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FACTORS INFLUENCING THE TRANSFORMATION AND  
FATE OF SULPHUR AND NITROGEN IN GRAZED  
HILL COUNTRY PASTURES

A thesis presented in partial fulfilment of the  
requirements for the degree of  
Doctor of Philosophy in Soil Science  
at Massey University

KARUPPAN SAKADEVAN

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*DEPT. OF SOIL SCIENCE*

*MASSEY UNIVERSITY*

15

*PALMERSTON NORTH*

## ABSTRACT

The increasing cost of agricultural grade sulphur and the high leaching losses of sulphate sulphur(S) from superphosphate fertilized pastures in New Zealand create a need to develop more efficient S fertilization techniques. The objective of the present study was to identify the main origins of the sulphate being leached from superphosphate fertilized hill country pastures with soils (Typic Dystrachrepts) developed from underlying sedimentary parent materials.

Origins of leached sulphate were categorized as S leached directly from fertilizer, from zones enriched in animal excreta and from the mineralization of soil organic matter. Mineralization studies, both in laboratory and in field were conducted to establish the extent of and the relationship between sulphur and nitrogen mineralization and the fate of mineralized nutrients in pasture soils that contrasted in their superphosphate fertilizer history.

In the preliminary laboratory study in which an open incubation technique was used to measure potential net mineralization, top soils (0-7.5cm) taken from sites that had received higher rates of superphosphate in the past, mineralized more soil organic sulphur and nitrogen than soils taken from sites that had received smaller amounts of superphosphate in the past. In addition top soils collected from low slope (0-12°) sites where a greater proportion of animal excreta is returned, mineralized more S and N than the soils from medium slope (13-25°) sites. The ratio of N to S mineralized was narrower (2.0 to 3.6) than the N to S ratio of the whole soil (7.1 to 8.9) suggesting that in these soils relatively more S remains in a mineral form in the soil and is more susceptible to leaching than N which is conserved in the soil.

Cylindrical, mini-lysimeters with ion exchange resin traps for collecting solutes from drainage water were developed to measure the net mineralization of soil organic S and N under field conditions. Leaching losses of S and N, pasture uptake of S and N and changes in mineral S and N pools in the soil at the same site were measured simultaneously and the rate of mineralization calculated. A laboratory evaluation of the lysimeter showed that the resin trap was capable of removing all the sulphate from

drainage water at several different flow rates. The main advantage of these lysimeters over the conventional methods of measuring the leaching losses of anions and cations in the field is that regular drainage collection was not necessary. By introducing mixtures of both anion and cation exchange resins in the trap in the lysimeter it was possible to monitor the amount of anions and cations in field drainage over long periods of time before it was necessary to change the resin mixtures.

In the initial field lysimeter study the net mineralization and pasture uptake of N (119 to 251 kg N ha<sup>-1</sup>) was 10 times more than that of S (12 to 27.5 kg S ha<sup>-1</sup>), yet approximately 10 times more sulphate S (2.0 to 17.3 kg S ha<sup>-1</sup>) than mineral N (0.19 to 1.3 kg N ha<sup>-1</sup>) was lost by leaching. Previous fertilizer history had a marked effect on the leaching losses of sulphate with seven times more S lost (2.1 vs 15.3 kg S ha<sup>-1</sup>) from sites which received greater rates of superphosphate and had higher stocking rates. During the initial seven month period S leaching losses on the low and high fertility sites were equivalent to 15% and 33% of the annual fertilizer application. More sulphate was leached from areas identified as animal camping areas. The lack of any change in sulphate below the 150mm soil depth during a period of active plant growth and no leaching suggested that any sulphate that moved below 150mm of the soil could be considered to be effectively lost from the system. Increased leaching losses of calcium and magnesium were associated with increased sulphate losses. The amount of calcium lost by leaching (4.75 to 12.5 kg Ca ha<sup>-1</sup>) was far greater than potassium (0.8 to 3.6 kg K ha<sup>-1</sup>), although twice the amount of potassium (240 kg K ha<sup>-1</sup> vs 120 kg Ca ha<sup>-1</sup>) was cycled through the plant-animal system. The amount of magnesium lost by leaching was greater than the amount of potassium lost by leaching.

In a second lysimeter study the direct effects of freshly applied fertilizer on the mineralization of S and N from soil organic matter, their plant availability and losses by leaching were studied under field conditions using <sup>35</sup>S labelled superphosphate. Fertilizer application significantly increased the mineralization of both organic S and N. The recovery and measurement of <sup>35</sup>S activity over a nine month period showed that major proportions of pasture S (85 and 86% of the pasture S for low and high fertility farmlets, respectively) and leached S (75 and 87% of the leached S for low

the mineralization of soil organic matter and not recently applied fertilizer. The amounts of both S and N mineralized from soil organic matter depends upon the past fertilizer history of the site and the present fertilizer application rate (22 and 40 kg S ha<sup>-1</sup> and 125 and 204 kg N ha<sup>-1</sup> for low and high fertility farmlets, respectively). Further, when the net mineralization of S was greater a greater proportion (59%) of mineralized S was lost by leaching than removed by pasture (39%). Irrespective of the amount N mineralized virtually all was removed by pasture. The results suggested that low N availability was a major factor limiting carbon fixation and the formation of organic S in these pasture soils.

In a third lysimeter study, field simulated sheep dung and urine events boosted pasture growth and S and N uptake by approximately (50%), whereas the leaching losses of S and N were not influenced by the their application.

A preliminary computer simulation model describing the mineralization of soil organic S, pasture S uptake and leaching losses in grazed pasture was developed. The preliminary model gave reasonable predictions of the changes in soil sulphate concentrations in the soil up to a depth of 25cm, pasture uptake of S and leaching losses of S at four pasture sites varying in their fertilizer history. Further refinement of the model is necessary before it can provide the basis for predicting fertilizer S requirement for hill country pastures.

The experimental results and model output confirm balance study predictions that large leaching losses of S occur and these are derived mainly from the mineralization of soil organic matter which accumulates in well fertilized soils. The extent of S losses appear to be a function of the general levels of soil productivity and the data suggested that only a small, probably less than 20% reduction in this loss could be achieved by changing to slow release S fertilizers.

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## CHAPTER-1

### INTRODUCTION

In New Zealand legume based pastures adequate supplies of plant available sulphur (S) are second only in importance to supplies of phosphorus. Sulphur requirements for pastures in New Zealand are estimated using a mass balance model developed by Sinclair and Saunders (1982). The model estimates the S gains from rainfall, the losses in animal products and leaching and the within system losses of S to unproductive areas by uneven transfer of S in excreta. A negative balance of S requires the addition of fertilizer S to maintain the equilibrium status of the pasture (Sinclair,1983).

Little research has been done to quantify the fluxes of S between various components of the pasture S cycle and verify that the estimates of S losses calculated by the model, particularly those relevant to immobilization of soil S, S leaching loss and animal excreta transfer, represent those occurring in practice. Such research is important as S becomes an increasingly costly input into New Zealand pastoral farming. Currently New Zealand imports S worth NZ\$40 million every year mainly for the fertilizer industry. At present about 90% of this S is applied to pastures as single superphosphate (SSP).

Recent research in this area by Saggar *et al.* (1990a) showed that an amount equivalent to 46-77% of the annual fertilizer S application to Southern North Island hill country pasture was lost by leaching. The extent of leaching loss increased with increasing rate (125-375 kg ha<sup>-1</sup>) of annual SSP application. These losses represent a very inefficient use of fertilizer S. Management strategies to reduce this loss could be developed if the origins of the leached S are identified.

Leached sulphate can originate 1. directly from the sulphate in the SSP fertilizer, 2. from dung and urine spots excreted by the grazing animals and 3. from the decomposition and mineralization of soil organic S, which includes plant litter, animal excreta and older soil organic matter (humus) which has built up through regular fertilizer application.

In hill country pastures the interaction between land slope and aspect on the camping behaviour of the grazing animals also effects the spatial distribution of the soil organic S and evidence indicates this influences S leaching loss (Saggar *et al.*, 1990a,b). In North Island hill country low slope areas commonly receive proportionately more dung and urine and can be expected to have potentially greater S leaching losses. Also on low slopes a greater proportion of rainfall water passes through soil profile and may increase the leaching losses of sulphate.

Although some information on the direct leaching loss of sulphate from fertilizer under field conditions (Smith *et al.*, 1983) and from dung and urine using repacked lysimeters (Hogg, 1981) exists, no detailed information exists on the amount of S mineralized from soil organic matter and the contribution this makes to pasture uptake and leaching loss. The relative fate of fertilizer and mineralized S as determined by pasture uptake and leaching may well be controlled by not only the factors mentioned above but also the availability of another plant growth limiting nutrient. For example in nitrogen (N) deficient legume based pastures fertilizer S may be used inefficiently by pasture until the mineralizable pool of soil N is increased through biological N fixation.

If the amount of S lost by leaching directly from fertilizer inputs could be quantified and the understanding improved of the processes resulting in indirect S losses by leaching from mineralized soil organic matter, plant litter and dung and urine spots, it might be possible to design procedures to reduce the overall S losses.

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

1. Determine the effect of fertilizer history and land slope on the net mineralization rates of soil organic S and N,
2. Develop techniques to measure net mineralization of S and N in grazed hill country pastures under field conditions,
3. Determine the effect of superphosphate application and excreta deposition on pasture production, S and N uptake and leaching losses under field conditions and finally,
4. To assemble this information to provide advice on how to use S fertilizer more efficiently on pasture soils.

Central to these studies was the availability of a series of sheep grazed research farmlets at the DSIR, Grasslands, Ballantrae Research Station which forms part of a long term study on the effects of varying rates of fertilizer application on grassland productivity. The importance of having such sites available to study the long term sustainability of the pastoral system cannot be over emphasised.

## CHAPTER-2

### REVIEW OF LITERATURE

#### 2.1 INTRODUCTION TO SULPHUR IN THE BIOSPHERE

Sulphur(S) is a nutrient essential for metabolism in plants, animals and microorganisms. In the biosphere it exists in a wide variety of compounds in various oxidation states ranging from -2 in sulphide to +6 in sulphate and is originally derived from the oxidative weathering of plutonic rocks. The oxidative weathering can take place chemically (Avrahanui and Golding, 1968; Zehnder and Zinder, 1980) and/or biochemically (Buchanan and Gibbons, 1974). Sulphur compounds of various oxidation states are further involved in a variety of chemical and biological reactions. In its various forms it can be a highly mobile element which can lead to deficiencies occurring in some terrestrial systems. It is the amounts, forms and reactions of these compounds in the soil which are of importance to agriculturists interested in plant nutrition.

#### 2.2 AMOUNT AND FORMS OF SULPHUR IN THE SOIL

The total S content and S forms present in surface soils varies widely depending on their geographical location (Freney, 1986). In mineral soils, the S content ranges from less than 20 to over 2000 mg S kg<sup>-1</sup> soil (Lowe and Delong, 1963; Korkman, 1973; Freney and Williams, 1980). In peat and swamp soils, with the majority of S present in organic residues, concentrations of up to 5000 mg S kg<sup>-1</sup> have been measured (Chae and Lowe, 1980; Freney and Williams, 1980). In saline soils values in excess of 6000 mg S kg<sup>-1</sup>, mostly as sulphate, are not uncommon (Delver, 1962; Dabin, 1972). In tidal marsh soils values as high as 35,000 mg S kg<sup>-1</sup> mostly as sulphide have been reported (Fleming and Alexander, 1961; Gallagher, 1969).

Most agricultural soils have S contents ranging from 50 to 1000 mg S kg<sup>-1</sup> in the surface 15 cm (Tabatabai and Bremner, 1972a,b; Bettany *et al.*, 1973). In subsoils, wide variation again occurs, depending particularly on drainage and rainfall. Values ranging from <10 mg S kg<sup>-1</sup> in the soils of silicious sands to as high as 10,000 mg S kg<sup>-1</sup> in the deeper horizons of soils from arid regions have been reported (Freney and Williams, 1983). The total amount of S in the surface metre of Australian soils have been estimated to range from less than 0.01 to over 500 tonnes S ha<sup>-1</sup> depending on soil type (Freney and Williams, 1980). Similar ranges could be expected for soils from other regions of the world. In New Zealand agricultural soils, the total S in the top 150mm ranges from 240 to 1360 mg S kg<sup>-1</sup> soil (Walker and Adams, 1958; Metson and Blakemore, 1978) depending upon the soil forming factors and upon fertilizer application and type of farming.

In well drained, non-calcareous soils of humid temperate regions, where annual rainfall exceeds evapotranspiration, most (>90%) of the S in the surface horizons appears to be in organic forms. The inorganic forms which are almost entirely sulphates are low (<10%) because sulphate is either leached or readily absorbed by plants (Donald and Williams, 1954; Walker and Adams, 1958; Williams and Steinberg, 1958; Freney, 1961;1986; Tabatabai and Bremner, 1972a,b; Fitzgerald, 1976;1978; Lambert *et al.*, 1988). Organic S generally decreases with soil depth except in soils in which organic matter has accumulated in the B-horizon and in soils which have formed under conditions where erosive deposition have led to buried profiles (Williams, 1974).

Soil organic S fractions provide the major long term S reserves for plant nutrition (Biederbeck, 1978), but because plants can only absorb inorganic sulphate, the rate of its production by organic matter mineralization and translocation are the key processes in the S cycle (Blair, 1971). As with nitrogen(N) and to a less extent with phosphorus(P), organic matter mineralization is a key source of sulphate in soils. Microorganisms present in the soil derive energy for respiration by oxidizing the carbon(C) of organic residues. Any S released during the process can either be utilized by microorganisms or left to enter the soil solution as sulphate ion or in a lower oxidation state. Clearly factors influencing the rate of organic matter turnover

are as important in determining the supply of S to plants as the forms and amounts of S in the soils. Thus the plant availability of soil organic S and its chemical characteristics should be considered in the context of understanding the S cycle in soil-plant-animal systems.

### 2.3 NATURE OF SOIL SULPHUR

In addition to the weathering of S bearing minerals the soil S is derived from the atmosphere as dry deposition and in precipitation.

Scott (1980) estimated that although about 44% of addition of S to atmosphere are as  $\text{H}_2\text{S}$ , it is rapidly converted in to  $\text{SO}_2$ ,  $\text{SO}_3$  and sulphate ions within the atmosphere. Till (1975) reported that  $\text{SO}_2$  concentration in air ranged from 0.3 to 4000  $\text{mg S m}^{-3}$ . Galbally (1980) reported  $\text{SO}_2$  uptake rates of 0.1 to 0.3  $\text{kg S ha}^{-1} \text{ year}^{-1}$  for desert and semiarid areas of Australia and 0.6 to 2.7  $\text{kg S ha}^{-1} \text{ year}^{-1}$  for temperate and tropical areas from the atmosphere by the plant.

Global additions of S in precipitation account for  $8.6 \times 10^6$  tonnes S  $\text{year}^{-1}$  (Davey, 1980). The pattern of deposition of S in precipitation is very uneven being concentrated near industrial areas (Peveerill, 1980) and in coastal regions (Walker and Gregg, 1975). An average value for coastal Australian sites (within 10 km of the coast) would appear to be 5  $\text{kg S ha}^{-1} \text{ year}^{-1}$  (Probert, 1976). The values can be expected to decline away from the coast to about 1  $\text{kg S ha}^{-1} \text{ year}^{-1}$  in central New Zealand (Walker and Gregg, 1975; Metson, 1979) and Northern table lands of N.S.W (Till, 1975). Till (1975) considered that much of the grazing areas in Australia received less than 1.5  $\text{kg S ha}^{-1} \text{ year}^{-1}$ . A similar value applies to most of the grazing area in New Zealand (Ledgard and Upsdell, 1991).

Plants and microorganisms are responsible for transforming these mineral forms of S in to organic forms and compounds of other oxidation states. Organic S in the form of root, plant litter, animal matter and excreta becomes the most important secondary inputs of S into soil. To understand the transformation of S in the soil it is therefore very important to know the forms of the various soil S fractions.

### 2.3.1 Soil Organic Sulphur

The total annual amount of C fixed for the earth is estimated to be  $1.5 \times 10^{11}$  tonnes (Trudinger, 1975). Based on an average C:S ratio of 100 (commonly the C:S ratio of the soil organic matter is 100:1) this would correspond to a rate of synthesis of organic S of about  $1-2 \times 10^9$  tonnes per annum making soil S an important pool for both plants and animals.

The mean C:N:S ratios for groups of individual soils from different regions of the world are very similar, for example agricultural soils seem to have a mean C:N:S ratio of about 130:10:1.3, native grass and woodland soils have ratios of the order of 200:10:1 and peat and organic soils have ratios, approximately 160:10:1.2 (Freney, 1986). Differences in C:N:S ratios of soils are due to the effect of parent material, weathering, pasture improvement and climate; examples have been reported by Walker and Adams (1958, 1959), Williams and Steinberg (1958), Lowe (1965), Bettany *et al.* (1973), Neptune *et al.* (1975), Mukhopadyay and Mukhopadyay (1975) and Lambert *et al.* (1988). Little is still known of the exact chemical nature of the organic S compounds in soils. Freney (1961) listed a wide variety of S containing compounds known to be produced by soil microorganisms, plants and animals (Table 2.1). Normally all these compounds are susceptible to decomposition and do not accumulate in uncombined forms. This creates difficulties in detecting their presence in soils. The existing knowledge about the nature of organic S in the soil is reviewed in the next section.

#### 2.3.1.1 Chemical Nature of Organic Sulphur

Some soil organic S occurs in amino acid form. In two podzolic soils amino acid S was found to account for 21-30% of the total organic S (Freney *et al.*, 1970). Approximately 60% of the amino acid S was cysteine. Apart from the amino acid S group little is known about the nature of the remaining organic S in soil even though it can amount to more than 60% of total organic S (Freney, 1967). Present

**Table 2.1 Empirical methods for extracting sulphur containing organic compounds from soils and their likely origin (Freney, 1961)**

S Containing Compounds	Method of Extractions	Origin of organic Sources
Amino acids	HI-S <sup>1</sup> and C-S <sup>2</sup> /R.N <sup>3</sup>	Proteins and Bacteria
Sulphonium compounds	HI-S	Microorganisms, red and green algae
Ester sulphate	HI-S	Microorganism tissue
Vitamin	C-S/R.N	Microorganisms
Sulphides	C-S/R.N	Plant litter
Sulphoxides	C-S/R.N	Microorganisms
Isothiocyanate	HI-S	Microorganisms and plant litter
Other compounds	HI-S and C-S/R.N	Microorganisms, plant litter and animal products

1 HI-reducible S (HI-S)

2 Carbon bonded S (C-S)

3 Raney-Ni S (R.N)

knowledge only permits a very broad grouping of organic S compounds on the basis of their reactions with reducing agents. These are as follows.

1. Organic S which is reduced to H<sub>2</sub>S by hydriodic acid(HI). This S is not bonded directly to C and is believed to be mainly ester sulphate such as C-O-S and C-N-S (Freney, 1961; Houghton and Rose, 1976).
2. Organic S which is not reduced by HI. This S is thought to be bonded directly to C such as C-S and C-S-S-C (Freney, 1961).
3. Organic S which is reduced to inorganic sulphide by Raney nickel. This makes up a substantial proportion the of C bonded fraction and may consist mainly of S in the form of amino acids (Freney, 1961; Freney *et al.*, 1975).

### 2.3.1.2 Hydriodic Acid Reducible Sulphur

Analysis covering a wide range of soils have indicated that the HI-reducible S fraction can account for as little as 30% of the total organic S or as much as 70% of total organic S (Williams and Steinberg, 1959; Freney, 1961; Lowe and Delong, 1963; Cooper, 1972; Tabatabai and Bremner, 1972b; Bettany *et al.*, 1973; Neptune *et al.*, 1975; Williams, 1975). This fraction appears to be readily hydrolysed to inorganic sulphate by acid or alkali and consequently has been considered by some workers (Lowe, 1965; Freney *et al.*, 1971; Cooper, 1972) to represent the most labile soil organic S fraction. This fraction could include aryl sulphates, sulphate esters of steroids, amino acid O-sulphate, ascorbic acid 2-O-sulphate which occurs in animal excreta, chondroitin sulphate which occurs in many invertebrates that inhabit soils, alkyl sulphate esters, occurring in a variety of microorganisms, and choline sulphate, occurring in lichens, algae, fungi and plants (Fitzgerald, 1976, 1978).

The environment in which a soil develops also may have a large effect on the proportion of total S present in the HI reducible pool. For example in Canadian soils the amount of HI reducible S decreases as the regional temperature falls and moisture (rainfall) increases (Bettany *et al.*, 1982). The amount and rate at which this fraction is mineralized to inorganic sulphate, and the amount of soil S cycled through this fraction annually has been the subject of little detailed study.

### 2.3.1.3 Carbon Bonded Sulphur

This fraction, in which S is directly bonded to C, is measured by the difference between the total organic S and that fraction of the total which is reduced to H<sub>2</sub>S by HI. About 50% of the C-bonded S occurs as amino acids (Freney *et al.*, 1970). This fraction is not hydrolysed into inorganic sulphate by hot acids or alkalis and would include mercaptans, disulphides, sulphones and sulphonic acids (Freney, 1986). The amounts of C-bonded S tend to decrease with soil depth and is more closely related to organic N than the HI reducible S fraction (Williams, 1974). Since the C-bonded S fraction in soil organic matter is resistant to reducing agents and correlated with several humus properties of soils this fraction is thought to be associated with the aromatic core of humic acids. For Australian soils Williams (1975) showed that the C-bonded S fraction accounted for about 84% of the soil organic S in a range of soils. The C-bonded S fraction accounted for about 84% of the soil organic S accumulated under clover pasture and 81% of organic S lost as a result of continuous cereal cropping (Williams, 1975). Presumably the loss results from increased soil erosion and from increased decomposition of soil organic matter brought about by continuous cultivation of soils.

Attempts have been made to measure C-bonded S directly by reaction of the soil with Raney Ni (Lowe and Delong, 1963; Freney *et al.*, 1970; Tabatabai and Bremner, 1972b; Scott and Anderson, 1976). This reagent reacts with all the reduced S bonded to C and oxidized S in the form of sulphoxides (R-C-SO-CH<sub>3</sub>), sulphonic acid (R-C-SO-OH) or sulphonic acid attached to aromatic nucleus or aliphatic sulphonic acid (Freney *et al.*, 1970). This fraction has been found to account for up to 60% of the total organic S. The amount of C-bonded S determined in this manner does not account for the difference between the total organic S and HI reducible S fraction (Lowe and Delong, 1963; Freney *et al.*, 1970). Studies in Australia (Freney *et al.*, 1975) and Scotland (Scott, 1981) showed a very good relationship between the amount of Raney Ni reducible S and amino acid S, suggesting that this extractant determines mainly amino acid S.

Fractionating soil organic S into discrete pools using reducing agents does not permit the biological significance of various fractions to be assessed (Bettany *et al.*, 1974, 1979). Some attempts have been made to develop extraction techniques which fractionate the more labile S from more inert components. For example, Bettany *et al.* (1979) used 0.1M NaOH-0.1M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> at pH 13 under nitrogen gas and dispersion (sonification), acidification and centrifugation to extract the labile pool. The fractionation method extracted 63-73% of the total organic S and the S was distributed as follows. Fulvic acid A,36%; fulvic acid B,3%; humic acid A, 13%; humic acid B,21%; humin >2µm, 15% and humin <2µm, 11%. Both fulvic acid A and B are believed to contain microbial metabolites and extra cellular enzymes. The humic acid A and B are regarded as chemically stable and more resistant to microbial degradation.

### **2.3.2. Soil Inorganic Sulphur**

Inorganic S is found in aerobic soils almost entirely as sulphate and this is the form in which S is absorbed by plant roots. Sulphur compounds of lower oxidation states such as sulphides and sulphites are usually restricted to wetland and submerged soils where anaerobic conditions exist. Where reduced S is found in well drained soils its presence could be indicative of atmospheric pollution (Wainwright, 1984) or possibly by a recent application of elemental S fertilizers. In time reduced S added to topsoil would be oxidized to sulphate. Accurate determination of the amount of these reduced forms of inorganic S in the soil is rarely possible, mainly because limitations of analytical procedures available.

#### **2.3.2.1 Soil Inorganic Sulphate**

Inorganic sulphate in the soil may occur as water soluble salts, adsorbed by soil colloids or as insoluble sulphates.

### 2.3.2.2 Water Soluble Sulphates

This is the form which is directly available for plant uptake. The charge on this solution sulphate is mostly balanced by  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$  and  $\text{K}^+$ . Extraction with water, sodium salts, lithium chloride, potassium chloride and calcium chloride solutions have been used for the determination of soluble sulphate. Calcium chloride is preferred because it does not disperse soil aggregates and the solubility of organic matter is lower in this reagent.

Considerable seasonal fluctuations occur in the amounts of soluble sulphate present in surface soils. This is mainly due to the influence of environmental conditions on microbial mineralization of organic S, leaching of the soluble sulphate and the uptake of sulphate by plant roots and microorganisms (Williams, 1968;1975). The sulphate content of soil is also affected by the application of fertilizers and to a lesser extent rainfall and irrigation. For soils of high or medium anion exchange properties the soluble sulphate often increases with soil depth (Williams, 1974; Probert, 1974; 1977). Subsoil sulphate is readily available to deep rooted plant species and may be important in reducing the incidence of S deficiency in cereal crops and deep rooted pasture species (Lipsette and Williams, 1971; Gillman, 1973; Walker and Gregg, 1975; Gregg and Goh, 1979).

### 2.3.2.3 Adsorbed Sulphate

Soils vary widely in their capacity to adsorb sulphate. Sulphate anions are adsorbed by ligand exchange with aquo( $-\text{OH}_2$ ) and hydroxyl( $-\text{OH}$ ) groups on the surface of soil colloids (Parfitt and Smart, 1978; Rajan, 1979; Bohn *et al.*, 1986). Sulphate adsorption is readily reversible and the amount of sulphate adsorbed is dependent on the concentration of sulphate in solution (Chang and Thomas, 1963; Chao *et al.*, 1962a; Kamprath *et al.*, 1956; Ensminger, 1954).

Conditions favouring the adsorption of sulphate includes

1. Lower pH increases the electrostatic potential of the adsorption plane (Williams and Steinberg, 1962; Harward and Reisenauer, 1966; Marsh *et al.*, 1983),

2. Higher clay contents are associated with greater amounts of iron and aluminium oxides having higher adsorption capacities (Ensminger, 1954; Marsh *et al.*, 1983),
3. Clay mineralogy, kaolinite and allophane kaolinite intermediates contain hydroxyl groups bonded to octahedral aluminium atoms which are active in sulphate adsorption. Soils which contain 2:1 lattice clays shows little capacity to adsorb and retain sulphate (Metson, 1979) and
4. More divalent cations, cations with higher valency are adsorbed more readily than cations with lower valency (Chao *et al.*, 1963) and create a less diffuse double layer which holds more sulphate ions.

Soils with low levels of native adsorbed sulphate invariably have negligible capacity to retain added sulphate (Barrow, 1969; Metson, 1979).

In surveys of New Zealand topsoils (0-200mm) Blakemore *et al.* (1968) and later Metson (1979) found that the levels of adsorbed sulphate were generally low (< 10 mg kg<sup>-1</sup> of soil) and often increased with increasing soil depth.

Adsorbed sulphate is readily available to plants and in many soils it provides a major source of plant available S (Freney and Spencer, 1960; Fox *et al.*, 1964; Williams and Steinberg, 1964; Barrow, 1967a). Adsorbed sulphate is readily displaced by phosphate. This is one of the reasons for low sulphate adsorption capacity of top soils which have received heavy dressings of superphosphate as fertilizer. The smaller sulphate adsorption capacity may also be associated with higher pH in surface soils.

Most methods for its determination involve the use of phosphate solutions as extractants. Calcium dihydrogen phosphate would be the most common and widely used (Searle, 1979) extractant for adsorbed sulphate in New Zealand.

#### **2.3.2.4 Insoluble Sulphate**

Several forms of insoluble sulphates are found in soils, including barium and strontium sulphates, SO<sub>4</sub><sup>=</sup> associated with calcium carbonate and basic iron and aluminium sulphates (Williams, 1975). Sulphate occurring in calcareous soils as co-crystallized impurity in calcium carbonate is probably the most common of these and in some Australian soils this may account for upto 95% of the total soil sulphur. In subsoil

horizons of calcareous soils it frequently accounts for 40 to 50% of the total sulphur. This fraction of soil S is determined by extraction with hydrochloric acid (Williams and Steinberg, 1962). This method may underestimate the amount of sulphate occurring in these forms due to the presence of barium and other forms of acid insoluble sulphate (Williams *et al.*, 1960).

### 2.3.3 Plant Available Sulphur in the Soil

Almost all of the sulphur taken up by plants is in the form of sulphate which is taken up from soil solution. This sulphate is in rapid equilibrium with adsorbed sulphate. The amount of soluble sulphate in soil solution at any time is the net result of complex interactions in the sulphur cycle. The major factors affecting the soluble sulphate in most grazed pastures are plant uptake, adsorption/desorption rates, immobilization/mineralization rates, leaching losses and fertilizer application rates (Freney and Spencer, 1960; Barrow, 1961a; Fox *et al.*, 1964a; Williams and Steinberg, 1964; Hasan *et al.*, 1970).

The rate of entry of sulphate from fertilizer to plant available sulphate is dependent on the type of fertilizer, available soil moisture and the time elapsed since application. Sulphate from gypsum and superphosphate is more likely to be available comparatively rapidly and in large doses (Till, 1980) compared with the slow release from the oxidation of elemental S (Shedley *et al.*, 1979; White and Currie, 1988). Under cool, temperate New Zealand conditions, particles of <150µm diameter are required for the elemental S to be effective for releasing sulphate to soil solution in the year of application. In environments in which moisture is growth limiting, the rate of oxidation to sulphate may be too slow to provide plant available sulphate at an adequate rate.

As mentioned earlier the amount of soluble sulphate varies widely between soil types (Blakemore *et al.*, 1968; Williams, 1974) and between seasons (Barrow, 1966; Williams, 1968). In addition to adsorbed sulphate in surface soil horizons, in some situations subsoil sulphate can play an important part in providing plant available S particularly for deep rooted plants (Gregg and Goh, 1978; Hue and Cope, 1987).

In general chemical analysis of soil as means of evaluating the S status of soils under field conditions have not been very helpful (Brogan and Murphy, 1980; Murphy, 1980; Spencer and Freney, 1980; Burmester *et al.*, 1981; Jones *et al.*, 1983). Those efforts made have invariably concentrated on extractable sulphate as the estimate of plant available S (Ensminger and Freney, 1966).

When the sulphate adsorption capacity of the soil is low, a 0.15% calcium chloride solution or distilled water is adequate to determine the plant available pool. In New Zealand 0.01M  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  (Saunders *et al.*, 1981) or 0.04M  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  (Searle, 1979) have been used to determine the sulphate in soil solution and adsorbed on surfaces and used to identify pastoral soils at risk of S deficiency (Saunders *et al.*, 1981). This extractant, however, has been found to be a poor indicator of S deficiency in not only pastoral soils in New Zealand but also in field grown crops in U.K. (Hoque *et al.*, 1987; Skinner, 1987).

Often the S tests have been evaluated in conjunction with greenhouse pot studies rather than under field conditions (Jones, 1986). Good correlations between extractable sulphate and plant uptake have been measured in many of these studies. This is mainly because in glasshouse studies losses of S by leaching can be controlled, the inputs of S through animal excreta and rainfall are eliminated and uniform conditions for S mineralization are maintained. In the field it is more difficult to control losses and gains to the soil sulphate pool. As a result the ability of soil tests to predict S response are far more variable. For example in a Californian field study Jones *et al.* (1983) reported that on clay loam and loam soils with C/S ratios ranging from 137 to 267 and organic matter from 3.1 to 8.6%, there was no significant relationship between subterranean clover-grass forage production and soil test S value. In Western Australia, Spencer and Glendenning (1980) in a field study also found no relationship between extractable S and yield of subterranean clover pasture. In tropical Queensland, however, the response of a tropical legume-grass mixture to gypsum was well correlated to  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  extractable sulphate concentrations (Probert and Jones, 1977). Rayment (1983) also found a good relationship between extractable sulphate and grass-legume mixture. In Canadian Prairie soils the immediately available S pool is considered to be extracted with water since the adsorbed sulphate is not present in significant amounts (Bettany *et al.*, 1982).

In summing up, the inaccuracy of chemical soil testing procedures to predict S requirements based on the levels of extractable sulphate can be due to a number of factors,

1. The potential of the soil to mineralize organic S during the growing season is not measured. With more than 95% of the soil S is in the organic fraction, failure to assess the contribution from this source seriously limits the usefulness of any chemical extractant.
2. Because sulphate is weakly held in many soils, a considerable degree of temporal variability is to be expected were, leaching is important (Ghani *et al.*, 1990). In such a situation it is difficult to see how the measurement of the sulphate at a single point in time could give a realistic indication of S supply to crops throughout the growing season. Soil testing is likely to be most useful when leaching of sulphate is low such as in the most arid part of the world (Hamm *et al.*, 1973) or where soils have high sulphate adsorption capacities.
3. Plant roots are capable of using sulphate to great depth. Soil samples for practical reasons are invariably collected from the top soil (0-75 or 0-150mm). Failure to account for subsoil reserves of plant available S in the past been used to explain why apparent S response sites did not respond to applied S.

Clearly a good knowledge of a soil and its properties and environmental conditions are necessary if soil test values derived from single chemical extractant are to be useful in predicting S responses. Under New Zealand conditions it is necessary to obtain information on organic S levels, subsoil sulphate, the soil infiltration characteristics, rainfall and past S fertilizer history to be able to predict S response using calcium phosphate extractable S values (Saunders *et al.*, 1981).

Having already discussed the various forms of S in the soil and the proportion of S in each fraction present in different environments and their plant availability, it is appropriate now to discuss the chemical and biochemical transformations that occur between these, various soil S fractions. Emphasis will be placed on transformations occurring in grazed pastures because of its importance to the objectives of this thesis.

## 2.4 TRANSFORMATION OF SULPHUR IN SOILS

The transformation of S in soil are many and varied and often the changes are cyclic. The element changes from inorganic to organic forms and back again due to the action of living organisms. Because the transformations are cyclic it is appropriate to discuss the S cycle before discussing the individual transformations.

The S cycle in a grazed pasture is an interactive system comprising soil, plants and animals and their interaction with climate. The S cycle for a well drained grassland soils in humid temperate climate was first proposed by Walker (1957). During the last three decade or so, S cycles for different agricultural systems have been developed by several workers (Till, 1975; Metson, 1979; Bettany *et al.*, 1982; Freney and Williams, 1983; Stevenson, 1986). A generalized S cycle for a grazed pasture is shown in Fig.2.1.

Considering the previous discussion (section 2.2) it is clear that soil organic pool is the largest reserve of S in a grazed pasture. Even though plants absorb a small amount of S as  $\text{SO}_2$ , the majority of atmospheric and fertilizer inputs of S must also pass through the soil pool before entering the plant and animal components of the cycle. The plant system contributes much to the S cycle because most of the carbon bonded S in soil organic matter is derived from plant litter. The grazing animal contributes S to the soil as primarily inorganic S in urine and both inorganic and organic S in dung.

As mentioned in section 2.3.3, one of the factors influencing the size of the sulphate pool is the balance between the organic matter formation and its decomposition. The rates of soil organic matter formation from plant and animal residues and its decomposition are essentially controlled by the activity of soil microorganisms. So it is appropriate to understand the factors which control the nature and activity of soil microorganisms.

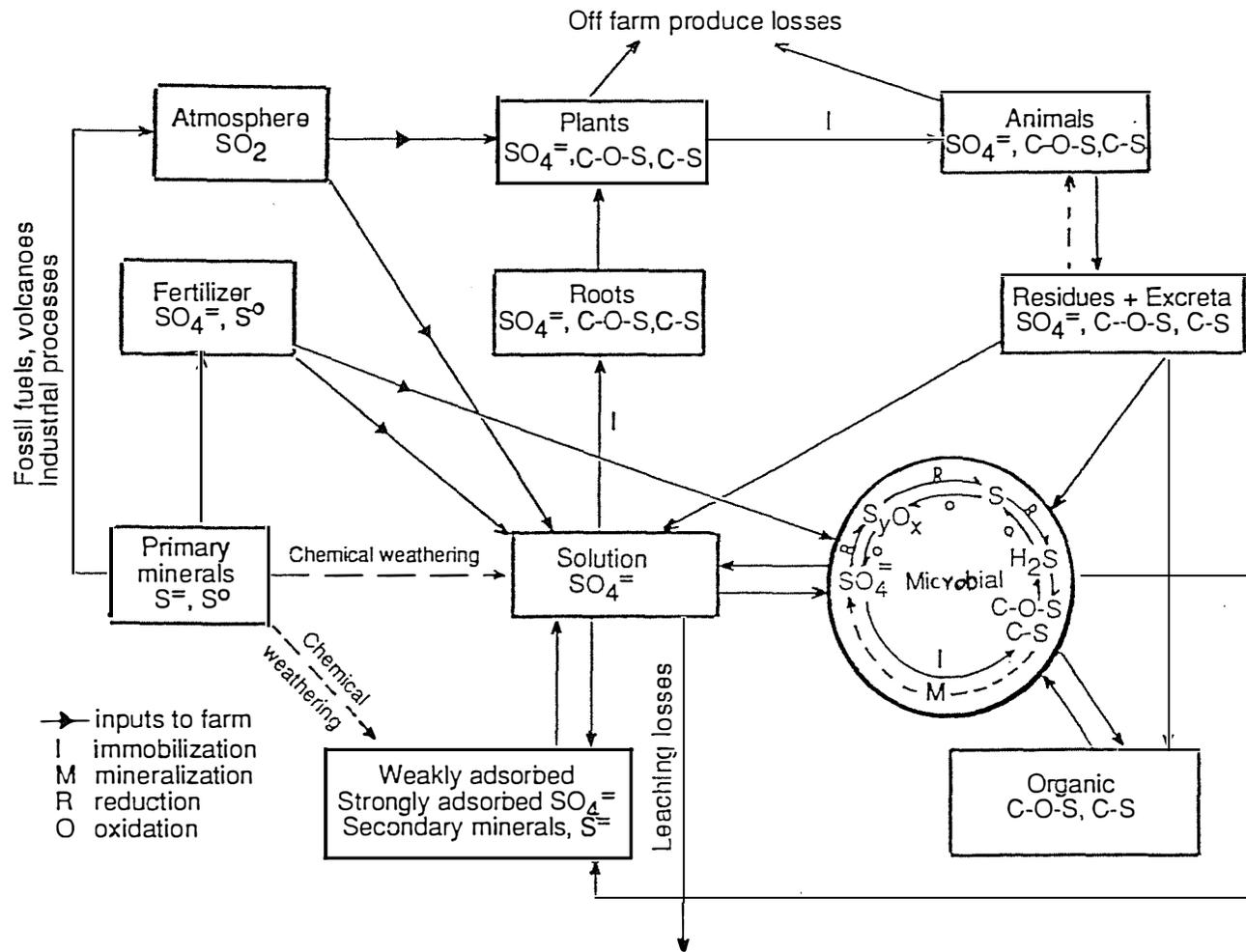


Figure 2.1

The S cycle (Hedley, M.J., 1990. Lecture notes of soil fertility and the environment, 89.412 Soil Science, Massey University).

### 2.4.1 Microbial Biomass Sulphur

Soil microorganisms contain S in the form of amino acids (C-bonded) and ester sulphates (HI-reducible S). This fraction is generally referred to as the microbial biomass S and in soil is considered to be both an important sink (immobilization) and a source (mineralization) of plant available S (Voroney *et al.*, 1981). The soil microbial biomass is included with the soil organic matter and contains about 2% of total C, N and S of the soil even though much of the other soil organic S compounds must pass through this pool before being available for plant uptake. Size and activity of the microbial biomass is affected by the soil nutrient status as well as by temporal and seasonal changes. Changes in the activity of biomass in response to environmental changes therefore have important implications in S availability for plant growth.

A major advance in estimating the size of the microbial biomass in soils came with the development of the chloroform-fumigation and extraction techniques of Jenkinson and Powlson (1976). The first attempt to measure biomass S was made by Saggar *et al.* (1981a) by fumigating soil with alcohol free chloroform and then extracting the soil with NaHCO<sub>3</sub> or CaCl<sub>2</sub> solution. This method has been used to determine biomass S in other soils although the extractant used varies (David *et al.*, 1982; Maynard *et al.*, 1983; Chapman, 1987; Ghani *et al.*, 1988). In bacteria the majority of S appears to be in amino acid form with only about 10% present as ester-S (Saggar *et al.*, 1981a). Again in fungi the majority of S is in the amino acid form. Fungi also contain a significant amount of organic sulphate as cholin sulphate (Fitzgerald, 1978).

#### 2.4.1.1 Factors Affecting Microbial Sulphur

Microbial activity is often limited by a lack of substrate and nutrient. This is evident by the fact that the addition of substrate (carbon source) to soil generally results in a rapid increase in microbial activity, total biomass and in short-term net immobilization. For example in incubation studies the incorporation of <sup>35</sup>S labelled sulphate into the soil organic S fraction can be increased by the addition of glucose

(Freney *et al.*, 1971; Saggar *et al.*, 1981b; M'Laren *et al.*, 1985; Ghani *et al.*, 1988). Under field conditions the main source of substrate for microbial growth is from plant residues, in the form of roots, stem and leaf litter and in grazed pasture 50% of substrate is returned in the form of dung and urine from the grazing animals. In a grazed pasture it was estimated that about 85% of the S taken up by above ground plant is returned to soil in these forms (Scott, 1985). More recent estimates (Saggar *et al.*, 1990a) would put this at a lower level with pasture utilization by animals commonly 70% of the above ground plant uptake.

In general soils that have the highest organic matter inputs also tends to have the greatest microbial activity and largest biomass. Practices which reduce organic return to soils will affect microbial activity, for example cultivation of natural vegetation such as forest and prairie reduces the soil biomass. Fertilizers in the organic form will on the other hand increase microbial activity more so than the inorganic forms because of the additional carbon substrate added. However, where inorganic S fertilizers stimulate plant growth, increased inputs of carbon will occur.

Saggar *et al.* (1981b) showed that the percent of total S present as ester-S in the microbial pool increases significantly as the sulphate content of the growing medium is raised. Thus it may be expected that additions of inorganic S fertilizers may also increase the microbial ester pool.

Even though the amount of S in the microbial pool has been quantified in a number of studies, no attempt has been made to measure the amount and rate at which S is cycled through this pool. The activity of this pool is important for a number of reasons discussed below.

1. Most of the plant S (both shoot and root) is cycled through this pool before becoming available for plant uptake,
2. About 75-90% of dung S must pass through this pool before becoming available for plant uptake and
3. Soil microflora and fauna activity must occur before organic S can be hydrolysed to plant available forms.

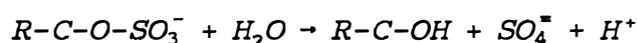
As discussed earlier the amount of plant available S at any time is the balance between the amount of S released as sulphate from soil organic matter by decomposition and the microbial need for S. Having discussed the factors affecting the form and activity of the organisms, it is now appropriate to discuss the processes of organic matter decomposition and the factors affecting it.

## 2.4.2 Mineralization by Microorganisms

The conversion of organic S to inorganic sulphate (mineralization) is regulated by same factors that control the activity of microorganisms and the functions of their extracellular enzymes. The chemistry of mineralization in different soils whether they be from forest or grassland ecosystems is almost identical (David *et al.*, 1982).

### 2.4.2.1 Mechanism of S Mineralization

The conversion of ester sulphate to inorganic sulphate is actioned by sulphohydrolase enzymes (sulphatases), which are produced by microorganisms, plants and mammals. The hydrolysis is given by the equation (Fitzgerald, 1978)



This can occur either intracellularly or in the periplasmic space, depending on the organism and substrate (Dodgen and Rose, 1975; Fitzgerald, 1978). Enzyme formation in pure systems is suppressed by the sulphate ion and S containing amino acids (Dodgen and Rose, 1975; Fitzgerald, 1976). The activity of sulphatase is thought to be inhibited by an accumulation of end product (Cooper, 1972) so that the amount of S mineralized by this mechanism depends on the sulphate level in the soil. It has been suggested (McGill and Cole, 1981) that the release of inorganic S from ester S by the sulphohydrolase enzyme is controlled by the microorganisms' need for S rather than energy. More extensive mineralization of organic S in cropped compared to uncropped soils has been attributed to the fact that by maintaining soluble sulphate at low concentrations in the cropped soils plants stimulate the production of sulphatase by rhizosphere microorganisms (Maynard *et al.*, 1985). In a pot experiment

with New Zealand soils of low S status sulphatase activity was a good indicator of mineralized S taken up by plants (Spier, 1977). In the absence of growing plants, however, Tabatabai and Bremner (1972a) showed in an incubation study no clear relationship between sulphatase level and sulphate production.

Although many aspects of S mineralization are still poorly understood (Scott, 1985) it is well established that the rate of S mineralization is regulated by same factors which influence the growth of microorganisms and their extra cellular enzymes. Soil temperature, moisture and water movement appear to play a regulatory role in the level of arylsulphatase activity in the soil (Speir, 1977; Neal and Herbein, 1983) and variation in these factors explain in part the difference in activity between cropped and fallow soils (Speir *et al.*, 1980). In planted soil however there is a greater opportunity for sulphohydrolase to be replaced either by plant roots and higher microorganism members associated with rhizosphere (Speir *et al.*, 1980), both of which are absent in a fallowed soil. It seems unreasonable to expect a strong relationship between sulphate released and aryl sulphatase activity because only part of the mineralized sulphate originates from ester sulphate fraction and arylsulphatase is only one of many enzymes involved in organic matter decomposition. Further research is required if the complex nature of S mineralization processes are to be unravelled in soils.

