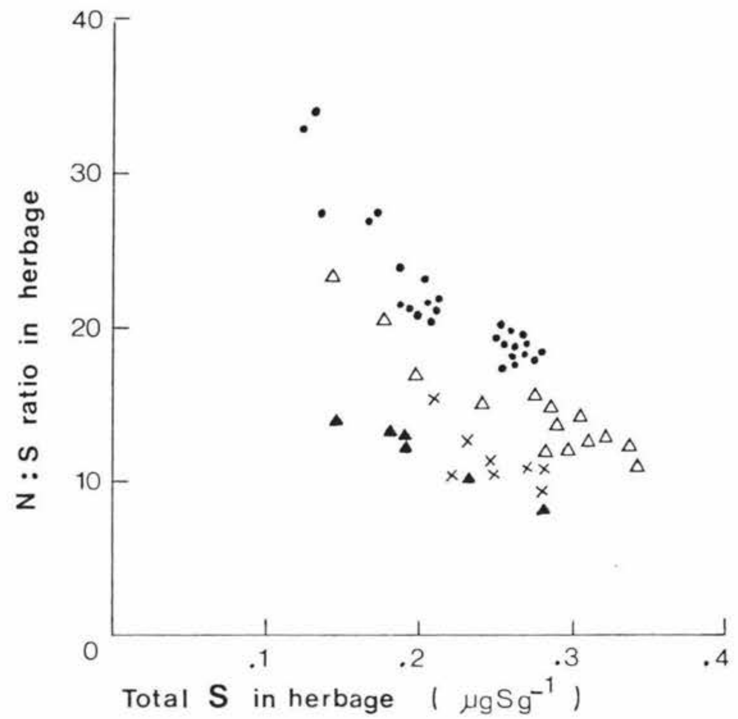


Figure 3.23 Relationship between N:S ratios and total sulphur in grass and clover

Key: Clover ●

Grass △ with high nitrogen status (> 3.5%N)

× with medium nitrogen status (2.5 - 3.4%N)

▲ with low nitrogen status (< 2.5%N)

sulphur deficiency is more likely to occur in early spring. Applications of sulphate-containing fertiliser such as superphosphate in the autumn months may fail to sustain levels of sulphur status in pasture in the following spring above the critical values proposed for near maximum (95%) dry matter production (McNaught and Christoffels, 1961). Reasons for this failure could include the leaching losses of sulphate and the slow mineralisation rate of soil organic sulphur during the winter months.

3.6 OVERALL CONCLUSIONS FROM THE SOIL AND HERBAGE SURVEY

The results obtained from the survey indicate that soil and herbage sulphur status can vary significantly throughout the year. In most cases, it is lower in spring than in autumn. Thus if sulphur deficiencies do occur, they may be most apparent in early spring. To determine the levels of plant available sulphur in Eastland soils, a calcium phosphate extractant can be employed and there was indirect evidence that phosphate extractable soil sulphur in the range of 11 to 13 $\mu g\ S\ g^{-1}$ may be taken as a soil test value below which a sulphur response is likely to occur.

Seasonal variations in sulphur response have been reported by various workers. For example, the more pronounced sulphur deficiency in spring has been observed by Metson (1972) on a low sulphate retaining gley podzol at Golden Bay in the Nelson province. This seasonal variation was attributed by this worker to: (i) the levels of plant available soil sulphur being depleted by leaching during winter and, (ii) the rate of mineralisation of soil organic sulphur in spring which may be too slow to keep pace with the sulphur requirements of pasture plants.

Contrasting findings have been obtained by During (1972) and During and Cooper (1974). Yield responses to sulphur applications on a highly sulphate retentive yellow-brown loam were absent in spring, but became significant in summer and early autumn, notably in late autumn, declined sharply in winter and disappeared again in spring. The absence of a spring sulphur response has been considered by these workers to be due to the strong ability of this soil to retain sulphate against leaching. Furthermore, the plant available soil sulphur pool in spring may have been partly supplied by the mineralisation of soil organic sulphur (During, 1972).

Overall, the incidence of sulphur deficiency may not undergo a similar seasonal cycle on all soils. On some soils, marked sulphur deficiency following autumn application of sulphate may not be apparent until summer, while on other soils, sulphur deficiency is likely to occur in spring. The degree of this spring sulphur deficiency will depend upon (i) the amount of sulphate applied in previous autum, (ii) the extent of sulphate leaching during the winter, (iii) the rate of mineralisation of soil organic sulphur in early spring and (iv) the rate of plant growth. For instance, sulphur responses to spring application of sulphate on low sulphate retentive yellow-brown pumice soils have been observed at sites which had been topdressed with sulphate (37.5kg S ha^{-1} as sulphate) in the previous autumn, suggesting that considerable leaching losses had occurred in this soil over winter (Toxopeus, 1970). In contrast, the absence of sulphur deficiency on another low sulphate retaining soil (Matapiro silt loam) even two years after sulphate application, was taken to indicate that there is little net movement of water for sulphate leaching in this heavy-textured soil under low rainfall (900 mm per annum) conditions (Saunders and Cooper, 1975).

Since there are many factors which can influence the incidence and degree of sulphur deficiency, it must be concluded that although the results of the soil and herbage survey suggest possible sulphur responses in spring, field trials will be the only sure way of confirming this.

CHAPTER 4

FIELD TRIALS

4.1 INTRODUCTION

The survey of Eastland pastures suggested a possible occurrence of sulphur deficiency in spring. The degree of this suspected sulphur deficiency would depend upon the amount of sulphate leached during winter and the sulphur fertiliser history. As spring advances, more sulphate is mineralised as a result of favourable environmental conditions for microbial activity (Barrow, 1961; Williams, 1968) and any sulphur deficiency may disappear as the rate of mineralisation matches the rate of plant demand for sulphur. Even if this situation does occur, the short-lived sulphur deficiency in early spring may be a crucial factor complicating pasture management, since it occurs at a critical time for animal nutrition.

Spring application of sulphur-free nitrogen fertiliser to provide extra dry matter for animal requirements during calving or lambing (During, 1972), might be expected to place further stress on the soil system to provide adequate sulphur for plant growth. This is because nitrogen and sulphur are required in a constant ratio for protein synthesis (Metson, 1973) and any increase in total nitrogen uptake caused by nitrogen fertilisation will increase plant demand for sulphur. In situations where the plant available soil sulphur pool is inadequate for plant sulphur requirements and inputs from other sources are insufficient, the use of nitrogen fertiliser without sulphur application may enhance the degree of sulphur deficiency or cause an imbalance in the N:S ratio in the herbage.

In this study, a series of short-term field trials were laid down in spring to: (i) confirm the suspected spring sulphur deficiency observed in the survey and (ii) investigate the effect of the spring application of nitrogen fertiliser on sulphur requirements.

4.2 METHODS AND MATERIALS

4.2.a SITES AND TRIAL DESIGNS

Five field trials were established on soils belonging to three soil groups: a yellow-grey earth, an intergrade between yellow-grey and yellow-brown earths, and a yellow-brown pumice soil. Site details are listed in table 4.1.

Since the degree of sulphur deficiency will depend upon (i) the extent of sulphate leaching and (ii) the sulphur fertiliser topdressing history, sites were chosen to include a range of these factors. Sites which had received sulphur-fortified superphosphate in the previous autumn were also selected, to assess how well sulphur applied in the elemental form had lasted over the winter, compared to sulphate applied in superphosphate.

Each trial comprised 16 plots (3 x 2m). The experimental design was a randomized complete block layout with four replicates. In each block, the following four treatments were applied:

(i) Control

(ii) plus N : Nitrogen as urea at 50 kg N ha^{-1}.

(iii) plus S : Sulphur at 50 kg S ha^{-1}.

(iv) plus N and S : Nitrogen (50 kg N ha^{-1}) and sulphur (50 kg S ha^{-1})

Sulphur was applied as a mixture of gypsum (25 kg S ha^{-1}) and elemental sulphur (25 kg S ha^{-1}).

A basal dressing of calcium monophosphate (50 kg P ha^{-1}) and potassium

Table 4.1 Description of sites used in field trials.

Site	Soil type	Soil group	Annual rainfall (mm)	Topdressing history
1	Matapiro sandy loam	Yellow-grey earth	900	Regular application of superphosphate every autumn including autumn 1980 (250 kg ha^{-1} of superphosphate) prior to the trial.
2	Otamauri sandy loam	Intergrade between yellow-grey and yellow-brown earths	1200	Regular autumn application of superphosphate. Sulphur-fortified superphosphate at a rate of 125 kg ha^{-1} applied in autumn 1980.
3	Taupo sandy silt	Yellow-brown pumice soil	1600	Regular application of superphosphate. Last application in summer 1980 (300 kg of superphosphate ha^{-1}) prior to the trial.
4	Taupo sandy silt	Yellow-brown pumice soil	1600	Sulphur-fortified superphosphate at a rate of 325 kg ha^{-1} applied in autumn 1980. Unknown topdressing prior to 1980.
5	Taupo sandy silt	Yellow-brown pumice soil	1600	Irregular application of superphosphate. The site had not received any sulpur-containing fertiliser for four years.

chloride (50 kg K ha^{-1}) was applied to all plots.

In trial 1, these treatments were applied on 29th August, 1980, the remaining trial sites received identical treatments on 3rd September,1980.

Grazing animals were excluded from all sites for the duration of the trials.

4.2.b SOIL AND HERBAGE SAMPLING

4.2.b.1 SOIL SAMPLING

Soil samples were taken from all plots at the beginning and at the conclusion of the field experiments.

Four soil cores (25mm diameter) were taken from each plot. Each core was divided into three depths (0-7.5, 7.5-15 and 15-30cm). Soil samples were bulked on the basis of similar soil depth and treatment.

4.2.b.2 HERBAGE SAMPLING

At each site, yield measurements were made by weighing herbage cut with a rotary mower.