Very little is known about S mineralization rates in field soils. Most of the work in USA (Tabatabai and AL-Khafaji, 1980), UK (Bristow and Garwood, 1984; M<sup>c</sup>Laren *et al.*, 1985), Canada (Maynard *et al.*, 1983), Australia (Freney *et al.*, 1971, 1975) and New Zealand (Ghani *et al.*, 1988) studied the mineralization rates of soils only under laboratory conditions. The practical significance of these results is uncertain because the apparent rate of mineralization of soil in laboratory depends upon the type of incubation system used (Maynard *et al.*, 1983). To provide effective information related to plant uptake and S fertilizer requirements, the mineralization study must be conducted under field conditions. In order to achieve this appropriate techniques need to be developed to measure the losses of S from soil by plant uptake and leaching and in so doing, determine the net mineralization of soil organic S and the rate of mineralization.

## 2.4.2.2 Factors Affecting Mineralization

As mentioned earlier, mineralization is essentially controlled by the activity of the microorganisms, which is controlled by several factors. These include the temperature, moisture, Ph and the availability of substrate and other nutrients.

### 2.4.2.2.1 Temperature

Laboratory studies have shown that mineralization of S is considerably retarded below 10°C (Stevenson, 1986), but increases with increase in temperature up to 40°C. Work in Iowa (Tabatabai and Al-Khafaji, 1980) showed that the quantity of S mineralized over a 6 week incubation period increased by a factor of 2.5 to 3.7 when temperature was raised from 20°C to 35°C. Similar effects of temperature on S mineralization have been reported by Williams (1967) and Ghani *et al.* (1988) for soils from Australia and New Zealand respectively. Under field conditions, the effect of temperature on the amount of S mineralized are not fully understood for agricultural ecosystems, because increased temperature also increases carbon fixation and S immobilization. Sulphate-S levels in pasture soils are often highest during moist cool periods when plant growth is slow (Ledgard *et al.*, 1991). The high levels of mineral S in summer due to S released from organic matter by desiccation under Australian cultivated soil conditions (Barrow, 1961a, 1966; Williams, 1967) is also an effect of temperature.

### 2.4.2.2.2 Moisture

In laboratory incubated soils moisture contents close to field capacity are optimal for S mineralization and the rate of sulphate production declines sharply at moisture contents above and below this point. The decline of S mineralization at high soil moisture contents could be expected to be due to the occurrence of anaerobic conditions (Williams, 1967). It has been shown that the effect of moisture on the mineralization of S and N was similar (Williams, 1967). When soils are dried and remoistened prior to incubation they release appreciably more sulphate than they do when incubated without prior drying (Williams, 1967). This occurs because drying

lyses some of the microorganisms and releases S. But Freney *et al.* (1975) showed that for Australian soils which presumably normally undergo severe wetting and drying in the field, drying and rewetting of planted soils in the greenhouse did not stimulate S mineralization. For New Zealand soils the effect of moisture on the mineralization of S has not been studied under either laboratory or field conditions, but West *et al.* (1989) studied the effects of laboratory and field drying on microbial P release in soils and concluded that soils prone to drought produced lysis resistant microbial populations whereas humid soils produce organisms susceptible to lysis on drying.

#### **2.4.2.2.3 pH**

Australian work in laboratory incubations (Williams, 1967) has shown that the amount of S mineralized is proportional to Ph up to 7.5. Above Ph 7.5 mineralization occurs more rapidly suggesting that chemical hydrolysis is also affecting the process. In some soils the amount of S mineralized was more related to the amount of calcium carbonate added, than to the Ph after incubation (Williams, 1967).

Addition of calcium carbonate to soils has been shown to lead to an increase in soluble sulphate on incubation (White, 1959; Nelson, 1964; Williams, 1967) because, in addition to increased mineralization, adsorbed sulphate may be desorbed from soil exchange sites because of the increased Ph (Chao *et al.*, 1965; Williams and Steinberg, 1962), and sulphate may be released from soil organic matter by chemical hydrolysis under alkaline condition (Barrow, 1960).

#### **2.4.2.2.4 Availability of Substrate and other Nutrients**

It has been suggested that the S content of organic matter recently added to soil rather than total soil S regulates S mineralization. It has been shown that sulphates usually accumulate in the soil when the C:S ratio is below 200 and is highly immobilized when the ratio exceeds 400 (Barrow, 1960). At ratios between 200 and 400 the picture is less clearcut. In a study investigating the effect of N addition on the S mineralization, Kowalenko and Lowe (1975, 1978) found that both immobilization and

mineralization occurred. This led them to the conclusion that simple generalization on the effect of changing the N:S ratio on S transformation should be avoided. Sulphur mineralization in presence of growing plants was greater than that which occurred in an identical fallow soil (Freney *et al.*, 1975; Barrow, 1967b; Cowling and Jones, 1970; Jones *et al.*, 1972a; Tsuji and Goh, 1979; Maynard *et al.*, 1985; Nicolson, 1970). The reason for this is partly due to increased rhizosphere activity in presence of plants.

No detailed information is available on the effect of rate of fertilizer application and the return of excreta by grazing animals on the amount of S mineralized in grazed pastures. The animal itself can be considered to be a mineralizing agent because on average about 35% of the organic S entering the animal is returned to the soil as sulphate (section 2.5.2).

#### **2.4.2.3 Relationship Between Sulphur and Nitrogen Mineralization**

Even though both S and N mineralization are the result of the decomposition of soil organic matter considerable controversy still exists in the literature regarding the factors influencing the relative rates of mineralization of the two nutrients.

In a comparison of New Zealand soils White (1959) reported that the relative rates of S and N mineralization from soil organic matter were similar and that they were released in the same ratio as that occurring in the soil organic matter. In contrast, most other incubation studies, for example in soils from Australia (Williams, 1967), Iowa (Tabatabai and Bremner, 1972a), West Indies (Haque and Walmsley, 1972) and Canada (Kowalenko and Lowe, 1975) the ratio of N to S mineralized was found to be much wider than the soil organic matter, suggesting that

1. The proportion of potentially mineralizable N pool may differ from S pool.
2. Sulphur and N may not occur in the same organic compounds or fractions of soil organic matter and thus may not be released at same time or rate (Freney, 1961; Biederbeck, 1978),

3. The inclusion of plant or animal residues with large N to S ratios would cause greater immobilization of S relative to N,
4. The processes affecting N and S mineralization may be different, especially the type of microorganisms and the stability of extra cellular enzymes (Biederbeck, 1978).

In all the above studies a closed soil incubation system was used. This allows for reimmobilization of mineralized S and N. When S is limiting microbial activity presumably the mineralized S reimmobilized. This would result in an apparently wider N/S ratio mineralized than present in the soil organic matter. The reverse is also possible. Recent studies (Tabatabai and Al-Khafaji, 1980; Maynard *et al.*, 1983; Ghani *et al.*, 1988), in which soils were leached periodically (open incubation system) with extractants such as 0.01M KCl and 0.15% CaCl<sub>2</sub> suggest that the ratio of N to S mineralized was very close to the N to S ratio of the soil organic matter (Table 2.2). In the open incubation system the mineralized products can be removed by leaching. This limits the reimmobilization of the mineralized products. In addition to the incubation system, there are a number of other factors, such as temperature, moisture, pH and the type of organisms, which can be used to explain the difference between the rates of N and S mineralization (Freney, 1986).

In all the New Zealand studies (White, 1959; Ghani *et al.*, 1988) the relationship between S and N mineralization has been examined only in laboratory incubation studies. Mineralization rates of S and N under field conditions have not been investigated in any detail. It is particularly important to measure these processes under legume based grazed pastures, the dominant agricultural land use, for which superphosphate is the main fertilizer applied and the only source of soil N is the fixation of atmospheric N.

### 2.4.3 Immobilization

Some authors considered this to be the consumption of inorganic S by soil microorganisms and eventual incorporation into humus. It also includes any S taken up and combined with carbon by plant roots and other microorganisms which remains

**Table 2.2 Effect of incubation system and period of incubation on the ratio of N to S mineralized and the ratio of N to S present in the soil from different regions of the world.**

Country	Number of soils examined	Incubation		N:S ratio of the soil	N:S ratio mineralized	Reference
		Period (Weeks)	System			
New Zealand	7	4	closed	6-14	10-37	White,(1959)
Australia	17	12	closed	4.4-9.6	10-45	Williams (1967)
Eastern N.S.W	1	14	closed	9(NF), 10(F)	19(NF), 13(F)	Barrow (1961)
Africa	1	4	closed	24	--	Hesse (1957)
Canada	4	14	closed	3-8	0-19	Kowalenko and Lowe (1975)
Western Saskatoon	2	2	open	6.6-10.6	3-5	Maynard <i>et al.</i> (1983)
West Indies	8	7	closed	7-12	0.3-10	Haque and Walmsley (1972)
USA	12	26	closed	4-8.5	3-9	Nelson (1964)
Mississippi Iowa	12	28	open	6-7.4	**	Tabatabai and Al-khafaji (1980)

\*\* lower than the N/S ratio of the soil, but dependent on the incubation temperature of the incubation system. NF= Unfertilized, F= Fertilized, - Not known.

below ground. Immobilization conserves  $\text{SO}_4^-$  against loss by leaching and the immobilized S provides a potential source of S for subsequent plant uptake (Voroney *et al.*, 1981). The biochemical pathways in the immobilization of sulphate are reasonably well understood and have recently been outlined (Scott, 1985). Under conditions where organic materials are rapidly accumulating, considerable amount of inorganic S are incorporated into soil organic matter. For example in South Australia vigorous legume growth is associated with the immobilization of S applied in superphosphate (Williams and Donald, 1957).

The incorporation of sulphate to organic S forms can be very rapid. In New Zealand, field work with  $^{35}\text{S}$ -labelled gypsum showed that about 40% of the S applied to a three year old pasture soil was converted into organic S in the top 0-50mm soil layer within six weeks of application (Gregg and Goh, 1979). Work in Australia showed that about 50% of the added  $^{35}\text{SO}_4\text{-S}$  was incorporated into organic forms in 168 days in a laboratory incubation study (Freney *et al.*, 1971). Added  $^{35}\text{S}$  was recovered in both ester S and C-bonded S fractions. When a carbon source was also added, the incorporation of sulphate into organic S was further increased (Freney *et al.*, 1971) demonstrating the importance of substrate for microbial activity. Several workers have demonstrated this phenomena (Maynard *et al.*, 1983; Ghani *et al.*, 1988).

Less is known about subsequent S transformations during the breakdown of plants, animals and microbial compounds which lead to S immobilization into soil humic and fulvic acids and humin materials (Bettany *et al.*, 1979). Studies in which rye plants were grown with labelled  $^{35}\text{S}$ -sulphate and the residues then incorporated into soil organic matter showed that appreciable amounts of labelled S were found in soil humic acid when sodium bicarbonate was used to extract the labelled organic matter (Freney *et al.*, 1971). When NaOH was used to extract the soil organic matter, however little  $^{35}\text{S}$  was found in humic acid fraction (Freney *et al.*, 1971; Scharpenseel and Krausse, 1963). This showed that most of the added S was incorporated in to more resistant C-bonded S fraction while some of the inorganic S was incorporated in to ester S, the quantity of ester S that may have been converted into C-bonded S and vice versa is not known.

Under steady state conditions the rates of immobilization and mineralization are balanced with organic soil S levels remaining comparatively constant. In many soils, however, the establishment of grass-clover association begins a phase of soil organic matter accumulation which is enhanced by the application of fertilizer P and S (Walker, 1956). Australian studies showed net immobilization of 10-15 kg S ha<sup>-1</sup>(0-150mm) year<sup>-1</sup> in several fertilized pastures for 3-27 years (Hingston, 1959). In New Zealand During and Cooper(1974) showed that about 30% of the fertilized S applied to yellow brown loam over a period of 5 years was immobilized in to soil organic matter.

#### 2.4.3.1 Biochemistry of Immobilization

In the process of immobilization sulphate ions are activated in a two step process, leading to the production of the energy-rich sulphate nucleotides APS (Adenosine 5'-phosphosulphate) and PAPS (3'-phosphoadenosine-5'-phosphosulphate) (Scott, 1985). The nucleotides are then used in the synthesis of S containing amino acids. The pathways are still uncertain, but it is thought that PAPS is reduced to sulphide via sulphite. The amino acid serine is then combined with sulphide to produce cysteine. Thiosulphate is readily used by microbes in place of sulphate and is thought to be a direct pathway. The overall reaction may be represented as follows.



Cysteine is then used as the building block for other S containing amino acids, which are then combined into proteins.

#### 2.4.4 Leaching of Sulphate

Soil S in the form of sulphate is lost from agricultural soils mainly by leaching. Sulphate leaching has been investigated in laboratory, greenhouse and field studies. Losses ranging from 0-100% of the applied S have been reported in different soils with various fertilizer and experimental techniques. The results of a number of these studies and the experimental techniques used are given in Table 2.3.

**Table 2.3 Experimental techniques used to evaluate sulphate leaching losses under greenhouse and field conditions.**

Soil group	Experimental techniques	Sulphur treatment (kg S ha <sup>-1</sup> )	Sulphate leached	Reference
Soils with widely varying characteristics	Soil leaching column study	45 as <sup>35</sup> S in gypsum	0-15% of fertilizer S	Chae <i>et al.</i> , (1962)
Podzol	Undisturbed soil leaching column study	Unfertilized	2 kg S ha <sup>-1</sup>	Peeverill and Douglas, (1976)
Podzol	Soil leaching column study	110 as gypsum 50 as SSP 31 as S°	90%,81% and 19-33% of fertilizer S	Hogg and Cooper, (1964)
Yellow grey earth	Greenhouse pot trial	106 or 264 in SSP	20% of fertilizer S	Muller and McSweeny,(1977)
Yellow grey earth	Field study	45 as SSP	15 kg S ha <sup>-1</sup>	Smith <i>et al.</i> ,(1983)

The amount of S lost by leaching depends upon soil texture, sulphate retention capacity, biological properties, the amount of water passing through the soil profile and factors which affect the size and rate of renewal of the solution sulphate pool in the soil.

#### **2.4.4.1 The Influence of Soil Texture**

Severe leaching of S occurs from sandy soils in Australia (Barrow, 1967b; Watson *et al.*, 1973; Lewis and Clarke, 1975), in New Zealand (Cooper and Hogg, 1966) and in USA (Rhue and Kamprath, 1973). This is due to the poor retention of sulphate (Cooper and Hogg, 1966) in these soils due to lack of organic matter to act as substrate for immobilization and the absence of hydrous Fe and Al oxides for sulphate adsorption. The low water retention capacity of these soils also leads to higher losses of sulphate. The lack of sulphate retention in a sandy soil was highlighted by Rhue and Kamprath (1973) where almost all of the applied S (sulphate and oxidized elemental S before leaching) was leached from the top 450mm of a sandy soil in 180 days, while in a silty loam of similar pH there was no downward movement of S was observed. A sand texture, however, is not the only prerequisite for S leaching (Till and McCabe, 1976).

#### **2.4.4.2 Factors Affecting the Accumulation of Soluble S-pool**

The amount of sulphate leached is influenced by all those factors that affect the soluble inorganic sulphate pool in the soil, namely, the timing of the last S fertilizer application, the form and size of the fertilizer S particle, factors affecting the net rate of mineralization and soil water characteristics (section 2.4.2.2).

The sulphate adsorption capacity of the soil has a major bearing on the rate of sulphate leaching. Work in New Zealand showed that under similar rainfall conditions (500-600 mm year<sup>-1</sup>) large differences in the movement of sulphate can occur in pasture soils with contrasting sulphate adsorption capacities (Gregg *et al.*, 1977). When sulphate adsorption capacity is negligible the mobility of sulphate can be as high as that of chloride (Aylmore and Karim, 1968). A recent study on the North Island hill country pasture soil in New Zealand with low phosphate adsorption

capacity (<30%), Saggar *et al.*(1990a) calculated that about 46 to 77% of S applied as superphosphate was lost by leaching depending on the rate of application of S. This leaching loss was more pronounced in the low slopes (camp areas) than in moderate hill slopes. In a similar study (Saggar *et al.*, 1990b) with the soil of high P retention showed that the loss was very low when the fertilizer application rate was low but it increased when the fertilizer application rate increased. In South Island, it was shown that when the fertilizer application rate was increased from 186 to 372 kg SSP ha<sup>-1</sup> year<sup>-1</sup> about 50% of the additional S applied was lost by leaching (Nguyen and Goh, 1990).

In some areas of New Zealand S applied to pastures in spring is less susceptible to leaching than S applied in autumn mainly due to a greater plant uptake and immobilization into soil organic matter, which reduces the soil solution sulphate before the next winter. In high rainfall environments this is reflected in increased S response in spring to spring applied S (Nguyen *et al.*, 1989). In another study it was shown that when the fertilizer was applied during previous spring about 11kg S ha<sup>-1</sup> was lost by leaching but when applied in late autumn the loss was increased by 4 to 5kg S ha<sup>-1</sup> (Smith *et al.*, 1983).

Work in U.K, where soils have little or no capacity to retain sulphate showed that losses of sulphate can represent a large proportion of S input. For example work at Rothamsted (Bromfield and Williams, 1974) showed that the amount of sulphate leached (50 kg ha<sup>-1</sup>) from an uncropped soil exceeded S inputs from rainfall and fertilizer. But this may not occur continuously for a long time. Cropping the soil reduced the leaching of sulphate significantly, but still substantial losses occurred (Bristow and Garwood, 1984).

Farming practices such as liming and phosphate fertilization both decreases the sulphate adsorption capacity and can accelerate sulphate leaching (Curtin and Smillie, 1986; Bolan *et al.*, 1988; Marsh *et al.*, 1988). Little work has been done to compare the losses of S by leaching from soils which have been fertilized with superphosphate and soils with other form of sulphate fertilizers, but such research is currently

underway at Massey University (Heng, 1991). But generally, soils with regular superphosphate application lose more S by leaching than soils with other sulphate fertilizers. Leaching and adsorption studies conducted in U.K showed that a sizeable, although a variable proportion, of added S was lost from the zone of root activity by leaching (Syers *et al.*, 1987).

The intensity and duration of rainfall affect the degree of wetting of the soil and thus the time taken to approach the maximum leaching rates. Singh *et al.* (1980) showed greater losses of S by leaching at greater rates of rainfall in lysimeter studies. The effect of previous rainfall can also affect the rate of leaching; e.g. Scotter (1978) found that preferential flow is most likely in saturated soils. In some cases preferential flow may lead to less sulphate leaching than if greater displacement of soil water occurs.

Despite many studies conducted in New Zealand, Australia and U.K on leaching losses of sulphate no quantitative information is available on the possible origin of this leached sulphate. In a grazed pasture, sulphate can be leached directly from fertilizer sulphate, sulphate in animal excreta and sulphate mineralized from soil organic matter. Even though lysimeter (Steele *et al.*, 1984), mole and tile drain (Smith *et al.*, 1983) and <sup>35</sup>S tracer (Gregg and Goh, 1979) studies have been used in field have measured indirectly the leaching losses of S, none of these studies measured the amount of S lost by leaching and the origin of the leached sulphate. For example in the experiment using <sup>35</sup>S labelled fertilizers (Gregg and Goh, 1979) the amount of S lost by leaching was not measured directly, instead it was calculated indirectly by balance from inputs and the percentage isotope recovery from the soil. In the experiment using mole and tile drain system (Smith *et al.*, 1983) to recover the leached sulphate, the amount of drainage moved below the mole drain was not accounted. In the lysimeter study (Steele *et al.*, 1984) not all drainage was collected, instead the drainage at the start and end of each rainfall event was collected and the average sulphate concentration was used to calculate leaching losses. Further studies are required to provide information on the actual amounts and origins of this leached sulphate. New techniques to measure these losses need to be developed. If the main

origin of the leached sulphate was identified management practices could be changed in order to reduce or minimize the losses of S by leaching. For example in situations where leached sulphate is derived mostly from fertilizer, elemental S fertilizer may be useful in reducing leaching loss. Elemental S based fertilizers have been successful in maintaining S supply to pastures in strongly leaching environments (Boswell, 1987).

## **2.5           SULPHUR CYCLING IN GRAZED PASTURE SYSTEM**

So far the literature review has considered the forms of soil S and the transformations of these forms that influences their fate in the soil. In grazed pasture systems, in addition to applied fertilizer, the grazing animal and its management, as it influences the return of plant litter and animal excreta, have a considerable influence on the fate of S (Saggar *et al.*, 1990a).

### **2.5.1           Fertilizer Sulphur Inputs**

In New Zealand, superphosphate (0 9 0 12, N-P-K-S) is the main fertilizer applied to legume based pastures in order to overcome key P and S deficiencies in pastures and stimulate nitrogen fixation by the legume component of the sward. Sulphur is particularly important because grasses depend upon clover for their nitrogen requirements. At the same time grasses are stronger competitors for S than clovers. When S supply limits clover growth nitrogen fixation rates are also limited. This in turn limits the nitrogen supply to the grass component of the sward. This in turn limits total pasture production. Overcoming the S limitation builds up soil organic matter by allowing more carbon to be fixed by growing plants and increases the accumulation of S in soil organic matter (Barrow, 1969). In the early stages of pasture development this build up of organic S may induce S deficiency (Walker and Adams, 1958) until immobilization and mineralization rates become balanced.

The cost of fertilizer transportation in recent years have made high analysis forms of S fertilizers more attractive to manufacture and distribute. To achieve high analysis S fertilizer it is preferable incorporate S into fertilizers in the form of elemental S (S<sup>0</sup>) rather than sulphate form. Elemental S is the most concentrated form of S and hence the addition of S<sup>0</sup> to higher analysis fertilizers will not greatly dilute other nutrients,

and unlike sulphate in superphosphate, the slow oxidation of S<sup>0</sup> may reduce the leaching losses of sulphate.

Research has indicated that fertilizers in the elemental S form can be suitable as a pastoral fertilizer in New Zealand provided specific particle sizes of S<sup>0</sup> are used (Boswell, 1985). Elemental S must be oxidized to sulphate in soils before it becomes plant available. The plant availability of S<sup>0</sup> applied to soil has been shown to be greatly affected by its particle size distribution (Fox *et al.*, 1964; Palmer *et al.*, 1983; Sinclair and Enright, 1983). Sulphuric acid grade S<sup>0</sup> of particle size range 100% <250µm and 50% < 150µm, is recommended by the Ministry of Agriculture and Fisheries for annual applications to pasture in warm temperate climate zones or biennial application in cool temperate climate zones.

In grazed pasture systems, S returned in plant litter and animal excreta (dung and urine) are the major above ground sources of recycled S for maintaining the fertility of soil.

### **2.5.2 Sulphur Returned in Plant Litter**

The amount of S involved in recycling from above ground plant litter depends on the amount of plant production and the amount of herbage utilized by the grazing animal (King and Hutchinson, 1976) which depends upon the stocking rate. In well grazed pastures with high stocking rate utilization can be as high as 90% (Gillingham and During, 1973) while in less intensively managed system pasture utilization by the grazing animal can be as low as 50% (Lambert *et al.*, 1983). With good grazing management ensuring high pasture utilization more S in the above ground herbage will be returned to the soil in the excreta. Under Australian conditions, 70% of net primary production of tops in intensively stocked pastures were utilized by grazing animals (Hutchinson, 1971). The amount of S cycled in root litter and exudate is dependent on the pasture species and the frequency and intensity of grazing.

The rate of release of S by mineralization of excised white clover tops and roots was

studied by Dalal *et al.* (1978). After 8 weeks about 44.4% of  $^{35}\text{S}$  applied in roots and 38% in tops was taken up by plants indicating that relative to tops root decompose quicker. But this trend may not follow for nonexcised root or for other plant species. The rate of cycling of S through plant litter is dependent on the S content of the plant and those factors that affect the decomposition of the litter. Root decomposition also provides plant available S as roots senesce or are harvested by root feeding arthropods and nematodes (Evans, 1971).

### 2.5.3 Sulphur Return in Animal Excreta

Sulphur cycling via grazing animals is considered to avoid the slow process of the decomposition of plant residues, effectively increasing the turnover rate of S cycle (Wilkinson and Lowery, 1973; Till, 1975). In part this is true as a large proportion of S (50-60%) in excreta is in an immediately plant available form (Till, 1975).

However, faecal S is mineralized more slowly than plant S (Barrow, 1961b). The trampling of dung by grazing animals, especially at high stocking rate, does encourage the decomposition process and in doing this reduces this difference. Inefficiencies, however results from the return of S in animal excreta. Dung and urine are not returned evenly, but to only a small part of the grazing sward (see section 2.5.2.2). This represents a loss of S from the soil-plant system. The ability of plants immediately after grazing to absorb S is often severely restricted. This leads to further reduction in the efficiency of S cycling because sulphate can be readily leached from dung and urine patches and is not incorporated into the organic matter or plant pool.

Of the S returned by the grazing animal approximately 40% of S is in dung and 60% of S in urine, respectively (Wilkinson and Lowery, 1973). The plant availability of S, in dung is dependent on the S content, its rate of breakdown and the distribution pattern of dung returned to the grazed pasture.

### **2.5.3.1      Dung and Urine Sulphur Content**

Values for S content of grazing animal dung range from a low of 0.07% (fresh weight) in fresh cow manures to a high of 0.4% S (fresh weight) in sheep dung. Faecal organic S consists of undigested protein, microbial protein S and compounds such as indican which are water insoluble and are somewhat resistant to microbial breakdown (Walker, 1957; During, 1984). The amount of S excreted in faeces is relatively constant, but the S content of the urinary excretion depends on the S content of herbage and season (Walker, 1957; Barrow, 1961b). According to During and Cooper (1974) and Till (1975), 50 to 60% of the S (mostly as sulphate) is excreted in urine when animals graze pastures adequately supplied with S, the remainder occurs as faecal S some of which is in the inorganic sulphate form susceptible to leaching (Walker, 1957; During, 1984).

The grazing animal can influence the losses from the plant available soil S pool in several ways. These include

1.      Losses in animal products
2.      Losses by transferring excreta and
3.      Losses of S by leaching from excreta deposits.

### **2.5.3.2      Dung and Urine Distribution by Grazing Stock**

A major factor influencing the accumulation of S in pastoral soils is the dung and urine distribution pattern which is dependent upon the type of grazing stock and the physical nature of the grazing environment. Sheep develop permanent, defined camp or resting areas where heavy rates of dung are deposited. Hilder (1964) studied the faecal return in the New England area of Australia using Merino sheep and found that stock camps, which comprised 3% of the total area, contained about 22% of the total faeces and that 10% of the total area contains 34% of the total faeces. Work of Gillingham and During (1973), with cattle, demonstrated that the campsites usually were freshly chosen at each grazing although some areas (eg. near shelter or gateway)

tend to receive high levels of excreta. Influence of topography and aspect on the pattern of excreta return from sheep have also been described by Gillingham (1980) and Saggar *et al.* (1990a).

Although it is recognized that campsites receive frequent applications of dung as evidenced predominantly by higher soil P and K levels than in the surrounding paddocks (Hilder and Mottershead, 1963; Rowarth, 1987; Saggar *et al.*, 1990a) there has been few attempts to quantitatively determine dung distribution patterns on the remainder of a grazed paddocks and its influence on pasture production and S leaching losses (Gillingham, 1980; Lambert *et al.*, 1983).

### **2.5.3.3 Decomposition of Dung Sulphur**

Mineralization of dung S is controlled by same factors that affect the mineralization of other forms of organic S. Barrow (1961b) reported that, like nitrogen, the rate of mineralization of S is closely related to the S content of the dung. The S not mineralized was considered to be due to the resistance of the organic matter to decomposition, rather than to organic matter decomposition and subsequent immobilization. Dung mineralization rates are more rapid in crushed samples than in pellet samples, which in turn, are greater than pad samples (Bromfield and Jones, 1970; Rowarth, 1987) and similarly arthropods such as earthworms (Barley, 1964) and dung beetles (Bomemissza and Williams, 1970) can be expected to enhance the mineralization rate through the action of comminution of the material and transporting it to the vicinity of microorganisms (Macfadyen, 1978). Similarly dung decomposition rates are slow in dry conditions compared to cold moist conditions. For example Hilder (1966) reported sheep pellets remaining for 10 weeks in cold moist conditions and for unspecified longer periods in dry conditions in Armidale. However in New Zealand, Rowarth (1987) reported that pellets samples decompose within 20 days by physical disappearance in cold moist winter periods, while longer periods (upto 60 days) were observed during summer. Even though much work has been done to study the decomposition and availability of dung phosphorus, little work was done to study the decomposition and fate of dung S in New Zealand under pastoral conditions.

#### **2.5.3.4 Urine in the Sulphur Cycle**

Most (70-90%) of the urine sulphur is in the sulphate form (Kennedy, 1974), either organic or inorganic. Non-sulphates in urine S is largely carbon bonded S. This is largely comprised of cysteine, methyl mercaptans, ethyl sulphides, thiocyanates and taurine derivatives.

Direct measurements of the distribution of urine by grazing animals are not available. In the absence of any definitive data, various authors have accepted that the distribution of urine is similar to that of dung (Petersen et al., 1956). The volume of urine excreted by the grazing animals can be expected to vary with the moisture content of the diet. Quinn (1977) reported urine outputs of 1-3 litres sheep<sup>-1</sup> day<sup>-1</sup> on pasture of similar quality. Even though much work has been done to study the availability of urine N and K, no precise information exists on the availability of urine S to plants and its leaching losses under field conditions. Nguyen and Goh (1990) indirectly calculated the amount of urine S lost by leaching (see section 2.5.3.3).

#### **2.5.4 Losses Through Animal**

The main losses of S through animal are in animal products and through the transfer to unproductive areas.

##### **2.5.4.1 Losses in Animal Products**

Only a small proportion of ingested S (usually less than 15%) is used by animals in the production of body tissues, milk and wool. The remainder (85%) is returned to the soil in the animals' excreta (During, 1984; Wilkinson and Lowery, 1973; Till, 1975).

#### **2.5.4.2 Losses by Transfer**

Large losses of S from the cycle (Fig.2.1) through the uneven return of dung and urine occur in grazed pastures. For example in hill country, excreta transfer to the areas of stock camps from the areas of steep and moderate slopes is well documented (During, 1984; Gillingham, 1978; Saggar *et al.*, 1990a).

#### **2.5.4.3 Losses of Sulphur from Dung and Urine Patches**

Goh and Nguyen (1991) estimated indirectly leaching losses of S from urinary patches around 70-80%. No direct measurements have been made to quantify such losses for either dairy or sheep grazed pastures in New Zealand.

The effect of freshly returned dung and urine on the availability of soil S to plant uptake and losses by leaching and the mineralization potential of soil organic S has also received little attention in New Zealand. The level of adsorbed sulphate can be reduced in the vicinity of a dung patch because dung increases the pH of the soil and in addition to S it contains phosphate and organic anions which compete for sulphate adsorption sites in the soil, all of those factors increased the leaching losses (During and Martin, 1968).

### **2.6 SUMMARY AND CONCLUSION**

From this review it is clear that most agricultural soils have S contents ranging from 50 to 1000 mg S kg<sup>-1</sup> soil. In New Zealand, agricultural soils contain 240 to 1360 mg S kg<sup>-1</sup> soil of which more than 90% occurs in the organic fraction. The inorganic S fraction is small because either sulphate can be immobilized into the soil organic matter or leached down the profile. The organic S fraction is the major, long term source for plant uptake and the rate of mineralization from and immobilization to organic matter are the key processes in the S cycle. Temperature, moisture, pH and availability of substrate are the main factors which affect the mineralization and immobilization processes. The rate of mineralization or immobilization also

determines the size of the plant available pool at any one time. By establishing the relative efficiencies and inefficiencies of these processes in the S cycle it may be possible to identify the pools and processes which limit the recycling of S to the plant available pool in agricultural systems. Such information is necessary for predicting S fertilizer requirements.

Even though mineralization of the organic S in the soil is considered to be the major long-term source for plant uptake and presumably for leached sulphate, no detailed studies have been done to quantify the proportion of mineralized S taken up by plants and lost by leaching under field conditions. The relationship between S and N mineralization has also not been studied for grazed pastures for which superphosphate is the main fertilizer applied to stimulate legume growth and the source of N is the fixation of atmospheric  $N_2$  by the legumes.

Further research is needed to study the relationship between the rates of mineralization of S and N for legume based grazed pastures and their contribution to plant uptake and losses under field conditions. To achieve this, it is necessary to know the spatial variability of mineralization rates in field soils. It is possible that the potential of field soils to mineralize S and N could be identified by conducting laboratory incubation studies. Field mineralization studies could then be established in areas that show different mineralization potentials.

In order to measure the net mineralization of S and N under field conditions, the amounts of soil sulphate and mineral N, the amounts of S and N removed by pasture and the amounts of S and N lost by leaching need to be measured simultaneously. The soil sulphate and mineral N pools and plant uptake of S and N can be measured directly by taking soil and pasture samples, respectively, over time, but for measuring leaching losses directly, field techniques which measures leaching of S and N in situ in undisturbed soil need to be developed. The net mineralization of S and N could then be calculated.

The literature review indicated that the level of nutrient inputs into grazed pastures influences pasture production, soil organic matter levels and therefore the rate of cycling of S and N. The field technique should be suitable for studying the effect of previous fertilizer applications on the fate of mineralized S and N and by use of radioactively labelled sulphur fertilizer would allow the fate of fertilizer and native soil S could be distinguished. Likewise the effect of fresh excreta return on the mineralization of S and N and their fate can also be studied. By establishing all the above information it is possible that the major origins of the S being taken up by pasture and lost by leaching can be identified.

The objectives of this thesis were therefore to study the mineralization of S and N in grazed pastures and the origins of the sulphate being leached from these grazed pastures.

## CHAPTER-3

### LABORATORY INCUBATIONS TO DETERMINE THE POTENTIAL OF SOILS TO MINERALIZE SULPHUR AND NITROGEN

#### 3.1 INTRODUCTION

A review of current literature (Chapter 2) indicates that at present the use of imported S fertilizer on pasture soils may be inefficient with large leaching losses occurring in certain circumstances. For example, recently Sagar *et al.* (1990a,b) predicted that about 14 to 77% of S applied as single superphosphate (SSP) to sheep grazed pasture in North Island of New Zealand was lost by leaching depending upon the rate of SSP application. In a South Island study Nguyen and Goh (1990) showed that when the SSP application rate was increased from 186 to 372 kg SSP ha<sup>-1</sup> year<sup>-1</sup> about 50% of the additional S applied was lost by leaching. At present few programmes to achieve reduced losses can be introduced because little detailed information exists on the possible origins of this leached sulphate. For example sulphate can be leached directly from fertilizer, sulphate in dung and urine patches and the mineralization of soil organic S, which has been accumulated over the preceding years by regular application of SSP. By identifying the main origins of leached sulphate, the potential for reducing S fertilizer input by changing, for example, the form of S or the time of application can be investigated.

Whereas information on the direct losses of sulphate by leaching from recently applied SSP under field conditions (Smith *et al.*, 1983) and sulphate losses by leaching from urine patches using repacked columns (Hogg, 1981) are available, no precise information exists on the amount of sulphate mineralized from soil organic matter and the percentage of this fraction that could potentially be lost by leaching.

It has been shown that large increases in soil organic matter occur in soils that developed under legume based pastures by regular application of fertilizer under Australian conditions (Donald and Williams, 1954; Williams and Donald, 1957; Barrow, 1969). This accumulation increases the more labile soil organic S and the mineralization potential of the soil for S. It is expected that the same build up of more labile fractions of soil organic S occurred in New Zealand soils, because

fertilizer was applied to increase the pasture development index. When mineralized, this labile S may be an important source of leached S.

To establish the potential losses of sulphate caused by leaching of recently mineralized soil organic S, a laboratory incubation study was conducted to measure S mineralization rates for soils where S had accumulated from different SSP application histories over the preceding 13 years and different rates of animal excreta returned to soils due to the effect of topography on animal behaviour. Since both carbon(C) and nitrogen(N) mineralization rates influence the rate of net S mineralization (McGill and Cole, 1981), the rates of mineralization of these two macronutrients were also measured. As part of the study a comparison of open (leached) and closed (unleached) incubation system was made because the amounts of S and N mineralized are affected by the type of incubation system used (Maynard *et al.*, 1983).

## **3.2 MATERIALS AND METHODS**

### **3.2.1 Description of Soils**

Eight surface soil samples (0-75 mm) (5 kg each) were taken from two slope categories, low (0-12°) and medium (13-26°), within each of four farmlets on Ballantrae, the Hill Country Research Station of DSIR, Grasslands, 20 kms north-east of Palmerston North in the southern Ruahine range. The total amounts of fertilizer P and S that had been added to each of the four farmlets and their codes are given in Table 3.1. Two farmlets had received SSP at rates of 576 (HF) and 125 (LF) kg ha<sup>-1</sup> year<sup>-1</sup> from 1975 to 1980 and 375 and 125 kg ha<sup>-1</sup> year<sup>-1</sup> from 1981 to 1988 and the remaining two farmlets received SSP at rates of 576 (HN) and 125 (LN) kg ha<sup>-1</sup> year<sup>-1</sup> from 1975 to 1980. A full description of the soils, pastures, animals and climate of the farmlets were given elsewhere (Lambert *et al.*, 1985a,b; 1988; 1990; Saggar *et al.*, 1990a). The soils were yellow-brown earth to yellow-grey earth intergrades (Typic Dystrocrepts) with P retention <30% and pH values of <6.00. Several of the physical and chemical properties of the

**Table 3.1 Amounts of P (kg ha<sup>-1</sup>) and S (kg ha<sup>-1</sup>) applied as single superphosphate to each farmlet from 1975-1988.**

Farmlet	Phosphorus		Sulphur		Total	
	1975-80	1981-88	1975-80	1981-88	1975-88	1975-88
HF	311	270	414	360	581	774
LF	68	90	90	120	158	210
HN	311	NIL	414	NIL	311	414
LN	68	NIL	90	NIL	68	90

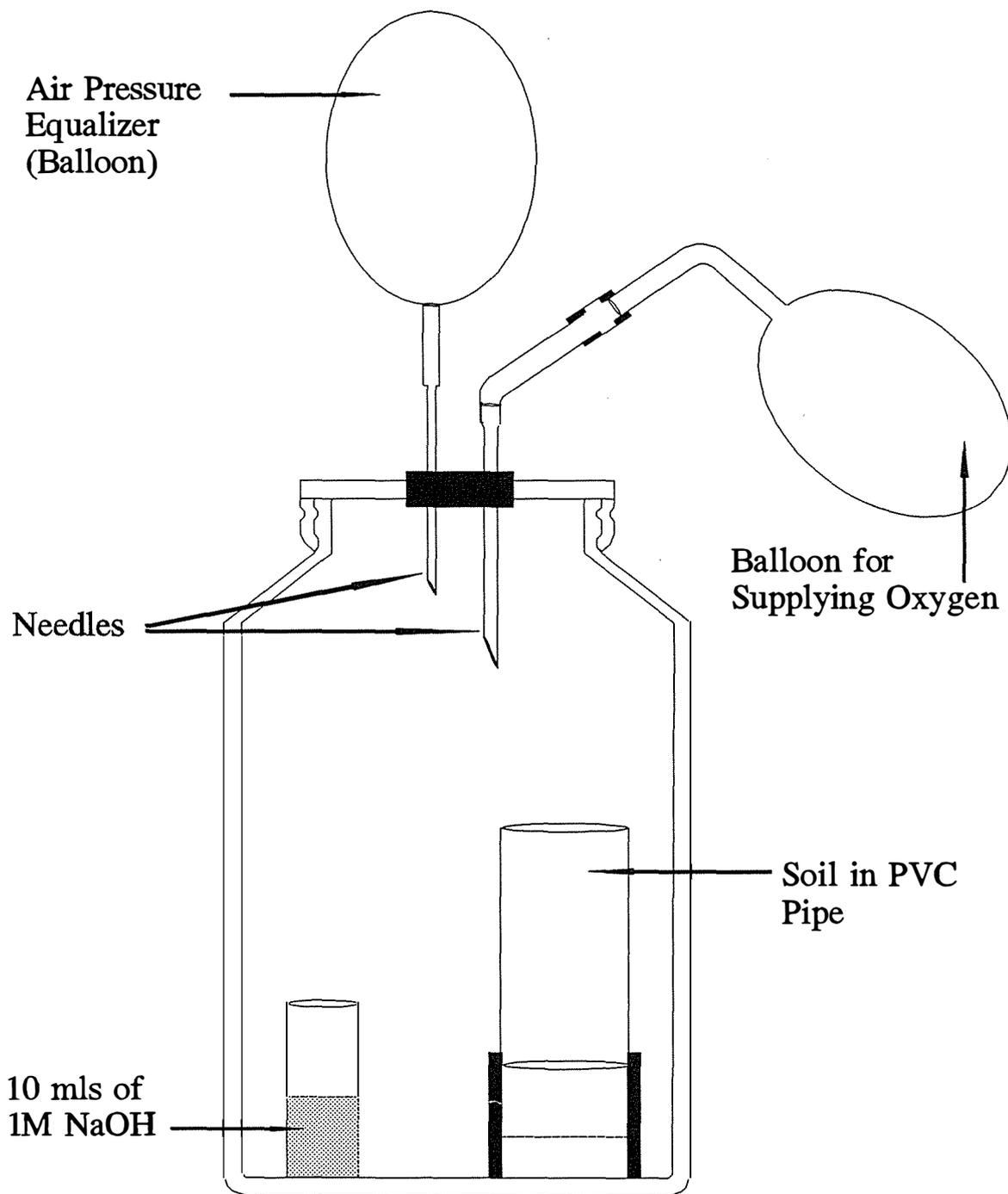
soils at the time of sampling are given in Table 3.2. The field moist soils were sieved to pass through a 2 mm sieve and stored at 4°C until required.

### 3.2.2 Incubation Techniques

Soil (25g oven dried) was placed in a 120mm length PVC pipe with an inner diameter of 22 mm that was covered at the bottom with a fine nylon mesh of size (200  $\mu\text{m}$ ). Triplicate soil columns were established for each of the eight surface soils. The soil moisture content was adjusted to 75% of the laboratory determined field capacity (Table 3.2). Soils were incubated under aerobic conditions in 1 litre preserving jars using the technique developed by Ruz (Ruz *et al.*, 1988). The incubation system is illustrated in Fig.3.1. The carbon dioxide ( $\text{CO}_2$ ) respired was absorbed in 10 mls of 1M NaOH kept in a small vial inside the jar. An air pressure equalizer in the form of a balloon was connected to the jar. When the balloon collapsed due to the consumption of oxygen ( $\text{O}_2$ ) by soil micro-organisms,  $\text{O}_2$  was supplied from outside until the balloon reinflated. The preparation of soil columns and the incubation conditions were the same for both 'open' and 'closed' systems. The incubation was continued for 140 days at a temperature of 18-20°C.

### 3.2.3 Leaching Procedures

After packing the soil columns and before incubation, the soil columns used for the 'open system' were leached with 0.01M KCl at a soil:solution ratio of 1:5 to remove inorganic nitrate( $\text{NO}_3^-$ ), ammonium( $\text{NH}_4^+$ ) and sulphate( $\text{SO}_4^{=}$ ) from soil solution. During the 140 day incubation these columns were leached at 14 day intervals with 0.01M KCl, at a soil:solution ratio of 1:5, and the concentration of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{=}$  in the leachate measured. After each leaching excess water was removed from soil cores by vacuum filtering by placing the cores on filter paper suspended on a sintered glass filter. A neutral solution, 0.01M KCl was preferred over a low pH solution of 0.15%  $\text{CaCl}_2$  which has been used by other workers (Barrow, 1961a; Maynard *et al.*, 1983). For the last two leaching events the soil columns had compacted and leaching took upto 1 day for some cores.

**Fig.3.1 Incubation System Used in the Experiment**

**Table 3.2 Physical and chemical characteristics of surface soils taken from low (LS) and medium (MS) slopes in each of the four farmlets before incubation.**

Farmlet	pH	Field capacity (%)	Bulk Density (Mg m <sup>-3</sup> )	Total soil			C:N	C:S	N:S	Extractable		
				C	N	S				NO <sub>3</sub> <sup>-</sup> N	NH <sub>4</sub> <sup>-</sup> N	SO <sub>4</sub> -S
				%						mg kg <sup>-1</sup> soil		
HF-LS	5.9	38.6	0.84	6.3	0.62	0.081	10.0	77	7.7	110	21.8	25.3
HN-LS	5.7	28.2	0.84	5.9	0.58	0.070	10.0	84	8.3	80	16.3	20.5
LF-LS	5.6	35.7	0.82	6.1	0.65	0.079	9.3	77	8.2	84	18.3	21.5
LN-LS	5.7	29.0	0.82	5.8	0.55	0.078	10.5	74	7.1	54	18	17.2
Mean				6.03	0.60	0.077	9.95	78	7.8	82	18.6	21.1
HF-MS	6.0	43.3	0.88	5.4	0.49	0.067	11.0	81	7.3	78	22.6	22.0
HN-MS	5.9	39.1	0.88	5.6	0.51	0.057	11.0	98	8.9	68	12.6	16.7
LF-MS	5.8	48.6	0.85	4.1	0.35	0.045	11.8	92	7.6	2.3	11.9	13.3
LN-MS	5.8	44.4	0.85	4.8	0.37	0.050	13.0	76	7.4	0.5	12.7	11.2
Mean				5.00	0.43	0.055	11.7	87	7.8	37	15.0	15.8
L.S.D <sub>&lt;0.01</sub>				0.22	0.01	0.001				4.0	1.0	1.0

The use of 0.01M KCl also avoids the potential precipitation of calcium sulphate that can occur with 0.15% CaCl<sub>2</sub> (Tabatabai and Al-Khafaji, 1980). In the closed incubation system the soil columns were not leached prior to and during incubation.

### 3.2.4 Analytical Measurements

The soil pH was measured with a soil:solution (water and 0.01M KCl) ratio of 1:2.5 using a glass electrode. The difference in pH values between water and 0.01M KCl were very small (<0.01 pH unit); values reported were obtained with water. Soil pH measurements were made at the start and at the end of the incubation study.