The presence of dung and urine patches can lead to a high variability in pasture measurements in the initial stages of field trials. To minimize this yield variation, which would have seriously affected the measurement of plant response in these short-term (3 months) field trials, herbage in the control plots was allowed to grow longer (15 cm) than would normally be the case before a cut was taken. By doing so, plants in other plots, especially those receiving nitrogen, were significantly taller than normal grazing height. Because of this, regrowth was seriously affected and the second harvest from these 'plus nitrogen' plots has been ignored.

Approximately one and a half months after laying down the trials, sites 1, 2 and 4 were harvested, while only grab samples were taken from sites 3 and 5 because of slow growth at these sites.

A second harvest was taken from all sites when the pasture height in the control plots had again reached 15 cm (about one month after the first cut).

At each harvest, the wet weight of herbage was measured and subsamples taken for moisture determination. All clippings were then discarded. Grab samples from unmown portions of each plot were taken for assessment of botanical composition and chemical analysis.

4.2.c CHEMICAL ANALYSES

4.2.c.1 SOIL ANALYSES:

Field moist samples were passed through a 2mm sieve to remove plant material. They were then frozen at -5°C until chemical analyses were conducted.

Soil pH, phosphate-extractable sulphur, calcium chloride extractable sulphur, phosphate retention and Olsen-extractable phosphate were determined using the methods previously described (Chapter 3).

4.2.c.2 HERBAGE ANALYSES:

Oven-dried (60°C for 48 hours) grass and clover samples were finely ground and analysed for total nitrogen, total sulphur and sulphate (Chapter 3).

4.3 RESULTS AND DISCUSSION

4.3.a DRY MATTER YIELD AND PASTURE COMPOSITION

4.3.a.1 PLUS SULPHUR TREATMENT

Significant responses in dry matter yield to sulphur application were observed at three out of the five sites (figure 4.1 and table 4.2). The sulphur responsive sites included those where there had been no recent

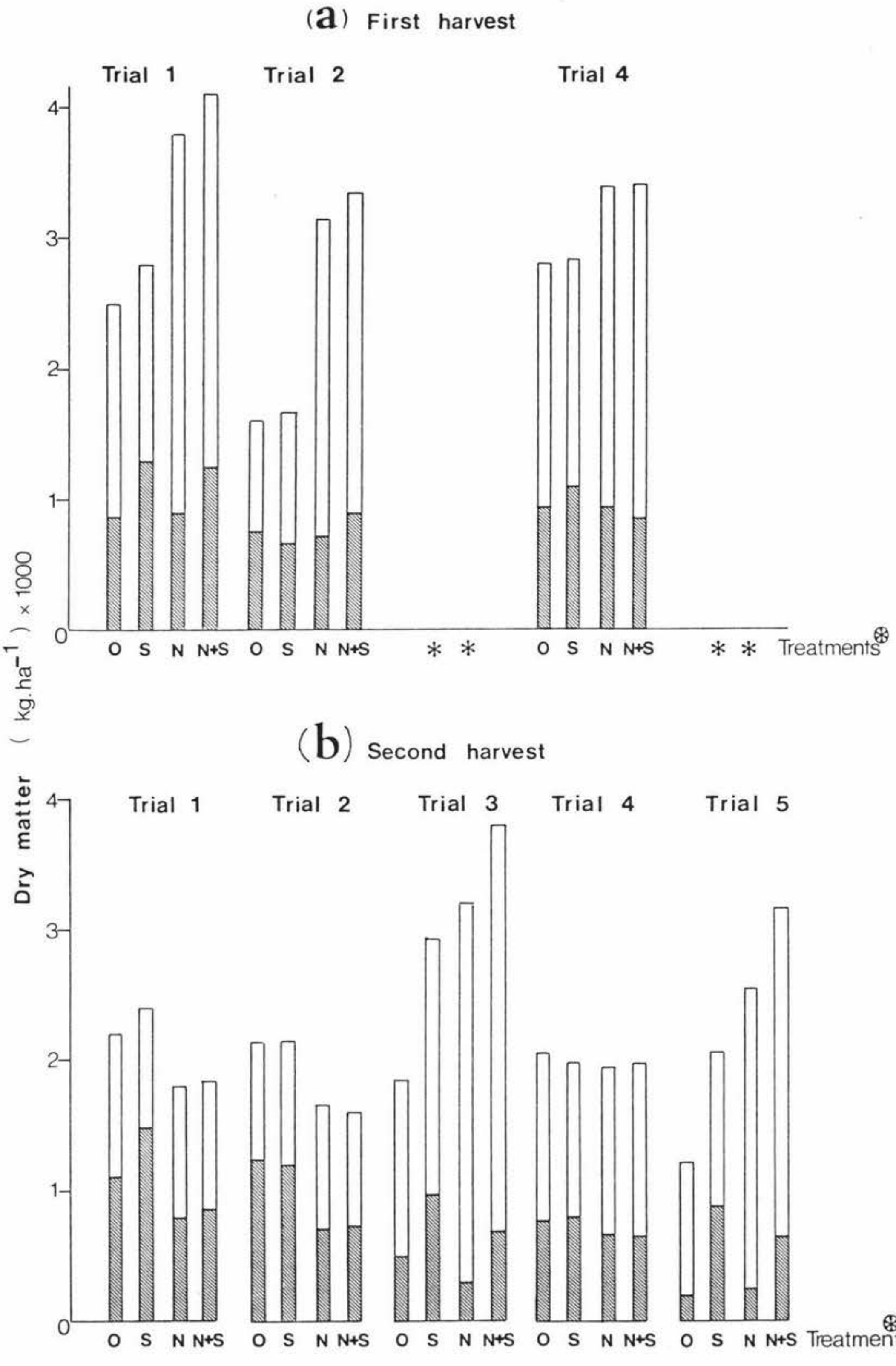


Figure 4.1 Average dry matter yields at two harvests from five field trials.

Key: ⊛ Treatments O = Control
S = 50kg S ha^{-1}
N = 50kg N ha^{-1}
N+S = 50kg N ha^{-1} + 50kg S ha^{-1}

▯ Grass
▨ Clover

** Because of the slow growth at these sites, yield measurements were not made at the first harvest.

Table 4.2 Effects of fertiliser treatment on the dry matter yield of mixed herbage.

Treatment	SITE 1		SITE 2		SITE 3		SITE 4		SITE 5	
	HARVEST		HARVEST		HARVEST		HARVEST		HARVEST	
	ONE	TWO	ONE	TWO	ONE*	TWO	ONE	TWO	ONE*	TWO
	kg D.M. ha^{-1}		kg D.M. ha^{-1}		kg D.M. ha^{-1}		kg D.M. ha^{-1}		kg D.M. ha^{-1}	
1: CONTROL	2507 aA**	2184 aA	1571 aA	2141 aA		1833 aA	2810 aA	2046 aA		1224 aA
2: + S	2859 bA	2444 bA	1653 aA	2151 aA		2963 bB	2841 aA	1996 aA		2034 bB
3: + N	3788 cB	1807 cB	3155 bB	1646 aA		3186 bB	3392 aA	1951 aA		2545 cC
4: + N + S	4078 dB	1824 cB	3355 bB	1586 aA		3809 cC	3438 aA	1973 aA		3169 dD

* No yield measurements were made. Grab samples only were taken for botanical composition and chemical analyses (section 4.2.b).

** Duncan's Lettering (Duncan, 1955): Common small letters are not significantly different at the 5% level of probability, capital letters at the 1% level of probability.

application of sulphur-containing fertiliser (site 5) and also those which had received regular applications of superphosphate each autumn (sites 1 and 3) (table 4.1). The magnitude of the sulphur responses obtained at sites 3 and 5 on a yellow-brown pumice soil was substantially higher than that obtained from site 1 on a yellow-grey earth (figure 4.1, table 4.2). These sulphur responses relate well to the levels of phosphate-extractable soil sulphur (figure 4.2) and herbage sulphur status (figure 4.3) in the control plots at each site.

In the absence of nitrogen, the yield response to applied sulphur was solely (site 1) or mainly (sites 3 and 5), the result of an increase in clover yield (figure 4.1, tables 4.3 and 4.4). The lack of response in grass growth is surprising, as the herbage sulphur concentrations in the control plots at each of these sites (tables 4.5 and 4.6) suggest that the grass was in fact sulphur deficient. A possible explanation is that this grass was also acutely nitrogen deficient, as evidenced both by low herbage nitrogen concentrations (tables 4.5 and 4.6) and also by the large response to added nitrogen at all sites (figure 4.1). Further discussion of this point is presented in section 4.3.a.2 (ii).

4.3.a.2 PLUS NITROGEN AND PLUS NITROGEN AND SULPHUR TREATMENTS

Although two yield cuts were made at sites 1, 2, and 4, data from the first cut only is discussed (See section 4.2.b.2).

4.3.a.2 (i) Nitrogen treatment

At all sites, the application of nitrogen in the absence of sulphur (+ N) greatly increased the total yield (figure 4.1). This increase resulted solely from an increase in grass growth (figure 4.1, tables 4.3 and 4.4). Nitrogen fertilisation reduced the clover component as a percentage of the mixed sward but it had no consistent effect on clover yield (figure 4.1, tables 4.3 and 4.4).

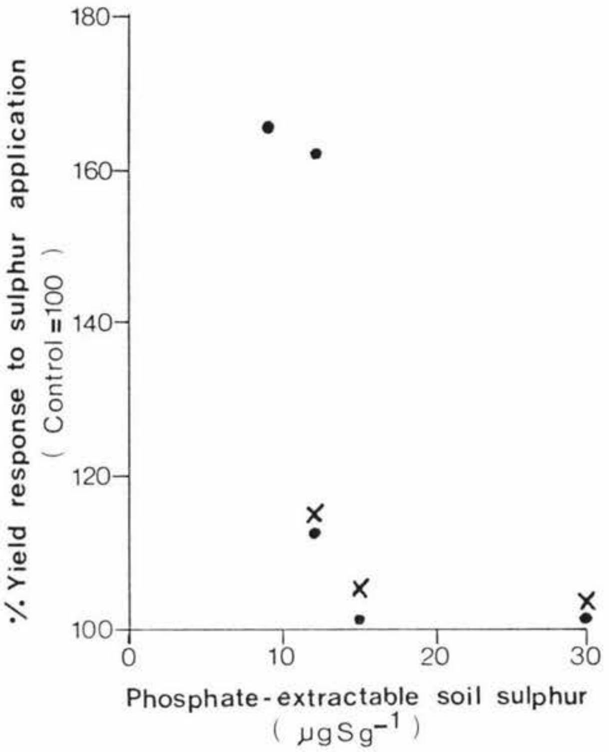


Figure 4.2 Relationship between percentage yield response to applied sulphur and the levels of phosphate extractable sulphur in soils (0 - 7.5 cm) sampled prior to the field experiments.

Key: x First harvest
● Second harvest

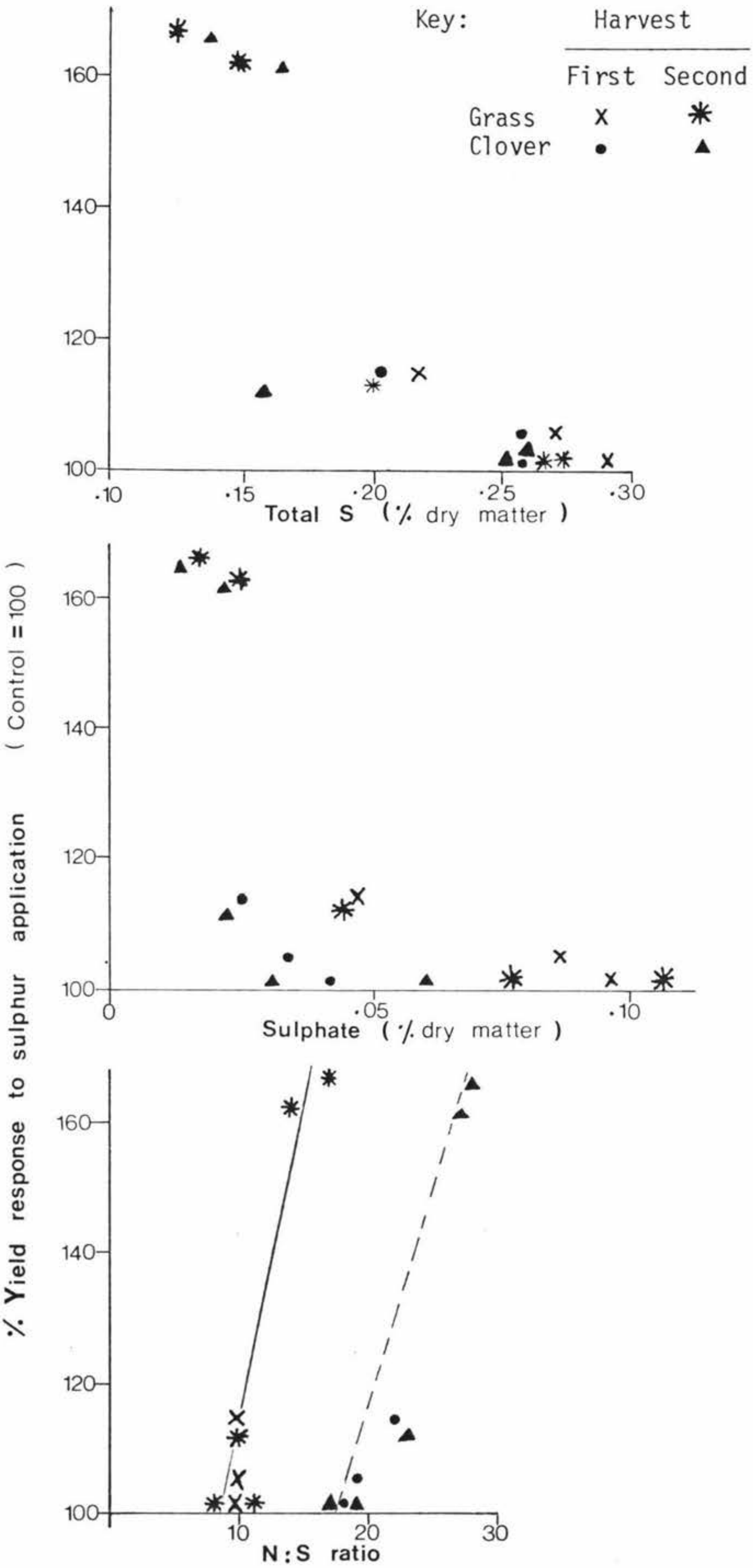


Figure 4.3 Relationship between percentage yield response to applied sulphur and sulphur status (total sulphur, sulphate and N:S ratio) of herbage samples taken from the control plot at the time of harvesting.

Table 4.3 Effects of fertiliser treatment on dry matter yield and botanical composition at the first harvest.

Treatment		GRASS		CLOVER	
		D.M. yield ($kg\ ha^{-1}$)	Composition (%)	D.M. yield ($kg\ ha^{-1}$)	Composition (%)
Site 1	0	1564 aA	62	880 aA	35
	S	1555 aA	54	1301 bB	45
	N	2894 bB	76	894 aA	24
	N + S	2868 bB	69	1240 bB	30
Site 2	0	811 aA	52	757 aA	48
	S	972 aA	59	669 aA	40
	N	2416 bB	77	725 aA	23
	N + S	2437 bB	74	905 aA	25
Site 3	0	*	66		32
	S		61		37
	N		87		10
	N + S		76		22
Site 4	0	1673 aA	59	935 aA	34
	S	1581 aA	56	1105 aA	39
	N	2155 aA	64	940 aA	28
	N + S	2343 aA	69	860 aA	25
Site 5	0	*	75		17
	S		53		41
	N		80		10
	N + S		75		19

* No yield measurements were made. Grab samples only were taken for botanical determination and chemical analyses (section 4.2.b).

Table 4.4 Effects of fertiliser treatment on dry matter yield and botanical composition at the second harvest.

Treatments		GRASS		CLOVER	
		D.M. yield ($kg\ ha^{-1}$)	Composition (%)	D.M. yield ($kg\ ha^{-1}$)	Composition (%)
Site 1	0	1063 aA	49	1121 aA	51
	S	955 aA	39	1489 bB	61
	N	1007 aA	56	800 cC	44
	N + S	953 aA	52	871 cC	48
Site 2	0	894 aA	42	1237 aA	58
	S	933 aA	44	1218 aA	56
	N	930 aA	56	716 bA	44
	N + S	849 aA	53	737 bA	47
Site 3	0	1293 aA	71	500 aA	27
	S	1960 bB	66	980 bB	33
	N	2818 cC	89	309 cC	10
	N + S	3072 cC	81	690 dA	18
Site 4	0	1030 aA	51	775 aA	37
	S	1025 aA	51	815 aA	41
	N	1070 aA	55	671 aA	35
	N + S	1183 aA	60	648 aA	33
Site 5	0	918 aA	75	209 aA	17
	S	1112 aA	55	880 bB	43
	N	2077 bB	82	243 aA	10
	N + S	2427 bB	77	634 cB	20

Table 4.5 Mean total sulphur, sulphate and nitrogen contents and nitrogen: sulphur ratios in grass and clover at the first harvest.

		GRASS					CLOVER				
Treatments		S	SO_4^{--}		N	N:S	S	SO_4^{--}		N	N:S
		%D.M.	%D.M.	% S*	%D.M.		%D.M.	%D.M.	% S	%D.M.	
Site 1	0	.217	.047	22	2.24	10	.203	.025	12	4.50	22
	S	.408	.164	40	2.54	6	.257	.066	26	4.75	19
	N	.203	.038	19	2.61	13	.203	.024	12	4.28	21
	N+S	.402	.164	41	2.60	7	.252	.063	25	4.49	18
Site 2	0	.271	.086	32	2.63	10	.256	.034	13	4.78	19
	S	.435	.152	35	2.53	6	.337	.074	22	4.77	14
	N	.263	.078	30	2.45	10	.251	.034	14	4.37	17
	N+S	.355	.138	39	2.52	7	.296	.066	22	4.41	15
Site 3	0	.193	.040	21	2.82	15	.201	.020	10	4.54	23
	S	.315	.131	42	3.63	12	.257	.046	18	5.07	20
	N	.181	.035	19	3.82	22	.177	.017	10	5.04	29
	N+S	.305	.118	39	3.85	13	.209	.043	21	5.22	25
Site 4	0	.291	.096	33	3.01	10	.258	.042	16	4.76	18
	S	.437	.165	38	3.15	7	.275	.058	21	4.66	17
	N	.281	.094	33	3.14	11	.255	.042	16	4.73	19
	N+S	.397	.164	41	3.10	8	.272	.066	24	4.81	18
Site 5	0	.173	.034	20	2.92	17	.194	.011	6	4.28	22
	S	.303	.129	42	3.19	11	.280	.038	13	4.94	18
	N	.150	.021	14	3.26	22	.184	.011	6	4.58	25
	N+S	.279	.117	42	3.43	12	.251	.045	18	5.15	21

* Sulphate (SO_4^{--}) expressed as a percentage of total sulphur.

Table 4.6 Mean total sulphur, sulphate and nitrogen contents and nitrogen:sulphur ratios in grass and clover at the second harvest.

		GRASS					CLOVER				
Treatments		S	SO_4^{--}		N	N:S	S	SO_4^{--}		N	N:S
		%D.M.	%D.M.	% S**	%D.M.		%D.M.	%D.M.	% S**	%D.M.	
Site 1*	0	.202	.045	22	2.02	10	.158	.020	13	3.67	23
	S	.413	.163	40	2.17	5	.255	.065	26	4.21	17
	N										
	N+S										
Site 2*	0	.265	.078	29	2.10	8	.252	.031	12	4.24	17
	S	.408	.165	41	2.03	5	.257	.043	17	4.27	17
	N										
	N+S										
Site 3	0	.149	.025	17	2.12	14	.163	.022	14	4.30	27
	S	.251	.057	23	2.33	9	.219	.029	13	4.72	22
	N	.134	.022	16	2.36	18	.152	.018	12	4.06	27
	N+S	.206	.050	24	2.34	11	.199	.024	12	4.36	22
Site 4*	0	.274	.107	39	2.85	11	.258	.060	23	4.89	19
	S	.322	.147	46	2.75	9	.266	.072	27	4.82	18
	N										
	N+S										
Site 5	0	.124	.017	14	2.06	17	.136	.014	10	3.79	28
	S	.203	.043	21	2.37	12	.201	.027	13	4.27	22
	N	.096	.015	15	2.15	23	.130	.014	10	3.67	29
	N+S	.200	.046	23	2.35	12	.170	.026	15	4.12	24

* Herbage from the N and N+S plots at the second harvest was not analysed because of growth depression (section 4.2.b).