The total S in the soil was determined by the method of Steinberg *et al.* (1962). The SO<sub>4</sub><sup>=</sup> formed was reduced with hydriodic acid mixture to hydrogen sulphide which was determined colorimetrically using a methylene blue finish (Johnson and Ulrich, 1959). Organic ester-S (HI-reducible S) in the soil was determined by the method of Freney *et al.* (1969). The difference between the ester-S and the initial calcium phosphate extractable SO<sub>4</sub><sup>=</sup> value was equal to organic ester-S. The C-bonded S was determined by the difference between the total organic S and the organic ester-S.

The total soil N was determined by Kjeldahl digestion and the NH<sub>4</sub><sup>+</sup> formed was measured using a Technicon Auto Analyzer (Technicon, 1976).

Pre- and post- incubation extractable NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were determined by extracting the soil with 2M KCl at a soil:solution ratio of 1:10 for 1h; the NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> concentrations in the extract were measured by the methods of Downes (1978) and Technicon (1976) using a Technicon auto analyzer.

Pre- and post- incubation extractable SO<sub>4</sub><sup>=</sup> contents of soil were determined by extracting soils with 0.04M Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> (Searle, 1979), and SO<sub>4</sub><sup>=</sup> concentrations in the extract were measured as above. The total soil carbon was measured using a Leco induction furnace.

The total S in the 0.01M KCl leachate from the open system was measured by evaporating 50 mls of solution to dryness and digesting with sodium hypobromide (Landers *et al.*, 1983). The SO<sub>4</sub><sup>=</sup> in the digest was determined as above. The difference between the total S and the SO<sub>4</sub><sup>=</sup> S was attributed to C-bonded S.

### 3.2.5 Presentation of Results

The net mineralization of C, N and S and change in HI-reducible S for the 140 day incubation period was calculated as follows for the open system

**Carbon:** The amounts of CO<sub>2</sub> released during 140 days of incubation.

**Sulphur:** The amounts of S leached from soils during the 140 days of incubation, plus the difference between the amounts of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>-extractable S (post and prior to incubation).

Mineralized S (mg kg<sup>-1</sup> soil) = Amount of S leached + extractable SO<sub>4</sub> (Final - Initial)

**Nitrogen:** Same as S.

**Ester sulphate-S:** The difference between the ester sulphur (HI-reducible S) before and after incubation.

Since the soils were not periodically leached in the closed system, the net mineralization of S and N was calculated as the difference between initial and final extractable soil S and N. For mineralized C and ester sulphur (HI-reducible S) the measurements were same as the open system.

Data representing total soil C, N and S, soil SO<sub>4</sub><sup>-</sup> and mineral N, the net mineralization of C, N and S and the decrease in HI-reducible S were subjected to analysis of variance to determine the simple and interactive effects of fertilizer history and land slope. Least significance differences were calculated to compare treatment effects.

## 3.3 RESULTS AND DISCUSSION

### 3.3.1 Characteristics of the Soils Prior to Incubation

In all four farmlets, soils from low slopes contained more C, N and S than that of medium slopes (Table 3.2), even though both slopes within each farmlet had received the same amount of S, as calcium sulphate in SSP for the preceding 13 years (Table 3.1). In addition to containing greater amounts of soil C, N and S, the C/N and C/S

ratios of low slopes were lower than those of medium slopes. These trends in soil nutrient content and ratios are due in part to the proportionately greater amounts of dung and urine returned to areas of low slopes (0-12°) (Gillingham and During, 1973; Gillingham, 1978) and to the fact that the C:nutrient ratio of excreta is narrower than the consumed pasture (Boswell, 1983) and plant litter returns.

Soils from low slopes contained more extractable  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  than the medium slopes (Table 3.2). This was particularly marked for  $\text{NO}_3^-$  in LF and LN farmlets where the soil  $\text{NO}_3^-$  concentrations of the low slopes were 84 and 54  $\text{mg kg}^{-1}$  soil, while in the medium slopes they were only 2.3 and 0.5  $\text{mg kg}^{-1}$  soil, respectively. Differences in inorganic S levels between the HF and LF farmlets were greater on medium than low slopes. On low slopes the amount of soil S accumulation resulted from both fertilizer S inputs and an above average return of excretal S per unit area. Accumulation of soil S on the medium slopes, where excretal return of S is less than S consumed by the grazing animal, is dependent primarily on S inputs from fertilizer (Saggar *et al.*, 1990a). Both HI-reducible S and C-bonded S were present in greater amounts in soils of the low slopes (Table 3.3) again reflecting the above average excretal return rates to these land units. The observed increase in soil HI-reducible S in soils of low slopes could be caused by ester formation due to short term excesses of soil  $\text{SO}_4^{=}$  mainly originating from dung and urine deposition, in which approximately 3-21% and 82-100% of total S respectively, is  $\text{SO}_4^{=}$  (Nguyen and Goh, 1990). Added  $\text{SO}_4^{=}$  can be incorporated into both the HI-reducible S and C-bonded S fractions (Freney *et al.*, 1971; 1975; Schindler *et al.*, 1986), with more entering the HI-reducible S fraction when C:S ratios of microbial substrate are narrow (Ghani *et al.*, 1988). In the long term however, most added  $\text{SO}_4^{=}$  is incorporated in to C-bonded S fractions (Donald and Williams, 1954).

**Table 3.3 Amounts of HI-reducible and C-bonded S before and after incubation in the open system for soils taken from four farmlets.**

Farmlet	HI-reducible S			C-bonded S*		
	Initial	Final	Decrease	Initial	Final	Decrease
	mg S kg <sup>-1</sup> soil					
HF-LS	146	107	39	638	638	nil
HN-LS	100	80	20	579	570	9
LF-LS	144	113	31	625	617	8
LN-LS	118	95	23	644	632	12
Mean**	127	99	31.2			
HF-MS	91	84	7	557	545	12
HN-MS	77	56	21	476	460	16
LF-MS	64	47	5	372	369	3
LN-MS	59	95	12	429	419	10
Mean**	73	62	15.3			
L.S.D p<0.01	5.5	2.8	4.9			

\* L.S.D was not calculated because the values were the difference between the total and the HI-reducible S.

\*\* Significance at p<0.01 for land slope.

### 3.3.2 Effect of Incubation System on Organic Matter Mineralization

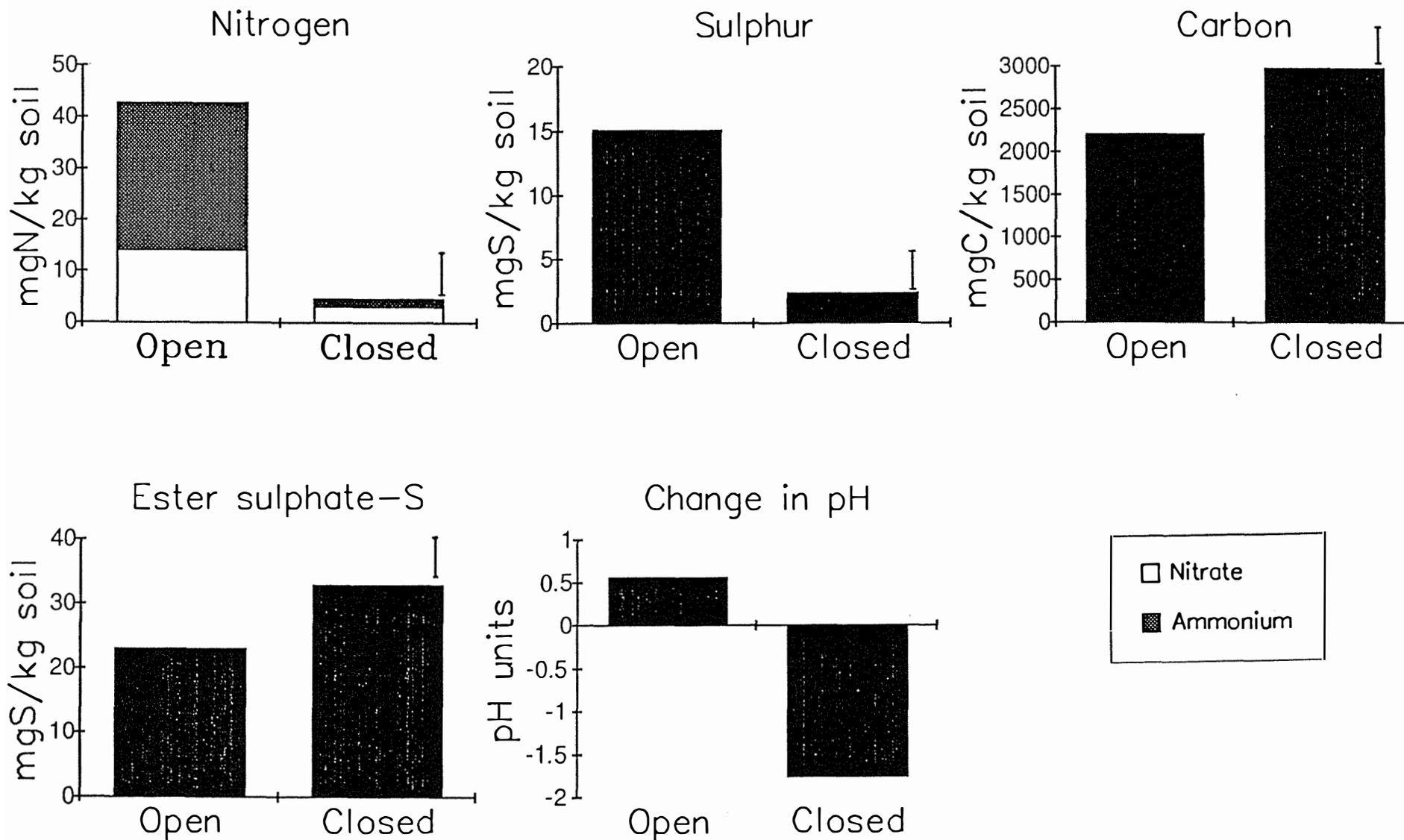
Four main differences in the amounts of C, N and S net mineralized in the eight soils were found between the open and closed incubation systems. The results discussed in this section are the means of 24 soil cores, comprising 3 replicates of each soil for each incubation system.

Firstly, the amount of S and N net mineralized were greater in the open than in the closed system (Fig.3.2). Either less S and N were mineralized in the closed system or because the S and N mineralized were not removed by leaching they were reimmobilized by microorganisms.

The latter explanation is probably correct because more CO<sub>2</sub> was evolved from the closed system indicating greater microbial activity. In a similar incubation study of Canadian Prairie soils Maynard *et al.* (1983) also found more S and N net mineralized in open than in closed systems.

Secondly in the open system more NH<sub>4</sub><sup>+</sup> was net mineralized than NO<sub>3</sub><sup>-</sup> while in the closed system the reverse occurred (Fig.3.2). The apparent lack of nitrification in the open system can be explained by either a limited supply of O<sub>2</sub> or an elevated chloride concentration during the biweekly leaching. Both inhibit the activity of nitrifying bacteria (Darrah *et al.*, 1985). As little as 11 μmoles Cl<sup>-</sup> g<sup>-1</sup> soil inhibits the nitrification process (Darrah *et al.*, 1985). Concentrations of upto 8 umoles g<sup>-1</sup> soil of Cl<sup>-</sup> would have been found in the columns during the leaching process. The formation of NH<sub>4</sub><sup>+</sup> can also be explained in part by the relatively coarse soil aggregates containing soil organic matter that are formed in the pasture soils. It is possible that mineralization occurs rapidly within these particles and micro regions of anaerobicity are created resulting in the accumulation of NH<sub>4</sub><sup>+</sup> (Swift, 1977). All of the above factors may be responsible for the apparent slow rate of nitrification observed in the study. Associated with the build up in NH<sub>4</sub><sup>+</sup> in the open incubation system was an increase in the pH while in the closed system the pH decreased (Fig.3.2). These pH changes are expected considering that

Fig.3.2 Effect of incubation system on the net-mineralization of S, N and C, change in HI-reducible S and pH during 140 days of incubation in soils from all four farmlets (see Table 3.1 for full description of symbols). Vertical bars=L S D, $p < 0.01$ .



ammonification generates net  $\text{OH}^-$  ions and ammonification and nitrification generates net  $\text{H}^+$  ions (Bolan *et al.*, 1991).

Thirdly more C was released in the closed than open system despite the fact that net mineralization of S and N was less in the closed system. The  $\text{CO}_2$  evolved was consistently greater in the closed system (data not shown) than in the open system throughout the incubation period of 140 days. As discussed earlier, either higher chloride levels or lower  $\text{O}_2$  concentrations in the open system may have caused reduced microbial activity. Alternatively, while recently mineralized S and N in the open system was removed by biweekly leaching, in the closed system mineralized S and N remained available for additional microbial growth and subsequently more  $\text{CO}_2$  was released. In both open and closed systems the  $\text{CO}_2$  evolution peaked between day 70 and 100 and then it decreased. The incubation was stopped at 140 days because increases in column packing density caused water to pond for approximately 1 day before leaching through the open system. This was seen as an undesirable change and the experiment was terminated.

Finally, the decrease in ester sulphur (HI-reducible S) was greater in closed than in the open system. This again reflects a greater rate of mineralization of S in the closed incubation system. This associated with the greater  $\text{CO}_2$  release in the closed system, supports the view that more organic S was turned over (mineralized and reimmobilized) in the closed system.

### **3.3.3 Mineralization Measured Using the Open Incubation System**

Although there was more microbial activity in the closed system mineralization was more easily quantified in the open system because the accumulated net mineralization of S and N can be measured in the open system. The remaining discussion concentrates on the open incubation system. During the 140 days incubation period, 11 to 25 mg S  $\text{kg}^{-1}$  soil (2 to 3% of the total organic S) and 25 to 65 mg N  $\text{kg}^{-1}$  soil (1% of the total organic N) were mineralized in the open incubation system (Table 3.4). The total amounts of soil

**Table 3.4 Net mineralization of carbon, nitrogen and sulphur and the change in pH for 140 days of incubation for the soils taken from four farmlets (mg kg<sup>-1</sup> soil).**

Farmlet	Sum of amounts in 0.01M KCl leachates*			Amount extracted post incubation			Net mineralization during incubation			C/N	C/S	Final pH	Increase in pH
	NO <sub>3</sub> -N	NH <sub>4</sub> -N	SO <sub>4</sub> -S	NO <sub>3</sub> -N	NH <sub>4</sub> -N	SO <sub>4</sub> -S	N	S	C				
HF-LS	139	19	29	19	5.0	21.7	50	25.2	2355	47	93	6.4	0.5
HN-LS	56	54	17	20	2.4	14.8	37	15.3	1768	48	116	6.5	0.8
LF-LS	82	62	20	21	2.2	19.4	65	18.1	2264	35	125	6.3	0.7
LN-LS	41	59	20	22	2.2	13.6	51	16.0	2138	42	134	6.2	0.5
Mean	80	49	21	21	2.9	17.4	51	17.7	2131				
HF-MS	93	21	27	18	5.9	13.7	38	18.3	2493	66	136	6.3	0.3
HN-MS	46	46	16	11	2.0	13.2	25	12.2	1826	72	150	6.6	0.7
LS-MS	8	27	16	6	2.7	10.0	29	12.4	2593	89	209	6.5	0.7
LN-MS	6	47	13	2	2.2	10.0	28	11.1	2401	85	216	6.2	0.4
Mean	38	35	18	9	3.2	11.1	30	12.6	2328				
L.S.D**	1.1	1.6	1.23	0.86	0	1.1	5.0	1.0	15.6				

\* Amount of mineral N and SO<sub>4</sub>-S leached before incubation was included, \*\* Significance at p<0.01

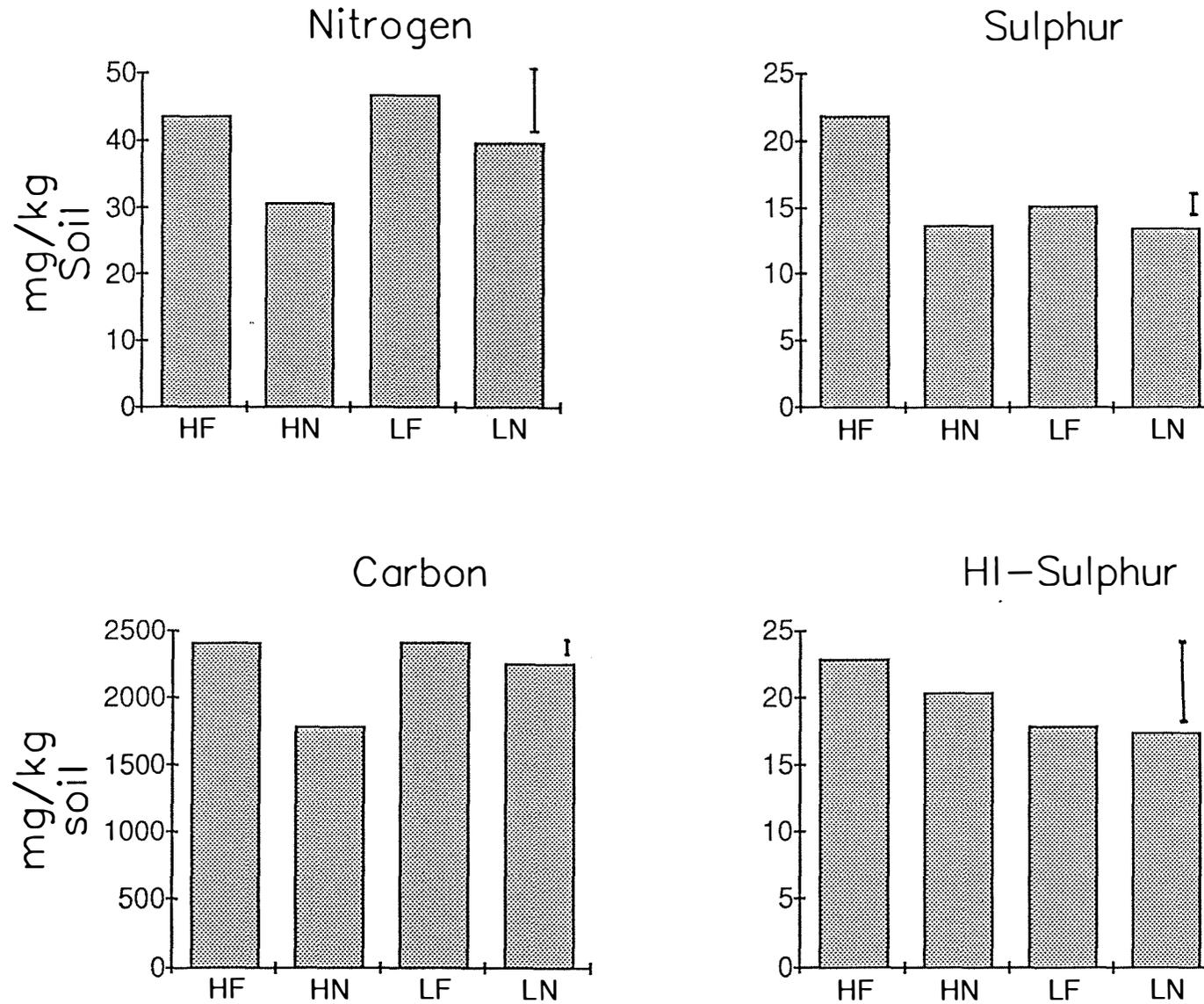
carbon released varied from 1768 to 2593 mg C kg<sup>-1</sup> soil. This constitutes 3 to 6% of the total soil organic C (Table 3.4). The amounts of N and S mineralized were much lower than those estimated by multiplying the amount of respired C by both C/N and C/S ratios of the total soil organic matter. Unlike mineralized C (CO<sub>2</sub>), the N and S mineralized (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>-</sup>) are not lost from the soil in gaseous forms and therefore remain susceptible to immediate reimmobilization by soil microorganisms.

The HI-reducible S content of the soil had decreased by the end of the incubation period by 5 to 39 mg kg<sup>-1</sup> soil (Table 3.3). Thus a significant amount of this S fraction was mineralized during the incubation period. Other studies (Frey *et al.*, 1971; Goh and Tsuji, 1979; McLaren *et al.*, 1985; Ghani *et al.*, 1988) have shown that the HI-reducible S fraction is an active pool, at least in short term S cycles. In contrast the net decreases in the larger C-bonded S fraction were much smaller (Table 3.3), indicating that, of the ester-S that was mineralized most was reimmobilized into the C-bonded S fraction.

### 3.3.4 Fertilizer History

The amounts of S mineralized were greater in soils from two farmlets (HF and LF) that had continuously received SSP for the preceding thirteen years (Fig.3.3) indicating that recently applied fertilizer contributes significantly to the readily mineralizable soil organic S pool. Greater amounts of S mineralization are also associated with a narrower soil C/S ratio (Table 3.2). Barrow (1961a) has already reported that SSP application increased the mineralization of S in Australian soils by increasing the fraction of easily decomposable soil organic matter. The extent of N mineralization was similarly related to S mineralization (Table 3.4; Fig.3.3), even though the amount of N mineralized in all four farmlets would be indirectly influenced by fertilizer application (Fig.3.3). For example, SSP application increased the production of the legume component of the sward (Lambert *et al.*, 1990) which could increase the fixation of atmospheric nitrogen by root nodules. Thus more N accumulated in the soil organic matter and subsequently more nitrogen was mineralized. Similarly the soils from HF and LF farmlets respired more CO<sub>2</sub> than the HN and LN farmlets which is again probably an indirect effect of the application of SSP (Fig.3.3).

Fig.3.3 Effect of fertilizer application on the net mineralization of S, N and C and the decrease in HI-reducible S during 140 days of incubation in the open system for soils from all four farmlets (see Table 3.2 for full description of symbols). Vertical bars=L S D, $p<0.01$ .

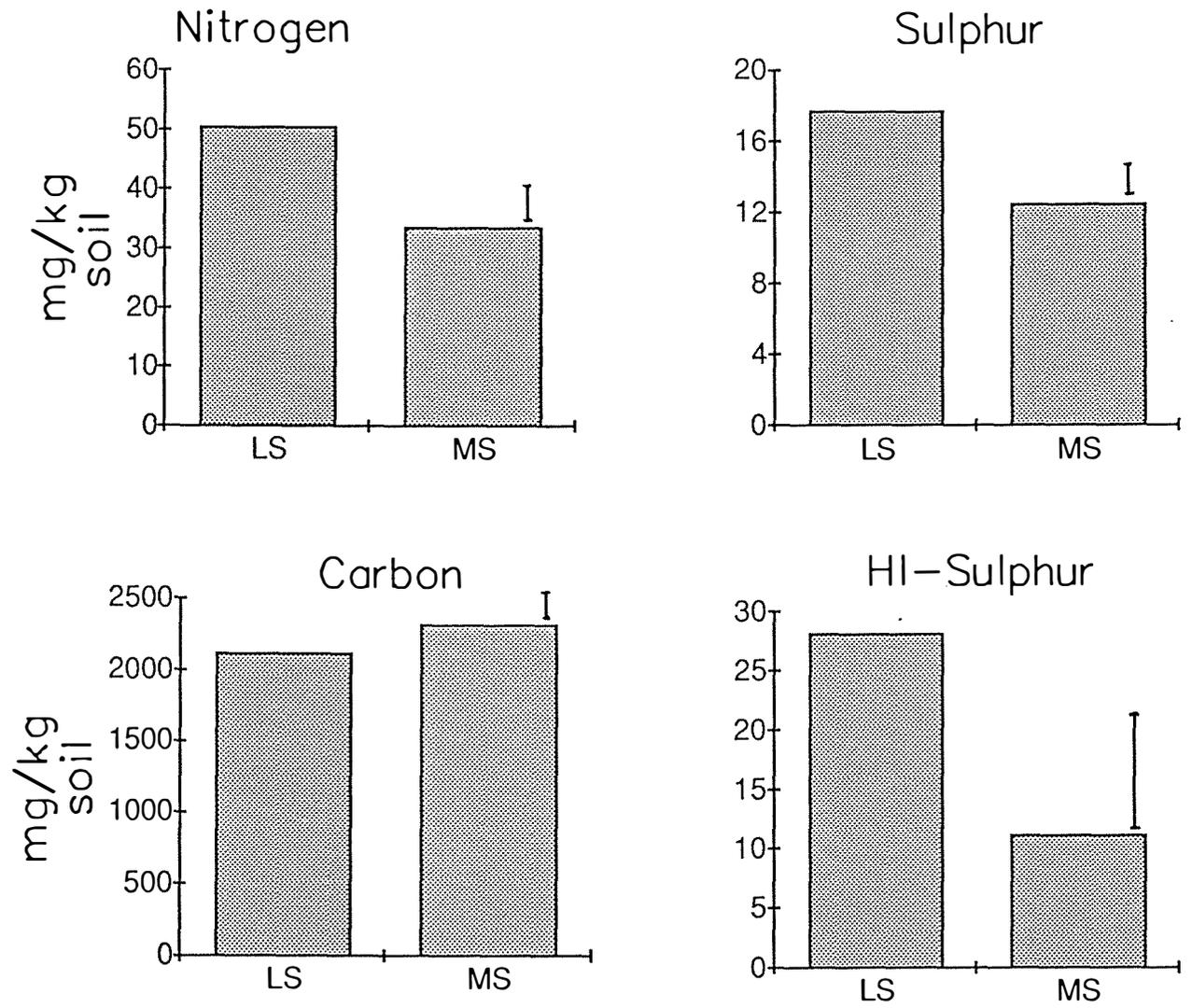


Even though fertilizer history influenced the accumulation of HI-reducible S, and considerable amounts of HI-reducible S were mineralized during the incubation, fertilizer history had no effect on the change in this fraction observed during the incubation (Fig.3.3). This might be due to rapid transformations of soil organic S, i.e. mineralization of HI-reducible S fraction and immobilization as carbon bonded S fractions during the incubation. Such transformations have been noted by other authors (Freney *et al.*, 1971;1975; McLaren and Swift, 1977; Maynard *et al.*, 1985; Nguyen and Goh, 1990).

### 3.3.5 Topography

The amounts of N and S mineralized were greater in soil samples taken from low slopes than medium slopes (Fig.3.4). In contrast the amounts of CO<sub>2</sub> evolved, an indicator of the microbial activity, was significantly greater in medium than low slope soils. The differences in the amounts of N and S mineralized can be explained, in part, by the differences in the C/N and C/S ratios of soil organic matter on the two slope classes if one assumes that mineralization is controlled by carbon availability and not N or S limitation. These were lower on low slopes (Table 3.2) indicating that the amounts of potentially mineralizable N and S in organic matter were greater in the soil from low slopes. This is due in part to the fact that more dung and urine were returned to the low slope areas through animal transfer (Saggar *et al.*, 1990a), and to the fact that the dung and urine have a narrower C:nutrient ratio than plant litter (Boswell, 1983). Infact Barrow (1961b) showed that the proportion of S mineralized from faeces is greater than proportion of S mineralized from plant material added directly to the soil. Higher C content of soils from medium slopes may lead to increased reimmobilization of mineralized N and S. Several authors (e.g. Saggar *et al.*, 1981b; Maynard *et al.*, 1985; McLaren *et al.*, 1985; Ghani *et al.*, 1988) have already shown that the addition of a C source increases the immobilization of soil solution sulphate. Evidence for greater SO<sub>4</sub><sup>=</sup> immobilization during the incubation of the medium slope soils is provided by the smaller net decrease in HI- reducible S per unit of CO<sub>2</sub> evolved from these soils.

Fig.3.4 Effect of land slope on the net mineralization of S, N and C and the decrease in HI-reducible S during 140 days of incubation in open system for soils from all four farmlets (see Table 3.2 for full description of symbols). Vertical bars=L S D,p<0.01.



### 3.3.6 Relationships between C, N and S mineralized

A positive relationship exists between the amounts of N and S net mineralized during incubation and the total soil N and S ( $r=0.739$  and  $r=0.775$ ) respectively (Fig.3.5a and 3.5b). This indicated that accumulation of N and S in soil organic matter and the narrowing of the C:N:S ratios by the addition of fertilizer and/or plant litter and animal excreta generally increased the mineralization of N and S. Some aspects of this phenomena are already presented in the literature e.g. an increase in total organic C and S contents increases the mineralization of S (Nelson, 1964), high organic matter content, particularly from soils with low C/N/S ratios increases the mineralization of S (Harward *et al.*, 1962; Haque and Walmsley, 1972; Bettany *et al.*, 1974; Kowalenko and Lowe, 1975) and the nature of organic N and S in the soil (Tabatabai and Al Khafaji, 1980).

From Figure 3.5c and 3.5d it becomes clear that the relationships between N and S net mineralized and the C/N and C/S ratios of the soils from different sites are curvilinear. For N, a simple relationship can be derived to show that the amount of N mineralized ( $N_{min}$ ; mgN kg<sup>-1</sup> soil) during the incubation can be related to the C/N ratio of the soil by the equation

$$N_{min} = C_t \left[ k \left( \frac{N}{C} \text{ soil} \right) - 0.4 \left( \frac{N}{C} \text{ mic} \right) \right]$$

where  $C_t = \text{CO}_2 \text{ evolved (mg kg}^{-1} \text{ soil)}/0.6$  (the calculated amount of soil carbon turned over,  $k$ , is a constant which determines the fraction of soil organic matter mineralized);  $(N/C_{soil})$  is the bulk soil N/C ratio, the constant 0.4 provides for the assumption that the microorganisms utilize only 40% of the carbon mineralized for growth, the remaining 60% is released as  $\text{CO}_2$  (Paul and Vanveen, 1978); and the  $(N/C_{mic})$  is the N/C ratio of the microbial biomass and is estimated to be 0.11 by assuming that biomass consists of 20% bacteria and 80% fungi (Shields *et al.*, 1974) and the C/N ratio in bacteria is on average 5 and in fungi is 10 (Follet *et al.*, 1981). This relationship is similar to the

Fig.3.5a Relationship between nitrogen mineralized and the total soil nitrogen during 140 days of incubation in open systems for soils from all four farmlets

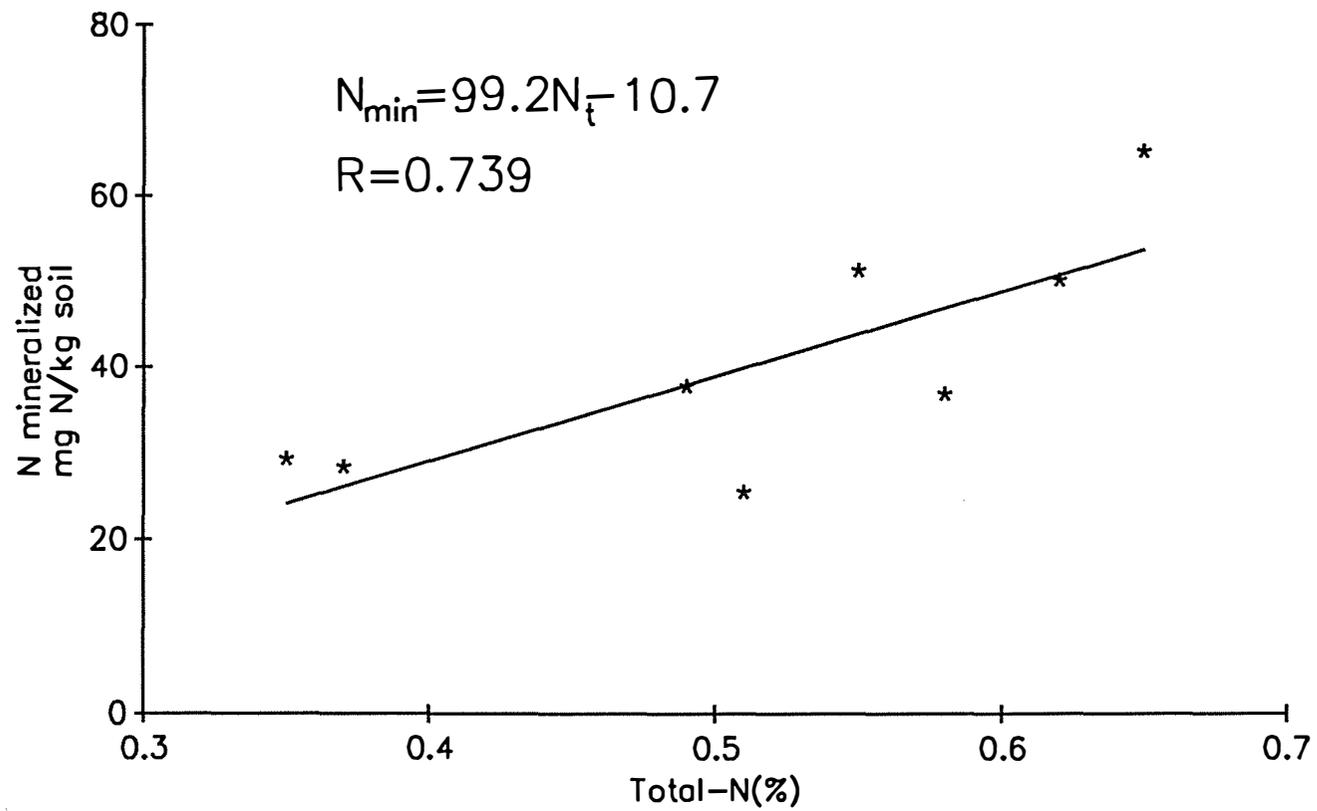


Fig.3.5b Relationship between sulphur mineralized and the total soil sulphur during 140 days of incubation in open system for soils from all four farmlets

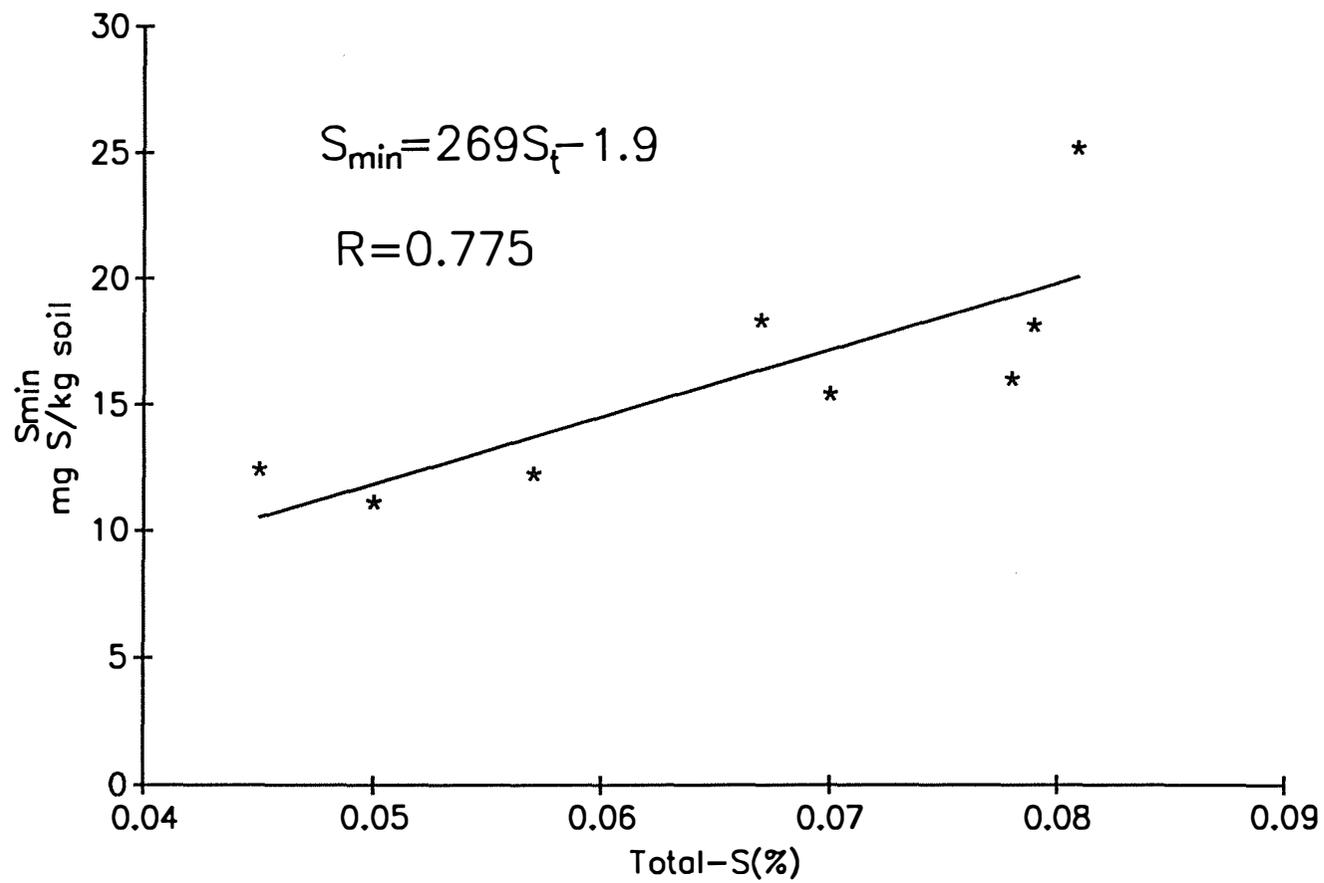


Fig.3.5c Relationship between nitrogen mineralized per unit of carbon turnover (mg N/mg C) and the soil N:C ratio during 140 days of incubation in open system for all four farmlets

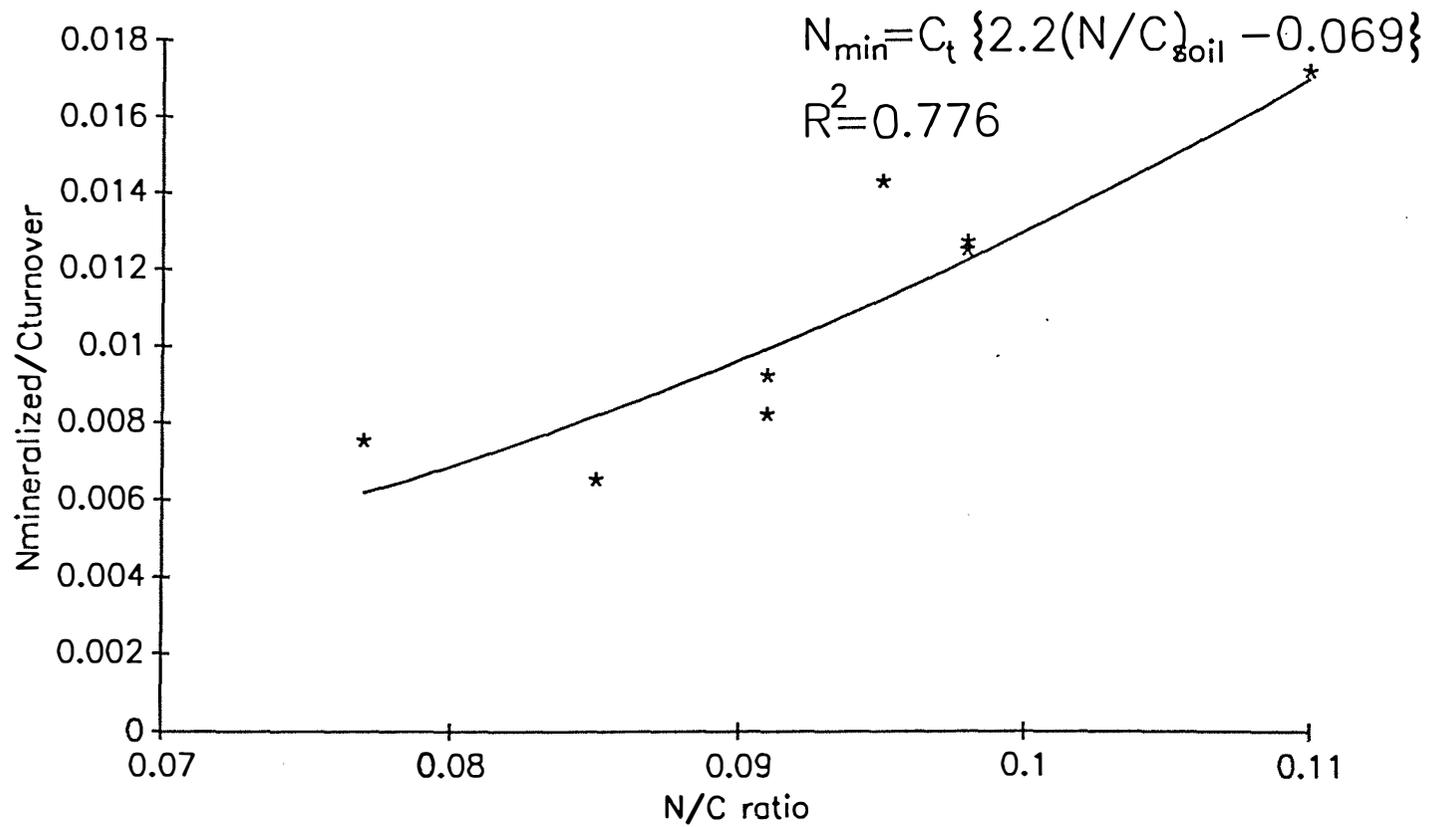
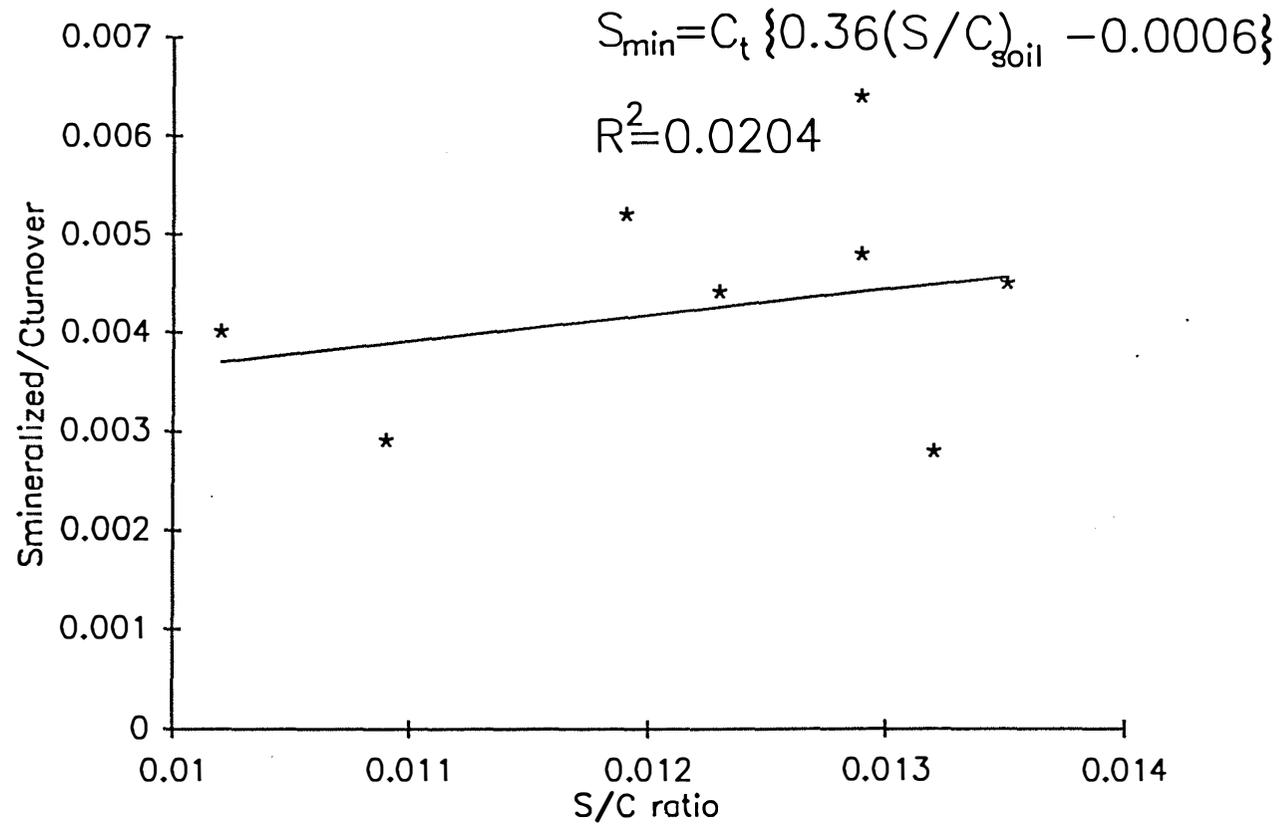


Fig.3.5d Relationship between sulphur mineralized per unit of carbon turnover (mg S/mg C) and the S:C ratio during 140 days of incubation in open system for soils from all four farmlets



relationship used by Fenchel and Blackburn (1979) and modified by White (1980) to describe phosphorus mineralization.

The curvilinear relationship provides a good explanation ( $r^2=0.766$ ) of N mineralization (Fig.3.5c) in the different soil samples. When constrained by the assumptions listed above, the relationship indicates that the mean N/C ratio of soil organic matter mineralized is approximately 2.23 times ( $k=2.23$ ) the bulk soil N/C ratio.

A similar relationship, derived to explain the observed S mineralization gave a poor explanation ( $r^2=0.0204$ ) of the amount of S net mineralized, using the S/C ratios of the soil samples and a value of 0.014 for the S/C ratio in microbial microorganisms derived from Chapman (1987). The reason for this could be that some soil organic S is mineralized irrespective of the soil microbial biomass demand for C. M<sup>c</sup>Gill and Cole (1981) suggested that the rate and extent of S mineralization is less related to C mineralization than N mineralization because S is also released from soil organic matter by biochemical processes which can be envisaged as extracellular enzymatic hydrolysis of organic ester sulphate (HI-reducible S). In support of this, it was shown that a substantial decrease (8-26%) in the HI-reducible S occurred during this incubation study (Table 3.3).

The ratios of CO<sub>2</sub>-C evolved to N or S mineralized (35-89 and 93-216 respectively) were greater than the total soil C:N and C:S ratios (9.3-13.0 and 74-92 respectively) of the eight soils. Either the C/N and C/S ratios of the readily mineralizable fraction of the soil are greater than that of the bulk soil organic matter or a significant fraction of the N and S mineralized was immediately reimmobilized as suggested earlier.

The ratio of N:S (2.0-3.6) mineralized was lower than that of the bulk soil organic matter (7.1-8.9) suggesting again that soil organic N and S are mineralized at different rates as noted by Kowalenko and Lowe (1975), or, relatively more N may be reimmobilized while more S remains in the soil solution. Ball *et al.* (1982) have already suggested that these hill country soils are N deficient with both plants and

micro-organisms strongly competing for mineral N supply. The results of this study support this view and suggest that relative to S, N conservation is greater.

### 3.4 GENERAL DISCUSSION AND CONCLUSION

The results from this study have shown that the open incubation system with periodical leaching of the soil during incubation offers an approach that simulates the removal of S and N by plants and leaching losses of these two nutrients under field conditions. In the closed incubation system mineralization can be greater but is not measurable because mineralized S and N are subjected to reimmobilization. The closed incubation system cannot be used to measure the accumulated net mineralization of S and N without the use of isotopic tracers of these nutrients. Carbon dioxide evolved alone overestimate the potentially mineralized S and N pool, because for a given substrate of constant C to nutrient ratio the S and N not removed by leaching are available for reimmobilization by microbial activity.

The study further showed that the rate of application of S and P fertilizer and the continuity of application to legume based hill pasture and the land slope had a large influence on the accumulation of N and S in soil organic matter and the amounts of readily plant available (extractable) mineral N and  $\text{SO}_4\text{-S}$ . In continuously fertilized soils, organic matter had narrower C/N and C/S ratios than discontinuously fertilized soils. The amounts of ester-S (HI-reducible S) and the fraction of the soil organic matter that was ester S also increased under continuous fertilizer application.

Continuously fertilized soils mineralized more S and N to readily available forms than soils from farmlets which had not received fertilizer in recent years. Most of the mineralized S was derived from the HI-reducible S fraction of the soil organic matter but some of the mineralized S were immobilized into the C-bonded S fraction of the soil organic matter. The ratio of N to S mineralized was low when compared to the N to S ratio of the soil organic matter. This suggested that N is conserved while S is readily released to the soil solution and mineralized S may be more relatively susceptible to leaching than mineralized N in these hill country pastures.

There were greater accumulations of S and N in soil organic matter on low slopes than on medium slopes and mineralization of S and N were greater in soils taken from low slopes when compared to medium slopes. This result was associated with the narrower C to N and C to S ratios in the soils from low slopes. The narrower C:N and C:S ratios of soils taken from low slopes mainly results from the greater deposition of dung and urine on the low slopes. These results and others reported by Barrow (1961b) support the conclusion that inputs of S through both fertilizer and excreta will increase the amount and mineralization potential of organic N and S in legume based pasture soils. In addition areas where more organic N and S accumulate (e.g. low slopes which are animal camping sites) are likely to be sites of increased N and S leaching.

These laboratory incubations clearly demonstrated that the potential of hill country soils to mineralize and perhaps leach S varies with the previous fertilizer history and land slope. The differences observed between different fertilizer histories and between different land slopes on mineralization potential are such that field studies should be undertaken to confirm that these differences are important under field conditions. The results from this laboratory incubation study will be important in deciding where to make S mineralization and leaching measurements in the field such that an accurate quantitative assesment of these process can be made. In order to measure mineralization under field conditions the losses of S and N by leaching and plant uptake should be measured. For measuring leaching losses appropriate techniques have to be developed, particularly for hill country pastures. The development of the technique will be examined in Chapter-4 and the field study on the mineralization of S and N will be examined in Chapter-5.2.

## CHAPTER-4

### DEVELOPMENT OF AN ION EXCHANGE RESIN TRAP LYSIMETER SYSTEM FOR MONITORING SULPHATE SULPHUR LOSSES BY LEACHING IN GRAZED HILL COUNTRY PASTURES.

#### 4.1 INTRODUCTION

Laboratory incubation studies carried out in Chapter-3 established that there was considerable variation in the capacity of hill country legume based pasture soils to mineralize organic S and N to plant available forms. This variation appeared to be dependent upon the previous fertilizer application rates and land slope which influences the extent of excreta return to soil from grazing animals. In general high pasture production under field conditions (Lambert *et al.*, 1988; Mackay *et al.*, 1988) was associated with soils which showed high mineralization levels in laboratory (Chapter 3). Under field conditions, however, the relationship between the extent of S mineralization and its quantitative fate to either plant uptake and/or leaching losses is poorly understood. Recent field studies (Saggar *et al.*, 1990a) indicated that the amount of S lost by leaching was the greatest from soils of low slopes which normally received the greatest amounts of S in excreta. It has subsequently been shown that these soils had high mineralization levels measured in laboratory incubations (Chapter 3). The study of Saggar *et al.* (1990a) did not identify the immediate origins of the leached S, although it is evident that as well as direct leaching of input sulphate (SSP and animal excreta) mineralized organic S was also a possible source of leached sulphate. Further field studies are therefore required to establish the contribution from each of these sources.

Mineralization studies conducted using incubation methods under controlled laboratory conditions cannot be extrapolated to explain the field situation, where the rate of mineralization can be changed by many factors such as variable soil temperatures, moisture contents, the availability of substrate, differences in soil structure and the rate of plant growth. Also the amount of sulphate formed in laboratory incubation studies depends on the type of incubation system and experimental conditions used (Chapter 3) (Maynard *et al.*, 1983).

In field studies both extractable soil sulphate and plant growth can be measured directly by taking soil samples and harvesting the plant. Sulphur leaching losses can be measured in various ways either directly or indirectly by balance studies. Smith *et al.* (1983) measured the leaching losses directly by measuring the sulphate in the drainage water collected from drained plots. Indirect balance methods are suitable for long-term (10 years) studies but are of little use for mineralization studies. Small lysimeters have been used to determine the leaching losses of nutrient anions such as S and N and cations such as Ca and Mg in low land soils (Steele *et al.*, 1984). The main draw back with lysimeter techniques is the necessity to collect and analyze large amounts of drainage water from a large number of replicated plots on a continuous basis. This difficulty could be overcome by the introduction of an ion exchange resin trap in to the lysimeter. This would reduce the number of samplings required for a particular period of time by trapping ionic nutrients from drainage water. Such a lysimeter system would be particularly useful for monitoring nutrient losses from remote hill country pasture.

The objective of the study reported in this Chapter was to design and test the efficiency of an ion exchange resin trap-lysimeter system to remove sulphate from drainage water using two undisturbed soil cores collected from low (LF) and high fertility (HF) farmlets at Ballantrae hill country research station. The net mineralization of S was also calculated by measuring the plant uptake and losses by leaching of S from soils of both farmlets over a 45 day period.

## **4.2 MATERIALS AND METHODS**

### **4.2.1 Construction of Lysimeters**

The lysimeters (Fig.4.1) were constructed by using 150mm diameter and 250mm long galvanized steel cylinders, 150mm diameter plastic plates, L-joints (20mm internal diameter), T-joints (25mm internal diameter) and 22mm internal diameter plastic pipes normally used to construct domestic waste water system (Hardie IPLEX, Palmerston North). A small hole (22mm diameter) was made near the edge of the plastic base

Fig.4.1 The Mini Lysimeter With Ion Exchange Resin Trap Used in the

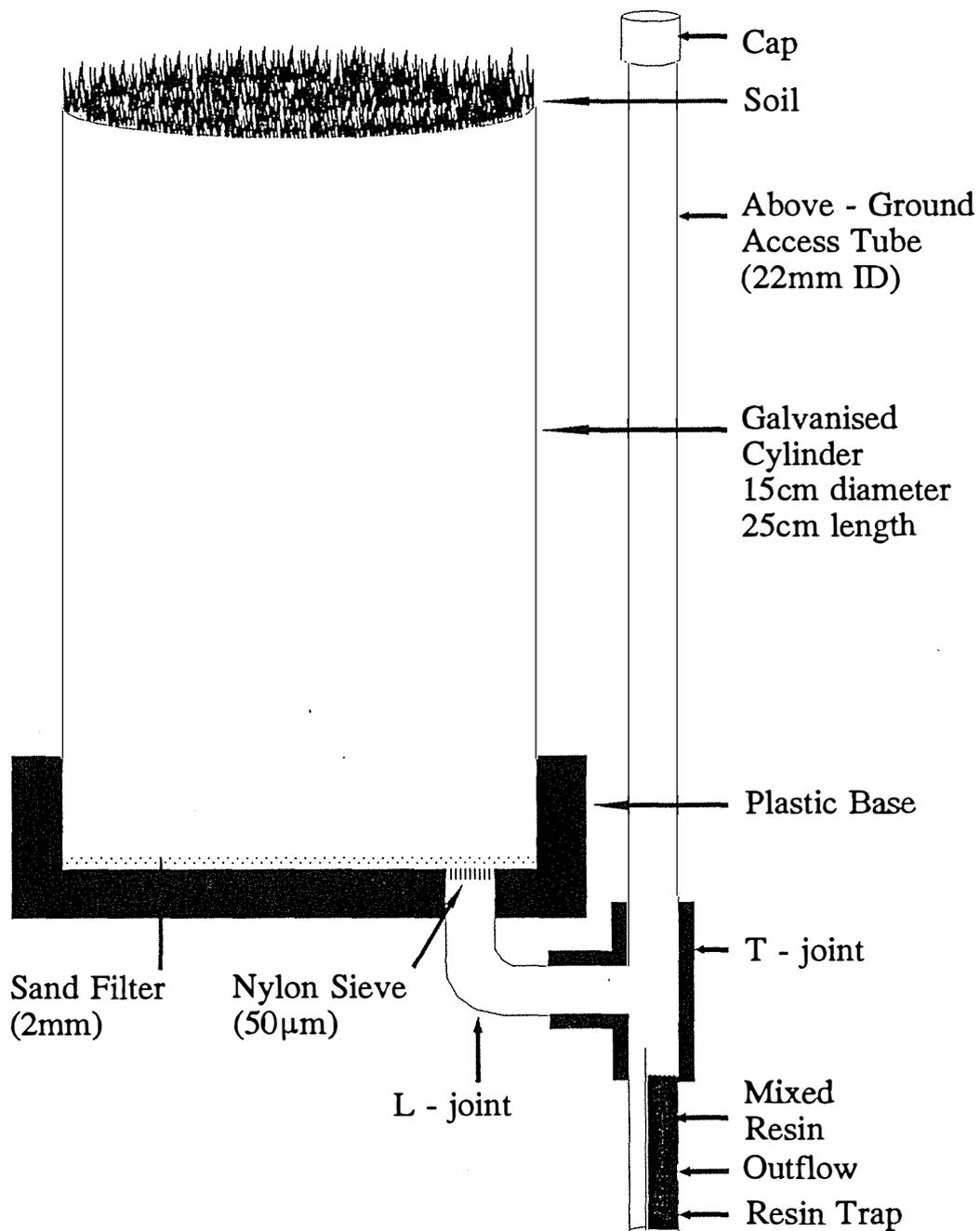


plate. The L-joint was glued in to the hole using a plastic glue (Novaki). While connecting the L-joint the pipe opening was covered with a fine nylon mesh ( $50\mu\text{m}$ ). The L-joint was again connected to the side arm of T-joint. This is connected to the resin trap which was 100mm long and an internal diameter of 22mm (Fig.4.1).

On 15 April, 1989 two galvanized steel cylinders were driven in to pasture soils on LF and HF low slope sites to a depth of 260mm (Ballantrae Hill Country Research Station, DSIR Grasslands) and then removed immediately. In order to minimise preferential flow of water, the soil surface with turf was kept 10mm above the cylinder height. Five soil cores were collected around each cylinder in the field, bulked in to two samples and used for sulphate determination. During the week before sampling 10mm of rainfall were recorded. Soil moisture content at the time of sampling for two sites is given in Table 4.2. A thin layer of sieved, acid (HCl) washed sand (1-2mm) was spread over the plastic base in order to act as a filter and allow free drainage and the soil cores were placed on plastic bases. The resin trap was divided into three compartments, the first for trapping sediments, the second for the anion exchange resin and the third for the cation exchange resin. In the preliminary laboratory experiment both anion and cation resin compartments were filled with anion exchange resin.

#### 4.2.2 Preparation of Anion Exchange Resin

The anion exchange resin used for trapping sulphate was 'Amberlite' resin IRA-400(Cl), a strongly basic anion exchanger. Its basic character is derived from quaternary ammonium groups. The density is  $710\text{g (wet) l}^{-1}$ . The exchange capacity of the resin is  $1.4\text{ meq ml}^{-1}$  wet resin, about 80 to 85% of the total exchange capacity can be utilized. Before filling the resin into the traps it was eluted (regenerated) with 1M HCl (1:10 ratio) for a minimum period of 5 hours to remove any background anions including sulphate present in the resin. The excess HCl was removed by washing several times with deionised water. The acid washed resin was eluted (regenerated) again with 1M NaCl to remove the excess  $\text{H}^+$  ions in the resin and washed with deionized water to remove the excess chloride and sodium. The

regenerated resin was always kept under water to keep it moist. About 20g of the regenerated resin was packed into each of the resin traps. The purpose of using an excess of resin was to provide a longer path length for drainage from the soil core at the highest flow rate to pass through the resin. Infact the resin compartment from which the effluent discharged out (the end compartment) was filled to capacity with the resin. The resin trap was constructed in such a way that all the drainage should pass through both the compartments in the resin trap. Another 20g of resin was used to prepare eluant NaCl solutions as standard blanks for subsequent sulphate analysis. After the leaching sulphate trapped by the resin was measured as described in section 4.3.2.

#### 4.2.3 Leaching

Both cores were leached with simulated rainfall using deionized water. The intensity of rainfall was calculated on the basis of rainfall records for the Ballantrae field farmlet from where the soil cores were collected and the lysimeters were installed (Chapter 5, 6 and 7). 99mm rainfall was recorded in one day in one single rainfall event at Ballantrae in 1988. Rainfall intensities around this value were chosen to test the efficiency of the resin trap to exchange anions at expected field drainage flow rates. The rates of flow used and their duration are shown in Table 4.1. The amount of simulated rainfall was calculated as follows:

Area of the soil core =  $176.8\text{cm}^2$

Total amount of rainfall for seven hours = 99mm

Rainfall per minute = 0.235mm

Amount of water added per minute = 4.17ml

A peristaltic pump was used to keep the flow rate constant throughout the leaching period which was seven hours for each leaching event. Effluent from the resin trap was collected in aliquot of 100ml for each core. After leaching the cores were left overnight in order to drain. The weight of the cores before and after leaching was measured in order to calculate the amount of water each core retained. The resin was removed from the resin traps and were eluted with 50ml of 1M NaCl. The concentration of sulphate in the NaCl eluate was measured by reducing the sulphate to  $\text{H}_2\text{S}$  using HI-reducing mixture and reacting the  $\text{H}_2\text{S}$  with bismuth nitrate to produce bismuth sulphide which was determined turbidimetrically using an auto analyzer

(CSIRO Division of Forest Research, Method No. PS17). Five leachings were carried out over a period of 45 days. The same procedure was used at each leaching event.

#### **4.2.4 Herbage and Soil Analysis**

Herbage was harvested twice during the experiment, first 15 days after starting the experiment and the second at the end of the experiment. Herbage was dried and weighed. A subsample of the dried, ground herbage was used to measure the S content. Herbage S content was measured after digesting the herbage using NaOBr (Tabatabai and Chae, 1982) and was diluted with 28ml of water and 2ml of formic acid. The sulphate formed was measured as mentioned above.

The initial extractable soil sulphate levels in samples of field soils were determined separately for the 0-75, 75-150 and 150-250mm soil depths as mentioned in Chapter-3. The extractable soil sulphate levels were also determined for soil samples removed from lysimeters at the end of the experiment

### **4.3. RESULTS AND DISCUSSION**

#### **4.3.1 Sulphate Leaching**

During the first three leaching events only 14mm of the total of 99mm rainfall was retained by the soil. The remaining 85mm drained from the soil (Table 4.1). A longer drying period between leaching (12days) was given for the last two leaching events, this increased the time taken for drainage water to appear from 1 hour to 1 hour and 40 minutes and increased the amount of rainfall retained to 24mm. The weight of the cores after leaching were similar to the initial field weight of the soil core when the experiment was commenced demonstrating that each core drained freely throughout the experiment in a manner similar to field conditions. At the soil/sand boundary at the bottom of each core the soil is however expected to be wetter than under field conditions since little suction will influence this area of the core in the laboratory. The amount of rainfall applied and the drainage collected were almost equal (steady state) for six hours for each leaching event. This showed that soil did not block the sand filter at any one leaching event or with successive leachings. The

1M NaCl eluate of the resin neither contain any suspended particles nor coloured indicating that the sand filter and nylon sieve were effective in trapping organic matter and sediments.

A total of 3 and 20 kg S ha<sup>-1</sup> sulphate-S was recovered in the 1M NaCl eluates of the ion exchange resin when the soils from LF and HF cores, respectively were leached. No sulphate was detected in the effluent that had first passed through the resin traps, suggesting that the resin was effective in exchanging sulphate ions even at a rate of drainage of 4.2ml minute<sup>-1</sup> equivalent to a drainage flow of 85mm for approximately six hours. The total exchange capacity of the resin in the trap was 23.8 milli equivalent (for 20g of resin). Less than 0.7 (<3%) milli equivalent of exchange capacity was used to exchange sulphate ions.

The amount of sulphate leached in the final leaching event was considerably lower than the first leaching event for both cores (Table 4.1) even though both leaching events received the same amount of rainfall. This showed that the amount of sulphate leached is influenced by both rainfall and the amount of sulphate present in the soil. The amount of sulphate leached in the soil core collected from HF site was greater than the soil core collected from LF site in all five leaching events (Table 4.1). This result reflects the different fertilizer histories of the two farmlets (HF= 375kg SSP ha<sup>-1</sup> year<sup>-1</sup> for 14 years and LF= 125kg SSP ha<sup>-1</sup> year<sup>-1</sup> for 14 years) and reflects the greater leaching loss of S from the high fertility farmlet predicted by Saggari *et al.* (1990a).

The amount of sulphate-S in 0-75 and 75-150mm soil depths in the soil core from HF farmlet decreased while the sulphate S in 150-250mm depth remained largely unchanged. This showed that mineralization in the surface layers and movement to and adsorption of sulphate at lower depths (subsurface layers) are the most likely mechanisms of S movement in these soils. A similar mechanism was suggested by Chao *et al.* (1962). Even though there was an increase in soil sulphate level at the 150-250mm soil depth in the soil core from HF farmlet, the increase was very small in the soil core from LF farmlet (Table 4.2).

#### **4.3.2 Drymatter Production and S Removed**

The herbage dry matter produced and the amount of S removed by herbage from the

**Table 4.1. Amount of net drainage collected and the amount of sulphate leached for soil cores collected from LF and HF sites (Leaching volume 4.2 ml/min, duration 7 hours/event, total applied 99 mm/event and for five events 495mm).**

Date of leaching	Drainage collected (mm)	Sulphate leached (mgS/core)	
		LF	HF
21-4-89	85.0	2.01	9.00
28-4-89	85.0	1.43	9.9
5-5-89	85.0	0.966	11.13
17-5-89	75.0	0.740	5.79
29-5-89	75.0	0.63	1.72
<b>Total</b>	<b>405.0</b>	<b>5.8</b>	<b>37.5</b>

**Table 4.2 Initial and final sulphate present in the soil for three depths, S lost by leaching, S removed by plant and the net mineralization of S for the soils from HF and LF sites.**

Farmlet	Depth (cm)	Soil Moisture	Soil sulphate kg S ha <sup>-1</sup>		Plant Uptake <sup>3</sup>	Leaching loss <sup>3</sup>	*Net mineralization <sup>3</sup>
		g/g soil	Initial <sup>1</sup>	Final <sup>2</sup>	kg S ha <sup>-1</sup>		
HF	0-7.5	0.44	37.1	29.7	5.1	20.0	16.1
	7.5-15	0.35	22.1	17.7			
	15-25	0.30	41.5	44.3			
LF	0-7.5	0.45	8.9	8.4	1.5	3.0	3.4
	7.5-15	0.37	9.4	7.6			
	15-25	0.31	20.7	21.9			

\* Net mineralization= Final Sulphate- Initial sulphate+ Plant uptake+ Leaching losses

1 Results are mean of four replicates (duplicate for two field samples).

2 Results are mean of duplicate samples taken from soil cores after leaching.

3 Individual results from a single core.

soil core from the HF farmlet (2092 kg DM ha<sup>-1</sup> and 5.1 kg S ha<sup>-1</sup>) were almost four times greater than that from the soil core from the low fertility farmlet (500 kg DM ha<sup>-1</sup> and 1.5 kg S ha<sup>-1</sup>) reflecting the different fertility status of the two farmlets.

#### **4.3.3 Net Mineralization of Sulphur**

The net mineralization of S was calculated from the difference between the initial and final extractable sulphate in the soil plus the amount of sulphate lost by leaching and the amount of S removed by plant. Table 4.2 showed that five times more S was mineralized in the soil from high fertility farmlet (16.1 kg S ha<sup>-1</sup>) than in the soil from low fertility farmlet (3.4 kg S ha<sup>-1</sup>). Overall the extractable sulphate pool in each soil core decreased (9.0 and 1.1 kg S ha<sup>-1</sup> for HF and LF cores, respectively) but the major part of the losses from the sulphate pool, caused by plant uptake and leaching (25.1 and 4.5 kg S ha<sup>-1</sup> for HF and LF cores, respectively), were replaced by mineralization of S (16.1 and 3.4 kg S ha<sup>-1</sup> for HF and LF cores, respectively).

#### **4.4 GENERAL DISCUSSION AND CONCLUSION**

Under intense simulated rainfall, the simple mini-lysimeter technique employing an anion exchange resin trap was effective in trapping all sulphate that leached from two soil cores taken from sites with contrasting fertilizer histories. The technique offers a number of advantages over present methods of measuring S mineralization in laboratory incubations or in glasshouse and field studies. They are

1. The method measures directly the losses of S by leaching under realistic conditions. For example if lysimeters are placed in the field, leaching can be studied with natural soil structure and conditions of variable soil temperature, moisture, rainfall intensity and drainage.

2. Because undisturbed soil cores were used, the physical and chemical changes occurring in the core are similar to those occurring in field soil. For example the soil infiltration characteristics, adsorption-desorption characteristics and mineralization-immobilization characteristics are similar to field soils. There may however be a wetter zone at the 250mm soil depth (at the soil/sand interface, core base) than in the natural continuous soil profile.
3. There is no need to collect samples immediately after heavy rainfall if the system is used in the field as has been necessary in the past.
4. Leaching losses and plant uptake of S can be measured simultaneously without disturbing the soil structure and estimates of soil sulphate can be made in soil cores immediately around the lysimeter cores. This is not possible in mineralization studies conducted in laboratory and glasshouse.
5. The amount of S lost from a specified area by leaching can be measured accurately by trapping all the ions using the ion exchange resin. The variability in the amount of S leached in the field can be overcome by using replicated lysimeters. Preliminary studies on the spatial variability of S leaching would be required to determine the appropriate diameter of the lysimeter.
6. Since leaching studies are normally conducted during winter, lysimeters can be inserted during summer or autumn and turf allowed to regrow to minimize edge effects on cores.
7. By introducing cation exchange resin both cations and anions lost by leaching can also be measured in the field.

The large differences in the dry matter production, S uptake and leaching losses of S from soil cores taken from HF and LF sites indicated that field studies using lysimeters would be worthwhile to quantify the actual S budgets in the field. The above results and the S losses predicted by Saggar et al., (1990a) indicate that large differences in S leaching losses can be expected in the field on pastures with different fertilizer histories.

## CHAPTER-5

### FIELD INVESTIGATION OF THE NET MINERALIZATION OF SULPHUR AND NITROGEN, THEIR RELATIVE PLANT UPTAKE AND LEACHING LOSSES IN GRAZED HILL COUNTRY PASTURES

#### 5.1 INTRODUCTION

The mini-lysimeter with ion exchange resin trap developed in Chapter-4 proved an effective method for calculating the net mineralization of organic S in undisturbed soil cores by measuring insitu, both plant uptake and leaching losses of S. Although the study reported in Chapter-4 used unreplicated cores the results indicated that a greater mineralization of S from soil organic matter lead to greater amounts of plant S uptake and S leaching loss. The undisturbed soil cores taken from LF and HF field sites at Ballantrae lost 3 and 20 kg S ha<sup>-1</sup> by leaching, respectively. This difference between the cores in soil sulphate leaching losses was in the same order of S loss as that predicted from field sites (46 to 77% of the applied S) by the model developed by Saggar *et al.* (1990a).

The objective of the study reported in this Chapter was to place a number of lysimeters at Ballantrae field sites to measure directly the S leaching losses under field conditions and compare the results to the leaching losses of S predicted by Saggar *et al.*(1990a). The net mineralization of soil organic S and pasture uptake were also studied. By installing lysimeters at sites on different topographic units and contrasting fertilizer history, it was possible to examine the influence of previous fertilizer application, rate and land slope on these S transformations. In applying the technique to field conditions provisions were also made to monitor the leaching losses of N (both nitrate and ammonium) and other cations such as Ca, Mg, K, Fe and Al. The net mineralization of N and its uptake by pasture was also investigated because the primary purpose of SSP application is to increase legume growth and N fertility of the pasture. Increased N availability in soil increases the rate of S cycling by increasing plant biomass production (M<sup>c</sup>Gill and Cole, 1981) and therefore S requirements of the pasture increase (Gilbert and Robson, 1984).

## 5.2 MATERIALS AND METHODS

### 5.2.1 Field Site

The experiment was carried out at Ballantrae, the Hill Country Research Station of DSIR Grasslands, Palmerston North from which soil samples and cores were collected for the previous two studies. A detailed description of farmlets used for the study, their soils, pastures, animals, climate and experimental procedures were discussed in Chapter-3. The fertilizer history of the experimental farmlet was described in Chapter-3. The annual rainfall for the farmlet is approximately 1200 mm. Four experimental sites were selected in two of the four farmlets on the basis of contrasting fertilizer history and land slope. These four sites along with the percentage distribution are given in Table 5.1.

The farmlets are 10-ha each and are set stocked with sheep. The last fertilizer application before the start of the experiment was made in December 1988. Since 1983 the low fertility farmlet was set stocked at 10.3 SU ha<sup>-1</sup> (SU= Stock unit defined by Coop, 1965) and the high fertility farmlet was stocked at 16.1 SU ha<sup>-1</sup>. These had increased from a base of 6.0 SU ha<sup>-1</sup> in 1975 when annual fertilizer input commenced.

### 5.2.2 Lysimeter Installation

The experiment was started on 31-5-1989. The lysimeters used in this study were similar to those described in Chapter-4. The installation of lysimeters in the field is described below.

Eight galvanized steel cylinders (150mm diameter and 250mm length) were driven into field soils at each of the four sites. Cylinders of this diameter were chosen because of their successful use in field studies carried out by Williams *et al.* (1990). After pushing the cylinders into the soils to a depth of 250mm, the cylinders were removed and fitted with plastic bases and resin traps (Chapter-4). Joints at the interface of the cylinder and base were sealed with silicone sealant. A plastic pipe was connected to the resin trap to provide above ground access to remove resins

**Table 5.1 The fertility, land slope and percentage occurrence of each slope class in each of the two farmlets.**

Fertility	Land slope(Angle)	Distribution %	Description
Low fertility	Low(0-12°)	33	LF-LS
Low fertility	Medium(12-26°)	42	LF-MS
High fertility	Low(0-12°)	23	HF-LS
High fertility	Medium(12-26°)	44	HF-MS

whenever necessary (see Fig.4.1). The whole system was reinserted in to the soil (Fig.5.1). Coarse sand was used to pack around the resin trap outlet to provide easy drainage to a small 20mm mole drain which was pulled away from each installation. The soil and turf were then carefully repacked around each cylinder. All the cores were covered with cages (0.5m<sup>2</sup>) to measure pasture production. Pasture yields were recorded from opposite end of the cage to the cylinder. After each harvest the cages were rotated with the lysimeter as the pivot. This allowed pasture growth to be measured (section 5.2.3.2) on a new area of pasture after each harvest and would include the effect of excreta on growth. In this way the lysimeters were always inside the cage so that no excreta entered inside the lysimeter.

### 5.2.3 Measurements

#### 5.2.3.1 Drainage

The predicted daily net drainage (D mm) for all the four sites was calculated using the following water balance equation.

$$D = R - E_t + w - w_{fc}$$

where **R**, Daily rainfall (mm); **E<sub>t</sub>**, Daily potential evapotranspiration (mm); **w**, depth of water (mm) for the soil measured at the beginning of the experiment; **w<sub>fc</sub>**, depth of water for the soil at field capacity (mm).

Daily rainfall was recorded at Ballantrae meteorological site. Rain gauges were also installed at all four sites and the rainfall was measured every week from the beginning of the experiment. This weekly rainfall was correlated to the accumulated weekly rainfall recorded at the meteorological site. Potential evapotranspiration was calculated using Priestly and Taylor (1972) equation and temperature (both air and soil) and sunshine hours recorded at the meteorological site. The volumetric water content of the field soil was measured at the beginning of the experiment and also when soil samples were taken for analysis during the experiment (Appendix-5.1). The volumetric water content of soils at field capacity were measured by determining soil water content and bulk density immediately after heavy rainfall. The water balance was calculated using a Multiplan spread sheet version 4.1.

### 5.2.3.2 Pasture Production

Pasture production at all sites was measured by harvesting the pasture grown under an exclusion cage (1m 0.5m). Pasture was harvested from one half of (Fig.5.1) the cage area (0.25m<sup>2</sup>). Weighed subsamples of pasture were dried at 60°C and the pasture dry matter yield recorded. Pasture production was expressed on a per hectare basis as follows

$$X = Y \times \frac{A}{B} \times \frac{10^4}{0.25} \times \frac{1}{10^3} \text{ kg DM ha}^{-1}$$

where

$X$ = Amount of dry matter produced (kg ha<sup>-1</sup>)

$Y$ = green weight of herbage produced (gm) in 0.25m<sup>2</sup> area

$A$ = Dry sample weight (gm)

$B$ = Green sample weight (gm)

Five harvests were taken (5/9, 6/10, 6/11, 30/11/89 and 8/1/90). Harvest intervals depended on pasture growth rates. The first harvest was not made until three months after the beginning of the experiment because winter pasture growth was slow. Thereafter harvests were made at approximately four week intervals. Separate pasture samples were dissected for species composition. A subsample of the oven dried mixed pasture was grounded and used to determine pasture S and N content (see analytical methods).

### 5.2.3.3 Ion Exchange Resin and Resin Care

The type of anion exchange resin (15g/trap) and its loading into the trap were described in Chapter-4. The cation exchange resin (15g/trap) used in this experiment was 'amberlite-IR120'. The exchange capacity of the resin was 1.9meq ml<sup>-1</sup>(wet) and 5.0meq ml<sup>-1</sup>(dry). Prior to use, both anion and cation exchange resins were first eluted (regenerated) with 1M HCl followed by 1M NaCl and then thoroughly washed with deionised water to remove background ions present in the resin and placed in the resin-trap compartments.

Fig.5.1 Exclusion cage and lysimeter installation in the field (A, Exchange resin trap access tube; B, Soil water suction cup sampler).



The resins were replaced four times during the experiment depending upon the frequency and intensity of rainfall. Each coincided with a harvest. After removing the resins from the trap, they were washed thoroughly with deionized water before eluting with 50mls of 1M NaCl. A portion of the eluant was used for the determination of  $\text{SO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and other cations such as  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^+$ ,  $\text{Fe}^{++}$  or  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ . Eluates from resin blanks were used to prepare standard curves for each element. The eluted resin was washed thoroughly with deionised water and used again for subsequent samplings.

#### **5.2.3.4 Soil Sampling**

Soil samples were collected from outside the lysimeters at the start of the experiment in early winter (1/6/89), mid winter(5/7), late winter(25/8), early spring(5/9), mid spring(6/11), late spring(30/11/89) and early summer (8/1/90 final). Samples were collected from 0-75, 75-150 and 150-250 mm soil depths. The extractable sulphate and mineral N contents were determined for field moist soils using the methods described in Chapter 3, section 3.2. Moisture content of the soil was also recorded at each sampling (Appendix-5.1). Soil bulk density was measured for all four sites at the beginning of the experiment (Appendix-5.2).

#### **5.2.4 Analytical Measurements**

The soil sulphate and mineral N were extracted and measured as mentioned in Chapter-3, section 3.2.4. The sulphate and mineral N in resin eluates were measured as mentioned in Chapter-3, section 3.2.4. Appropriate matrices were used for the preparation of standard curves in the determination of S and N in soil and resin eluates.

The concentrations of cations in the resin eluates were measured using atomic absorption spectroscopy. Appropriate ionic suppressants (Sr, Cs and K ) were used for the determination of  $\text{Ca}^{++}$ ,  $\text{K}^+$  and  $\text{Fe}^{++}$  or  $\text{Fe}^{3+}$ . The final solution for the determination of cations was acidified with 1ml of 1M HCl per 50ml.

Pasture S content was determined as described in Chapter-4, section 4.2. Pasture N content was determined by digesting the sample with a mixture of concentrated  $H_2SO_4$ ,  $K_2SO_4$  and Se (a micro Kjeldal method) and the N was measured using an auto analyser. Final results for the above analyses are expressed as the mean of eight replicate measurements derived from eight replicate lysimeters.

### **5.2.5 Statistical Analysis**

Soil sulphate, mineral N, the amount of S and N lost by leaching, the pasture S and N content and net mineralization of S and N were subjected to analysis of variance (Hull and Nie, 1981) to determine the statistical significance of the simple and interactive effects of site location and soil depth.

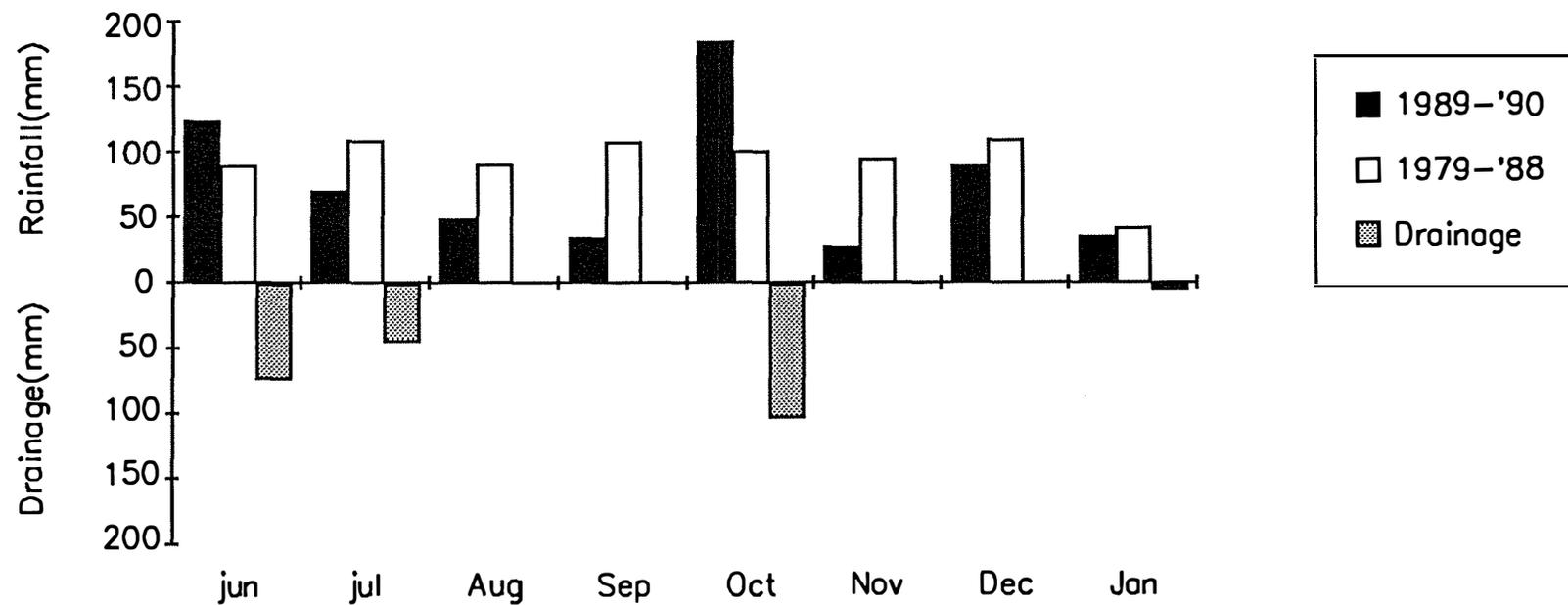
## **5.3 RESULTS AND DISCUSSION**

In a grazed pasture, the net mineralization of any nutrient in the soil under field conditions can be calculated at any one site by measuring the changes in the amount of that nutrient in the plant available pool (in the soil), the amount of nutrient taken up by plant and lost by leaching and the amount of nutrient returned in excreta which could be potentially available for plant growth. Such measurements for both S and N are now discussed before an attempt is made to calculate the net mineralization of these two nutrients.

### **5.3.1 Rainfall and Drainage**

The total rainfall (625mm) during the experimental period was lower than the long-term average (754mm) for that period (Fig.5.2). The winter (June to August 1989) rainfall in particular was lower than the long-term average. Drainage occurred in only three of the seven months of measurement (Fig.5.2). The total drainage during winter (118mm) was greater than the total drainage during spring (103mm), but the intensity of drainage was greater during spring. In spring drainage occurred over a period of 17 days whereas in winter drainage extended over a longer period (42

Fig.5.2 Rainfall and predicted net drainage for the period from Jun. 1989 to Jan. 1990 and the long term (1979-1988) average rainfall for the same period



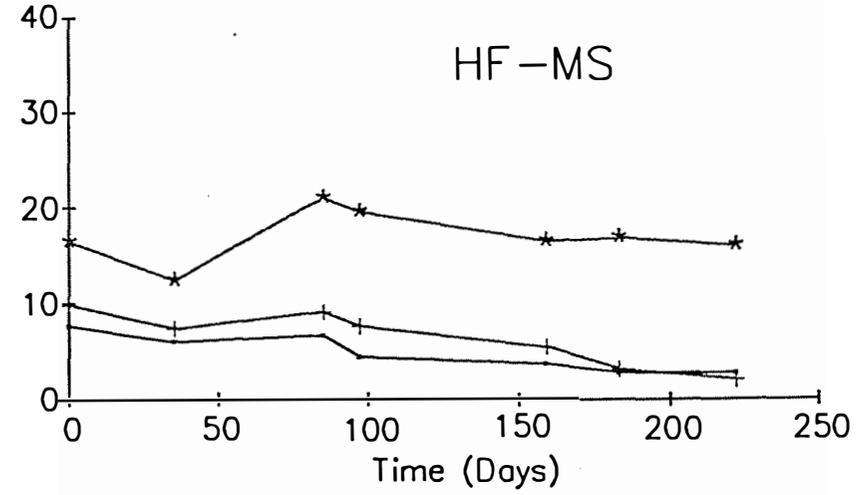
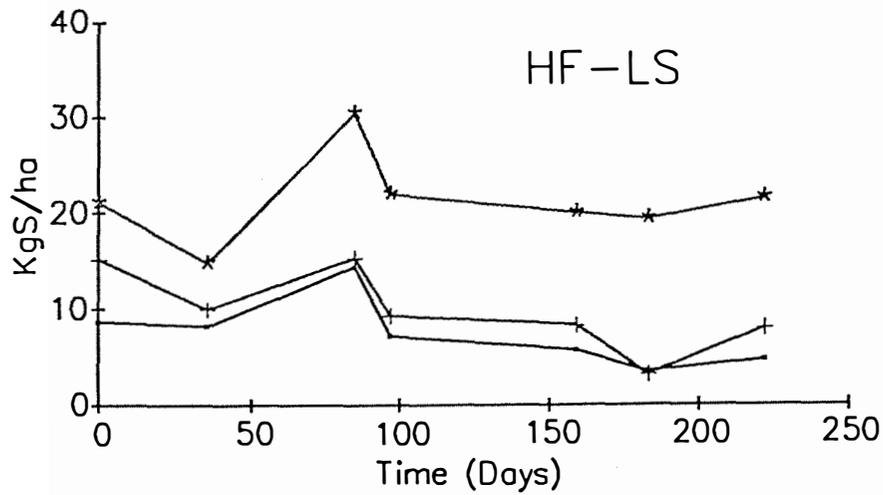
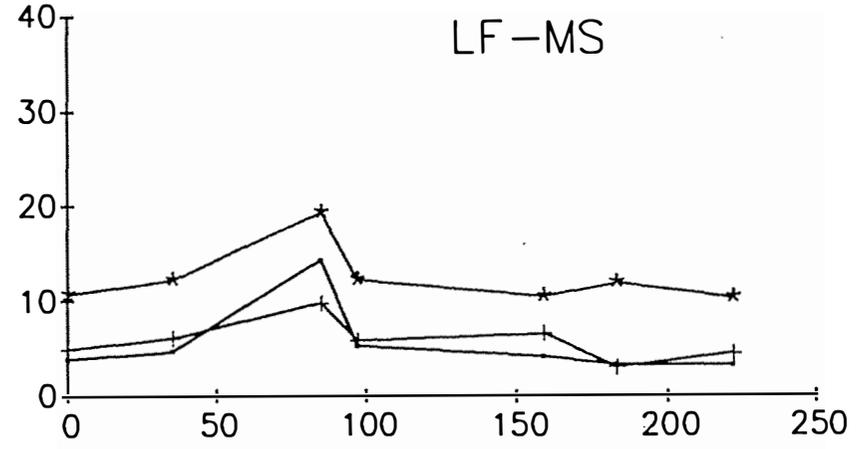
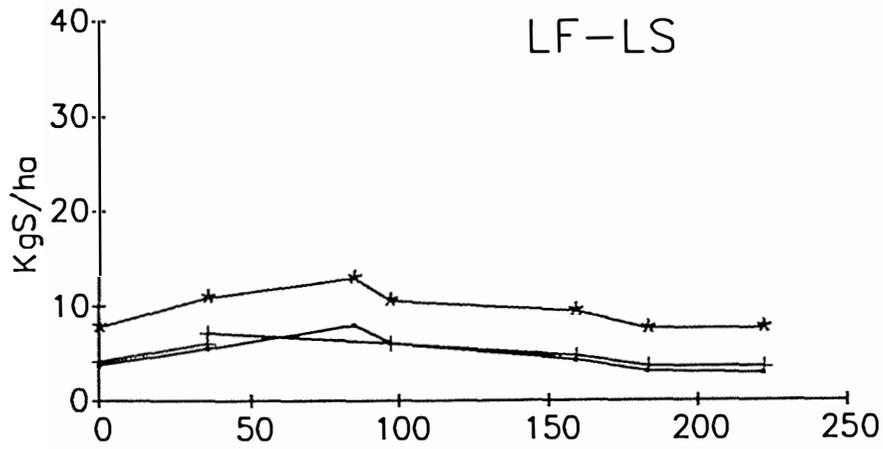
days). The significance of this drainage pattern on sulphate leaching and soil sulphate levels are discussed in a later section (section 5.3.2). Even though the rainfall intensity was greater in spring than in winter, no runoff occurred in spring. In a similar study conducted on a Tokomaru silt loam Heng *et al.* (1991) also did not observe any surface runoff for a rainfall of  $7.2 \text{ mm hr}^{-1}$  for 6 hours, even though for the same time the soil remained at its field moisture holding capacity. The rainfall intensity during the experimental period for these sites never exceeded  $4 \text{ mm hr}^{-1}$ .

### 5.3.2 Soil Sulphate

At the beginning of the experiment average extractable soil sulphate for the profile (0-250mm) were higher at high fertility sites ( $45.0$  and  $34.1 \text{ kg S ha}^{-1}$  for low and medium slopes, respectively) than at low fertility sites ( $15.8$  and  $19.5 \text{ kg S ha}^{-1}$  for low and medium slopes, respectively) (Appendix-5.3). In the high fertility farmlet the amount of sulphate present at the low slope was greater than the amount of sulphate present at medium slopes even though both slope categories have same fertilizer history. At the low fertility farmlet, however, there was no difference between the amounts of sulphate present in the soil at low and medium slopes. At all sites the amounts of sulphate S present in the soil fluctuated throughout the experimental period (Fig.5.3). During the period of maximum plant growth in spring and early summer (Sep. to Early Jan.) the amount of sulphate in the upper 150mm of the soil steadily decreased (Fig.5.3). This is due to the depletion of sulphate in the top 150mm soil depth by plant uptake and microbial immobilization. Sulphate in the 150-250mm soil depth was consistently higher than those at 1-150mm soil depths during this period. The greater amount of sulphate S in the subsoil than in the surface layers is due also, in part, to the sorption of sulphate by iron and aluminium hydrous oxides surfaces in the absence of  $\text{HPO}_4^-$  ions that in the top soil may compete with sulphate ions for sorption sites (Bolan *et al.*, 1988). Further, because of lower root (Barker *et al.*, 1988) and microbial activities in the lower soil layers the sulphate concentration at this depth is influenced to a much lesser degree by organic matter turnover, mineralization and immobilization processes. Seasonal changes in the rate of uptake of S by plant roots and soil microbial activity brought about by changes in soil temperature and moisture (rainfall) (Harward and Reisenauer, 1966; Metson, 1979) will lead to more frequent or greater fluctuations in the amount of sulphate in the top soil.

Fig.5.3. Soil sulphate present for the depths 0-75 mm (—), 75-150 mm (—+—) and 150-250 mm (—\*—) at all sites from Jun. 1989 to Jan. 1990. Soil samplings were done on 31/5/89, 4/7, 24/8, 5/9, 6/10, 30/11 and 8/1/1990. The L.S.D values are given in

Appendix-5.3.