** Sulphate (SO_4^{--}) expressed as a percentage of total sulphur.

4.3.a.2 (ii) Sulphur plus nitrogen treatment

The two sites (2 and 4) which did not respond to sulphur application in the absence of nitrogen still showed no response to sulphur when nitrogen fertiliser was applied (figure 4.1, table 4.2) suggesting that the soil sulphur status was adequate for pasture requirements even with the greater demand from the increased grass growth.

At the three sulphur responsive sites (1, 3 and 5), sulphur application in the presence of nitrogen fertiliser resulted in a greater dry matter yield than where nitrogen was applied alone (figure 4.1, table 4.2). This yield response was produced mainly by an increase in clover growth (figure 4.1, tables 4.3 and 4.4) and was of similar or lower magnitude to that obtained with sulphur in the absence of nitrogen. The fact that grass did not respond to added sulphur, even in the presence of adequate nitrogen, would suggest that the supply of sulphur from the soil was adequate for grass growth even though the concentrations of sulphur in the herbage had dropped to very low levels on some of the plus nitrogen treatments (tables 4.5 and 4.6). Further discussion is presented in section 4.3.c.2 (ii).

4.3.b SOIL ANALYSES

4.3.b.1 PREDICTION OF SULPHUR RESPONSE

The levels of phosphate-extractable soil sulphur in the control plots at each site were consistent with the yield responses obtained (figure 4.2, table 4.7).

In comparison with site 3, where 300 kg ha^{-1} of superphosphate was applied in autumn 1980, 325 kg ha^{-1} of sulphur-fortified superphosphate was applied to site 4 in autumn of the same year. However, the high levels of phosphate-extractable soil sulphur (30 µg S g^{-1}) and especially the high Olsen extractable soil phosphorus level (40 µg P g^{-1}) at site 4,

Table 4.7 Levels of phosphate-extractable sulphur, calcium chloride extractable sulphur, adsorbed sulphur, Olsen-extractable phosphorus, phosphate retention and soil pH in soil profiles at the start of field trials.

Trial	Soil depth (cm)	PO_4-extractable sulphur (μg S g^{-1})	$CaCl_2$-extractable sulphur (μg S g^{-1})	Adsorbed* sulphur (μg S g^{-1})	Olsen-extractable phosphorus (μg P g^{-1})	Phosphate retention (%)	Soil pH
1	0 - 7.5	12	6	6	15	32	5.6 - 5.8
	7.5 - 15	8	3	5	7	28	
	15 - 30	5	2	3	4	25	
2	0 - 7.5	15	5	10	15	41	5.4 - 5.5
	7.5 - 15	9	3	6	7	35	
	15 - 30	7	4	3	3	27	
3	0 - 7.5	12	4	8	24	54	5.8 - 6.0
	7.5 - 15	8	2	6	10	60	
	15 - 30	8	1	6	6	65	
4	0 - 7.5	30	14	16	40	70	5.0 - 5.2
	7.5 - 15	18	4	14	18	78	
	15 - 30	13	3	10	8	74	
5	0 - 7.5	9	3	6	9	73	5.6 - 58
	7.5 - 15	6	1	5	5	80	
	15 - 30	4	1	3	3	74	

* Adsorbed sulphur is calculated as the difference between the sulphur extracted by calcium phosphate and calcium chloride solutions.

suggest that in fact this site had a markedly different fertiliser history besides the application of sulphur-fortified superphosphate in the previous autumn.

4.3.b.2 LEACHING PATTERNS

Indirect evidence of sulphate leaching can be obtained by comparing the levels of phosphate-extractable soil sulphur and Olsen-extractable soil phosphate at sites 3 and 5 (table 4.7), which were developed from the same parent material under the same rainfall conditions but have different fertiliser histories (table 4.1). While there was no great difference between these sites in the levels of phosphate-extractable sulphur, the amount of Olsen-extractable phosphorus at site 3, with a long history of superphosphate applications, was much higher than that obtained from site 5, which had received less frequent fertiliser applications.

Further evidence of sulphate leaching can be obtained by comparing the levels of phosphate-extractable sulphur from lower depths (7.5-15cm and 15-30cm) in sulphur-treated plots with those in control plots (figure 4.4, table 4.8). Substantial amounts of sulphate leached down from the topsoil within three months of application (figure 4.4). This downward movement of sulphate applied in the spring emphasizes that leaching can be a problem if sulphur in a water-soluble form is applied prior to winter.

4.3.c HERBAGE ANALYSES

4.3.c.1 PREDICTION OF SULPHUR RESPONSE

The degree of plant response to sulphur application related well to the sulphur status (sulphate, total sulphur and nitrogen:sulphur ratios) of the herbage in the control plots (figure 4.3).

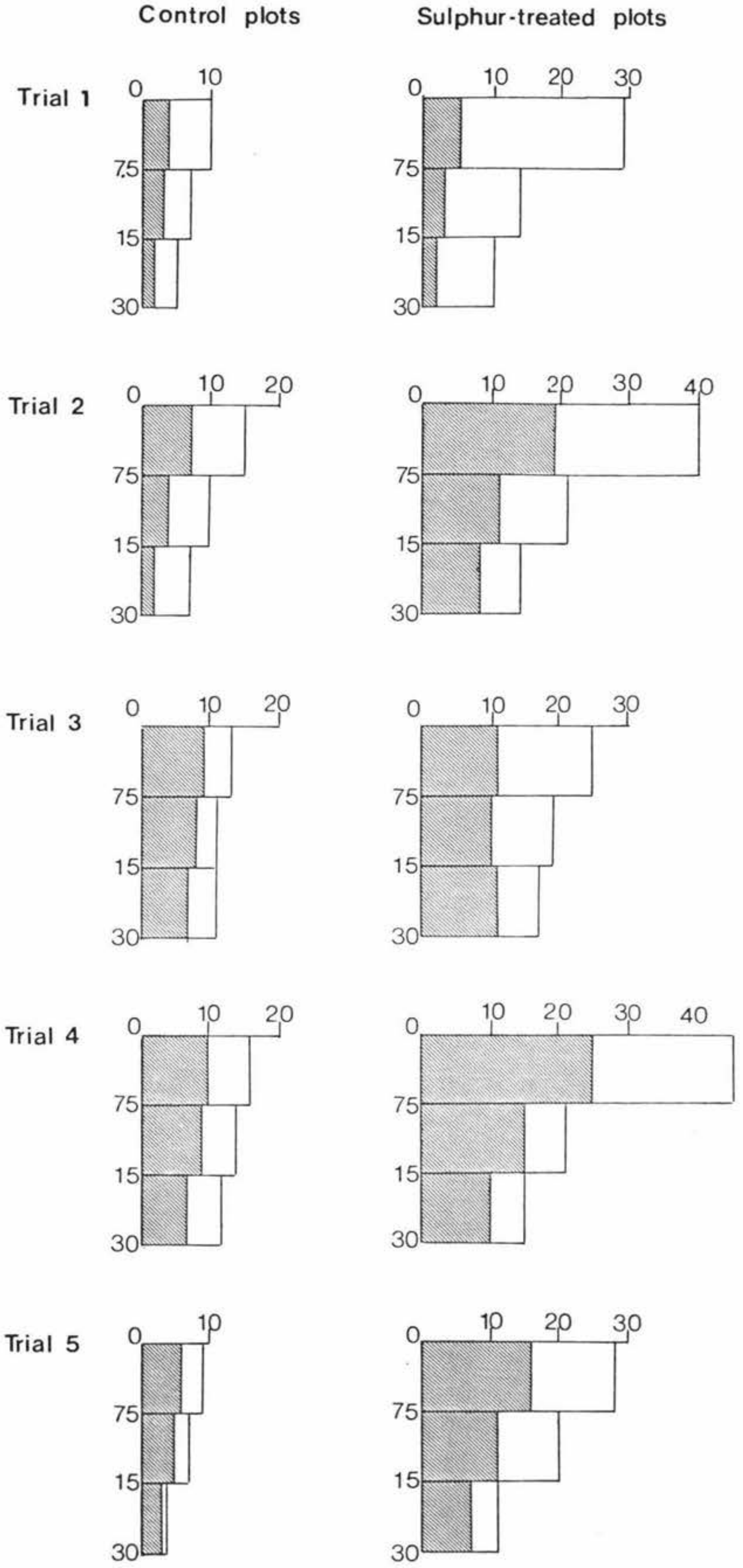


Figure 4.4 The distribution of extractable sulphur with depth in soil profiles at the conclusions of field experiments.

Key: S(μg S g^{-1} soil)

depth (cm)

▨ Adsorbed sulphur

☐ Phosphate extractable sulphur

Table 4.8 Levels of phosphate-extractable sulphur, calcium chloride extractable sulphur, adsorbed sulphur and soil pH in soil profiles of the control and sulphur-treated plots at the conclusions of field trials.

		CONTROL PLOTS				+ S PLOTS			
Trial	Soil Depth (cm)	Phosphate extractable sulphur ($\mu g\ S\ g^{-1}$)	$CaCl_2$ extractable sulphur ($\mu g\ S\ g^{-1}$)	Adsorbed sulphur ($\mu g\ S\ g^{-1}$)	Soil pH	Phosphate extractable sulphur ($\mu g\ S\ g^{-1}$)	$CaCl_2$ extractable sulphur ($\mu g\ S\ g^{-1}$)	Adsorbed sulphur ($\mu g\ S\ g^{-1}$)	Soil pH
1	0 - 7.5	10	6	4	5.9-6.1	29	24	5	5.8-6.2
	7.5 - 15	7	4	3		14	11	3	
	15 - 30	5	3	2		10	8	2	
2	0 - 7.5	15	8	7	5.0-5.1	40	21	19	5.0-5.1
	7.5 - 15	10	6	4		21	10	11	
	15 - 30	7	5	2		14	6	8	
3	0 - 7.5	13	4	9	5.7-6.0	25	14	11	5.7-5.9
	7.5 - 15	10	2	8		19	9	10	
	15 - 30	10	3	7		17	6	11	
4	0 - 7.5	16	6	10	5.1-5.2	45	20	25	5.1-5.2
	7.5 - 15	14	5	9		21	6	15	
	15 - 30	12	4	7		15	4	11	
5	0 - 7.5	9	3	6	5.7-6.1	28	12	16	5.6-5.9
	7.5 - 15	7	2	5		20	9	11	
	15 - 30	4	1	3		11	4	7	

4.3.c.2 EFFECT OF FERTILISER ON HERBAGE COMPOSITION

4.3.c.2 (i) Plus sulphur treatment

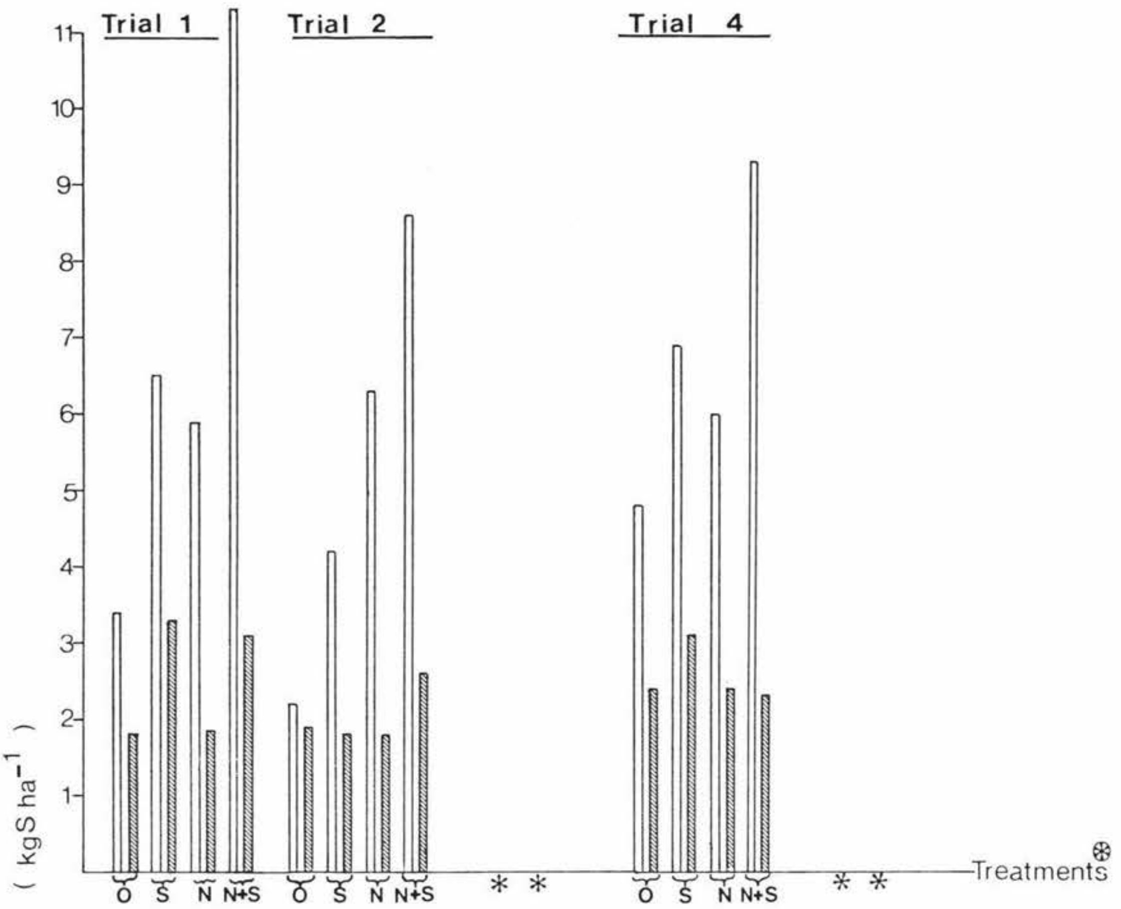
Concentrations of sulphate, total sulphur and nitrogen in herbage as well as the uptake of sulphur and nitrogen increased at the three sulphur responsive sites (1, 3 and 5) as a result of sulphur application (figures 4.5 and 4.6, tables 4.5, 4.6 and 4.9). Even at sites 2 and 4, where no yield response was recorded (figure 4.1), sulphur fertilisation increased the sulphur concentrations in grass and clover (tables 4.5 and 4.6) as well as the sulphur uptake in grass (table 4.9) but it did not increase either the concentration or uptake of nitrogen by herbage (tables 4.5, 4.6 and 4.9).

As in the survey of the previous year, it was observed that clover had a lesser ability than grass to: (i) take up sulphate from soil solution, even when the sulphur supply was adequate (figure 4.5) and (ii) accumulate sulphur in the sulphate form. Up to 46 percent of the total sulphur in grass could be accounted for by this fraction, while in clover it was always below 28% (tables 4.5 and 4.6).

The increase in nitrogen uptake by herbage, especially clover (figure 4.6, table 4.9), at the three sulphur responsive sites, suggests that sulphur is important not only for clover growth but also for nitrogen fixation (McNaught and Christoffels, 1961; Metson, 1973; Andrew, 1977).

As a consequence of sulphur application, the ratios of total nitrogen to total sulphur (N:S ratio) in herbage from the first harvest at the three sulphur-responsive sites (1, 3 and 5) were reduced (table 4.5) to within the optimum range for plant production proposed by McNaught and Christoffels (1961). However at the second harvest, the ratios at sites 3 and 5 were wider (table 4.6) than the critical levels.

(a) First harvest



(b) Second harvest

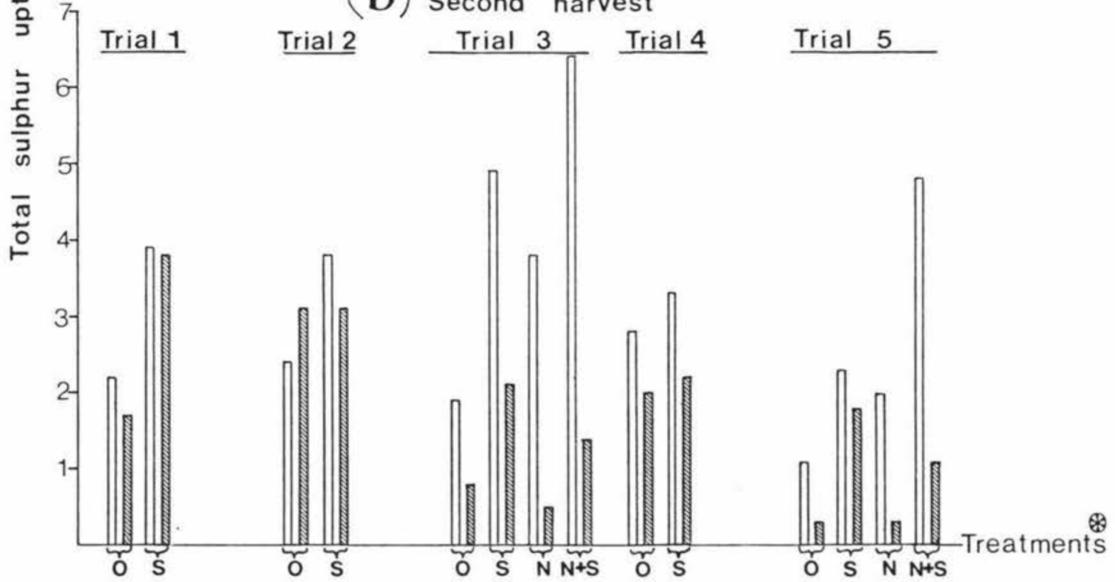


Figure 4.5 Total sulphur uptake in pasture herbage.

Key: ⊛ Treatments
O = Control
S = 50kg S ha^{-1}
N = 50kg N ha^{-1}
N+S = 50kg N ha^{-1} + 50kg S ha^{-1}