Soil sulphate S in low fertility sites increased during the initial period (31/5 to 4/7/89) of the experiment (early winter), but in high fertility sites the sulphate S decreased (Fig.5.3). This decrease may be due to immobilization and greater leaching of sulphate in these two HF sites in the absence of significant plant growth. Immobilization of sulphate is possible in HF farmlet because the initial sulphate in the two high fertility sites were as high as 24 and 17.6 kg S ha<sup>-1</sup> in the top 150mm of the soil (Appendix-5.3) which is almost 2 to 3 times more than the sulphate in the low fertility sites (8.0 and 8.7 kg S ha<sup>-1</sup>, respectively) (Appendix-5.3). Previous S balance studies in New Zealand and Australia have shown that, when rainfall was low large amounts of applied sulphate were incorporated in to soil organic matter (Goh and Gregg, 1982; Goh and Tsuji., 1979; Freney *et al.*, 1975).

Further evidence for immobilization of sulphate was that even though there was considerable drainage (73mm) (equivalent to 100% of water stored in the top 150mm of the soil) during this period the amount of sulphate lost by leaching was low (4.0 and 3.5 kg S ha<sup>-1</sup> for low and medium slopes) compared to the amount of sulphate (24 and 17.6 kg S ha<sup>-1</sup> for low and medium slopes) (Appendix-5.3) present in the top 150mm of the soil (Appendix-5.3). The greater sulphate concentration in the soil might have also decreased the mineralization of soil organic sulphur because the rate of sulphate production by biochemical enzymatic hydrolysis of ester sulphate in soil decreases as the concentration of the sulphate in the soil solution increases (Cooper, 1972; Fitzgerald, 1976).

The concentrations of sulphate S increased to its highest level at the end of winter (24-8-1989) at all sites (Fig.5.3) and thereafter the concentrations steadily decreased, particularly for the 0-150mm soil depths due to increased plant uptake and leaching, which occurred in mid spring (Oct.1989, for a period of 17 days, Fig.5.3). After the leaching events in spring (Oct.1989) the sulphate concentrations are constant in the 150-250mm soil depth at all sites during the period of maximum plant growth (Fig.5.3).

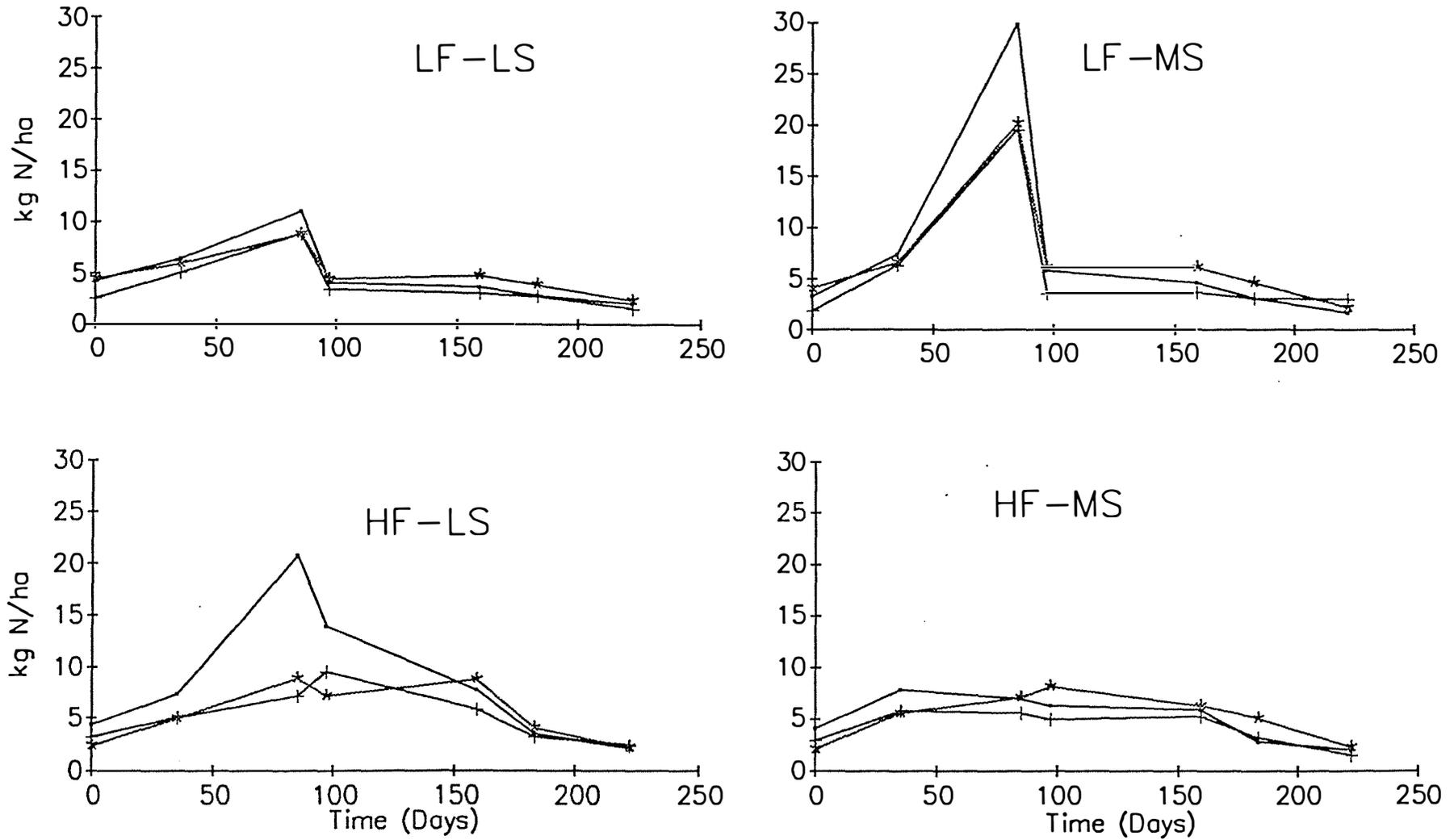
At low fertility sites the amount of sulphate present in the soil (0-250mm) at the beginning (1-6-1989) and at the end (8-1-1990) of the experiment was almost same (Fig.5.3, Appendix-5.3), showing that mineralization of organic S replenished the soil

solution sulphate lost by leaching and pasture uptake during that period. At high fertility sites the soil sulphate level (0-250mm) had decreased by the end of the experiment. Nearly all of this decrease was observed in the upper 0-150mm of the soil, showing that plant and leached S was derived in part from the sulphate pool and the remainder from the mineralization of soil organic S. During the period of rapid plant growth the amount of sulphate present in the 150-250mm soil depth showed little change. Although previous studies have demonstrated that subsurface  $\text{SO}_4^{2-}$  is available to plants (Gregg and Goh, 1979) the extent to which this pool contributes to the overall S nutrition of the plant depends on soil texture and bulk density as it influences the quantities and activity of plant roots in the subsoil and to lesser degree the extent of refluxing of the subsoil sulphate to the topsoil when the soil water table increases (Risk and Boswell, 1988). The small changes in the amount of sulphate S in 150-250mm soil depth at all four sites during a period when there was no leaching occurred (19/9/89 to 8/1/90), plant growth depleted soil sulphate level at 0-150mm soil depth but not at 150-250mm depth indicating that once sulphate moved beyond the top 150mm of the pasture soil it is essentially not available for plant uptake.

### 5.3.3 Mineral Nitrogen

Unlike S, at the beginning of the experiment mean soil mineral N ( $\text{NO}_3^- + \text{NH}_4^+$ ) contents of low ( $10.3 \text{ kgN ha}^{-1}$ ) and high fertility ( $9.8 \text{ kgN ha}^{-1}$ ) sites (Appendix-5.4) were very similar as they were between slope classes within low and high fertility sites. Like S, however, the amount of mineral N (both nitrate and ammonium) increased during winter and there after decreased throughout the spring and early summer (Fig.5.4). This coincided with rapid plant uptake. For HF sites this increase in mineral N in winter occurred before the increase in soil  $\text{SO}_4\text{-S}$  (Fig.5.3). Ammonium was the dominant inorganic N form present at all sites and made up 100% of the inorganic N in spring and summer. Nitrate was present only in the winter months (Table.5.2, Appendix-5.4). These trends are typical of seasonal observations of mineral N content of soil under grasslands (Jackson *et al.*, 1988). Rapid immobilization of nitrate or denitrification however are not suitable

Fig.5.4. Soil mineral nitrogen present for the depths 0-75 mm (—), 75-150 mm (—+—) and 150-250 mm (—\*—) at all sites from Jun. 1989 to Jan. 1990. Soil samplings were done on 31/5/89, 4/7, 24/8, 5/9, 6/10, 30/11 and 8/1/1990. The L.S.D values are given in Appendix-5.4.



**Table 5.2** Amounts of Nitrate (N) and Ammonium (A) present at three depths in the soil for all the four sites during the experiment. No nitrate was observed in some of the samplings.

Farmlet	Soil Depth (mm)	31-5-89	4-7-89		24-8-89		5-9-89	6-11-89	30-11-89	8-1-90	
		mg N kg <sup>-1</sup> soil									
		A	N	A	N	A	A	A	A	A	
LF-LS	0-75	7.5	1.5	9.8	4.1	14.9	5.6	6.4	5.1	3.7	
	75-150	3.5	1.4	5.9	3.9	7.9	3.4	4.6	3.8	2.2	
	150-250	3.8	1.5	6.8	3.0	4.1	2.6	4.1	3.3	2.1	
LF-MS	0-7.5	5.8	1.6	11.6	8.1	42.9	7.9	8.1	5.6	3.1	
	7.5-15	2.6	1.6	7.3	6.6	19.5	3.6	5.2	4.4	4.2	
	150-250	3.5	1.7	5.9	4.7	12	3.5	5.2	4	1.9	
HF-LS	0-7.5	7.3	6.6	9.6	9	18.4	12.6	13.1	5.9	3.5	
	7.5-15	4.4	4.7	4.4	5.2	4.4	7.3	7.9	4.3	3.2	
	150-250	2	3.5	3.5	4.2	4.1	2.6	7.35	3.4	1.8	
HF-MS	0-7.5	7.2	9.7	12.2	6.5	5.6	6	7.8	4.9	3.5	
	7.5-15	4.1	8.3	8.5	4.7	3	3.9	7.2	4.4	2.1	
	150-250	1.8	6.9	5.7	3.1	2.9	3.7	5.4	4.3	1.9	
	<sup>1</sup> L S D <sub>p&lt;0.01</sub>	0.82	2.0	1.9	2.3	5.2	0.96	0.65	1.0	0.85	

1 for comparison of means between depths

explanations for the absence of nitrate in these soils in the spring. Microbial heterotrophs prefer ammonium as a N source and are able to out compete the nitrifying bacteria for the ammonium ions (Jones and Richards, 1977). Ammonium rather than nitrate is also central to microbial growth and decomposition (Paul and Juma, 1981). However it is not clear which form of inorganic N,  $\text{NO}_3^-$  or  $\text{NH}_4^+$  is preferred by pastures. Previous work (Jackson *et al.*, 1989) shows that ammonium is the dominant N source for not only microbes but also plants. Earlier laboratory incubation results (Chapter-3.3.2) showed that considerable amounts of ammonium rather than nitrate was the major byproducts of mineralization of soil organic matter. But the absence of nitrate during spring and early summer may be due to the rapid removal of nitrate by plants during active periods of plant growth. The decrease in the amounts of mineral N throughout the spring resulted from plant uptake and immobilization by microorganisms and was not the result of leaching, since most of the mineral N was in the form of ammonium and retained on cation exchange sites rather than nitrate which is susceptible to leaching. This shows that the presence of ammonium as the major inorganic N species would limit the amount of N lost by leaching in these hill country pastures. In fact very little N was lost (section 5.3.4).

#### 5.3.4 Leaching Losses of S and N

Over the seven months of measurement more S and N were leached from high fertility sites ( $15.3 \text{ kg S ha}^{-1}$  and  $1.3 \text{ kg N ha}^{-1}$ ) than low fertility sites ( $2.1 \text{ kg S ha}^{-1}$  and  $0.24 \text{ kg N ha}^{-1}$ ) (Table 5.3). Land slope did not affect leaching losses from low fertility sites. The reasons for the low fertility medium slope site behaving like a low slope campsite are discussed in section 5.3.6. At the high fertility farmlet more S and N were lost from the low slope than the medium slope. As expected S leaching loss was much greater on the HF farmlet where soil solution sulphate was greater than  $8 \text{ mg l}^{-1}$  (measured using suction cups) for most of the year. At the LF site, where leaching much less, soil solution sulphate concentrations were  $<2 \text{ mg l}^{-1}$  throughout the year. Even though the net drainage during winter was slightly greater than during spring at both slope classes of each farmlet (Fig.5.2 and Table 5.3) different patterns for the downward movement of S through the different soil profiles emerged at the two sites. A greater amount of S ( $1.2$  and  $1.3 \text{ kg S ha}^{-1}$  for low and medium slopes) was lost by leaching at the low fertility farmlet during winter, while

**Table 5.3 Predicted net drainage and the amounts of sulphate and mineral N lost by leaching in winter and spring at all four sites.**

Farmlet	winter			spring			total		
	drainage	S	N	drainage	S	N	drainage	S	N
	mm	kg/ha		mm	kg/ha		mm	kg/ha	
LF-LS	136	1.2	0.29	99	0.78	0	235	2.0	0.29
LF-MS	146	1.3	0.17	130	0.91	0	276	2.2	0.19
Average	141	1.3	0.23	115	0.85	0	256		
LSD p<0.01	12	0.2	0.1	22	0.23		31	0.34	0.2
HF-LS	138	6.6	1.5	120	10.7	0	258	17.3	1.5
HF-MS	132	5.9	1.1	102	7.1	0	234	13.2	1.1
Average	135	6.3	1.3	111	8.9	0	246	15.3	1.3
L.S.D p<0.01	14	2.5	0.3	13	2.3		24	3.3	0.6

most of the S (10.7 and 7.1 kg S ha<sup>-1</sup> for low and medium slopes) lost by leaching at the high fertility farmlet occurred during spring (Table 5.3). Accelerated plant growth that occurred in the low fertility farmlet during spring compared to winter is likely to have had a much greater impact on soil sulphate levels, which never exceed 2mg l<sup>-1</sup> and so reduce the potential for leaching. This showed the pool size and the pasture S demand also influences the leaching losses of sulphate.

Rapid movement of sulphate down the soil profile has been observed in a number of studies both in laboratory (Chao *et al.*, 1962; Hogg, 1981) and in the field (Till and May, 1971; Gregg and Goh, 1978, 1979; Smith *et al.*, 1983; Heng *et al.*, 1991). Drainage water from a mole and tile drain system on a similarly low sulphate retaining soil (Smith *et al.*, 1983) contained 15 kg S ha<sup>-1</sup> for a total winter-spring drainage of 165mm when the fertilizer was applied in late autumn at a rate of 43 kg S ha<sup>-1</sup> as SSP. The loss in the present experiment (15.3 kg S ha<sup>-1</sup>) was associated with 250mm drainage and the last fertilizer application was done in the previous spring at a rate of 45 kg S ha<sup>-1</sup>. Heng *et al.* (1991) in an experiment conducted at the same site with mole and tile drain as Smith *et al.* (1983) measured a total loss of 17 kg S ha<sup>-1</sup> by leaching for winter-spring drainage of 350mm from plots receiving 50 kg S ha<sup>-1</sup> SSP. If the losses of S by leaching in the present experiment are expressed as a percentage of annual S application rate then 13%, 14%, 38% and 29% of the S applied was leached from LF-LS, LF-MS, HF-LS and HF-MS sites. These values are lower than the leaching losses of S predicted by Saggar *et al.* (1990a) for the same sites. This is due in part to the fact that leaching was not measured for the full year and because rainfall during the experiment was lower than the long-term average for which the losses were predicted. No measurements were made of the S leached directly after fertilizer application. Such measurements are made in a later study (Chapter-6).

The amount of N lost by leaching (0.25 and 1.3 kg N ha<sup>-1</sup> for low and high fertility farmlets, respectively) was very small (Table 5.3) in terms of the total amount of N being cycled in the soil-plant-animal system (estimated during this experiment to be 232 and 467 kg N ha<sup>-1</sup> year<sup>-1</sup> for low and high fertility farmlets, respectively). In a later section the reason for this small loss of N are discussed in terms of N inputs and the fact that the pasture growth is limited by N availability. Higher leaching (50 to

70 kg N ha<sup>-1</sup> year<sup>-1</sup>) rates have been recorded for irrigated and fertilized pastures stocked at a rate of 14 and 20 SU ha<sup>-1</sup> (Quin, 1977;1982; Steele *et al.*, 1984; Heng *et al.*, 1991). In the present study the effect of grazing animals on leaching losses of S and N were not established because all the lysimeters were completely isolated from excreta return. Even though the effect of grazing animals on leaching losses was not known in this study, it was shown that excreta returned in sheep grazed hill pastures did not increase the immediate leaching losses of nitrogen (see Chapter-7). A previous study (Lambert *et al.*, 1982) in these farmlets showed that N losses by surface runoff and drainage were 12 and 14 kg N ha<sup>-1</sup> for low and high fertility farmlets, respectively. During the present experiment little or no surface runoff occurred (section 5.3.1).

### 5.3.5 Leaching Losses of Cations

Calcium(Ca) was the dominant cation lost by leaching. Nearly 50% of the total cation molar charge measured in the drainage water during the experiment was Ca (Table 5.4). The dominance of Ca in leachate reflects the dominance of this cation in these sedimentary soils and the higher concentrations of Ca in the drainage from the HF sites indicates that Ca contained in superphosphate fertilizer probably contributes significantly to the leached Ca pool. The amount of Ca lost (12.5 kg Ca ha<sup>-1</sup>) by leaching was lower than the amount (40 kg Ca ha<sup>-1</sup>) draining from a lowland yellow grey earth pasture (Heng *et al.*, 1991). This may be a function of the drainage system or that yellow grey earths in general have higher base saturation than yellow brown earth/yellow grey earth intergrades, the hill soils in this study. The lower Ca leaching loss observed in this study was also associated with lower N leaching (1.5 kg N ha<sup>-1</sup>) losses than the 20 kg N ha<sup>-1</sup> leached in the study of Heng *et al.* (1991).

The amount of magnesium(Mg) and potassium(K) lost by leaching were greater in high than low fertility farmlet though the amount (molar charge) leached were lower than Ca at all sites (Table 5.4). It would appear that increased H<sup>+</sup> ions generated by

**Table 5.4 Amounts of cations leached for all the four sites between Jun. 1989 and Jan. 1990**

Farmlet	Amount of cations leached				
	Kg/ha				
	Ca	Mg	K	Al	Fe
LF-LS	5.00	0.78	0.78	1.36	2.95
LF-MS	4.75	0.28	1.21	1.09	0.89
Average	4.9	0.53	1.00	1.2	1.9
LSD <sub>p&lt;0.01</sub>	0.45	0.36	0.56	0.49	0.85
HF-LS	12.49	1.91	3.62	0.53	0.56
HF-MS	6.37	1.19	3.09	1.49	1.22
Average	9.4	1.6	3.4	1.0	0.90
LSD <sub>p&lt;0.01</sub>	3.2	0.74	0.64	0.85	0.48

increased N cycling (Bolan *et al.*, 1991) in HF farmlet exchanged with and cause increased  $Mg^{++}$  and  $K^+$  leaching in this farmlet. Also increased anion leaching will enhance the greater leaching of  $Mg^{++}$  and  $K^+$  in the high fertility farmlet. The amount of  $K^+$  lost by leaching in terms of annual K cycling ( $240 \text{ kg K ha}^{-1}$  observed during the experiment for HF farmlet) in sheep grazed pastures was very low ( $0.78$  to  $3.6 \text{ kg K ha}^{-1}$ ), lower than the amount of  $Ca^{++}$  lost by leaching ( $4.8$  to  $12.5 \text{ kg Ca ha}^{-1}$ ) for which the annual turnover is about  $125 \text{ kg Ca ha}^{-1}$ . Over this experimental period a greater amount of K was taken up by pasture ( $100$  to  $180 \text{ kg K ha}^{-1}$ ) and returned to soil by sheep than Ca ( $53$  to  $95 \text{ kg Ca ha}^{-1}$ ), most of the K returned in excreta by sheep to the soil is retained by displacing  $Ca^{++}$  and  $Mg^{++}$  from exchange sites. The amount of K lost is even lower than the amount of Mg lost from some sites. The small amount of K leached was consistent with the findings of other studies (Hogg, 1981; Smith *et al.*, 1983; Steele *et al.*, 1984; Williams *et al.*, 1990) conducted in New Zealand.

In the present study the summed amounts of cation charge leached was not balanced with the measured summed amounts of anion charge leached. This is partly because some of the main anions ( $Cl$ ,  $HCO_3^-$  and  $OH^-$ ) and the cation ( $Na^+$ ) could not be measured from the  $0.5M$  NaCl resin eluate and because the oxidation states of Fe and Al species appearing in the leachate is unclear. In fact, the drainage water collected from  $0$ - $250\text{mm}$  soil depth using porous suction cups contained about  $3$  to  $5 \text{ mg Cl l}^{-1}$  of water. The higher amounts of Fe and Al during winter period may be due to the initial disturbance of the soil cores when they were inserted in the field, or may be due to reduced conditions during winter. While the anions and cations could not be balanced the amounts of both anion and cation leached were greater in high fertility farmlets than in low fertility farmlets.

At this stage it is useful to note that the amount of Ca lost by leaching from both LF and HF sites are lower than the amount of Ca applied in the fertilizer to the soil but increased fertilizer application is definitely causing accelerated leaching losses of Mg and K from these hill country soils even though these nutrients were not applied in the fertilizer. The mechanism of cation leaching in grazed pasture is unclear, but

these results showed that the amounts of K returned to soil in excreta particularly in urine is much higher than the amounts of Ca and Mg returned but the losses of K by leaching were much lower than the amounts of Ca and Mg lost by leaching. The results along with the results of Heng *et al.* (1991) suggest that in sheep grazed pasture both fertilizer and excreta K exchanges with Ca and probably with Mg and enhances the leaching losses of both Ca and Mg. The accelerated losses of Mg and K in the HF farmlet may be due to an enhanced recycling of Mg and K through plant and animal because of a greater growth and stock numbers. This aspect is investigated further in Chapter-7.

### **5.3.6 Pasture Production**

For the seven month period, pasture production (Average of 8 replicates) at high fertility sites was greater (2 times) than at low fertility sites (Table 5.5). Land slope did not effect the pasture production at the high fertility farmlet, but at the low fertility farmlet the medium slope produced more pasture than the low slope. The increase in pasture production at this particular site can be explained by the effect of the prevailing North Westerly wind on the camping behaviour of the grazing animal. In the low fertility farmlet the low slope site was exposed to the full force of the westerly wind. Whereas the medium sloped easterly aspect was sheltered, received greater excretal returns as a result was more fertile than the low slope site. Sagar *et al.* (1990a) have already reported that wind direction prevailing from North West influenced stock behaviour and excretal return in this hill country.

Late winter pasture growth rates were very low (3.2 to 14.2 kg DM ha<sup>-1</sup> day<sup>-1</sup>). Thereafter growth rate steadily increased and by late spring it ranged from 48 to 73 kg DM ha<sup>-1</sup> day<sup>-1</sup>. By early summer growth rates had slowed because of moisture stress (see Chapter-8).

### **5.3.7 Pasture S and N Concentration**

Pasture S and N concentrations are dependent upon the plant availability of soil nutrients, amount of fertilizer application, pasture yield, plant species composition,

**Table 5.5 Pasture production from June. 1989 to Jan. 1990 at all four sites.**

Farmlet	Harvest					Total Production kg DM ha <sup>-1</sup>
	5/9	6/10	6/11	30/11	8/1/90	
	Late winter	Spring			Early Summer	
	kg DM ha <sup>-1</sup>					
LF-LS	307	425	628	1168	1246	3774
LF-MS	378	759	1133	1454	1465	5198
Average	343	592	881	1311	1356	4486
LSD <sub>p&lt;0.05</sub>	50	205	293	190	102	312
HF-LS	1370	1506	1580	1740	2109	8307
HF-MS	1375	1475	1609	1766	2294	8519
Average	1373	1490	1595	1753	2202	8413
LSD <sub>p&lt;0.05</sub>	25	53	42	73	202	293

**Table 5.6 Effect of fertilizer history and land slope on pasture S and N concentrations and N/S ratios.**

Farmlet	5-9-1989			6-10-89			6-11-89			30-11-89			8-1-1990		
	Late winter			Spring									Early summer		
	%S	%N	N/S	%S	%N	N/S	%S	%N	N/S	%S	%N	N/S	%S	%N	N/S
LF-LS	0.28	3.22	11.5	0.32	3.65	11.4	0.31	3.29	10.6	0.25	3.20	12.8	0.21	2.43	11.6
LF-MS	0.28	3.20	11.8	0.32	3.61	11.3	0.32	3.72	11.6	0.24	3.01	12.5	0.21	2.04	9.7
Average	0.28	3.21	11.7	0.32	3.63	11.4	0.32	3.51	11.5	0.25	3.1	12.7	0.21	2.24	10.7
LSD P<0.01	0.03	0.2		0.01	0.2		0.02	0.5		0.01	0.2		0.02	0.6	
HF-LS	0.33	3.61	10.9	0.34	3.93	11.6	0.35	3.67	10.5	0.30	3.34	11.1	0.29	2.46	8.5
HF-MS	0.32	3.59	11.2	0.32	4.05	12.6	0.38	3.82	10.1	0.29	3.01	10.4	0.27	2.51	9.3
Average	0.33	3.6		0.33	4.0		0.37	3.74		0.30	3.18		0.28	2.49	
LSD p<0.01	0.01	0.1		0.01	0.1		0.03	0.25		0.01	0.3		0.01	0.3	

season of sampling, slope and aspect. The higher S and N concentrations of mixed pasture at HF sites reflects the higher fertility of these sites (Table 5.6). At all sites the concentrations of S and N in pasture increased from Jun. to Oct. and thereafter steadily decreased. The decrease was associated with an increase in pasture production in spring and decrease in soil sulphate and mineral N in the top 150mm. By Jan. the pasture S and N concentrations were lower than the critical S and N concentrations of 0.23% and 3.00%, respectively (Jones *et al.*,1972; M<sup>c</sup>Naught, 1970) even though pasture production decreased during this period suggesting that adequate S and N were not supplied for maximum plant growth.

The N/S ratio of mixed pasture samples ranged from 10-12 from early winter till the end of spring at all sites (Table 5.6). By early summer it decreased to less than 10. According to Metson (1973) N/S ratios of 14 or greater occur when either S is deficient or N is more than adequate; while a value of 11 indicates inadequate N and more than adequate S. Pasture S concentrations were always greater than 0.25% in late winter and throughout spring. Thus the low N/S ratios indicate that more than adequate S was supplied, because the pasture S concentrations was always greater than 0.25%. Concentrations above 0.25% S are adequate for maximum growth of a mixed clover-rey grass pasture (Metson and Saunders, 1978). The low N/S ratio and low N and S concentrations in early summer indicate that adequate S and N were not available from the soil for maximum pasture production suggesting that the low soil moisture content during the summer reduces the availability of both S and N by reducing N and S transport to roots and the mineralization rates of S and N.

### **5.3.8 Sulphur and N Removed in Pasture**

The total amounts of S and N removed in pasture were much greater at high fertility sites ( 25.3 and 26.6 kg S ha<sup>-1</sup>, 267 and 282 kg N ha<sup>-1</sup> for low and medium slopes, respectively) than low fertility sites (9.8 and 13.5 kg S ha<sup>-1</sup>, 113 and 155 kg N ha<sup>-1</sup> for low and medium slopes) (Fig.5.5 and 5.6). In the low fertility farmlet greater amounts of S and N were removed by pasture from the medium than low slope area. The reason for this apparent anomaly have been discussed in section 5.3.6.

Fig.5.5 Cumulative amounts of sulphur removed by pasture from Jun. 1989 to Jan. 1990 at all sites. Harvests were made on 5/9/89, 6/10/, 6/11, 30/11 and 8/1/90.  
 (Vertical bars = L S D,  $p < 0.01$ ).

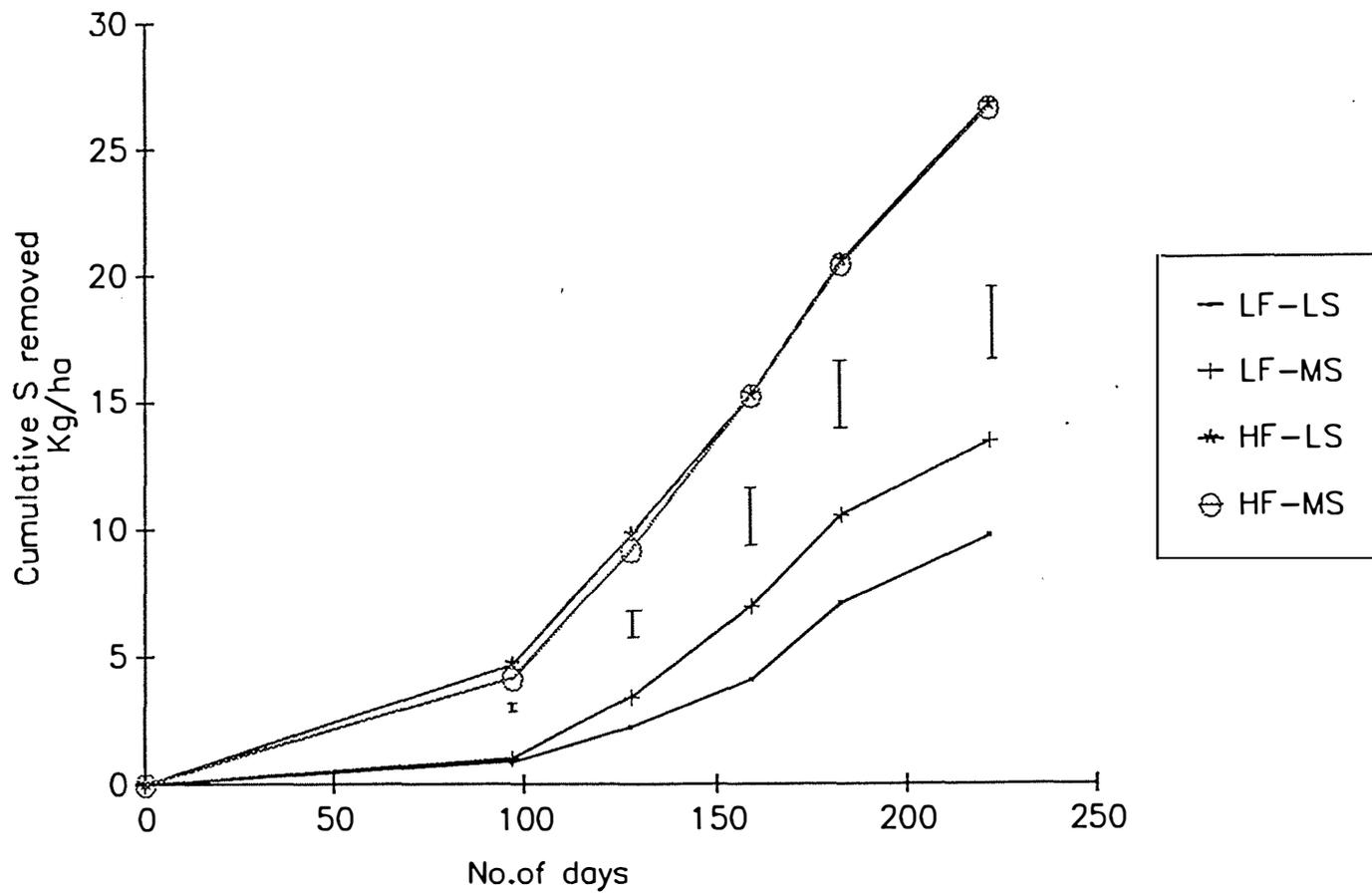
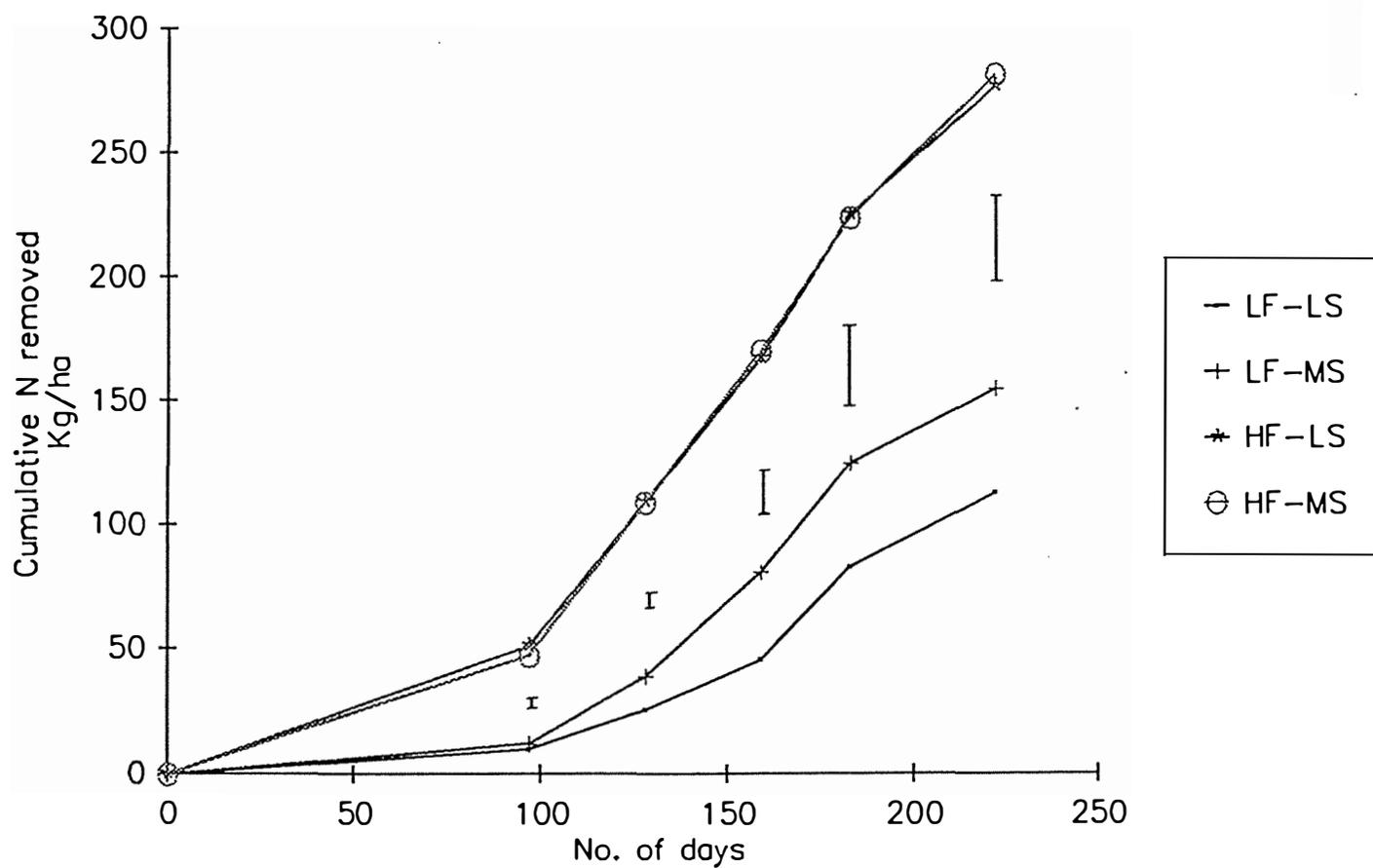


Fig.5.6 Cumulative amounts of nitrogen removed by pasture from Jun. 1989 to Jan. 1990 at all sites. Harvests were made on 5/9/89, 6/10, 6/11, 30/11 and 8/1/90. (Vertical bars = L S D,  $p < 0.01$ ).



By the end of spring pasture uptake of S and N had decreased the amounts of soil sulphate and mineral N in the upper 0-250mm of soil at high fertility sites. The magnitude of the decrease was much less than the amount of S and N taken up by pasture. This suggests that mineralization of organic S and N also contributed to the plant available pool during this period. Since the amount of N removed by pasture was far greater than the change in mineral N concentration it is reasonable to assume that most of the N taken up by pasture was mineralized from soil organic matter and a small amount of N derived from the fixation of atmospheric N by legumes (section.5.3.9). As mentioned in section 5.3.2, the sulphate in the 150-250mm soil depth changed little, suggesting that pasture obtained nearly all of its S requirements from the top 150mm of the soil.

The rates of S and N removed by pasture were as low as 9.3g S and 0.1kg N ha<sup>-1</sup> day<sup>-1</sup> in winter and as high as 125g S and 1.6kg N ha<sup>-1</sup> day<sup>-1</sup> in late spring at low fertility sites. At high fertility sites the amounts of S and N removed were as low as 45g S and 0.5kg N ha<sup>-1</sup> day<sup>-1</sup> during winter and as high as 220g S and 2.42kg N ha<sup>-1</sup> day<sup>-1</sup> during late spring. The rate of S and N removed by the pasture increased approximately 14 times from winter to spring at low fertility sites, but in high fertility sites it increased only five times during that period. This suggests that both S and N were limiting pasture production less in HF farmlet during winter because low soil and air temperature were two main factors limiting pasture production. During this period, the higher sulphate concentrations in soil increased the potential for leaching losses of both S and N to occur from the HF farmlet.

### **5.3.9 Net Mineralization of S and N**

The calculation of net mineralization of S and N is complicated by the fact that sheep excreta was allowed to return to the cage areas where pasture production and soil mineral S and N measurements were made but not to the cylinder where drainage measurements were made (see Fig.5.1). The effect of excreta return on pasture growth therefore needs to be considered first.

### 5.3.9.1 Quantitative Estimation of Excreta Return

Distribution of excreta in grazed pastures is dependant upon factors such as stocking rate, camping behaviour, grazing pattern, animal type and frequency of excretion (Wilkinson and Lowery, 1973; Gillingham *et al.*, 1980). For S returned in sheep excreta it has been calculated that the ratio of S excreted in dung:urine is 40:60 (Wilkinson and Lowery, 1973). They also reported that an increase in the concentration of S in pasture increases the amount of S in urine. In the case of N it has been shown that about 30% of the N is excreted in dung and the remaining 70% returned in urine (Barrow and Lambourn, 1962). At the Ballantrae farmlets pasture utilization has been estimated at 70%. Therefore it is assumed that 70% of the pasture S is consumed by the sheep and 15% of the consumed S and N is removed in animal product (Wilkinson and Lowery, 1973). The amounts of S and N that is returned in excreta is given in Table 5.7. In hill country the return of nutrient in excreta per unit surface area is confounded by land slope, regional climate and their influence on the grazing and camping behaviour of the sheep (Saggar *et al.*, 1990a). Of the excretal return it was assumed using the data of Gillingham *et al.* (1980) that 60%, 30% and 10% of dung and 55%, 31% and 14% of urine were returned to low, medium and steep slopes, respectively. Calculations on the amount of  $\text{SO}_4^{=}$  returned to both low and medium slope are given in Appendix-5.3. A similar calculation was also made for N (Wilkinson and Lowery, 1973; Gillingham *et al.*, 1980). The amount of S and N ingested by the animal and returned in excreta is given in Table 5.7. Even though considerable amounts of sulphate and readily available N are returned in excreta, the amounts of this excretal S and N taken up by pasture plant are low (about 7% of S and 6% N in urine and 1.9 % of S and 3.7% N in dung over 150 days of pasture growth, see Chapter-7). Remaining excretal S and N enters the soil organic S and N pools and becomes plant available over a longer period. Goh and Nguyen (1990) also reported only 7% recovery of urinary S by mixed ryegrass-white clover pasture after 270 days. The immediate and direct contribution of excreta S and N to plant uptake and growth can be considered small (see Chapter-7).

**Table 5.7. Amounts of dry matter and S and N consumed and the amounts of readily available S and N returned in excreta in whole farmlets and the calculated amounts of excretal S and N taken up by pasture.**

Farmlet	Pasture consumed*			S and N returned in excreta		Plant uptake of Excreta S and N	
	kg/ha						
	Dry matter	S	N	S	N	S	N
LF-LS	2642	6.9	79.3	6.8	64.4	0.45	3.8
LF-MS	3632	9.5	108.5	2.9	27.5	0.21	1.7
HF-LS	5815	17.7	186.2	15.3	137.0	1.1	8.0
HF-MS	5963	18.6	196.7	6.2	57.2	0.4	3.5

\* Assuming 70% ingestion of total pasture production.

### 5.3.9.2 Net mineralization of S and N

The net mineralization of S was calculated using the following formula.

$$S_m = (S_f - S_i) + P + L - E$$

Where

$S_m$  = Sulphur net mineralized (kg S ha<sup>-1</sup>) for an experimental period.

$S_f$  = Soil sulphate S (kg S ha<sup>-1</sup>) at the end of the experimental period as measured by extracting the soil with 0.04M Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>.

$S_i$  = Soil sulphate S (kg S ha<sup>-1</sup>) at the beginning of the experimental period as measured by extracting the soil as mentioned above.

$P$  = Total S removed by plants (kg S ha<sup>-1</sup>) over the experimental period.

$L$  = Total S lost by leaching (kg S ha<sup>-1</sup>) over the experimental period.

$E$  = Total excretal S taken up by plants and lost by leaching (kg S ha<sup>-1</sup>) over the experimental period.

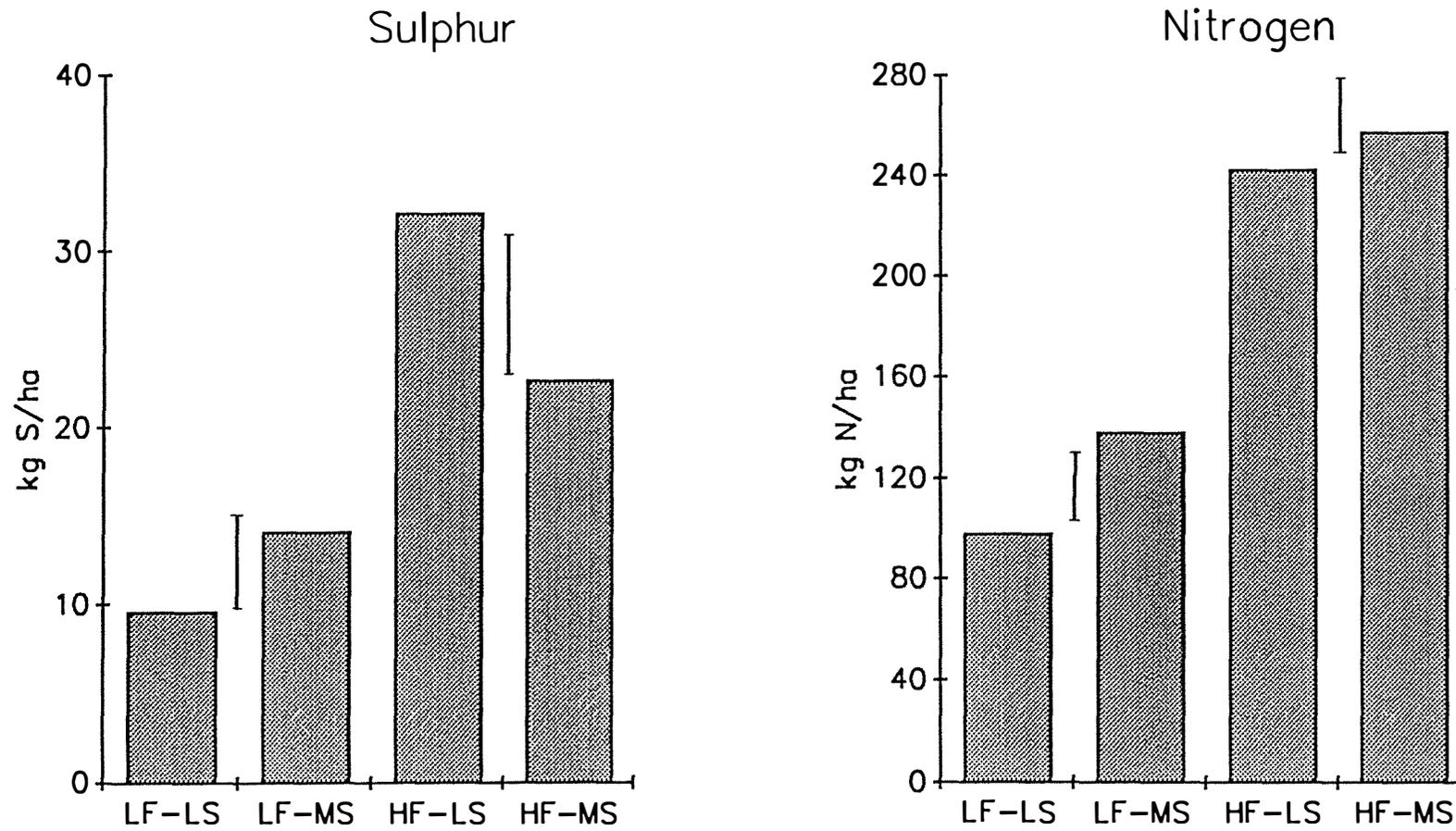
The net mineralization of N was calculated in the same way as S. Mineral N in the soil at the beginning and at the end was measured using 2M KCl extract and the pasture uptake of N includes an unknown amount of N (usually < 10% of the total pasture N) contributed by clover fixation (see same section below). The same procedure was used to calculate the net mineralization of S and N for various seasons during the experiment. An illustration of the calculation of the net mineralization of S and N is described in Table 5.8 for LF-LS and HF-LS sites. Based on the results in Chapter 7 and those of Goh and Nguyen (1991) it was estimated that 7% of total excretal S and N deposited was recovered in plant uptake over the whole experimental period (217 days, Jun. 1989 to Jan.1990).