▯ Grass
▨ Clover

** Because of the slow growth at these sites, yield measurements were not made at the first harvest.

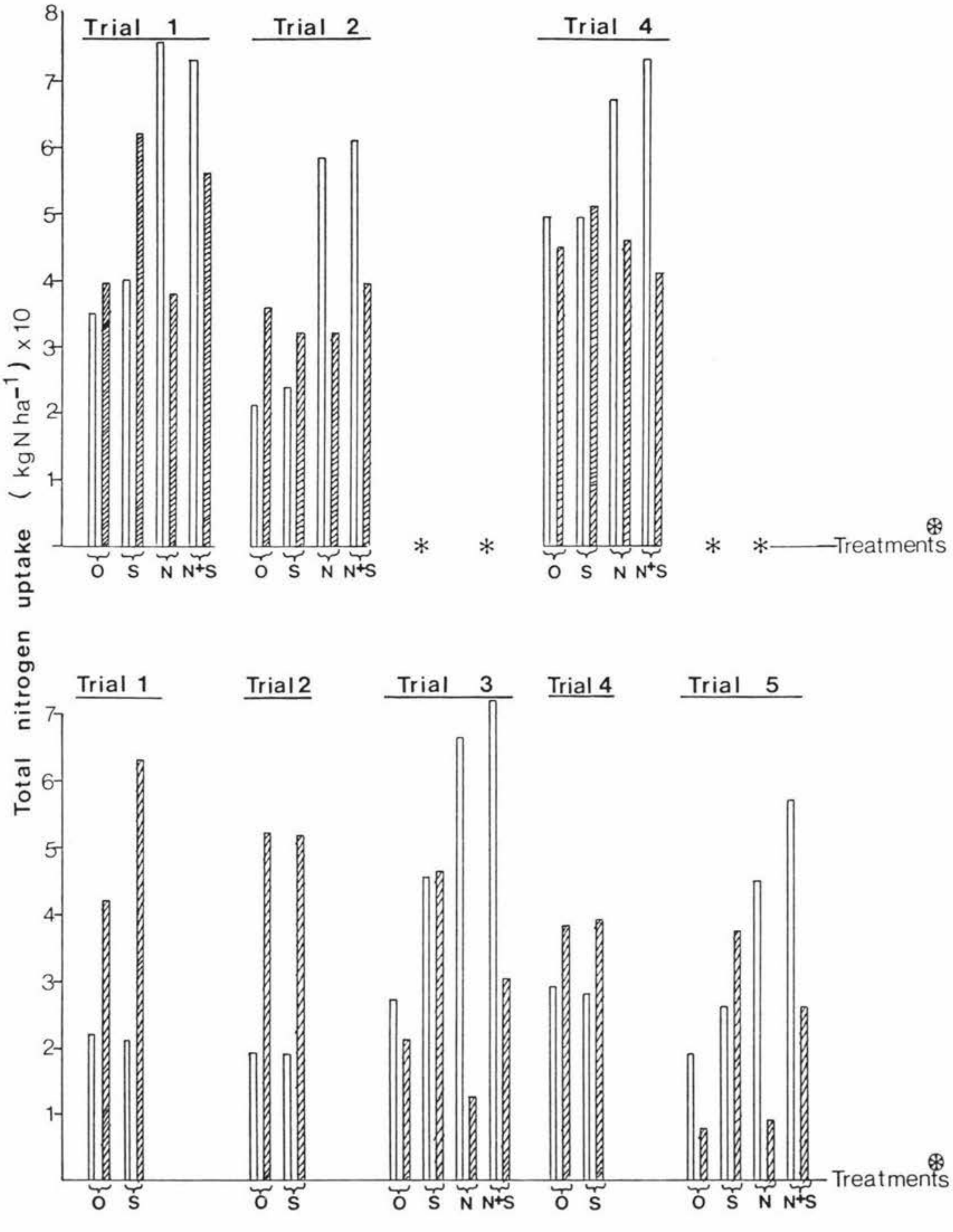


Figure 4.6 Uptake of total nitrogen in pasture herbage.

Key: ⊛ Treatments O = Control
S = 50kg S ha-1
N = 50kg N ha-1
N+S = 50kg ha-1 + 50kg S ha-1

▯ Grass
▨ Clover

** Because of the slow growth at these sites, yield measurements were not made at the first harvest.

Table 4.9 Effect of fertiliser treatment on uptake of total sulphur and total nitrogen in pasture herbage.

		FIRST HARVEST				SECOND HARVEST			
		GRASS		CLOVER		GRASS		CLOVER	
Treatment		S	N	S	N	S	N	S	N
		kg ha^{-1}		kg ha^{-1}		kg ha^{-1}		kg ha^{-1}	
Site 1	0	3.4 aA	35.1 aA	1.8 aA	39.6 aA	2.2 aA	21.4 aA	1.7 aA	41.7 aA
	S	6.5 bB	39.8 aA	3.3 bB	61.8 bB	3.9 bB	20.7 aA	3.8 bB	52.7 bB
	N	5.9 bB	75.5 bB	1.8 aA	38.2 aA				
	N + S	11.3 cC	72.8 bB	3.1 bB	56.1 bB				
Site 2	0	2.2 aA	21.3 aA	1.9 aA	36.3 aA	2.4 aA	18.8 aA	3.1 aA	52.4 aA
	S	4.2 bB	24.4 aA	1.8 aA	31.9 aA	3.8 bB	18.9 aA	3.1 aA	51.8 aA
	N	6.3 cC	58.4 bB	1.8 aA	32.1 aA				
	N + S	8.6 dD	61.4 bB	2.6 aA	39.4 aA				
Site 3	0					1.9 aA	27.3 aA	0.8 aA	21.4 aAC
	S					4.9 bB	45.6 bB	2.1 bB	46.1 bB
	N					3.8 cC	66.3 cC	0.5 cA	12.5 cA
	N + S					6.4 dC	71.8 cC	1.4 dC	30.1 dC
Site 4	0	4.8 aA	49.3 aA	2.4 aA	44.5 aA	2.8 aA	29.1 aA	2.0 aA	38.1 aA
	S	6.9 bAB	49.4 aA	3.1 aA	51.2 aA	3.3 bA	27.7 aA	2.2 aA	39.2 aA
	N	6.0 abA	66.7 abA	2.4 aA	44.5 aA				
	N + S	9.3 cB	72.8 bA	2.3 aA	41.2 aA				
Site 5	0					1.1 aA	18.8 aA	0.3 aA	7.8 aA
	S					2.3 bB	26.4 aA	1.8 bB	37.4 bB
	N					2.0 bB	44.5 bB	0.3 aA	8.9 aA
	N + S					4.8 cC	56.9 cC	1.1 cC	26.1 cC

The widening of N:S ratios could be attributed to the stage of plant maturity at this cut (McNaught, 1970).

4.3.c.2 (ii) Plus nitrogen treatment

The amounts of sulphur removed by pasture plants in nitrogen-treated plots were higher than those in the control plots (figure 4.5, table 4.9). This was caused mainly by the increase in total sulphur uptake by grass (figure 4.5). Reasons for this increase may include:

(i) The stimulatory effect of ammonium ions from urea fertiliser on sulphate uptake (Rehm and Caldwell, 1970).

(ii) An increase in the proliferation of grass roots due to nitrogen fertilisation (Grunes et al., 1958) giving a greater exploitation of the soil volume.

(iii) Nitrogen addition may result in a greater mineralisation of soil organic sulphur through an increase in plant growth and microbial activity (Freney, 1967; Nelson, 1973).

Although nitrogen application increased total sulphur uptake in pasture, sulphur and sulphate contents in grass samples taken from sulphur-responsive sites (tables 4.5 and 4.6) were reduced. This reduction could be due to a dilution effect through increased yield (figure 4.1).

Addition of nitrogen to sites 3 and 5 significantly increased yield (figure 4.1) but led to very wide N:S ratios (18:1 to 23:1) in mixed herbage (table 4.10). Such effects may have implications on the nutritive value of this herbage to animals since the N:S ratios are wider than the optimum range (10:1 to 15:1) which has been proposed as necessary to satisfy the sulphur needs of ruminants (Moir, 1970; Bray and Till, 1975; Goodrich et al., 1978). According to these workers, an insufficiency in dietary sulphur can reduce feed utilisation and animal production in terms of liveweight gain, wool growth and milk yield.

Table 4.10 Effect of fertiliser treatment on the nitrogen:sulphur ratio of mixed herbage.

		N:S ratios of mixed herbage	
Treatments		HARVEST ONE	HARVEST TWO
Site 1	0	14	16
	S	10	11
	N	15	
	N + S	9	
Site 2	0	14	13
	S	9	10
	N	11	
	N + S	9	
Site 3	0	17	18
	S	15	13
	N	22	18
	N + S	15	13
Site 4	0	13	14
	S	10	12
	N	13	
	N + S	10	
Site 5	0	18	19
	S	14	16
	N	22	23
	N + S	14	14

4.3.c.2 (iii) Nitrogen plus sulphur treatment

The addition of nitrogen and sulphur together led to a higher sulphur uptake than when either element was applied alone (figure 4.5, table 4.9). This is probably due to the stimulatory effect of nitrogen on the growth of grass (figure 4.1) which is more effective than clover in taking up sulphate from soil solution (section 4.3.c.2 (i)).

More importantly, the addition of sulphur together with nitrogen reduced the N:S ratios of the mixed herbage compared to when nitrogen was applied alone (table 4.10). There was however very little difference in N:S ratios between the plus sulphur and nitrogen plus sulphur treatments at all sites (table 4.10).

4.4 CONCLUSIONS

Significant yield responses to spring application of sulphur were observed at three out of the five trials conducted in the Eastland region. Of these three trial sites, two had received regular applications of superphosphate including one in the autumn immediately prior to the commencement of the trial. These sulphur responses together with the low levels of soil and herbage sulphur and the evidence of downward movement of sulphate within the soil profile suggest that (i) substantial amounts of sulphate from superphosphate can be leached during winter and (ii) the autumn application of superphosphate at an annual rate which provides 25 to 33 kg S ha^{-1} may not be sufficient to safeguard these sites against spring sulphur deficiency. Since the levels of Olsen-extractable soil phosphorus at these two sites were in the range of 15 to 24 $\mu g\ P\ g^{-1}$, it is probable that the amount of phosphorus applied in the current autumn application of superphosphate is sufficient to correct phosphorus deficiency in the following spring. Thus the use of sulphur-fortified superphosphate at similar rates in the autumn may be able to provide not only adequate phosphorus, but also sulphur in an immediately available form for autumn growth and also in a slowly-released form to minimize sulphate leaching during the winter.

It was found that whether yield response to sulphur application was significant or not, sulphur addition always resulted in:
(i) increased total sulphur concentrations in grass and clover,
(ii) increased total sulphur uptake by pasture herbage and (iii) the narrowing of N:S ratios. Such effects are expected to improve feed utilisation and animal production through the increase in dietary sulphur.

The increased grass growth due to nitrogen application may increase the amount of sulphur recovered from the soil system since grass is more competitive than clover in taking up sulphate from soil solution.
This may be why nitrogen application in the absence of sulphur did not appear to aggravate the effect of sulphur deficiency on pasture growth as evidenced by the fact that yield responses to sulphur application in the presence of nitrogen fertiliser were of similar or lower magnitude than those obtained with sulphur in the absence of nitrogen fertiliser.