Over the 217 day period 27.5 kg S ha<sup>-1</sup> and 251 kg N ha<sup>-1</sup>, respectively, were mineralized at the high fertility farmlet and 12 kg S ha<sup>-1</sup> and 119 kg N ha<sup>-1</sup>, respectively, were mineralized at the low fertility farmlet (Fig.5.7). The greater amounts of S and N mineralized at HF sites reflect the greater amounts of fertilizer previously applied and the impact this has had on legume growth, nitrogen fixation,

**Table 5.8 Calculation of the net mineralization of S and N during the periods of early winter and late spring for LF-LS and HF-LS sites (the symbols are described in text).**

Season	Nutrient	Farmlet	$S_i$	$S_f$	P	L	E	$S_m$	
			kg ha <sup>-1</sup>						
Winter	S	LF-LS	15.8	22.5	0.3	0.75	0.0	7.7	
		HF-LS	44.0	33.0	1.6	3.6	0.8	-6.6	
	N	LF-LS	11.3	17.6	3.6	0.2	0.1	10.0	
		HF-LS	10.0	17.5	18.2	0.8	0.7	25.8	
Spring	S	LF-LS	16.8	14.4	3.0	0.0	0.1	0.5	
		HF-LS	34.0	31.9	5.3	0.0	0.2	3.0	
	N	LF-LS	11.5	6.1	37.8	0.0	1.2	31.1	
		HF-LS	22.5	6.7	58.1	0.0	1.8	40.5	

Fig.5.7 Net mineralization of S and N from Jun. 1989 to Jan. 1990 at all sites (Vertical bars=LSD,  $p<0.01$ )



pasture production, carrying capacity and the amount of dung and urine returned. Compared to the LF farmlet for an additional 250kg SSP ha<sup>-1</sup> year<sup>-1</sup> applied, which is equivalent to an addition of 30 kg S ha<sup>-1</sup> year<sup>-1</sup>, an additional 22.5 kg S ha<sup>-1</sup> was mineralized at the HF low slope. At the medium slope of LF and HF sites the difference (7.5 kg S ha<sup>-1</sup>) was much smaller reflecting the smaller amounts of dung and urine returned to the medium slopes. Also compared to the LF farmlet additional amounts (144 and 119 kg N ha<sup>-1</sup>) of N were mineralized at low and medium slopes and available for pasture uptake at the HF farmlet.

Fertilizer and excretal S inputs have increased the amount of S in the labile sulphate ester pool. It has already been demonstrated (Chapter-3) that fertilizer and excretal deposition increased the ester sulphate pool, the pool from which most of potentially mineralized S originates in these soils.

There was no difference in the amounts of S and N net mineralized at low and medium slopes in the low fertility farmlet. The effect of the prevailing North Westerly wind on animal camping behaviour and the impact this had on excreta return at these two sites explains the lack of difference found at this site. At the high fertility sites the amount of S net mineralized was significantly greater on the low slope (Fig.5.7). This difference did not extend to the amounts of N mineralized.

Although net mineralization of S and N was observed over the eight months of the study, net mineralization of S and N was not continuous over that period (Table 5.9). In early winter net immobilization of S occurred in high fertility sites while N was mineralized at all sites (Table 5.9). This immobilization of S occurred because the decrease in extractable soil sulphate could not be accounted for in the plant uptake or losses by leaching. It is unclear why the pattern of S and N turnover should differ in early winter. For mid to late winter net mineralization of both S and N occurred at all sites. Within a short period between late winter to early spring (15 days) net immobilization of both S and N was observed. With one exception (Table 5.9), from early spring onwards net mineralization of both S and N was observed at all sites. The ratio of N to S mineralized were approximately 10 and 9.5 for low and high

**Table 5.9** Amounts of S and N net mineralized\* during the experiment  
(31/5/1989 to 8/1/1990) for all four sites

Farmlet	31/5-4/7		4/7-25/8		25/8-5/9		5/9-6/11		6/11-30/11		30/11-8/1/90	
	S	N	S	N	S	N	S	N	S	N	S	N
	kg ha <sup>-1</sup>											
LF-LS	7.7	10.0	6.5	16.5	-5.3	-15.5	-2.0	34.0	0.5	31.1	2.3	29.0
LF-MS	4.7	15.6	19.7	55.9	-18.3	-52.7	4.9	67.2	2.3	36.0	1.0	29.7
HF-LS	-6.8	25.8	32.4	46.4	-21.1	0.7	15.1	89.0	3.0	40.5	8.3	49.8
HF-MS	-3.6	28.8	16.7	28.4	-5.4	5.8	13.1	117.3	6.6	41.6	5.9	56.9

minus sign indicates net immobilization during the period.

fertility sites, respectively, which unlike the ratio of N to S mineralized in the laboratory study (N to S ratio of 2 to 3), is very close to the N to S ratio of the soil organic matter in these soils (Chapter-3, Table 3.2 and 3.4). While the total C, N and S for the soil around each of the 48 individual lysimeters were not measured the total C, N and S in the bulked soil samples for each site were measured. Using the means of the four site data sets no significant relationship between C/N and N mineralized or C/S and S mineralized could be found to explain the amounts of N and S mineralized at each site.

The total amount of N net mineralized for the individual lysimeters was strongly correlated to the total pasture production (Fig.5.8). In this study the exact amount of N mineralized from soil organic matter was slightly over estimated, since the total amount of N removed by pasture included an unknown amount of N fixed from the atmosphere by the legumes. This amount is likely to be small, because total N uptake by legumes was less than 10% of the total pasture production and not all the N taken up by legumes is derived from the fixation. Legumes in established pastures may derive about 50% of their N requirements from soil (Field and Ball, 1978). The correlation coefficient ( $r=0.981$ ) for the relationship between the net mineralization of N and the total pasture production (Fig.5.8) was not changed much from the correlation coefficient ( $r=0.970$ ) obtained for the relationship between the net mineralization of N and the pasture production other than legumes (Fig.5.9). This showed that a majority of the pasture N was derived from the mineralization of the soil organic matter. The linear nature of the regression indicates that N availability was limiting pasture production even on the high fertility low slope site and probably explain why little N was leached from these hill country pastures.

In the case of S, at mineralization rates of  $<15 \text{ kg S ha}^{-1}$  the majority of S was taken up by pasture (Fig.5.10). At higher mineralization rates a much greater fraction of S was lost by leaching. The data indicates that at the high fertility sites S is not limiting pasture growth, but is being utilized inefficiently because of limited supply of N for pasture growth. This aspect will be examined and discussed in greater detail in Chapter-6.

Fig.5.8 Relationship between N net mineralized and pasture dry matter production from Jun. 1989 to Jan. 1990 at all sites. Values for 40 individual lysimeters.

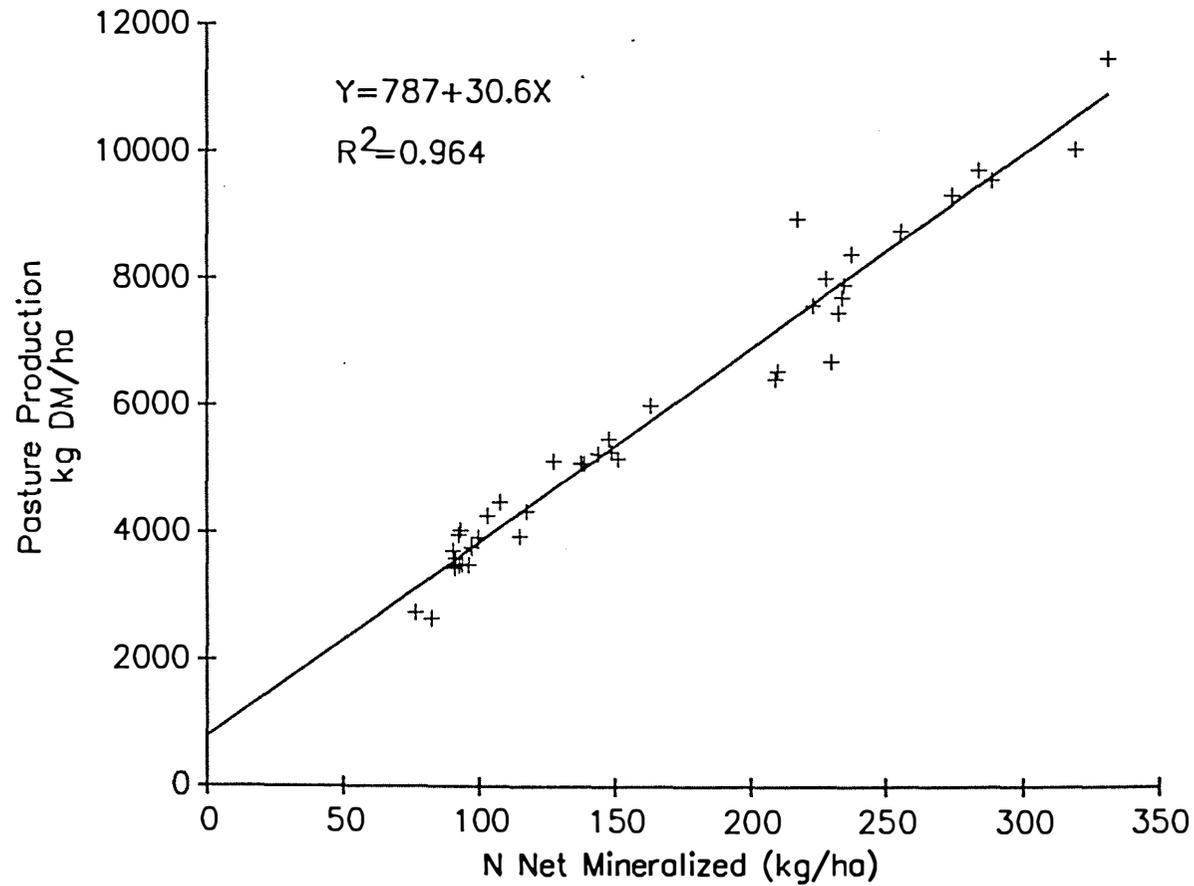


Fig.5.9 Relationship between nitrogen net mineralized and pasture dry matter other than legumes produced from Jun. 1989 to Jan. 1990 at all sites. Values for 40 individual lysimeters.

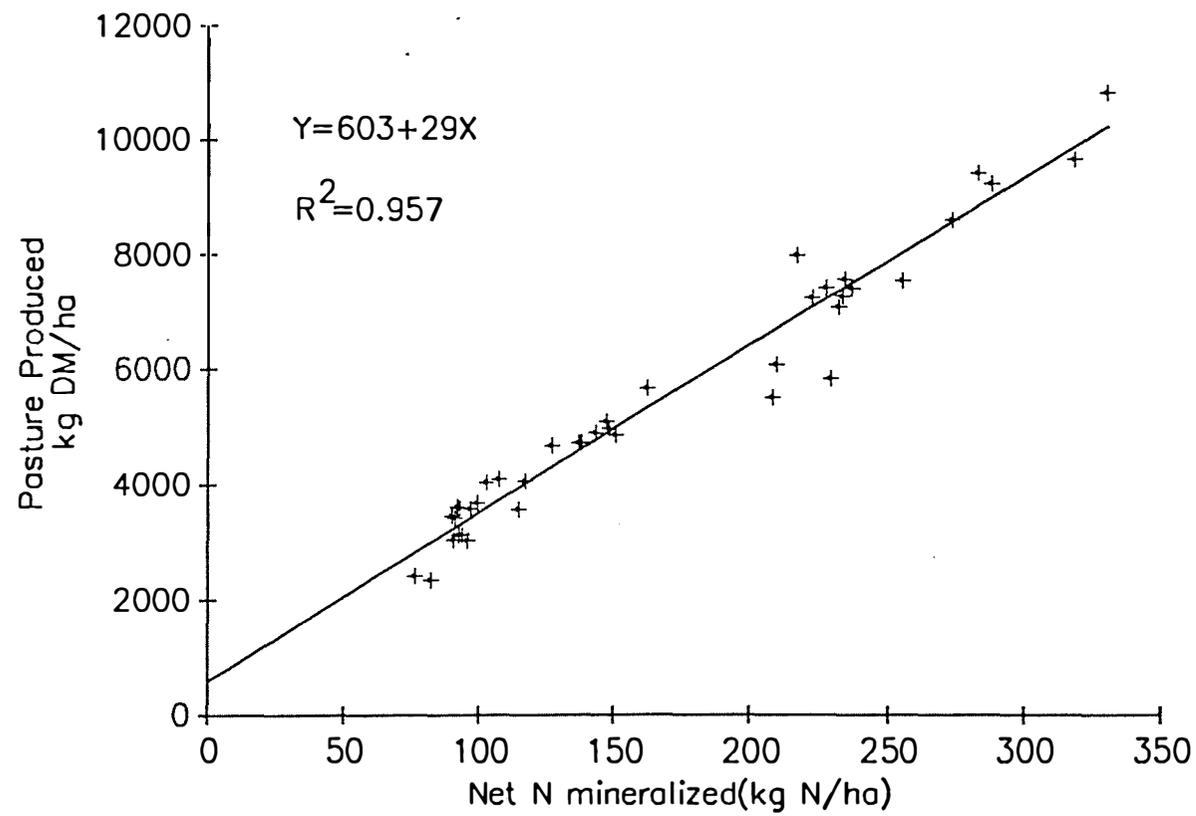
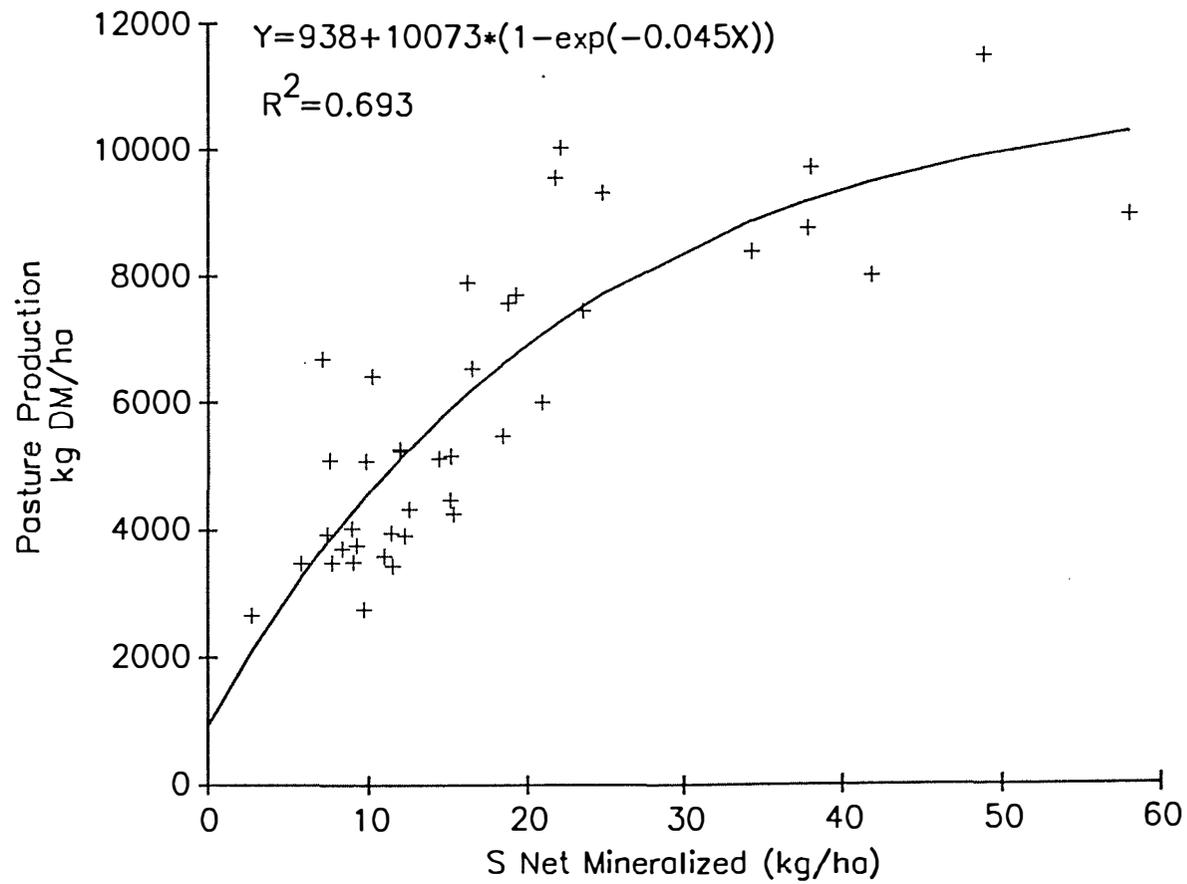


Fig.5.10 Relationship between S net mineralized and pasture dry matter production from Jun. 1989 to Jan. 1990 at all sites. Values for 40 individual lysimeters.



## 5.4 GENERAL DISCUSSION AND CONCLUSION

The mini-lysimeters with ion exchange resin traps developed in Chapter-4 are effective for measuring the leaching losses of both anions and cations in hill pastures under field conditions. The technique allows the net mineralization of S and N in the field to be calculated by establishing losses by leaching to be added to the N and S taken up by pasture and that remaining in the soil solution. Previously calculation of net mineralization of S and N under field conditions has not been measured mainly because there has been no direct measurement of the losses of S and N by leaching. The lysimeter method was successfully used to calculate the mineralization of S and N in presence of grazing animals. The study clearly showed that a greater mineralization of S increased the leaching losses of S but a greater mineralization of N increased the uptake of N.

Application of 375 kg SSP ha<sup>-1</sup> year<sup>-1</sup> to the high fertility farmlet, a three fold increase in S application over the low fertility farmlet (125 kg SSP ha<sup>-1</sup> year<sup>-1</sup>), doubled the pasture production of the high fertility sites and increased S leaching losses by approximately 7 times. Nitrogen leaching was not increased. This demonstrates that cycling of S in low fertility farmlet was more efficient with a greater proportion of the S returned in excreta and mineralized from soil organic matter being either taken up by pasture or soil microorganisms. Less S remained in the soil solution to be lost by leaching. Although N mineralization doubled the amount of N lost by leaching, the amount of N lost by leaching was insignificant in terms of agricultural efficiency. In general N was efficiently used in both low and high fertility farmlets. Increased SSP application also increased the leaching losses of Ca, Mg and K.

It has been shown that although approximately 10 times more N than S was taken up by pasture and cycled via animal to soil, sulphate and not nitrate was the dominant anion in the drainage waters. The concentration of ammonium in the drainage was also low. An average of ten times more S than N was found in the drainage waters below 25cm depth suggesting that in hill country pastures of even high fertility, N cycling is more efficient than S cycling and that much of the mineralized N is used

by pasture and microorganisms. Nitrate leaching in these hill country pastures does not appear to be an important process affecting the soil N levels, the N economy of the sward and contributes only small amounts to fresh water and aquatic ecosystems. Nitrogen was the key nutrient limiting plant biomass production in the hill country pasture used in this study. Sulphur plays a secondary role so that much of the S mineralized was lost by leaching from the system.

The amounts of sulphate and mineral N present in the soil throughout the experimental period clearly showed that in the low fertility farmlet most of the S and N taken up by pasture and lost by leaching was derived from the mineralization of soil organic matter. In the high fertility farmlet there was a greater source of S and N in the mineral pools in the soil solution. For the majority of the growing season the mineral S and N present below 150mm of the soil showed little availability for plant uptake. Mineral S and N below 150mm of the soil can be regarded as lost from the plant-animal cycle.

An issue not examined in this Chapter was the fate of freshly applied fertilizer S and the relative contributions of freshly applied fertilizer S and mineralized S to plant uptake and the quantities of each lost by leaching. The direct effect of freshly applied fertilizer S has on the mineralization of soil organic S and N was also not examined in this study. These aspects will be examined in the next Chapter where further studies are carried out using the same mini-lysimeters.

## CHAPTER-6

### FATE OF FERTILIZER SULPHUR APPLIED TO GRAZED HILL COUNTRY PASTURES

#### 6.1 INTRODUCTION

In the previous field study it was shown that variable amounts of S and N were mineralized from pasture soils, depending upon their past fertilizer history ( Chapter 5). The study showed that most of the N mineralized was utilized by plants leaving an insignificant amount of mineral N in the soil solution which was lost by leaching. In contrast, substantial amounts of the S mineralized were lost from the soil by leaching.

The influence of a current fertilizer application on the amounts of S mineralized, taken up by plants and lost by leaching has not been studied. It has been suggested that the losses of S immediately after fertilizer application may represent a substantial proportion of S losses from these hill country pastures (Saggar *et al.*, 1990a). Further studies are required to provide information on the proportions of mineralized and fertilizer S taken up by plant and lost by leaching. Such information can be obtained by using  $^{35}\text{S}$  labelled fertilizer and by monitoring the transformation of  $^{35}\text{S}$  in soil and the movement of the tracer to plants and drainage water.

In New Zealand (Gregg and Goh,1979) and Australia (Till and May,1971), only a limited number of field studies have used  $^{35}\text{S}$  labelled fertilizer to investigate the fate of fertilizer S applied to grazed pastures. In each of the studies conducted the recovery of fertilizer S in soil-plant-animal system did not include a direct measurement of  $^{35}\text{S}$  losses by leaching. Generally the  $^{35}\text{S}$  unaccounted for or the difference between the applied and recovered  $^{35}\text{S}$  was assumed to be lost from the soil by leaching. Fertilizer leaching losses calculated from mass balances can overestimate the actual losses because applied fertilizer may influence the mineralization of soil organic S (priming effect) which can also be lost along with fertilizer S. Neither the work of Gregg and Goh,(1979) nor Till and May,(1971) examined the effect of the

previous fertilizer history on the mineralization of soil organic S and subsequent plant uptake and losses by leaching. In both the above studies radioactively labelled gypsum was used to trace the movement of S in the soil-plant-animal system rather than  $^{35}\text{S}$  labelled SSP, the common S fertilizer for pastoral system in New Zealand and Australia. The presence of phosphate may enhance the losses of sulphate by leaching in some soils (Bolan *et al.*, 1988). Therefore under certain situations, experiments using gypsum may underestimate the losses of S by leaching from fertilizers containing both S and P. Compounding this effect pasture growth may be P responsive, thus SSP fertilization rather than gypsum may lead to an increased plant uptake of S.

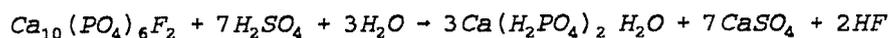
The objective of this study was to investigate the fate of recent (fresh) fertilizer S applied to legume based hill country pastures as  $^{35}\text{S}$  labelled SSP. In addition the effect of freshly applied fertilizer on the mineralization of soil organic S and N and subsequent plant uptake and losses by leaching under field conditions were also investigated. By working at more than one site it was possible also to examine the effect that the rate of fertilizer application and the residual effect of previously applied fertilizer had on plant uptake, losses by leaching and the mineralization of soil organic S and N.

## 6.2 MATERIALS AND METHODS

The study built on the previous field experiment ( Chapter-5), that investigated the mineralization rates of organic S and N, plant uptake and losses by leaching of these two nutrients from two slope categories in fertilized grazed hill pastures ( Chapter-5). Of the eight cores monitored in the previous study in each of the two farmlets and two slopes, 4 cores were topdressed with radioactively labelled  $^{35}\text{S}$ -SSP and the remaining 4 cores remained unfertilized. Cores not receiving fertilizer enabled the residual effect of the previous fertilizer applications to be examined

### 6.2.1 Preparation of Radioactively Labelled $^{35}\text{S}$ Superphosphate

Apatite rock reacts with concentrated sulphuric acid and produces SSP. The stoichiometric equation for the reaction is



According to the stoichiometric equation the amount of sulphuric acid required for 100% acidulation of one gram of rock which contains 18.45% of phosphorus is

$$\frac{686 \times 1}{1008} = 0.681\text{g}$$

Where 686 is the amount of sulphuric acid (g) required to acidulate completely one molecular weight (1008) of apatite rock. In the experiment the SSP was prepared by using 50:50 mixture of Nauru:Christmas Island rocks which contains approximately 15% phosphorus. So the amount of sulphuric acid required to acidulate 1g of this mixture is

$$\frac{0.681 \times 15.00}{18.45} = 0.553\text{g}$$

The volume of concentrated sulphuric acid required for 100% acidulation

$$\frac{0.553}{1.84} = 0.301\text{ml}$$

where 1.84 is the specific gravity of concentrated sulphuric acid. The acid is normally diluted to 65% by addition of water. The amount of 65% sulphuric acid required for 100% acidulation

$$\frac{0.301}{0.65} = 0.466\text{ml}$$

Two separate quantities of SSP were prepared for both low and high fertility farmlets. For both low fertility sites, 1.4 grams of phosphate rock was mixed with 0.625ml of 65% sulphuric acid which had been previously labelled with 5mCi  $^{35}\text{S}$ -sulphate. Approximately 2 grams of SSP were prepared. For both high fertility sites, 4.2 grams of rock was mixed with 1.96ml of 65% sulphuric acid previously labelled with 5mCi

<sup>35</sup>S-sulphate. Approximately 6 grams of SSP was prepared. Before mixing, the sulphuric acid was warmed to about 60-70°C. After acid addition, drops of water were added to improve the uniformity of mixing. The mixture was then dried in the oven at 60°C.

### **6.2.2 Application of Fertilizer**

To avoid the loss of labelled SSP the fertilizer was not granulated in a drum. Granulation was simulated by weighing exactly 0.073g of radioactively labelled SSP in to gelatin capsules. Three capsules of fertilizer were placed on each core in low fertility sites at a rate of 125 kg SSP ha<sup>-1</sup> (see Figure of cage and core placement, section 5.2). Similarly 0.134g of radioactively labelled SSP was weighed into gelatin capsules and five capsules of fertilizer were placed on each core in high fertility sites at a rate of 375 kg SSP ha<sup>-1</sup>. The amounts of labelled fertilizer sulphur applied, the activity of the added <sup>35</sup>S and the specific activity of the fertilizer for each of the four sites are presented in Table 6.1. The fertilizer was applied on 12 January 1990.

### **6.2.3 Rainfall, Drainage and Pasture Measurements**

The daily rainfall was measured throughout the experiment at all four sites. Predicted net drainage was calculated for each site (calculations are described in Chapter-5, section 5.2.3.1). In addition, two additional mini-lysimeters with drainage water collection vessels (instead of resin trap) were inserted in each of the four sites and the drainage water was collected. The amounts of drainage collected at each site were compared with the predicted net drainage.

The pasture was harvested depending upon growth. A total of six cuts were made for the period from January to October 1990. Pasture samples were oven dried at 60°C and the dry matter weighed. The bulk sample was ground and a subsample was used to determine total N and S and the <sup>35</sup>S activity.

**Table 6.1 Initial sulphate and mineral N present in the soil, fertilizer sulphate and  $^{35}\text{S}$  activity applied to each core and the specific activity of fertilizer S for all four sites.**

Farmlet	Soil Sulphate*	Soil Mineral N*	Fertilizer S Applied	Activity of $^{35}\text{S}$ Applied	Specific Activity of Fertilizer S <sup>#</sup>
	kg ha <sup>-1</sup>		mg S/core	cpm/core	cpm/mgS/core
LF-LS	14.1	6.2	24.75	10.17E+08	4.11E+07
LF-MS	18.2	7.0	24.75	10.17E+08	4.11E+07
HF-LS	34.3	6.7	72.89	11.85E+08	1.63E+07
HF-MS	28.1	5.7	72.89	11.85E+08	1.63E+07

\* Soil sulphate and mineral nitrogen were determined when radioactively labelled superphosphate was applied. The values were for the top 25cm of the soil.

# Specific activity = activity of  $^{35}\text{S}$  applied / Amount of S applied.

Resin collection from the resin trap lysimeter (as in Chapter 5, section-2) coincided with pasture harvests which were approximately at five week intervals. The resins were eluted with 50ml 1M NaCl as described in Chapter-4, section 2.2.3. The amounts of sulphate, mineral N and  $^{35}\text{S}$  activity in the eluates were measured in order to calculate the losses of S and N by leaching.

Each time the resin was changed in the lysimeter, soil samples were collected from all four sites from outside the cores. All four pasture cage sites were topdressed with SSP at the same time the cores were topdressed, equivalent to the labelled SSP applied to the cores. When cage sites were topdressed the core surfaces were completely covered using plastic saucers. Soil samples were collected in the cage sites from Jan. to Oct. 1990. Extractable sulphate and mineral N were measured for three soil depths (0-75, 75-150 and 150-250mm) ( Chapter-5, Section 5.2).

### **6.2.5 Analytical Measurements**

The pasture S and N content, the concentrations of sulphate and mineral N in the resin eluates and the extractable soil sulphate and mineral N were measured as described in Chapter-5, section 5.2. The  $^{35}\text{S}$  activities of the pasture and the resin eluates were measured by counting the activity of the herbage digest or the eluate of the resin using a Beckman LS 3801 liquid scintillation counter. The scintillation cocktail for measuring the activity of  $^{35}\text{S}$  was prepared as mentioned in the following section.

### **6.2.5 Preparation of Scintillation Cocktail**

Two litres of cocktail were prepared by mixing 8g of 2,5-diphenyl oxazole (POP), 0.2g of dimethyl 1,4-di-[2-(5-phenyl oxazolyl)]-benzene (POPOP), 1340ml of toluene and 660ml of triton-X 100. This cocktail was stirred for a minimum of 6 hours. The activity of  $^{35}\text{S}$  was measured in a clear emulsion of 10 mls of cocktail and 1ml of the resin eluate (or the diluted herbage digest). All measurements of radioactivity were corrected for decay and normalized to the day on which the  $^{35}\text{S}$  labelled SSP was applied to the cores. A standard reference solution which was prepared from the labelled SSP by dissolving labelled SSP in dilute hydrochloric acid. Quench correction curves were prepared for each type of counting matrix.

## 6.3 RESULTS AND DISCUSSION

When fertilizer S is applied to grazed pasture, it rapidly enters the S cycle. Sulphur, first enters to the soil solution sulphate pool. The rate of entry of fertilizer S to sulphate pool depends upon, among other factors, the soil moisture which is influenced by the amount of rainfall. Once S enters the sulphate pool, the fate is determined by several factors such as plant uptake, leaching losses in drainage waters, immobilization by soil microorganisms and adsorption onto soil sesquioxide surfaces (Rhue and Kamprath,1973; Freney *et al.*,1975; M'Laren *et al.*,1985). In order to monitor the fate of fertilizer S all of the components mentioned above should be studied.

### 6.3.1 Rainfall and Drainage

Drainage is a major vector for S loss, which is influenced by the amount of rainfall. The monthly rainfall during the experimental period (from Jan. 1990 to Oct. 1990) ranged from <50mm during Feb. to >250mm during Mar. 1990. Except for the months of Feb. and Sep. drainage occurred at all four sites (Fig.6.1) throughout the experiment. The total rainfall during the experiment was higher (948mm) than the long term average (800mm), in particular the rainfall was higher than the corresponding period for the year 1989 (616mm). Winter rainfall during the experiment was also higher than the year 1989 for the same period. The predicted net drainage was significantly correlated to a 1:1 relationship with the measured drainage collected from the lysimeters at all sites (Fig.6.2). About 91.1% of the variation was explained by the relationship. The close relationship between the predicted and measured drainage also showed that surface runoff was negligible. Thus a simple water balance model predicts drainage events and their size adequately.

### 6.3.2 Pasture Production

Increases in pasture production will influence the efficiency of S fertilizer use by removing more S in the above ground plant material and causing a greater transfer of S away from the site of uptake; plus extra 'root carbon' (Nei and Tinker,1980) may be generated, increasing the immobilization of soil solution  $\text{SO}_4^-$ .

Fig.6.1 Rainfall and predicted drainage from Jan. to Sep. 1990, rainfall for the year 1989 and the long term average rainfall (1979-1989) for the same period.

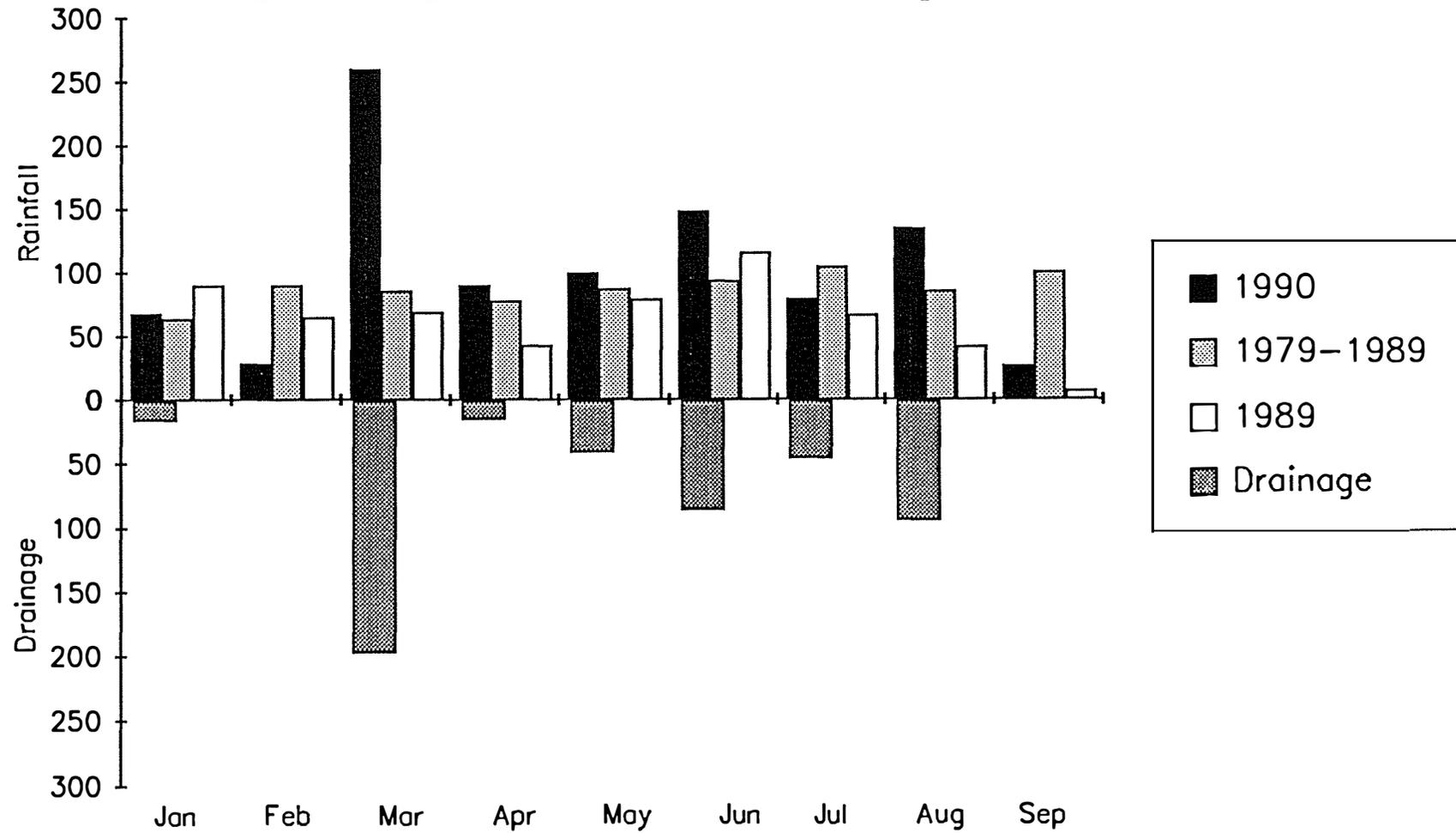
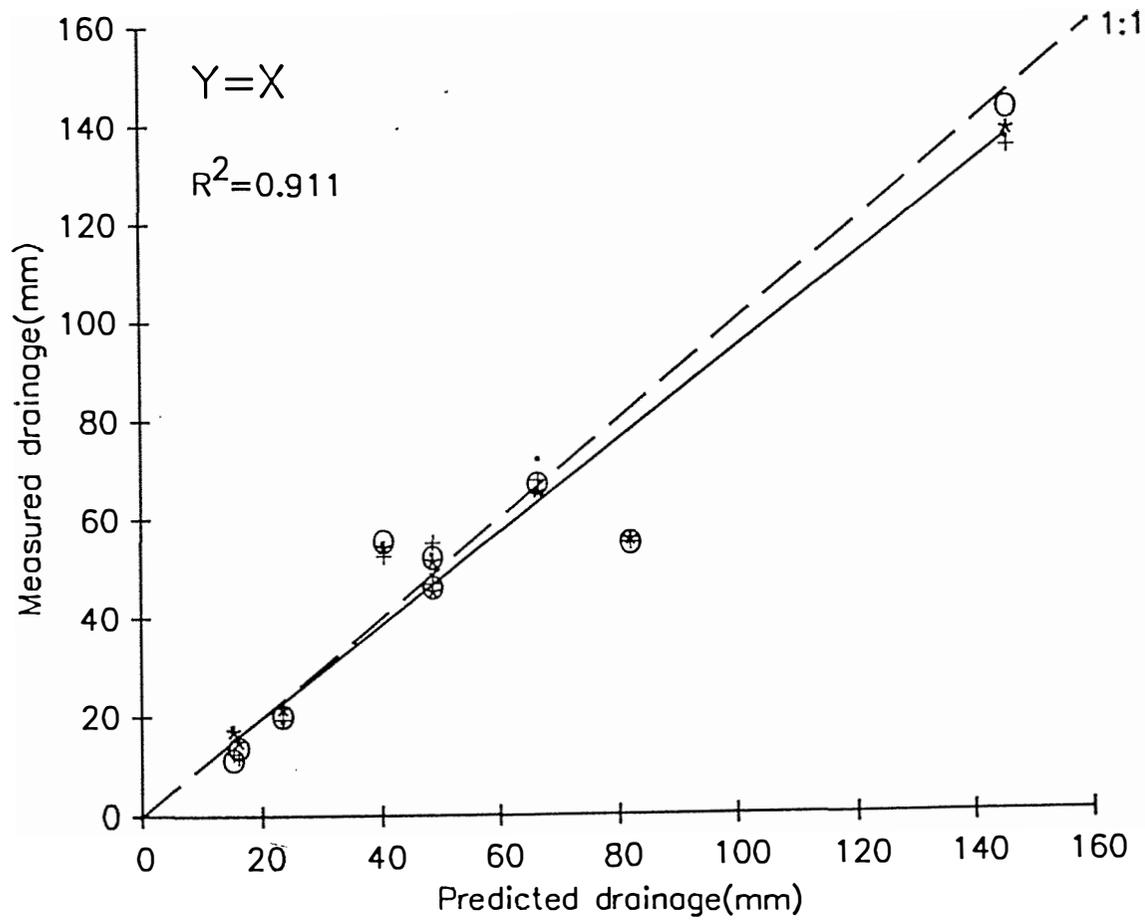


Fig.6.2. Predicted and measured drainage for the experimental period across all four sites. Symbols referred to four different sites.



Throughout summer (8/1/1990 to 26/3/1990) fertilizer application did not increase pasture production at any site (Table 6.2). Superphosphate is primarily applied to stimulate legume growth and biological N fixation. But the P and S applied might have not been fully available during the early periods after application due to dry conditions which prevailed during summer preventing SSP dissolution and/or the pasture uptake of P and S. Differences in pasture responses to applied fertilizer were first observed in autumn. By spring total pasture production for the 9 month period was greater ( $p < 0.01$ ) in the fertilized than in the unfertilized plots at all sites (Fig.6.3). Winter growth rates were slow ( $5.5 \text{ kg DM ha}^{-1} \text{ day}^{-1}$ ) compared to summer ( $29.6 \text{ kg DM ha}^{-1} \text{ day}^{-1}$ ), autumn ( $17.9 \text{ kg DM ha}^{-1} \text{ day}^{-1}$ ) and spring ( $12.9 \text{ kg DM ha}^{-1}$ ). The positive effect of freshly applied fertilizer on pasture production had a cumulative effect over the nine months of measurement. The fertilized plots at low fertility sites produced an average of 24% more pasture than the unfertilized plots, while at high fertility sites the fertilized plots produced an average only of 10% more pasture. Also, fertilizer caused a greater absolute increase in pasture production at the low fertility sites. This indicated that the residual effect of previously applied fertilizer was more pronounced in high fertility sites than in low fertility sites and pasture growth was less responsive to freshly applied fertilizer at this farmlet. This residual effect of previously applied fertilizer on pasture production was observed in earlier studies by Stephen,(1970), Gregg and Goh,(1979), Nguyen *et al.* (1989) and Lambert *et al.* (1990) for soils of both the South Island and the North Island of New Zealand. In fact Stephen,(1970) did not observe growth responses even after withdrawing S application for several years but Lambert *et al.* (1990) observed 1.5% and 5% decreases in pasture production during seven years after ceasing SSP application to the low and high fertility farmlets at Ballantrae. Nguyen *et al.* (1989a) observed a much greater decline (19%) in pasture production in the first year after cessation of SSP application to irrigated pasture.

Mean pasture production was higher (18%) at high than at low fertility sites for the nine month period. There was no significant difference in pasture production between low and medium slopes at the high fertility farmlet, but the medium slope in the low fertility farmlet produced more pasture than the low slope. This increased growth on

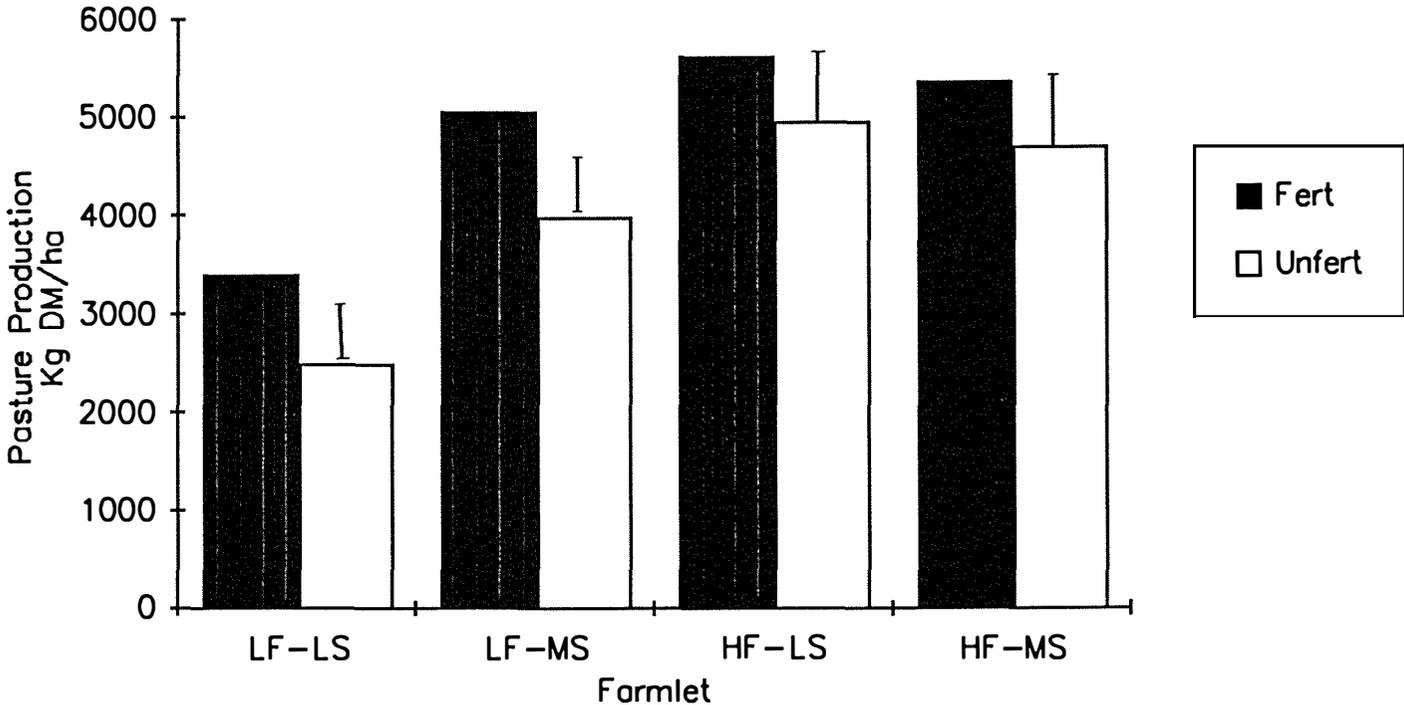
**Table 6.2** Amounts of pasture produced in fertilized and unfertilized plots at each site from Jan. to Oct. 1990.

Farmlet	Treatment	8/1 to 26/3	27/3 to 31/5	1/6 to 16/8	17/8 to 10/10
		kg DM ha <sup>-1</sup>			
LF-LS	Fert	2067	803	224	318
	Unfert	1724	505	101	173
LF-MS	Fert	2781	1089	341	865
	Unfert	2344	808	209	538
L.S.D*		566	260	123	295
L.S.D**		400	184	87	208
HF-LS	Fert	2389	1662	643	953
	Unfert	2689	1189	467	601
HF-MS	Fert	1622	1966	877	924
	Unfert	1924	1246	642	911
L.S.D*		869	478	139	409
L.S.D**		615	338	98	289

\* L.S.D. for fertilized and unfertilized treatments within a slope category.

\*\* L.S.D. for slopes and fertilized and unfertilized treatments within a farmlet.

Fig.6.3 Pasture production for fertilized and unfertilized plots at all sites during the period from Jan. to Oct. 1990  
(Vertical bars=LSD,  $p < 0.01$ ).



the easterly facing medium slope was mainly due to camping behaviour of the grazing animal brought about by the effect of the prevailing north westerly wind. This has already been discussed in Chapter-5, section.5.3.6.