Spring application of nitrogen fertiliser in the absence of sulphur fertiliser did however produce very high N:S ratios (about 22:1) at two sulphur deficient sites. In such situations, the nutritional value of the extra feed produced by a tactical application of nitrogen fertiliser may be lowered. In that case, the use of ammonium sulphate could be considered.

Further research is needed to evaluate the agronomic effectiveness of various topdressing alternatives aimed at overcoming leaching losses and maintaining an adequate level of sulphur for pasture growth in the Eastland region.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

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

1. A review of literature indicates that the plant available soil sulphur consists of the readily-soluble sulphate and adsorbed sulphate fractions. The size of this pool at any one time may govern the level of pasture productivity and is the net balance of various inputs and outflows. If the relative magnitudes of these gains and losses of sulphate can be determined, it may be possible to identify the major factors responsible for the onset of sulphur deficiency in a given agricultural system. In many inland areas of New Zealand, where atmospheric sulphur additions are insufficient to offset sulphur losses associated with leaching, immobilisation and uneven transfer of animal excreta, sulphur deficiency can occur, unless sulphur-containing fertiliser is applied to augment the plant available soil sulphur pool. This deficiency can occur in both unimproved and improved pastures. In unimproved situations, net sulphur immobilisation and leaching are the major processes depleting the plant available soil sulphur pool, while the occurrence and magnitude of sulphur deficiency in improved pastures, with comparable stocking rates, seems to be mainly dependent upon the extent of sulphate leaching.

2. To evaluate the sulphur status of Eastland pastures, two sampling surveys of soil and herbage, one in autumn and the second in the following spring, were carried out. The relative importance of such factors as the anion retention capacity of soil, rainfall patterns and sulphur fertiliser history in affecting soil and

plant sulphur status was assessed.

3. A preliminary glasshouse experiment using ryegrass as an indicator plant showed that 0.01M calcium phosphate solution at pH 4 can be used as a criterion of sulphur status in the soils covered by the survey, since soil sulphur extracted with this phosphate solution was more closely related to yield response in the glasshouse than the sulphur removed by a 0.01M calcium chloride extractant.

4. The levels of phosphate extractable sulphur in most of the soils surveyed varied throughout the year, being lower in spring than in autumn. The decrease in soil sulphur levels during winter was observed even at sites with low annual rainfalls (900-1000 mm) and in soils with anion retention capacities as high as 70% as measured by the phosphate retention test. Although the levels of Olsen-extractable soil phosphorus also tended to decrease over winter, this decrease was not nearly as great, suggesting that sulphate being the more weakly adsorbed anion had been leached more readily.

   Soil sulphur levels in autumn reflected the pattern of sulphur fertiliser history more markedly than in spring.

5. Soils with high phosphate retention tests were shown to have a high ability to accumulate adsorbed sulphate and vice versa. This relationship was not linear because the levels of adsorbed sulphate were generally low (< 10 µg S g^{-1}) over a wide range (10 - 70%) of phosphate retention. For any given level of phosphate retention capacity below 70%, the greater spread of adsorbed sulphate values in autumn compared to spring suggests that such soils are unable to retain during winter any adsorbed sulphate which may have accumulated over the summer-autumn period.

6. The decrease in the levels of phosphate extractable sulphur with depth down to 30 cm observed in most of the Eastland soils, suggests that there may be no great advantage in sampling to 30 cm, compared with 0 - 7.5 cm, to assess soil sulphur status in Eastland pastures.

7. The results obtained from the herbage survey were consistent with those obtained from the glasshouse trial and soil survey in showing that the plant sulphur status, whether expressed in terms of total sulphur, sulphate, or N:S ratios tended to be lower in spring than in autumn.

8. To confirm the suspected spring sulphur deficiency observed in the survey, five field trials were laid down in the spring of the following year on soils belonging to three soil groups: a yellow-grey earth, an intergrade between yellow-grey and yellow-brown earths and a yellow-brown pumice soil.

   Significant yield responses to spring application of sulphur were recorded at three out of the five field sites and the magnitude of sulphur response obtained at sites on a yellow-brown pumice soil was substantially higher than that obtained from a yellow-grey earth site. These sulphur-responsive sites included those where there had been no recent application of sulphate containing fertiliser and those which had received regular autumn applications of sulphate at annual rates of 25 to 33 kg S per hectare. The spring sulphur responses together with the low levels of soil and herbage sulphur in the control plots at these sites suggest that leaching can be a problem if sulphur in a water-soluble form (sulphate) is applied prior to winter.

9. Sulphur applications not only increased dry matter yield at the three sulphur-responsive sites but also resulted in:
(i) increased total sulphur concentrations in grass and clover,
(ii) increased total sulphur uptake by pasture herbage and
(iii) the narrowing of N:S ratios. Such effects are expected to improve feed utilisation and animal production through the increase in dietary sulphur.

10. Spring application of sulphur-free nitrogen fertiliser greatly increased dry matter yield but did not appear to aggravate the effect of sulphur deficiency on pasture growth at the sulphur-deficient sites as evidenced by the fact that yield responses to sulphur application in the presence of nitrogen fertiliser were of similar or lower magnitude than those obtained with sulphur in the absence of nitrogen fertiliser. However, spring fertilisation of sulphur-free nitrogen can lead to very wide N:S ratios (18:1 to 23:1) in mixed herbage at the sulphur-deficient sites. In such situations, there may be a decrease in the nutritive value of the extra feed produced by a tactical application of nitrogen fertiliser.

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APPENDICES

Appendix I: Description of survey sites: Central Hawkes Bay area: Autumn sampling.

Site	Soil type	Soil group	Parent material	Annual rainfall (mm)	Sulphur fertiliser history
1	Makaretu silt loam	yellow-brown earth	pumiceous mudstone and pumiceous sandstone	1400	Never topdressed with superphosphate. Lime (1250 kg ha^{-1}) applied six months prior to soil collection.
2	Makaretu silt loam	yellow-brown earth	pumiceous mudstone and pumiceous sandstone	1400	Superphosphate applied in 1977, January 1978 and November 1978.
3	Kopua stony silt loam	intergrade between yellow-brown earth and yellow-brown loam	old alluvium from volcanic ash and greywacke	1200	Large amount of superphosphate applied in spring 1978 and small amount was applied in autumn 1979.
4	Kopua stony silt loam	"	"	1200	Never topdressed with superphosphate.
5	Waipawa silt loam	yellow-grey earth	argillite and loess	900	550 kg ha^{-1} of superphosphate applied in autumn 1979.
6	Waipawa silt loam	"	"	900	125 kg ha^{-1} of superphosphate applied in autumn 1979.

Appendix II: Discription of survey sites: Gisborne area: Autumn sampling.

Site	Soil type	Soil group	Parent material	Annual rainfall (mm)	Sulphur fertiliser history
7	Mahia fine sandy loam	intergrade between yellow-brown pumice soil and yellow-brown loam	Gisborne ash on mudstone	1400	Long history of regular spring application of superphosphate.
8	Whangaehu silt loam	a steepland soil related to intergrade between yellow-grey and yellow-brown earths	argillacous sandstone and mudstone	1400	Superphosphate applied in spring 1978 and autumn 1978.
9	Taihape silt loam	a steepland soil related to intergrade between yellow-grey and yellow-brown earths	mudstone	1016	Four years of spring application.
10	Taupo sandy silt loam	yellow-brown pumice	Taupo ash	1016	Never topdressed.
11	Taupo sandy silt loam	"	"	1016	Superphosphate application every 2 years for 10 years.
12	Ngaroma sandy silt	yellow-brown pumice soil	Taupo ash on rhyolite, greywacke and sandstone	1800	Well topdressed.
13	Ngaroma sandy silt	"	" "	1800	Never topdressed.
14	Whangaehu silt loam	a steepland soil related to intergrade between yellow-grey and yellow-brown earths	argillaceous sandstone and mudstone	1400	Never topdressed.

Appendix III: Description of survey sites: Central Hawkes Bay area: Spring sampling.

Site	Soil type	Soil group	Parent material	Annual rainfall (mm)	Sulphur fertiliser history
15	Ruahine stony silt loam	steepland soil related to yellow-brown earth	mixed volcanic ash and greywacke	1600	10 years of superphosphate application. Autumn application in 1979.
16	Ruahine stony silt loam	"	"	1600	18 years of superphosphate application.
17	Te Mata sandy loam	steepland soil related to Rendzina soils from limestone	limestone	900	Regular autumn application of superphosphate (375 kg ha^{-1}) since 1969.
18	Te Mata sandy loam	"	"	900	Regular autumn application of superphosphate since 1968.
19	Kopua stony silt loam	Appendix I, site 3			
20	Waipawa silt loam	Appendix I, site 5			
21	Waipawa silt loam	Appendix I, site 6			

Appendix IV: Description of survey sites: Gisborne area: Spring sampling.

Site	Soil type	Soil group	Parent material	Annual rainfall (mm)	Sulphur fertiliser history
22	Whangaehu silt loam	a steepland soil related to intergrade between yellow-grey and yellow-brown earths	argillaceous sandstone and mudstone	950	Superphosphate (250 kg ha^{-1}) applied in October, 1978. Intermittent applications prior to that.
23	Otamauri sandy loam	intergrade between yellow-grey and yellow-brown earths	pumiceous ash on sandstone	950	Superphosphate (250 kg ha^{-1}) applied in October 1978. Intermittent applications prior to that.
24	Mahoenui silt loam	a steepland soil related to yellow-brown earth	banded mudstone and sandstone	1780	Autumn application of superphosphate (250 kg ha^{-1}) since 1969. Sulphur fortified superphosphate (250 kg ha^{-1}) in autumn 1976 and 1978.
25	Mahoenui silt loam	"	"	1780	Autumn application of superphosphate (250 kg ha^{-1}) since 1968. Sulphur fortified superphosphate (250 kg ha^{-1}) in autumn 1976 and 1978.
26	Whangaehu silt loam	a steepland soil related to intergrade between yellow-grey and yellow-brown earths	argillaceous sandstone and mudstone	1143	Superphosphate applied every autumn for 9 years at 125 kg ha^{-1}.
27	Gisborne sandy loam	yellow-brown pumice	Gisborne ash	1016-1143	Autumn application of superphosphate every two years at 250 kg ha^{-1}.