### 6.3.3 Herbage Sulphur and Nitrogen Concentrations

The S and N concentrations of the pasture are indicators of the S and N status of the pasture. This reflects the soil's ability to supply S and N for maximum plant production. The amounts of S and N removed by pasture is a function of S and N concentrations of the pasture and the pasture growth rates. Sulphur and N concentrations of the mixed pasture were low during summer and the concentrations reached maximum during autumn. In winter they decreased slightly and were lower than the autumn (Table 6.3 & 6.4). During early spring the pasture S and N concentrations were low and almost equal to the S and N concentrations of summer. The low S and N concentrations during summer is due in part to greater pasture growth rates and also due to the declining mineralization rates as moisture becomes increasingly limiting ( Chapter-5). The pasture S and N concentrations in spring of this experiment were lower than the spring S and N concentration measured during the previous year ( Chapter-5, section 5.3) even though pasture production was also lower. The greater leaching losses of S during the period from Jan. to Aug. 1990 prior to spring growth occurring might explain the lower S and N concentrations (see section 6.3.5 on leaching). Nguyen *et al.* (1989) has<sup>ve</sup> already shown that pasture S concentrations decreased in spring due to winter leaching even in situations where fertilizer was applied in the autumn.

Pasture S concentrations were lower than the critical S concentration of 0.25% at low fertility sites during the summer and early autumn. Despite adequate S levels at the end of April, the concentrations of N remained lower than the critical N concentration of 3.00% at low fertility sites until end of May. At high fertility sites, the concentrations of S and N were in general higher than at low fertility sites with the concentration of S adequate through the nine months of measurement. Nitrogen concentrations were lower than the critical N concentration (3.00%) in the first (16-2-

**Table 6.3 Pasture S concentrations for fertilized and unfertilized plots for all four sites from Jan. to Oct. 1990.**

Farmlet	Treatment	16/2	26/3	30/4	31/5	16/8	10/10
		%S					
LF-LS	Fert	0.24	0.20	0.32	0.36	0.32	0.26
	Unfert	0.21	0.24	0.30	0.37	0.30	0.25
LF-MS	Fert	0.23	0.23	0.33	0.38	0.35	0.26
	Unfert	0.20	0.31	0.33	0.40	0.35	0.27
HF-LS	Fert	0.30	0.28	0.37	0.39	0.31	0.30
	Unfert	0.27	0.35	0.43	0.42	0.33	0.26
HF-MS	Fert	0.25	0.32	0.37	0.40	0.35	0.25
	Unfert	0.26	0.41	0.38	0.44	0.39	0.24

**Table 6.4 Pasture N concentrations for fertilized and unfertilized plots for all four sites from Jan. to Oct. 1990.**

Farmlet	Treatment	16/2	26/3	30/4	31/5	16/8	10/10
LF-LS	Fert	2.51	2.19	2.76	2.92	3.10	2.60
	Unfert	2.33	2.03	2.47	3.10	3.25	2.31
LF-MS	Fert	2.49	2.14	2.56	3.22	3.43	2.75
	Unfert	2.26	2.37	2.77	3.39	3.80	2.62
HF-LS	Fert	3.13	3.25	3.28	3.53	3.68	2.88
	Unfert	2.16	2.77	3.30	3.74	3.78	2.72
HF-MS	Fert	2.40	2.99	3.16	3.53	3.48	2.55
	Unfert	2.71	3.15	3.43	3.73	3.72	2.81

Fig.6.4 Amounts of S removed by pasture in fertilized and unfertilized plots at all four sites during the period from Jan. to Oct. 1990 (Vertical bars=LSD,  $p < 0.01$ ).

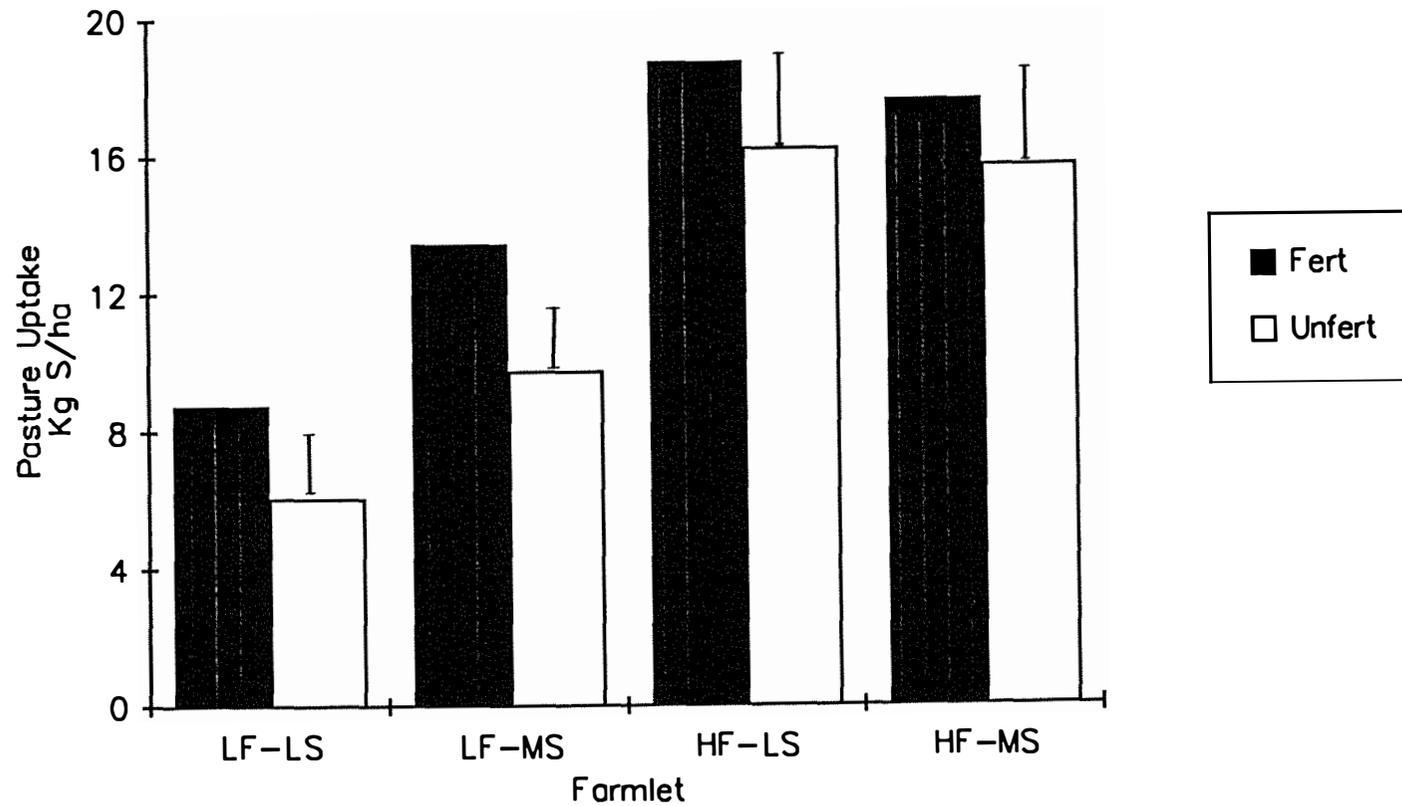
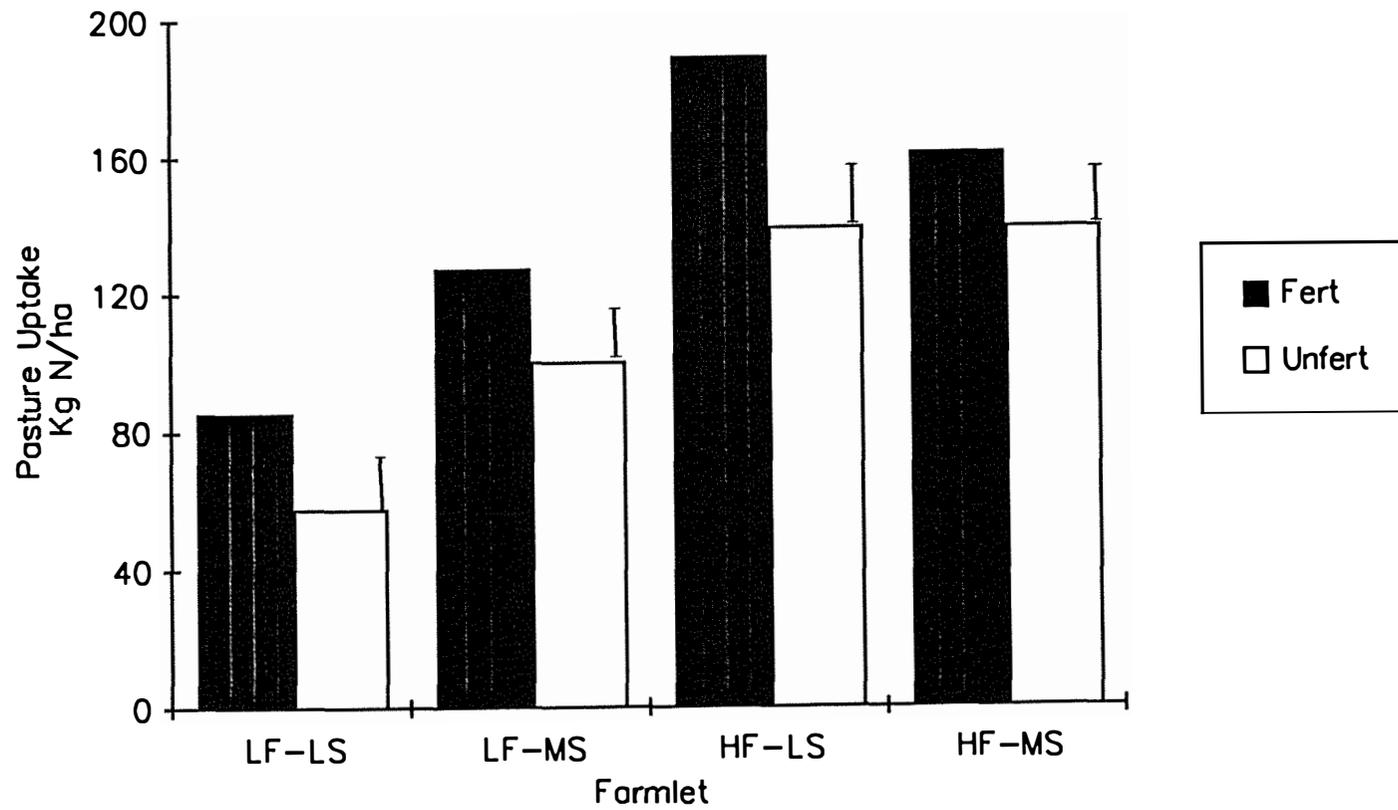


Fig.6.5 Amounts of N removed by pasture for fertilized and unfertilized plots at all sites during Jan. to Oct. 1990.  
(Vertical bars=LSD,  $p < 0.01$ ).



1990) and the last (10-10-1990) cuts. Although the rate of fertilizer application is to maintain N fixation through increasing plant S and P status, fertilizer application did not consistently maintain pasture S and N concentrations at a high level in the fertilized plots (Table 6.3 and 6.4).

#### **6.3.4 Sulphur and N Removed by Pasture**

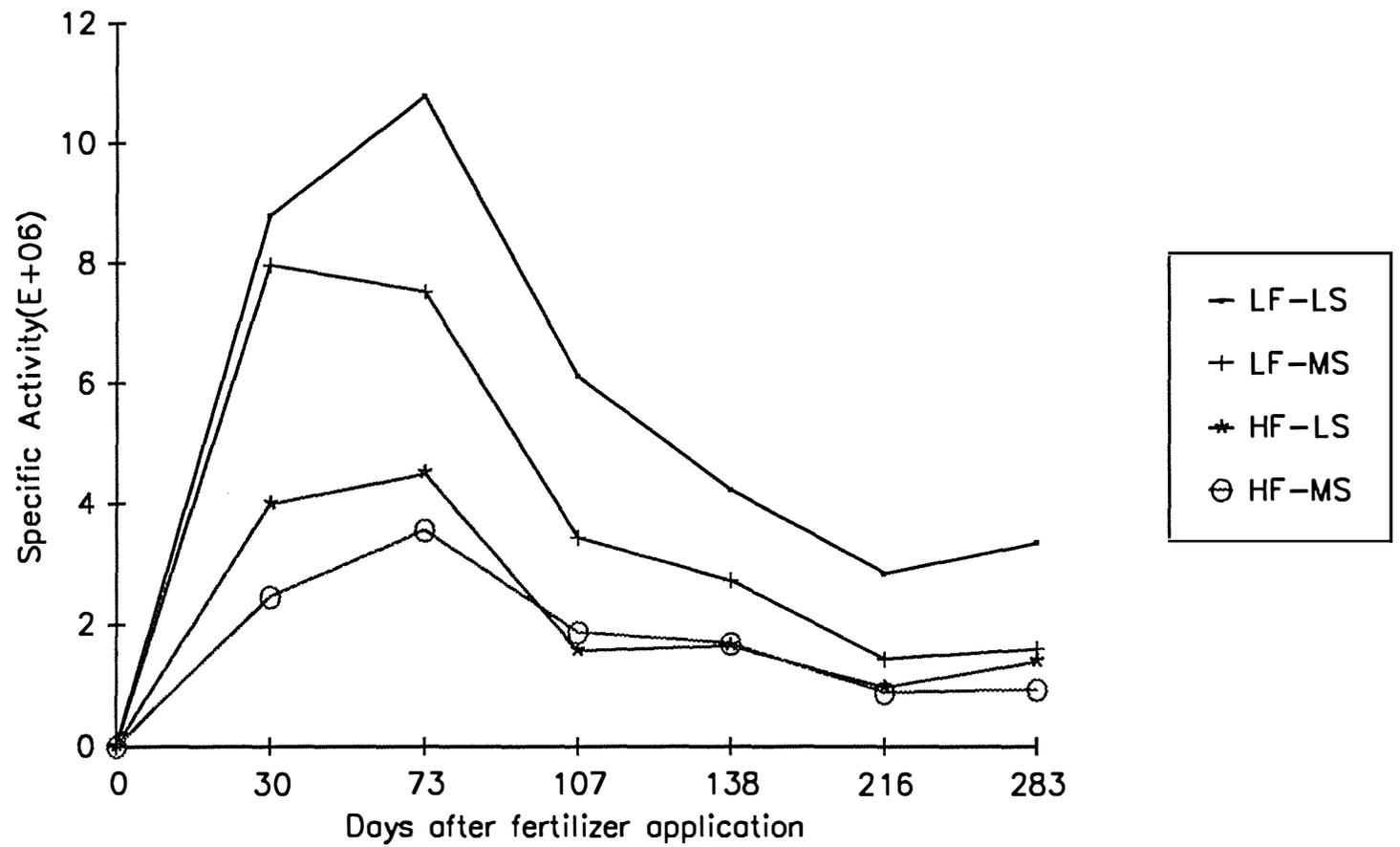
The total amounts of S removed by pasture was greater ( $p < 0.01$ ) in fertilized plots than in unfertilized plots at low fertility sites (Fig.6.4). At high fertility sites the total amounts of S removed by pasture was not significantly different between fertilized and unfertilized plots. This reflects the smaller response to freshly applied fertilizer at the two high fertility sites. Freshly applied fertilizer has a much more important role in supplying S directly to pasture at the low fertility sites. In the high fertility farmlet there was no significant difference in pasture S uptake on low and medium slopes. But in the low fertility farmlet more S was removed in medium slope than in low slope. The reason for this was discussed in section 6.3.3.

The total amounts of N removed by pasture was significantly increased ( $p < 0.01$ ) by fertilizer application at all sites (Fig.6.5). This showed that freshly applied fertilizer encouraged greater mineralization of N and more pasture uptake at the fertilized plots. Greater amounts of N were taken up by pasture at the two high fertility sites than at the two low fertility sites. Pasture removed more N on low slopes than on medium slopes at the high fertility farmlet, but at the low fertility farmlet pasture at medium slope removed more N than the low slope. The reason for this reversal was discussed earlier and is reflected in the higher fertility status of the medium slope site as shown by the initial soil test results presented in Table 6.1.

##### **6.3.4.1 Contribution of Soil and Fertilizer S to S Removed by Pasture**

The specific activity of pasture samples at all harvests were always much lower than the specific activity of the fertilizer S applied (LF=4.11E+07 and HF=1.63E+07

Fig.6.6 Changes in specific activity of S-35 in pasture with time at all sites during the period from Jan. to Oct.1990.



**Table 6.5** Amounts of <sup>35</sup>S activity, % fertilizer S removed, amounts of fertilizer and soil S removed by pasture and the percentage contribution of fertilizer and soil S to pasture at all sites from Jan to Oct 1990.

Farmlet	<sup>35</sup> S activity removed (cpm/core)	% fertilizer S removed*	S uptake by plant			% contribution to plant S	
			Total	Fertilizer**	Soil#	Fertilizer <sup>1</sup>	Soil <sup>2</sup>
			kg S ha <sup>-1</sup>				
LF-LS	1.12E+08	11.0	8.8	1.5	7.3	17	83
LF-MS	1.17E+08	11.5	13.5	1.7	11.8	13	87
HF-LS	7.88E+07	6.7	18.4	2.7	15.7	15	85
HF-MS	6.56E+07	5.6	17.7	2.3	15.4	13	87

\* % fertilizer S removed by plant = Activity removed by plant X 100/Total activity applied

\*\* Fertilizer S removed = Amount of fertilizer S applied X percentage fertilizer S removed/100

# Soil S removed = Total S removed by plant - Fertilizer S removed by plant

1 % contribution of fertilizer S = Fertilizer S taken up by plant X 100/total S taken up by plant

2 % contribution of soil S = Soil S taken up by plant X 100/total S taken up by plant

cpm  $\text{mg}^{-1}$  S) at the beginning of the experiment (Fig.6.6), indicating that S taken up by pasture was not derived solely from freshly applied fertilizer and freshly applied SSP meets only part of the pasture S requirements. The considerable amounts of non fertilizer S taken up by pasture during the growing period must have been derived from the mineralization of soil organic matter. Immobilization of S into soil organic matter and the downward movement of sulphate out of the rooting depth of pasture plants are the other two fates of fertilizer S. To quantify the amounts of plant S derived from the fertilizer S pool and from the soil organic matter by mineralization, the percentage fertilizer S removed by pasture was calculated using the accumulated activity of  $^{35}\text{S}$  removed by pasture harvested from each core and the original activity and specific activity of SSP applied to each core at the beginning of the experiment. The total amount of activity removed by pasture from Jan. to Oct. 1990, the percentage of fertilizer S in the pasture, the amount of fertilizer and soil S taken up by pasture and the percentage contribution of fertilizer and soil S to total pasture S uptake are presented in Table 6.5.

The absolute amounts of fertilizer S taken up by pasture were greater (2.7 and 2.3 kg S  $\text{ha}^{-1}$  for low and medium slopes, respectively) at high fertility sites than at low fertility sites (1.5 and 1.7 kg S  $\text{ha}^{-1}$  for low and medium slopes, respectively) (Table 6.5). The amounts of fertilizer S taken up by pasture as a percentage of applied S, however, was greater (11.0% and 11.5% in low and medium slopes, respectively) at low fertility sites than at high fertility sites (6.7% and 5.6% for low and medium slopes, respectively). This indicates that pasture at low fertility sites is more dependent on freshly applied fertilizer than at high fertility sites.

At high fertility sites S from the mineralization of organic matter, that has accumulated from regular topdressing of SSP and dung and urine return by grazing animal, provided a greater absolute amount of pasture S (15 to 16 kg S  $\text{ha}^{-1}$ ) than soil at low fertility sites (7 to 12 kg S  $\text{ha}^{-1}$ ). Thus the rate at which fertilizer was applied over the preceding years and the current rate of fertilizer application had a major affect on the mineralization of S from soil organic matter. Even though the amounts of both fertilizer and soil S taken up by pasture were greater in the high fertility sites

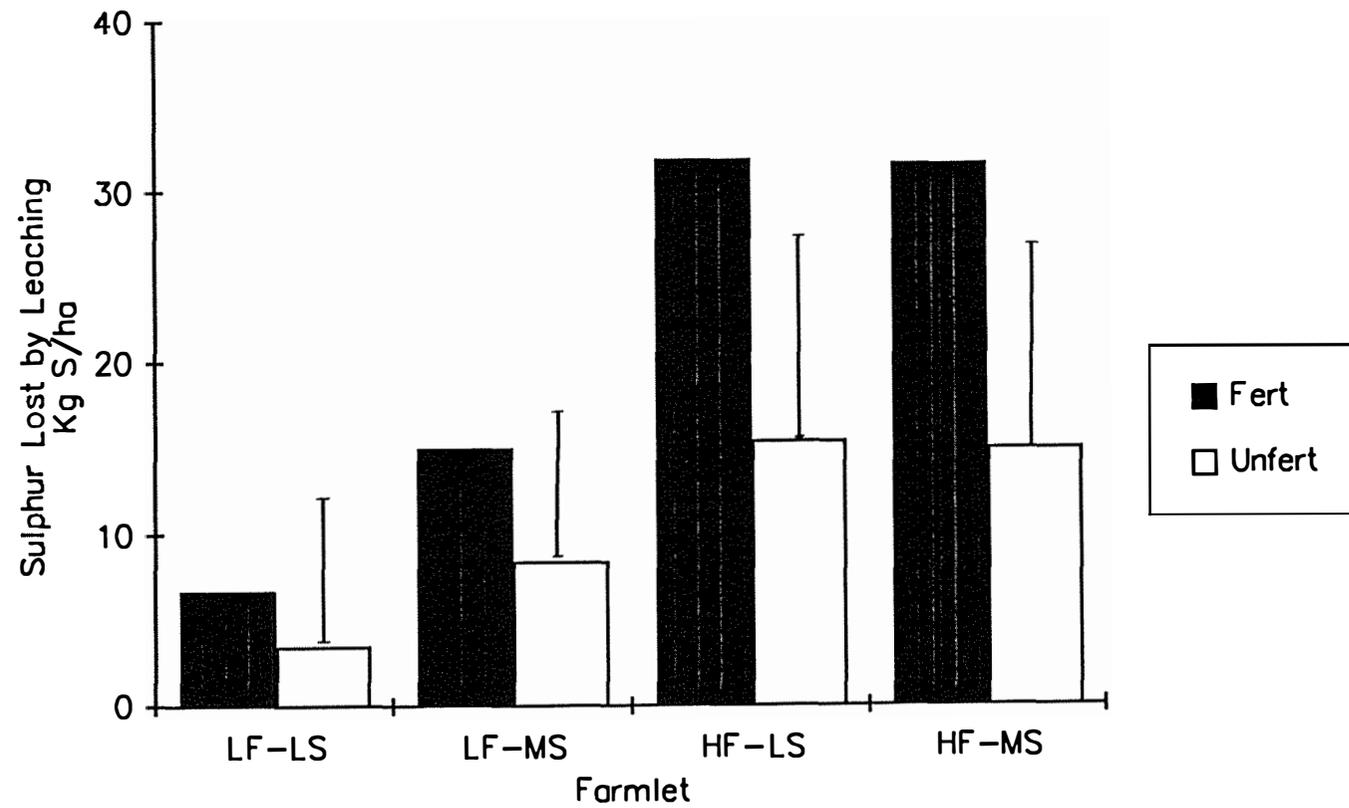
than in the low fertility sites, pasture derived similar proportions of S from fertilizer and soil S in both low and high fertility farmlets. On average pasture derived 14.6% and 13.6% of their S from fertilizer and the remaining 85.4 and 86.4% from the soil at the low and the high fertility sites (Table 6.5).

While both fertilizer and soil S were taken up by pasture (Table 6.5), most of the N (86 and 87% of the mineralized N for low and high fertility farmlets) taken up by pasture was derived from the mineralization of soil organic matter. Only a small amount of plant N (<10%) was derived directly from fixation of atmospheric N by the clover component of the pasture (see discussion in Chapter 5, section-5.3. Field and Ball,(1982) suggested that clover substitute almost half of their mineral soil N uptake for N fixation in meeting their N requirements for growth. The different rates of mineralization of N in both low and high fertility farmlets indicates that the extent of N availability in pasture depends on the past SSP fertilizer history.

### **6.3.5 Sulphur Lost by Leaching**

Freshly applied SSP significantly ( $p < 0.01$ ) increased (16.6 kg S ha<sup>-1</sup> more) the losses of S by leaching in high fertility sites (31.9 vs 15.3 Kg S ha<sup>-1</sup> for fertilized and unfertilized plots, respectively), but this increase (4.8 kg S ha<sup>-1</sup> more) was not significant at low fertility sites (Fig.6.7). The amounts of S lost by leaching from low fertility sites (10.9 and 6.1 kg S ha<sup>-1</sup> for fertilized and unfertilized plots, respectively) were also lower than high fertility sites. Previous fertilizer history also had a large impact on the losses of S by leaching (Fig.6.7). Where fertilizer was not applied (unfertilized), approximately 2.5 times more S was lost by leaching at high fertility farmlet than at the low fertility farmlet (15.3 vs 6.1 kg S ha<sup>-1</sup> for high and low fertility farmlets, respectively) during the 9 months of measurement from Jan. to Oct. 1990. Where SSP was freshly applied (fertilized) approximately 4 times more S was lost by leaching at the high fertility farmlet than at the low fertility farmlet (31.9 vs 8.9 kg S ha<sup>-1</sup> for high and low fertility farmlets, respectively). This again demonstrates the marked impact that the rate of SSP application has on S losses by leaching.

Fig.6.7 Amounts of S lost by leaching from fertilized and unfertilized plots all sites during the period from Jan. to Oct. 1990 (Vertical bars=LSD,  $p < 0.01$ ).



Even though the total drainage for summer and autumn (269mm) was more (19%) than the total drainage for winter (226mm) at all sites, the losses of S by leaching from both fertilized and unfertilized plots was greater in winter. Extractable sulphate concentrations remained similar (Fig.6.11) for both periods, but the longer less intensive drainage events during winter (Fig.6.1) probably caused the greater leaching in winter.

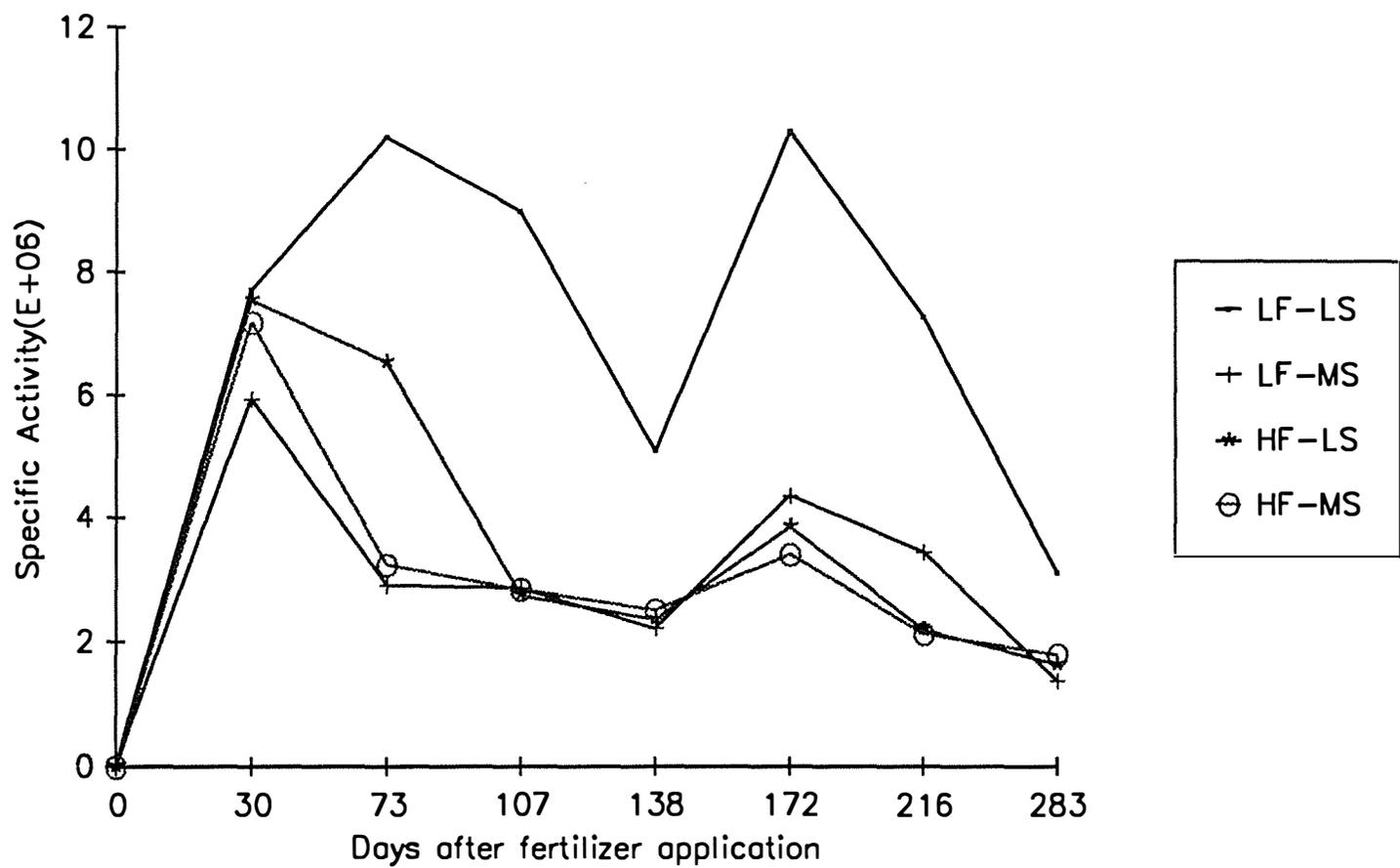
The leaching losses reported in this study were similar to the results reported by Smith *et al.* (1983), showing that withholding fertilizer application to sheep grazed pasture on Tokomaru silt loam can reduce the losses of S by leaching (4 to 5 kg S ha<sup>-1</sup>) but still substantial losses occur. In the present study the losses were reduced by 50% when the fertilizer application was discontinued after one year. In the study of Smith *et al.* (1983) the losses were reduced by 30% by withholding fertilizer application for one year. The fertilizer history for the site studied by Smith *et al.* (1983) was different from that of the present study and the drainage was monitored only for winter by Smith *et al.* (1983). Fertilizer was not applied continuously during the previous years. Also the drainage was collected at a depth of 450mm. In the present study drainage was monitored over a longer period of time (485mm drainage for a period of 9 months) and it was collected at a depth of 250mm. This indicates that there may be some adsorption of sulphate at 250-450m soil depth in the study of Smith *et al.* (1983).

The total losses of S by leaching for the 9 months of measurement expressed as a percentage of annual SSP application were 48.5%, 77.7%, 77.6% and 76.8% for the LF-LS, LF-MS, HF-LS and HF-MS sites respectively for a total drainage of 495mm. These losses are in close agreement with the S losses (46% to 78%, depending upon the land slope and fertilizer history) calculated from a mass nutrient balance model by Saggart *et al.* (1990a) for this hill country pasture. These losses include both soil and fertilizer S lost by leaching.

#### **6.3.5.1 Contribution of Soil and Fertilizer S to Leaching Losses**

The specific activity of S in the leachate was lower than the specific activity of the applied fertilizer throughout the experiment (Fig.6.8). This again shows that not all

Fig.6.8 Changes in specific activity of S-35 in leachate with time at all sites during the period from Jan. to Oct.1990.



**Table 6.6** Amounts of <sup>35</sup>S activity, % of applied fertilizer S leached, amounts of soil and fertilizer S lost by leaching and the % contribution of fertilizer and soil S to leaching losses at all sites from Jan. to Oct. 1990.

Farmlet	<sup>35</sup> S activity leached (cpm/core)	% fertilizer S leached*	S leached			% contribution to leached S	
			Total	Fertilizer**	Soil#	Fertilizer <sup>1</sup>	Soil <sup>2</sup>
			Kg S ha <sup>-1</sup>				
LF-LS	9.40E+07	9.2	6.7	1.3	5.4	19	81
LF-MS	5.92E+07	5.8	15.1	0.8	14.3	5	95
HF-LS	2.53E+08	21.4	32.0	8.8	23.2	28	72
HF-MS	2.18E+08	18.4	31.7	7.6	24.1	24	76

\* %fertilizer S lost= activity lost by leaching X 100/total activity applied

\*\* Fertilizer S lost= Amount of fertilizer S applied X percentage fertilizer S lost by leaching/100

# Soil S removed = Total S removed - fertilizer S removed

1 % contribution of fertilizer S= Fertilizer S lost by leaching X 100/total S lost by leaching

2 % contribution of soil S= Soil S lost by leaching X 100/total S lost by leaching

the S lost by leaching was derived directly from fertilizer. Soil S was also lost. Here also it is necessary to quantify the amounts of fertilizer and soil S lost by leaching based on the activity of  $^{35}\text{S}$  removed and the total amounts of S lost by leaching. The total  $^{35}\text{S}$  activity, the amounts of fertilizer and soil S lost by leaching and the percentage contribution of fertilizer and soil S to leaching losses are given in Table 6.6. Approximately 7 times more fertilizer S was lost by leaching from the high fertility farmlet (8.8 and 7.6 kg S ha<sup>-1</sup> for low and medium slopes, respectively) than from the low fertility farmlet (1.3 and 0.8 kg S ha<sup>-1</sup> for low and medium slopes, respectively). As a percentage of applied fertilizer S the losses of S by leaching were approximately 3 times more from the high (21.4% and 18.4% for low and medium slopes, respectively) than low fertility farmlet (9.2% and 5.8% for low and medium slopes, respectively) (Table 6.6).

In contrast the contribution from freshly applied fertilizer to total pasture uptake (Table 6.5) at both the low and high fertility sites were very similar (14%). The small S loss by leaching from freshly applied fertilizer at the LF sites demonstrate the efficient manner in which applied S is utilised within the low fertility system. In contrast in the high fertility system where no response to added fertilizer S was measured, the S losses by leaching were much greater.

At all sites pasture S uptake and losses by leaching accounted for only 19 and 26% (15 vs 45 kg S ha<sup>-1</sup>) of the applied fertilizer S for low and high fertility farmlets, respectively (Fig.6.10). The amount of S remaining in the extractable sulphate pool was very small (2.7 and 10.7 kg S ha<sup>-1</sup> for low and high fertility farmlets, respectively, Fig.6.11). Thus the majority of the fertilizer S was either immobilized into soil organic S or adsorbed by soil sesquioxides in the subsoil and not extractable (81 and 74% for low and high fertility farmlets, respectively) in 0.04M Ca(HPO<sub>4</sub>)<sub>2</sub>. Immobilization of fertilizer S was also observed by Gregg and Goh,(1979).

The amounts of N lost by leaching (Fig.6.9) were much less than the losses of S by leaching and when expressed as a percentage of the N taken up by pasture (ranging from 60 kg N ha<sup>-1</sup> for LF-LS unfertilized, to 190 kg N ha<sup>-1</sup> for HF-LS fertilized )

Fig.6.9 Amounts of N lost by leaching from fertilized and unfertilized plots at all sites during the period from Jan. to Oct. 1990 (Vertical bars=LSD,  $p < 0.01$ )

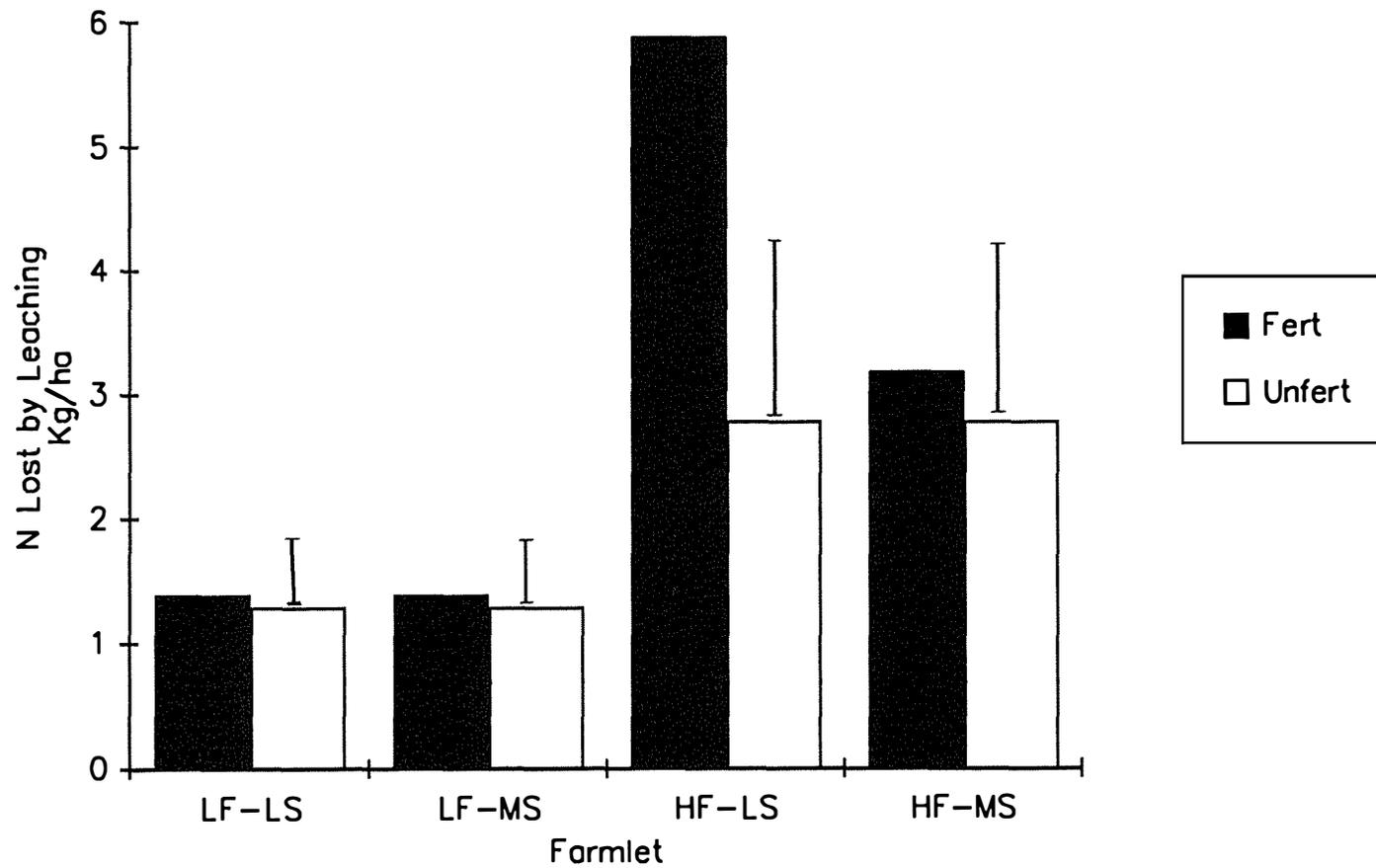
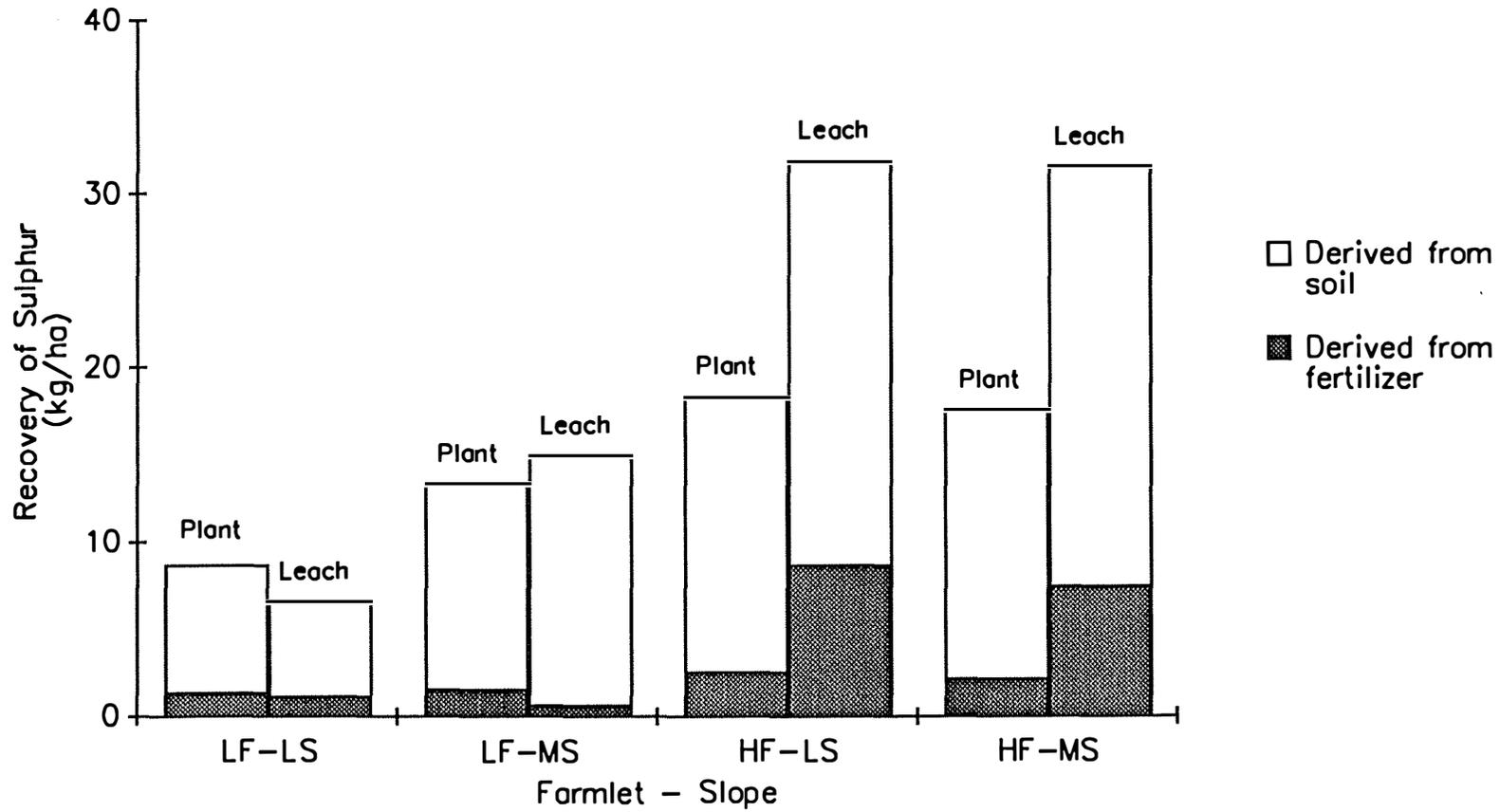


Fig.6.10 Amounts of fertilizer(F) and soil(S) sulphur removed by pasture and lost by leaching between Jan. to Oct. 1990 at LF-LS, LF-MS, HF-LS and HF-MS sites.



the amounts lost were small at all sites (Fig.6.9). The amounts of N lost by leaching were only slightly greater than the losses observed in the preliminary field experiment (Chapter 5). The slightly greater loss of N by leaching in the present experiment (Jan-Oct) may be due to a greater loss during summer and autumn than in winter and spring period when the preliminary experiment was conducted. Even though the amounts of N lost by leaching were very small in terms of the total amount of N uptake by pasture, and so from an agricultural standpoint, of little significance at high fertility sites the amounts of nitrogen lost by leaching in the present experiment approached  $6 \text{ kg N ha}^{-1}$ . These values are much lower than those calculated by Field *et al.* (1985) for intensive cattle grazed lowland pastures ( $73 \text{ kg N ha}^{-1}$ ) and measured by Steele *et al.* (1984) for intensive beef-cattle systems ( $88 \text{ kg N ha}^{-1}$ ). The losses in this study are again lower than the losses ( $15 \text{ to } 20 \text{ kg N ha}^{-1}$ ) observed in a series of experiments conducted on the Tokomaru silt loam under permanent pasture grazed intensively by dairy cattle (Sharpley and Syers, 1979) and sheep (Turner *et al.*, 1979; Heng *et al.*, 1991). The N losses by leaching measured in this study represent the first estimates of likely losses of N from less intensively farmed hill country farming systems. The losses from low fertility sites ( $< 2 \text{ kg N ha}^{-1}$ ) would be indicative of the N losses from larger tracks of South and North Island hill country where stocking rates are  $< 12 \text{ SU ha}^{-1}$  and fertilizer inputs have been low for the past 10 years.

### 6.3.6 Soil Sulphate and Mineral Nitrogen

Immediately after fertilizer application (second soil sampling on 15-2-1990) which occurred on 18-1-1990 the soil sulphate concentrations increased in the top 0-75mm soil depth at all sites (Fig.6.11). This increase was very small for low fertility sites and particularly marked at the high fertility sites. After this initial increase, sulphate concentrations decreased slowly with time (Fig.6.11). The soil sulphate at 150-250mm soil depth was generally greater than the top two layers (Fig.6.11) except for the early stages after fertilizer application. In the low fertility farmlet the sulphate concentrations for 150-250mm soil depth was always greater than the top two layers, even immediately after fertilizer application (Fig.6.11). The buildup of sulphate in the 150 to 250mm soil depth indicates that sulphate in the soil solution of the top two

Fig.6.11. Soil sulphate present for the depths 0-75 mm (—), 75-150 mm (—+—) and 150-250 mm (—\*—) at all sites from Jan. to Oct. 1990. Soil samplings were done on 8/1, 15/2, 26/3, 30/4, 11/6, 14/7, 23/8 and 10/10. The L.S.D values are given in

Appendix-6.1.