Appendix IV contd: Description of survey sites: Gisborne area: Spring sampling.

Site	Soil type	Soil group	Parent material	Annual rainfall (mm)	Sulphur fertiliser history
28	Taupo sandy silt	yellow-brown pumice	Taupo ash	1524-1780	Autumn application of superphosphate at 250 kg ha^{-1}. Last applied in autumn 1979.
29	Ngaroma sandy silt	"	Taupo ash on rhyolite, greywacke and sandstone	1524	Autumn application of superphosphate every alternate year for the last 20 years at 250 kg ha^{-1}. Last applied in autumn 1978 at 375 kg ha^{-1}.
30	Ngaroma sandy silt	"	"	1524-1780	Autumn application of superphosphate every alternate year for the last 20 years at 250 kg ha^{-1}. Last applied in autumn 1979 at 375 kg ha^{-1}.
31	Ngaroma sandy silt	"	"	1780	Annual application of superphosphate at 250 kg ha^{-1} since 1971. Last applied in spring 1978.

Appendix V: Colourimetric determination of total nitrogen in herbage digests. (M.A. Turner, pers.comm. 1979)

I Reagents:

(i) Neutralising solution: Dissolve 80g of sodium hydroxide in deionised water and make up to 1 litre.

(ii) Wash solution: Dilute 143 ml of digestion mixture with deionised water to 2 litres.

(iii) Phenol nitroprusside solution: Dissolve 0.025g sodium nitroprusside and 6.2g of phenol in deionised water and make up to 100 ml.

(iv) Hypochlorite solution: This is made up by mixing the two following solutions.

(a) 7.45 ml of commercial Janola and 2 g of sodium hydroxide, made up to 100 ml with deionized water.

(b) 19.10 g of anhydrous sodium carbonate, made up to 100 ml with deionized water.

II Analytical Procedures:

(i) 1.5 ml of the digested sample is mixed with 7 ml of deionised water, 1.5 ml of wash solution and 4.14 ml of the neutralising solution.

(ii) 0.5 ml of the mixture prepared from the first step is mixed with .5 ml of phenol nitroprusside and 1 ml of hypochlorite solution. The absorbance of the resulting solution is then measured at 625 nm.

Appendix VI: Average dry matter yield of grass (g/pot) at two harvests on nine soils in the glasshouse trial.

Sites	1		2		3 *			4		6		7		8		11		12	
Harvests	1	2	1	2	1	2	3	1	2	1	2	1	2	1	2	1	2	1	2
Control pot	1.30[†] aA	2.99 aA	1.80 aA	3.68 aA	1.60 aA	3.34 aA	8.65 aA	2.27 aA	3.90 aA	2.01 aA	3.47 aA	1.53 aA	3.58 aA	2.05 aA	3.32 aA	1.37 aA	3.28 aA	1.63 aA	2.92 aA
- S pot	1.03 bB	0.96 bB	1.77 aA	1.51 bB	1.60 aA	3.31 aA	4.81 bB	1.69 bB	0.88 bB	1.73 bAB	1.06 bB	1.25 bB	1.20 bB	2.08 aA	1.57 bB	0.74 bB	0.82 bB	1.44 bB	1.17 bB
- P pot	0.51 cC	0.50 cC	1.46 bB	2.71 cC	0.98 bB	2.99 bB	5.15 cC	1.67 bB	2.49 cC	1.53 cB	2.22 cC	0.81 cC	1.55 cC	2.03 aA	3.31 aA	0.27 cC	0.49 cC	1.33 cC	1.89 cC

[†] Duncan's Lettering (Duncan, 1955): Common small letters are not significantly different at the 5% level of probability, capital letters at the 1% level of probability.

[*] Site 3: Since there was no significant difference in dry matter yield between the control and minus sulphur pots at the first and second harvests, a third harvest was taken on 18th November, 1979.

Appendix VII: Chemical analyses of soils collected in the autumn survey.

Site	Depth (cm)	Phosphate-extractable sulphur µg S/g soil	Calcium chloride-extractable sulphur µg S/g soil	Adsorbed sulphur µg S/g soil	Olsen-extractable phosphate µg P/g soil	Phosphate retention %
1	0-7.5	16.1	7.1	9.0	7.5	68
	7.5-15	15.2	7.1	8.1		70
	15-30	14.0	6.5	7.5		67
2	0-7.5	19.5	10.0	9.5	17.4	59
	7.5-15	18.0	7.5	10.5		58
	15-30	15.0	7.5	7.5		58
3	0-7.5	50.2	19.1	31.1	20.0	82
	7.5-15	37.3	12.2	25.1		81
	15-30	37.0	13.0	24.0		88
4	0-7.5	11.0	8.5	1.5	17.1	59
	7.5-15	8.2	7.1	1.1		59
	15-30	7.0	6.5	0.5		56
5	0-7.5	27.3	27.0	0.3	30.2	24
	7.5-15	16.1	15.0	1.1		26
	15-30	13.5	13.0	0.5		22
6	0-7.5	15.4	13.0	2.4	16.1	21
	7.5-15	12.6	12.1	0.5		18
	15-30	7.1	7.0	0.1		15
7	0-7.5	15.0	12.5	2.5	17.4	52
	7.5-15	13.2	8.1	5.1		56
	15-30	13.0	7.5	5.5		47
8	0-7.5	19.2	18.1	1.1	38.4	29
	7.5-15	18.1	16.0	2.1		28
	15-30	11.5	7.0	4.5		23
9	0-7.5	13.0	12.5	0.5	17.4	11
	7.5-15	11.2	11.1	0.1		11
	15-30	11.3	11.2	0.1		11
10	0-7.5	12.5	11.0	1.5	13.0	33
	7.5-15	9.1	8.1	1.0		35
	15-30	7.3	6.2	1.1		22
11	0-7.5	11.0	9.0	2.0	10.5	33
	7.5-15	9.1	8.1	1.0		35
	15-30	7.3	6.2	1.1		22
12	0-7.5	23.0	21.0	2.0	25.5	53
	7.5-15	15.1	9.1	6.0		57
	15-30	9.2	7.1	2.1		68
13	0-7.5	12.0	11.5	0.5	13.0	39
	7.5-15	11.1	9.1	2.0		38
	15-30	10.3	6.1	4.2		48
14	0-7.5	8.1	7.1	1.0	7.0	16
	7.5-15	6.2	6.1	0.1		15
	15-30*					

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*Due to the presence of a hard pan below a depth of 15cm, soil samples were not taken beyond this point.

Appendix VIII: Chemical analyses of soils collected in the spring survey.

Site	Depth (cm)	Phosphate-extractable sulphur µg S/g soil	Calcium chloride-extractable sulphur µg S/g soil	Adsorbed sulphur µg S/g soil	Olsen-extractable phosphate µg P/g soil	Phosphate retention %
15	0-7.5	40.1	5.1	35.0	11.5	94
	7.5-15	87.5	7.0	80.5		97
	15-30	>100	7.0	93.0		98
16	0-7.5	12.2	4.5	7.5	10.5	80
	7.5-15	15.1	5.5	9.5		82
	15-30	65.0	7.1	58.0		92
17	0-7.5	6.2	6.0	0.1	5.5	15
	7.5-15	9.1	6.1	3.0		14
	15-30	8.3	5.2	3.1		14
18	0-7.5	6.2	6.0	0.2	9.8	14
	7.5-15	5.5	5.0	0.5		12
	15-30	7.0	5.1	2.0		14
19	0-7.5	18.1	6.0	12.1	12.2	91
	7.5-15	26.3	6.2	20.1		91
	15-30	33.2	8.2	25.0		93
20	0-7.5	13.1	10.0	3.1	21.4	21
	7.5-15	11.2	9.1	2.1		23
	15-30*					
21	0-7.5	6.5	6.3	0.2	10.4	17
	7.5-15	8.1	7.1	1.0		18
	15-30	7.1	4.5	2.5		12
22	0-7.5	11.5	11.0	0.5	21.9	24
	7.5-15	8.2	6.1	2.1		22
	15-30	7.3	6.3	1.0		17
23	0-7.5	24.0	19.0	5.0	18.1	33
	7.5-15	13.1	11.1	2.0		32
	15-30	8.2	7.0	1.2		25
24	0-7.5	12.1	11.5	0.5	12.6	29
	7.5-15	6.2	5.7	0.5		27
	15-30	6.2	5.7	0.5		23
25	0-7.5	11.0	9.0	2.0	18.5	26
	7.5-15	7.2	6.1	1.1		22
	15-30	6.1	5.0	1.1		20
26	0-7.5	11.1	11.0	0.1	22.9	23
	7.5-15	7.3	6.1	1.2		21
	15-30	6.1	5.0	1.1		18
27	0-7.5	12.1	9.1	3.0	22.2	37
	7.5-15	7.0	6.0	1.0		37
	15-30	7.1	5.5	1.5		33
28	0-7.5	11.6	9.1	2.5	22.2	60
	7.5-15	9.2	7.2	2.0		66
	15-30	8.3	6.2	2.1		64

Appendix VIII: contd.

Chemical analyses of soils collected in the spring survey

Site	Depth (cm)	Phosphate-extractable sulphur µg S/g soil	Calcium chloride-extractable sulphur µg S/g soil	Adsorbed sulphur µg S/g soil	Olsen-extractable µg P/g soil	Phosphate retention %
29	0-7.5	11.0	8.0	3.0	11.1	55
	7.5-15	8.3	4.8	3.5		60
	15-30	7.1	6.1	1.0		62
30	0-7.5	11.5	9.0	2.5	21.2	39
	7.5-15	9.1	7.1	2.0		40
	15-30	8.1	5.0	3.1		71
31	0-7.5	11.5	8.0	3.5	14.0	40
	7.5-15	10.6	7.1	3.5		45
	15-30	7.5	6.0	1.5		55

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* Due to the presence of a hard pan below a depth of 15 cm, soil samples were not taken beyond this point.