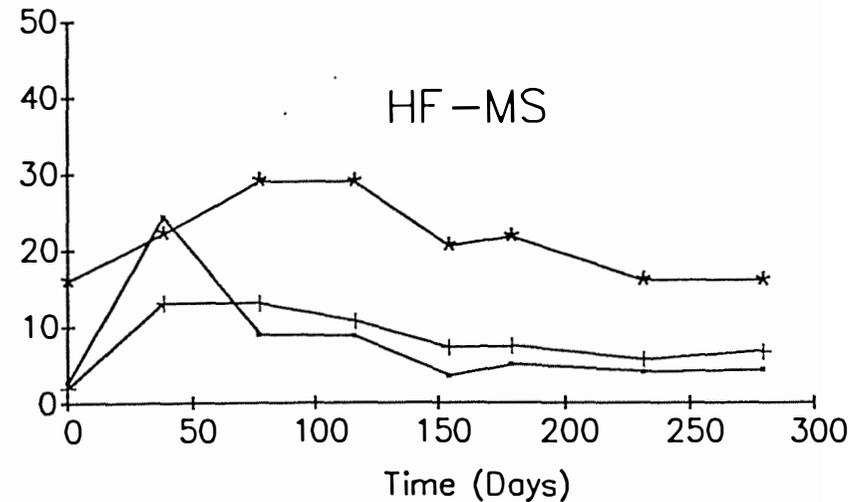
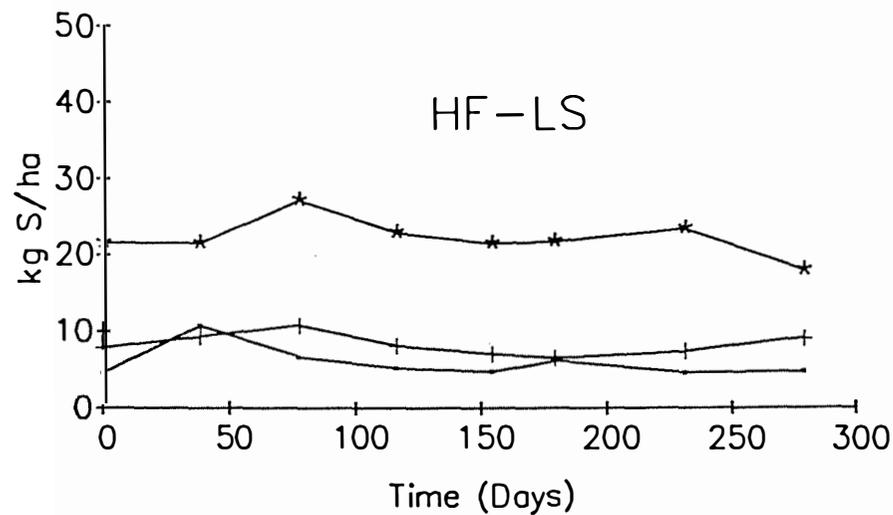
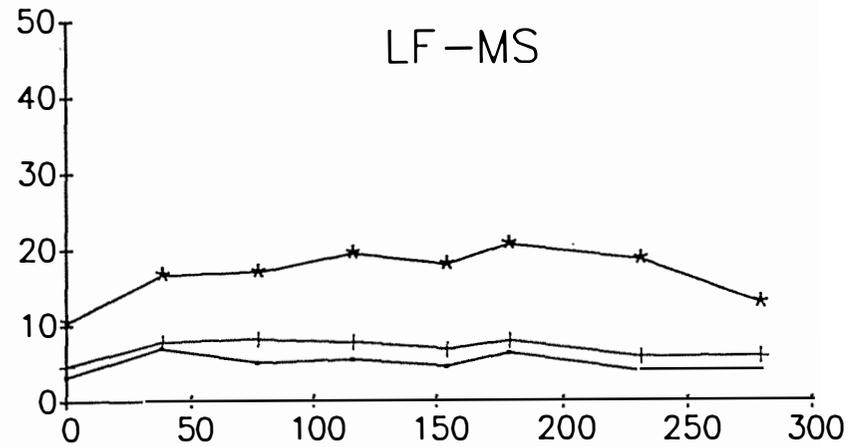
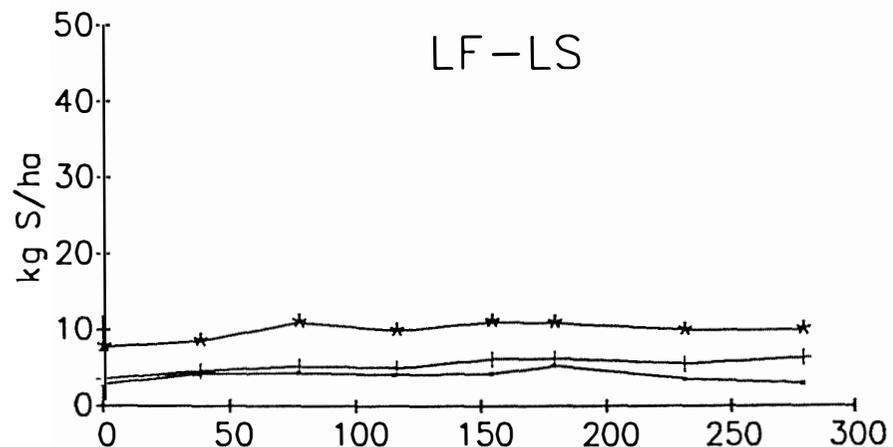
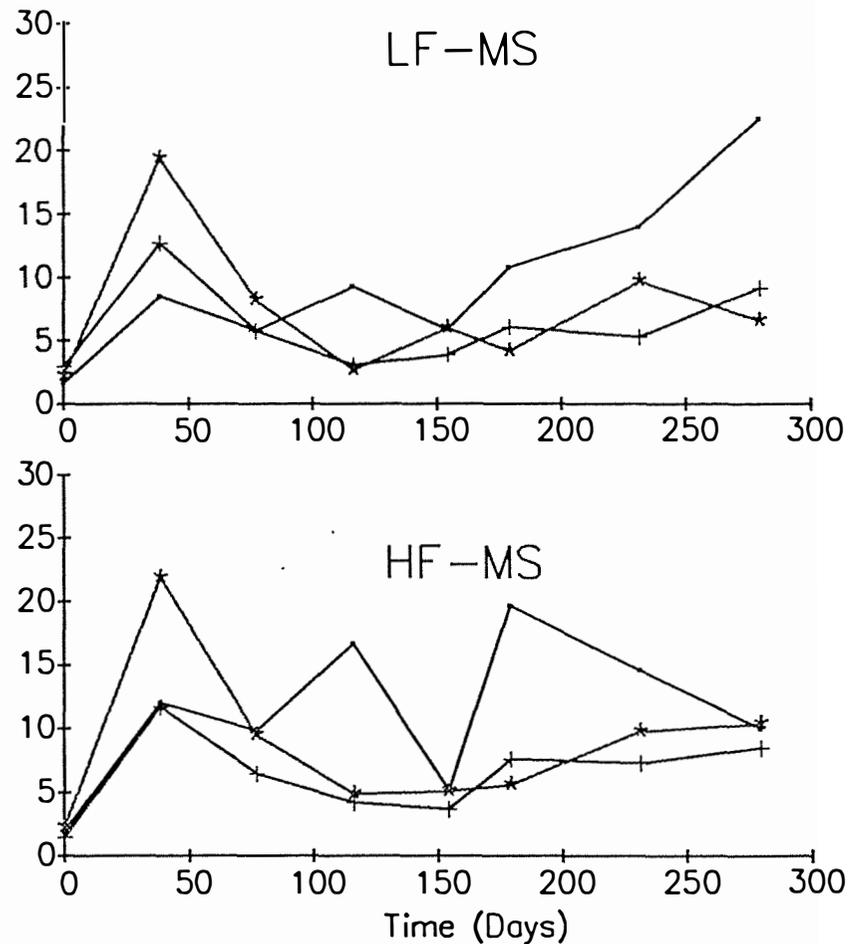
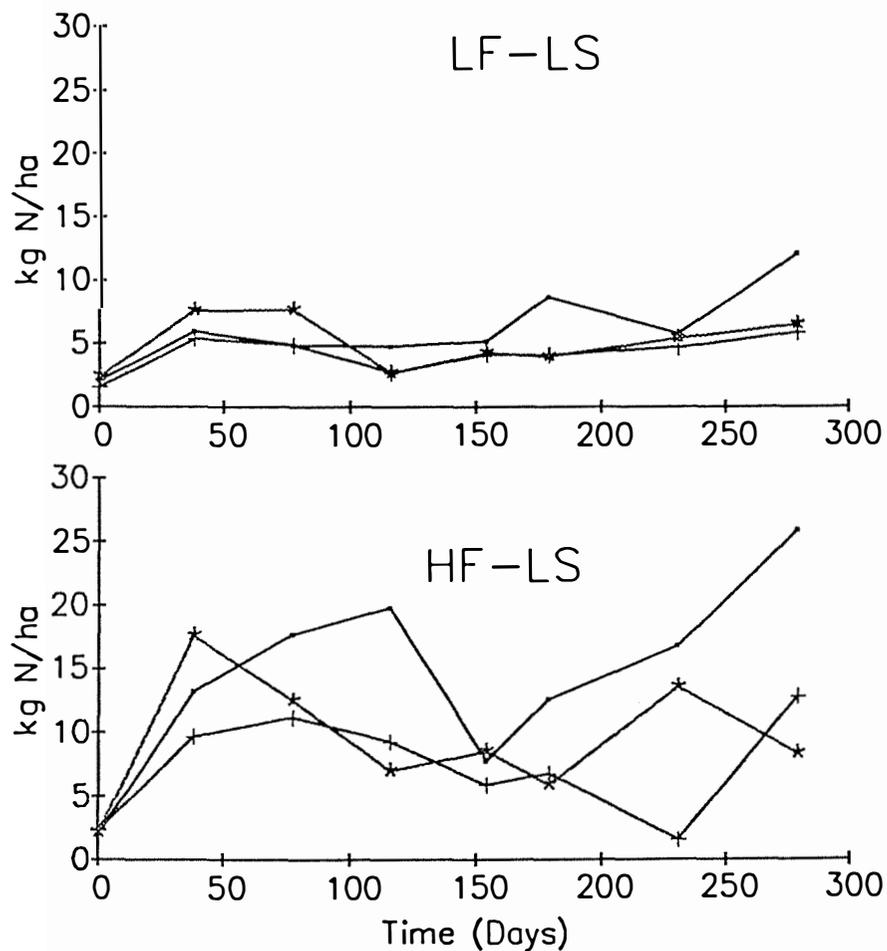


Fig.6.12. Soil mineral nitrogen present for the depths 0-75 mm (—), 75-150 mm (—+—) and 150-250 mm (—\*—) at all sites from Jan. to Oct. 1990. Soil samplings were done on 8/1, 15/2, 26/3, 30/4, 11/6, 14/7, 23/8 and 10/10. The L.S.D values are given in Appendix-6.2.



layers (0-150mm) leached to this soil depth is not significantly depleted by pasture growth. Infact considerable amounts of sulphate were leached beyond 250mm soil depth and collected in the resin between each successive soil sampling (Table 6.6). The amounts of mineral N were greater in top layer than the other two layers (Fig.6.12). This trend was similar to that reported in the previous study period (June 1989 to Jan 1990). Ammonium was the dominant form of mineral N present in the soil at all four sites. This was particularly marked for the low fertility sites where the nitrate form was very low. Nitrate N did accumulate during summer and late spring, but was still present at much lower levels than ammonium.

### 6.3.7 Net Mineralization of S and N

The amounts of S and N net mineralized were calculated using the formula described in Chapter-5. In this experiment the amounts of S and N returned in excreta need not be considered because both pasture uptake and losses by leaching of S and N were not influenced by excreta return because no excreta was allowed to return to the lysimeter cores from which both pasture uptake and leaching losses of S and N were measured. It was also possible to separate the S uptake by pasture and losses by leaching of both fertilizer and soil S because the fertilizer S was labelled with  $^{35}\text{S}$ . A modified equation for calculating net mineralization of S is given below.

$$M_s = E_{sF} - E_{sI} + P_{ss} + L_{ss}$$

where

- $M_s$ = Sulphur mineralized from Jan to Oct 1990 (kg S ha<sup>-1</sup>)
- $E_{sF}$ = Final soil sulphate extracted with 0.04M Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> (kg S ha<sup>-1</sup>)
- $E_{sI}$ = Initial soil sulphate extracted with 0.04M Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> (kg S ha<sup>-1</sup>)
- $P_{ss}$ = Total soil S taken up by plant from Jan to Oct 1990 (kg S ha<sup>-1</sup>) from Table 6.5
- $L_{ss}$ = Total soil S lost by leaching from Jan to Oct 1990 (kg S ha<sup>-1</sup>) from Table 6.6

The net mineralization of N was calculated as mentioned above, except the extractant used was 2M KCl (see Chapter-5) and also included a small amount of N fixed from atmosphere by legumes.

It was established that most of the extractable soil sulphate present at the end of the experiment was soil derived sulphate and not fertilizer derived sulphate because during the last leaching and pasture growth period (1-9-1990 to 10-10-1990) isotopic data showed that less than 2% of the S taken up by pasture or lost by leaching was derived from the fertilizer. Thus the fertilizer made little contribution to the extractable sulphate pool and this amount (2% of the pool) was not considered in the calculation of the amount of S mineralized.

The amounts of S net mineralized was greater (40.2 and 39.5 kg S ha<sup>-1</sup> for low and medium slopes, respectively) at the high fertility sites than (15.7 and 28.3 kg S ha<sup>-1</sup> for low and medium slopes, respectively) at the low fertility sites, demonstrating that previous fertilizer history had caused more S to accumulate in the soil organic matter which in turn had a major influence on the mineralization of soil organic S (Table 6.7). An average of 44% of the mineralized S was taken up by pasture at the low fertility sites while an average of 39% of the mineralized S was taken up by pasture in high fertility sites. About 42% of the mineralized S was lost by leaching in the low fertility farmlet and 60% of the mineralized S was lost by leaching in the high fertility farmlet (Table 6.7). The remaining mineralized S accumulated in the inorganic sulphate pool. This showed that when the mineralization rate was greater, a greater amount of mineralized S was lost by leaching while at a low rate of mineralization a greater amount of mineralized S was taken up by pasture.

The amounts of N net mineralized was greater (204 kg N ha<sup>-1</sup>) at the high fertility sites than at the low fertility sites (125 kg N ha<sup>-1</sup>) again reflecting the long term effect that previous fertilizer have had on legume growth and nitrogen fixation. Irrespective of the amounts of N mineralized most of the mineralized N was taken up by pasture and the losses of N by leaching were very low (<2% of the total mineralized). This confirms the results from the earlier field experiment which demonstrated a linear relationship between N mineralized and pasture dry matter production.

**Table 6.7 Net mineralization of S and N from soil organic matter and the percentage of mineralized S and N removed by pasture and lost by leaching at all four SSP fertilized sites from Jan. to Oct. 1990.**

Farmlet	Net mineralization		% plant uptake <sup>1,*</sup>		% leached <sup>1,**</sup>	
	kg ha <sup>-1</sup>		S	N	S	N
	S	N				
LF-LS	15.7	100	46	86	34.4	1.3
LF-MS	28.3	149	42	86	50.0	1.1
HF-LS	40.2	224	39	85	58.0	2.0
HF-MS	39.5	184	39	88	61.0	1.5

\* Total S and N removed by plant X 100/Net mineralization.

\*\* Total S and N leached X 100/Net mineralization.

1 The recovery of mineralized S and N by plant and leaching losses is not 100%. The remaining S and N is accumulated in the soil solution.

Assuming that extractable soil sulphate and mineral N concentrations were the same in both fertilized and unfertilized plots at the end of the experiment, the amounts of S and N net mineralized in the unfertilized plots were 10, 20, 22 and 21 kg S ha<sup>-1</sup> and 72, 122, 172 and 159 kg N ha<sup>-1</sup> for the LF-LS, LF-MS, HF-LS and HF-MS sites respectively. These values were lower than the amounts of S and N net mineralized in the fertilized plots (Table 6.7) suggesting that freshly applied fertilizer has a stimulating and priming effect on the mineralization process. The proportions of mineralized S removed by pasture and/or lost by leaching in the unfertilized plots could not be quantified because during the period of plant growth extractable soil sulphate decreased indicating that a substantial part of pasture uptake and leaching could have been derived from this pool. Most of the N taken up by pasture was derived from the mineralization of soil organic N because the initial soil mineral N level was very low compared to the total amount of N taken up by pasture (see Table 6.1 and Fig 6.5) and leaching losses were small.

#### 6.4 GENERAL DISCUSSION AND CONCLUSION

The results from these lysimeter studies showed that for the study period of 9 months from Jan. to Oct. 1990, the losses of S from SSP fertilized hill country farmlets ranged from 48 to 77% of the annual fertilizer application depending upon the rate of annual fertilizer application and the past fertilizer history and the bulk of this loss was derived from the mineralization of soil organic matter and not directly from freshly applied fertilizer. These leaching losses were in accordance with the predicted losses for these hill country systems (Saggar *et al.*, 1990a). Freshly applied fertilizer increased both the mineralization of S from organic matter and leaching losses of S. On the other hand withholding fertilizer application significantly reduced S losses by leaching.

Previous fertilizer history had a major effect on the fate of freshly applied fertilizer S. At the low fertility farmlet which had a history of 125 kg SSP ha<sup>-1</sup> year<sup>-1</sup>, a greater proportion of the freshly applied fertilizer S was removed by pasture compared to the proportion lost by leaching. At the high fertility farmlet which had a history of 375

kg SSP ha<sup>-1</sup> year<sup>-1</sup>, a greater amount and percentage of freshly applied fertilizer S was lost by leaching rather than pasture uptake. Even though the high fertility farmlet had higher pasture production than the low fertility farmlet, the losses of S by leaching were nearly four times greater than the low fertility farmlet suggesting that at low fertilizer application rate, more efficient use of both fertilizer and soil S is made without a major loss of S by leaching. By measuring the fate of the <sup>35</sup>S labelled fertilizer it was possible to demonstrate that most of the S removed by pasture and lost by leaching were derived from the mineralization of soil organic S which was influenced by the current fertilizer application. Less than 12% of the freshly applied fertilizer S was removed by pasture. But most (74 to 81%) of the applied S in SSP was either immobilized in to soil organic matter in top soil or adsorbed by soil sesquioxides in the sub soil. Direct losses of S by leaching from freshly applied fertilizer represents < 22% of applied S and was lower in the low fertility farmlet. This suggests that there is only limited scope for reducing S losses directly from applied fertilizer. It is clear from this study that most of the leached sulphate and that removed by pasture originated from the mineralization of soil organic S.

This study has shown that there is a fundamental difference in cycling of S and N in these sheep grazed hill country pastures and that N rather than S limits pasture production. With N, irrespective of the level of pasture productivity maintained by different fertilizer strategies, nearly all of the mineralized N was taken up by pasture. The fraction of mineralized N lost by leaching was very small (<2%) showing that even though both N and S are biologically mobile nutrients, N is conserved in these soil-plant systems, while more S is available in the soil solution and susceptible to leaching. In these legume based pasture system where superphosphate is used to supply both P and S and the only nitrogen source is the fixation of atmospheric N<sub>2</sub>, the system is continuously under N stress and any N released by mineralization from soil organic matter is either utilized by plants or microorganism immediately and keeping the soil mineral N level very low and the quantities available for leaching low. Since S is not limiting pasture production, all S as sulphate in excess of the pasture requirements is susceptible to leaching.

Increasing the N status of the soil without increasing the S application rate may offer a solution for reducing the leaching losses of S from grazed hill country pasture. Normally in legume based grazed pastures the N status is increased by increasing the S status through SSP application. Either more efficient N fixing legumes are required or perhaps current levels of N fixation could be maintained with fertilizers of lower S:P ratios. If the N status of the pasture increased without increasing the S status, more pasture will be grown fixing more carbon, translocating more carbon to the root and to the soil which would immobilize more sulphate in the soil. More plant growth also increases the uptake of sulphate from the soil.

Alternatively the leaching losses of S may be reduced by applying fertilizer material which provide both S and N. The proportion of pasture S derived from fertilizer (<17%) did not vary much with the rate of fertilizer application but the proportion of leached S derived from fertilizer was greater at high fertility sites (28 and 24%) than in low fertility sites (19 and 5%). Therefore at higher rates of fertilizer application not only is more S leached as mentioned earlier but more of this leached S is directly derived from fresh fertilizer applications.

The data generated from the isotopic studies in this Chapter will be more fully discussed in Chapter 8, where attempts are made to estimate the actual rates of mineralization and immobilization of S in these pasture soils.

## CHAPTER-7

### THE INFLUENCE OF SHEEP EXCRETA ON THE PASTURE UPTAKE AND LEACHING LOSSES OF SULPHUR IN GRAZED HILL COUNTRY PASTURES.

#### 7.1 INTRODUCTION

In the previous Chapter (Chapter-6), investigating the fate of fertilizer S applied to grazed hill country pastures, it was shown that most of the S removed by pasture plants (85-86%) or lost by leaching (75-87%) was derived from the mineralization of soil organic matter and not from a current superphosphate application. The amount of S mineralized was influenced by previous superphosphate topdressing history. The study however did not examine the contribution of recently returned excreta from the grazing animals to pasture uptake and to the losses of S by leaching. As approximately 70% of S removed by pasture may be ingested by the grazing animal and returned to the pasture in excreta on an annual basis (Saggar *et al.*, 1990a), this represents a large flux of S that is potentially available for pasture uptake. Little information is available on the efficiency with which this excretal S is reutilized by pasture.

Nutrient cycling through grazing animals was for a long time considered beneficial to the fertility of grazed pastures (Walker, 1956; Sears *et al.*, 1965; Till *et al.*, 1987). However, more recently it has been recognised as an inefficient process resulting in considerable loss of effective nutrients from productive areas of paddocks (Carran *et al.*, 1982; Goh and Nguyen, 1991; Hedley *et al.*, 1990; Saggar *et al.*, 1990a) which may accelerate leaching losses.

Unlike N and K, for which the majority (>70%) of the excreted nutrients are in the urine, S is distributed approximately 40% in dung and 60% in urine (Wilkinson and Lowery, 1973; Syers *et al.*, 1987). A knowledge of the fate of both dung and urine S, once deposited on the soil is therefore important for determining long term S fertilizer requirements.

The fate of S in sheep dung and urine, after deposition to soil, has been investigated by a few researchers in New Zealand and overseas using either a balance approach in laboratory simulations (Hogg, 1981) or radioactively  $^{35}\text{S}$  labelled dung and urine in field studies (Kennedy and Till, 1981a; Goh and Nguyen, 1991). The results in the laboratory using repacked soil columns (Hogg, 1981) established that a greater amount of S was lost by leaching in the urine treated lysimeter when compared to the control treatment. It is debatable whether results from repacked soil columns are applicable to naturally structured field soils. In field studies on pasture soils (Goh and Nguyen, 1991) it was shown that about 16 to 20% of the simulated sheep urine S was recovered in pasture (above ground plant material and root) but a substantial amount of S was not recovered and suggested that it was lost by leaching. The amount of S lost by leaching was not quantified by direct measurement.

Under normal field conditions it is very difficult to establish average influences of excreta return on pasture production, nutrient uptake and leaching losses of nutrients because of the spatial variability with which excreta is deposited by the grazing animals. For example Petersen *et al.* (1956) have shown that if random deposition is assumed little more than 16% of a flat paddock will receive excreta in any one year, Jackman (1960) assumed completely random behaviour by grazing animals to estimate that with 19 sheep  $\text{ha}^{-1}$  about 30% of grazed area would receive urine over a year. When topography and climate influence the animal camping behaviour this area may be even less (Gillingham, 1978; Lambert *et al.*, 1983; Saggar *et al.*, 1990a). The mini lysimeters installed in the field at Ballantrae (Chapters 5 and 6) provided an opportunity to study the effect of individual excreta return on the pasture uptake and leaching losses of S in grazed hill country pastures.

The objective of this study was to investigate the effect of excreta return, both dung and urine, on pasture production, pasture uptake and leaching losses of S in fertilized grazed hill country pastures. The effect of excreta return on the amounts of N and K removed by pastures and lost by leaching was also investigated because N and K are major plant nutrients returned in excreta along with S.

## 7.2 MATERIALS AND METHODS

This experiment was a continuation of the earlier field experiment investigating the origins of leached sulphate in fertilized grazed hill country pastures which was described in Chapters 5 and 6. Of the four sites used for the previous studies, the LF-LS site was selected for this study, because the pasture response to and the losses of nutrients by leaching from applied excreta can easily be identified due to the low fertility of the site. The sixteen mini-lysimeters installed at this site were divided randomly to take four treatments, namely

1. Control, for which no fertilizer had been applied for the previous eighteen months
2. Fertilizer, applied at the rate of 125 kg SSP ha<sup>-1</sup>, which was applied along with the normal annual top dressing in January, 1990.
3. Fertilizer applied as above plus dung applied in early winter (in this Chapter it is referred to as dung treatment).
4. Fertilizer applied as above plus urine applied in early winter (in this Chapter it is referred to as urine treatment).

Each treatment was replicated four times.

### 7.2.1 Application of Dung and Urine

The dung and urine used in the experiment were collected in early winter from approximately 20 ewes from the experimental site, and applied to the cores on the same day (21-06-1990), during light rain. The chemical composition of nutrients in both the composite dung and urine samples are given in Table 7.1. About 225g of fresh dung (774, 115 and 376 kg N, S and K ha<sup>-1</sup>, respectively) which is equivalent to the amount of dung excreted by a grazing sheep for one defecation (Sears and Newbold, 1942) was applied to each core in treatment 3, and 150 mls of fresh urine (280, 21 and 146 kg N, S and K ha<sup>-1</sup>, respectively) which is equivalent to the amount of urine excreted by the grazing sheep for one urination event (Sears, 1950,1953; Quinn, 1977; Hogg, 1981) was applied to each core in treatment 4. To simulate one

urination event urine was applied to the cores from a height of 2 feet above each core. At the time of application the soil moisture content was 0.78g water/g soil and urine drained rapidly into all lysimeters with negligible runoff occurring. Urine was also applied to one of the lysimeters which contained a collection vessel instead of a resin trap (see Chapter-6, section-6.2).

The partitioning of S between dung and urine during winter collection differs from the S partitioning between dung and urine proposed by Wilkinson and Lowery (1973). The concentration of S in urine was very low (0.0246%) compared to dung (0.273%) which represents an excretal return of 0.3g S sheep<sup>-1</sup> day<sup>-1</sup> in urine and 1.1g S sheep<sup>-1</sup> day<sup>-1</sup> in dung and a partitioning of 79% S in dung and 21% S in urine. But earlier S analysis of spring dung and urine samples take from the same site showed much higher S concentration (0.13%) in urine and 0.3% S in dung. This represents a partitioning of 46% and 54% S in dung and urine respectively. It is important therefore in experiments simulating the effect of dung and urine return to use a sample which is representative of season, site and resident animals. Irrespective of the total S concentration in urine, the sulphate concentration as a fraction of total S was 70% in both winter and spring. In dung the sulphate concentration as a fraction of total S content increased from 9% in winter to 14% in spring. Similar results were also observed for N and K, in which both N and K were distributed in both dung and urine (Table 7.1).

## **7.2.2 Measurements**

### **7.2.2.1 Rainfall and Drainage**

Rainfall and predicted and measured net drainage for the site were obtained from the values reported in Chapter-6 for the period from Jun. to Sep. 1990. Equipment failure prevented rainfall measurements, however, no drainage was measured during this period.

### **7.2.2.2 Pasture Production**

The amount of pasture produced in all the four treatments was measured as described in Chapter-6. Pasture was harvested 21 days before dung and urine application. After

**Table 7.1 Chemical composition of major plant nutrients in dung and urine and the amounts of nutrients applied to both dung and urine treatments.**

Nutrients in dung and urine		Composition	Amounts applied to each lysimeter Kg ha <sup>-1</sup>
Dung		g kg <sup>-1</sup> dung	
1	Moisture	200%	--
2	Ammonium-N (2M KCl)	0.110	4.7
	Ammonium-N (Water)	0.100	4.2
3	Nitrate-N (2M KCl)	nil	nil
	Nitrate-N (Water)	nil	nil
4	Total N	18.3	774
5	Sulphate (Cal.Phos)	0.27	11.5
	Sulphate (Water)	0.243	10.3
6	Total Sulphur	2.73	115
7	Total Calcium	12.5	530
8	Total Potassium	8.85	376
9	Total Magnesium	3.21	136
Urine		g litre <sup>-1</sup>	
1	Ammonium-N	0.336	28.5
2	Nitrate-N	nil	nil
3	Total-N	3.3	280
4	Total-S	0.246	20.9
5	Sulphate-S	0.171	14.5
6	Calcium	0.038	5.7
7	Potassium	1.9	146
8	Magnesium	0.076	6.5

application three harvests were taken over 150 days. The first harvest after dung and urine application was made at the end of winter (21-8-90, two months after dung and urine application or 81 days after the previous harvest), the second during the middle of spring (16-10-90) and the third during the late spring (17-11-90). Pasture S, N and K concentrations were measured.

### 7.2.2.3 Resin Replacement

Resin samples in the lysimeter traps (see Chapter 4, 5 and 6) were replaced with new resin before the application of dung and urine. Immediately after dung and urine application (2 days) the resin was replaced with new resin. Thereafter the resin was replaced depending on the frequency and intensity of rainfall and predicted drainage volumes. After removal to the laboratory, the resins were eluted as described in Chapter-6 and the concentrations of  $\text{SO}_4^-$ , mineral N and basic cations such as Ca, Mg and K in the eluates were measured.

### 7.2.3 Analytical Measurements

The pasture S and N concentrations were measured as mentioned in Chapter-5. Pasture K, Ca and Mg concentrations were measured by digesting pasture sub samples with concentrated  $\text{HNO}_3$ , then evaporating the digest to dryness at  $250^\circ\text{C}$ . 5ml of 2M HCl were added to the dried digest sample and then diluted to 50mls with deionised water. The amounts of K, Ca and Mg in the final solution were measured using atomic absorption spectroscopy. Appropriate ionic suppressors such as Cs and Sr were added to the final solution at  $1000\text{mg l}^{-1}$ .

The amounts of  $\text{SO}_4^-$ , mineral N,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$  and  $\text{K}^+$  in the resin eluate were measured as mentioned in Chapter-5.

### 7.2.4 Statistical Analysis

Analysis of variance was performed on pasture produced in each harvest and the total pasture produced for 150 days, pasture S, N and K concentrations for all the three harvests, the total amounts of S, N and K removed by pasture and the total amounts of S, N, K, Ca and Mg lost by leaching to determine the statistical significance of the

simple and interactive effects of fertilizer and dung or urine applications. In the discussion, treatments which are significantly different from each other at  $p < 0.01$  are denoted by \*\*\*, significantly different at  $p < 0.05$  are denoted by \*\* and non significant by NS.

## 7.3 RESULTS AND DISCUSSION

### 7.3.1 Pasture Production

Application of fertilizer alone did not increase pasture production until late spring (Table 7.2.). From the outset, application of dung or urine with fertilizer increased pasture production ( $p < 0.01$ ). Urine treated plots initially produced more pasture than dung treated plots, reflecting the presence of readily plant available S, N and K in the urine, and this effect carried over to total pasture production for winter and spring. Addition of dung with fertilizer did not significantly increase pasture production over fertilizer alone, despite the addition of over  $700\text{kg N ha}^{-1}$  in the dung.

Even though the amounts of S, N and K applied to the cores in dung treatment was greater than the amount of these nutrients applied to the cores in urine treatment, the readily available forms of S, N and K such as sulphate, ammonium and soluble K applied were greater in the urine treatment than in the dung treatment (Table 7.1). Dung has to decompose before the majority of the nutrients become available for pasture growth.

In this experiment, which was conducted mainly during winter and spring it took 60 days for the dung to physically disappear and chemically decompose. Rowarth (1987) reported that faecal pellets decomposed completely in 20 days and pad samples in 30 days during winter, a period when earthworms are active. Similar faecal decomposition studies elsewhere showed that arthropods such as earthworms (Barley, 1964) and dung beetles (Bornemissza and Williams, 1970) enhance mineralization through the action of comminution of the material and transporting it to the vicinity of soil microorganisms (Macfadyen, 1978). Rowarth (1987) also showed that in summer much longer periods are required for decomposition of dung to take place.

**Table 7.2. Pasture dry matter response to fertilizer plus dung and urine application for a period of 150 days.**

Treatment	Late Winter (21/8/90)	Mid Spring (16/10/90)	Late Spring (17/11/90)	Total
	Kg ha <sup>-1</sup>			
Control	102	175	429	707
Fertilizer	226	316	882	1425
Fertilizer+D	289	532	921	1742
Fertilizer+U	430	667	1170	2268
L S D <sub>p&lt;0.01</sub>	164	221	255	470

Moisture generally limits the activity of earthworms at this time. The effectiveness of freshly returned dung as a source of S, N and K for pasture growth would therefore be limited during this period.

Over the whole winter-spring period pasture production was increased by 100%, 150% and 220% in fertilized, dung and urine treatments respectively, compared to the control. Compared to fertilizer alone, pasture production was increased in dung and urine by 22% (NS) and 59% (\*\*\*), respectively. The poor pasture production in unfertilized and excreta-free control treatment demonstrates the significance of both fertilizer application and animal excreta return in stimulating pasture growth at this low fertility site.

With a stocking rate of 10 SU ha<sup>-1</sup> for the experimental site, the annual input of dung and urine is approximately 4925 kg fresh dung ha<sup>-1</sup> and 4380 litres of urine ha<sup>-1</sup> respectively (see Appendix-7.1). About 60% of dung and 55% of the urine is returned to low slopes which constitute 33% of the total area (Gillingham, 1980; Saggar *et al.*, 1990a). This gives an amount equal to 2950 kg of fresh dung which covered an area of 0.232 ha (0.02m<sup>2</sup>/event), and 2190 litres of urine, which covered an area of 0.258 ha (0.018m<sup>2</sup>/event). The total low slope area in the LF farmlet was 0.33 ha. It is evident from the calculations that some areas of the low slope are likely to receive both dung and urine deposition or multiple dung and urine depositions and the whole of the low slope area probably receives dung and/or urine. The combined effect of dung and urine on pasture production was not studied, but the values calculated separately for dung and urine showed that the fertilizer alone treatment produced 1425kg DM ha<sup>-1</sup> whereas application of fertilizer plus dung or urine increased the pasture production to an average of 2100kg DM ha<sup>-1</sup> for 150 days. This amount may be further increased on an annual basis. Over the time period studied dung and urine return are likely to be responsible for up to 700kg DM ha<sup>-1</sup> by excreta on low slope areas, which represents a yield increase of 50%.

### 7.3.2 Sulphur, N and K concentrations in pasture

Application of dung and urine to fertilized pastures had an immediate and positive effect on the concentrations of S and N in pasture (Table 7.3). With S this effect

**Table 7.3 Effect of fertilizer and fertilizer plus dung or urine on pasture S, N and K concentrations for all treatments in three harvests.**

Treatment	Late Winter (23-8-1990)			Mid Spring (16-10-1990)			Late Spring (18-11-1990)		
	S	N	K	S	N	K	S	N	K
	%								
Control	0.30	3.25	0.84	0.25	2.31	1.12	0.26	2.14	2.08
Fertilizer	0.31	3.10	1.06	0.26	2.60	1.41	0.24	2.26	2.16
Fertilizer+D	0.38	4.32	1.55	0.27	2.82	1.76	0.25	2.37	2.39
Fertilizer+U	0.37	4.83	1.39	0.26	3.03	1.70	0.25	2.27	2.45
L S D <sub>&lt;0.01</sub>	0.05	0.52	0.49	0.07	0.24	0.21	0.06	0.39	0.64

was short lived, reflecting the smaller amounts of this nutrient in both dung and urine. The effects of dung and urine on the N dynamics of the sward persisted till late spring. While S and N concentrations decreased into spring, the reverse was true for K. Both dung and urine had a positive effect on K concentration. This effect persisted until late spring, 120 days after application. For dairy pasture, Williams *et al.* (1990) showed that the concentration of K in the pasture increased (2.0% and 2.5% for control and urine treated plots, respectively) immediately after urine application and it decreased to the concentration of the pasture which was not affected by urine after 130 days. It is clear from this study that while S and N concentrations decreased with increased pasture production, the concentration of K increased as pasture production increase. These seasonal changes in the pasture nutrient composition have been documented by Metson and Saunders (1978).

### 7.3.3 Sulphur, N and K Removed in Pasture

Both fertilizer and fertilizer plus dung or urine increased the amounts of S and N removed by pasture ( $p < 0.01$ ) (Table 7.4). The effect of fertilizer plus dung or urine was greater than fertilizer alone on S and N uptake by pasture, reflecting the effect of greater application of readily available S and N in dung and urine. In general the amounts of S and N removed by pasture were in the order urine > dung > fertilizer > control for a period of 150 days (Table 7.4). While the increased N uptake by pasture in the fertilizer only treatment must have resulted from increased organic matter mineralization and/or N fixation brought about by the effect of fertilizer on legume growth, the organic and inorganic N in dung and urine provides an immediate sources of N for pasture uptake. The effects of dung and urine return on the S uptake by pasture have not been studied in detail for fertilized pastures in New Zealand. However, the effects of urine and to a lesser extent dung on the N dynamics of a sward have been studied in great detail. The classical work of Sears (Sears *et al.*, 1965) first demonstrated the large positive effect of urine, and more recently Ball *et al.* (1979) working with a sheep/cattle pasture and Williams *et al.* (1990) on dairy pastures, have shown the effect of urine N on pasture production.

**Table 7.4** Effect of fertilizer and fertilizer plus dung or urine on the amounts of S, N and K removed in pasture during 150 days.

Treatment	Sulphur	Nitrogen	Potassium
	Kg ha <sup>-1</sup>		
Control	1.9	16.5	12.7
Fertilizer	3.6	34.8	23.6
Fertilizer+D	4.8	50.0	35.5
Fertilizer+U	6.3	67.0	45.1
L S D <sub>p&lt;0.01</sub>	1.0	14.0	11.2

Both dung and urine had a large positive effect on K uptake by pasture (Table 7.4). Williams *et al.* (1989) also showed that urine application increased the K uptake by pasture. Despite the fact that nearly two and a half times as much K was applied in dung as in urine (Table 7.1), the K uptake was not increased in dung treatment compared to urine treatment (Table 7.4). This demonstrates the higher, short term availability of urine K as compared to dung K. The amounts K removed by pasture were significantly greater in dung and urine treatments than in the control and fertilizer treatments (Table 7.4) but there was no difference in the amounts of K removed by pasture between dung and urine treatments and between the control and fertilizer treatments. In high fertility lowland pastures more K and N uptake can be expected, but as discussed below, the percent recovery of excretal nutrients may not differ from those measured in this study. For example over a longer experimental period (240 days) greater amounts of K and N (345kg N ha<sup>-1</sup> and 297kg K ha<sup>-1</sup>) were taken up by urine affected pasture in the study of Williams *et al.* (1990) than in the present study. In the study of Ball *et al.* (1979) the amount of N removed by urine affected pasture during 53 days in spring was again higher (143 to 202 kg N ha<sup>-1</sup>) than this study.

In the study apparent recoveries by pasture of the S and N applied in excreta was very low (1.9% and 3.7% of S and N applied respectively, in dung and 7.3% and 6.2% of the S and N applied respectively, in urine). This showed that very small amounts of S and N applied in excreta were used by pasture. In the South Island using <sup>35</sup>S labelled urine (Goh and Nguyen, 1990), the recovery of urine S from grazed pasture was 7% of that applied for a period of over 270 days. The amount of urine N recovered by pasture was also low, in keeping with the findings of this study, and that of Williams *et al.* (1990), where the amount of N recovered by the pasture from urine was even lower (<5%) than the value reported in the present study. Ball *et al.* (1979) reported much greater recoveries (23 to 37%) when urine was mixed with urea.

The amounts of K applied in dung and urine that were subsequently recovered by pasture (<1% in either dung or urine) were even lower than S and N. This showed that pasture derived K mainly from soil, but excreta application boosted the pasture production and hence more soil K was removed.

### 7.3.4 Leaching Losses of S, N and K

Leaching losses of nutrients from an urination event can occur by direct flow of urine through the soil macropores, such as earthworm channels and root cracks (Williams *et al.*, 1990), or by subsequent percolation of rain water through the nutrient rich urine affected soils. Williams *et al.* (1990) identified that a substantial proportion (up to 40%) of cow urine may move directly out of the top soil by macropore flow. In order to examine the extent of macropore flow of urine through the soil in the lysimeter or test for a cylinder/soil edge effect, drainage water was collected from the lysimeter with a drainage collection vessel immediately after urine application (just after application). The soil moisture content at the time of urine application was  $0.78\text{g g}^{-1}$  soil.

The amount of drainage water collected from the lysimeter (just after application) was equal to the amount of urine applied to the surface. There were no increases in the concentrations of S, N and K found in the drainage water collected immediately after urine application, suggesting piston displacement of soil water by the applied urine. The lack of any increase in the concentrations of S, N and K on the resin traps in the lysimeter treated with dung and urine collected two days after application confirmed that sheep urine applied to the surface did not pass beyond the 250mm soil depth as preferential flow down macropores and cracks or as edge flow around the cylinder edge of the lysimeter.

Application of fertilizer increased the amount of S lost by leaching (Table 7.5). An amount equivalent to 13% of the fertilizer S was lost by leaching for the period from late June to late August. The addition of dung or urine along with fertilizer, which amounts to an additional  $20.9\text{kg S ha}^{-1}$  in urine and  $115\text{ kg S ha}^{-1}$  in dung, actually resulted in decreases in the losses of S by leaching. These lower S losses must be due largely to increased immobilization of S in soil and the small increased uptake of S by pasture receiving dung and urine in addition to fertilizer (Table 7.4). This suggests that S leaching losses are not related to pasture production, but that in these N deficient soils given an adequate supply of N, S can be conserved more effectively.

**Table 7.5. Effect of fertilizer and fertilizer plus dung or urine on the amounts of S, N and K lost by leaching during 150 days.**

Treatment	Sulphur	Nitrogen	Potassium
	kg ha <sup>-1</sup> (molar charge ha <sup>-1</sup> )		
Control	0.9 (56)	0.36 (26)	0.7 (18)
Fertilizer	3.0 (188)	0.36 (26)	0.7 (18)
Fertilizer+D	2.2 (138)	0.28 (20)	1.5 (38)
Fertilizer+U	2.8 (175)	0.28 (20)	0.7 (18)
L S D <sub>p&lt;0.01</sub>	1.1 (69)	0.10 (7)	1.0 (26)

Addition of 774kg N ha<sup>-1</sup> in dung and 280kg N ha<sup>-1</sup> in urine did not increase the amount of N lost by leaching (Table 7.5). Losses of N were even lower than the amounts of S lost by leaching from either dung or urine applied plots. This supports and confirms our previous results suggesting that N is by and large conserved in these hill soils (Chapters 3, 5 and 6). In comparison S is readily lost from the soil solution (Chapter 5 and 6). Previous studies of the losses of N by leaching from grazed pastures have in general shown that much greater losses (65% of the total N applied in urine for 18 days) of N occurred (Ball *et al.*, 1979) and have been attributed mainly due to the preferential movement of urine by macropore flow down cracks and channels to drainage tiles (Sharpley and Syers, 1979; Heng *et al.*, 1991; Williams *et al.*, 1990; Steele *et al.*, 1984) in nitrogen rich lowland environments.

The amount of K lost by leaching was not influenced by either fertilizer application or the return of dung and urine (Table 7.5). The amount of K lost by leaching in this experiment (on average 0.7kg K ha<sup>-1</sup>) was lower than the amounts (35 to 55% of the applied K in urine) lost in the study of Williams *et al.* (1989). In that study most of the K was lost by preferential flow down macropores. But in low K environment of these hill pastures preferential movement of urine did not occur.

### 7.3.5 Leaching losses of Calcium and Magnesium

The equivalent amounts (moles of charge) of calcium(Ca) and magnesium(Mg) lost by leaching in all four treatments were greater than the equivalent amount of K lost by leaching (Table 7.5 and 7.6). This can be explained by considering the native exchange capacity (centimolar charge kg<sup>-1</sup> soil) of the individual cations in these soils. The exchange capacity of K (1.00 centimolar charge kg<sup>-1</sup> soil) was lower than the exchange capacity of both Ca(6.5 centimolar charge kg<sup>-1</sup> soil) and Mg(2.5 centimolar charge kg<sup>-1</sup> soil). Even though the amount of K (3700 molar charge ha<sup>-1</sup>) applied in urine was much greater than Ca the amount of Ca (160 molar charge ha<sup>-1</sup>) and Mg (540 molar charge ha<sup>-1</sup>) applied most of the applied K in urine was retained by the soil while Ca and Mg (soil and urine) were lost by leaching. It is

**Table 7.6. Effect of fertilizer and fertilizer plus dung or urine on the amounts of Ca and Mg lost by leaching during 150 days.**

Treatment	Ca	Mg
	Kg ha <sup>-1</sup> (molar charge ha <sup>-1</sup> )	
Control	3.9 (195)	1.7 (142)
Fertilizer	5.4 (270)	2.1 (175)
Fertilizer + D	6.6 (330)	2.4 (200)
Fertilizer + U	8.3 (415)	3.0 (250)
L S D <sub>p&lt;0.01</sub>	2.6 (130)	0.7 (58)

probable that urine K exchanges with soil Ca and Mg, so that the amount of Ca and Mg leached immediately after urine application (190 vs 70 molar charge ha<sup>-1</sup> Ca and 100 vs 50 molar charge ha<sup>-1</sup> Mg for urine and fertilizer treatments) significantly increased compared to the fertilizer treatment but the amount of K lost by leaching was not significantly increased (18 vs 18 for fertilizer vs fertilizer plus urine). Heng *et al.* (1991) demonstrated that K applied in fertilizer was retained by the soil in exchange for Ca and Mg which were lost by leaching.

#### 7.4 GENERAL DISCUSSION AND CONCLUSION

The results from this study quantifies common visual observations that the return of excreta by grazing animals to fertilized hill pastures boosts pasture growth and increases the pasture uptake of S and N in the vicinity of deposition. The proportions of excretal S and N taken up by pasture however were low. Even though greater amounts of K were applied in excreta, the proportion of excretal K taken up by pasture was even lower than the proportion of excretal S and N taken up by pasture, despite the fact that K fertilizer has not been applied to this hill country pasture since the fertilizer trial began in 1975. This may reflect the greater pool of plant available K present in these soils relative to S and N, in relation to the amount of S, N and K deposited in excreta.

Preferential flow of urine through macropores to soil depths below 25cm following urination was not a factor determining the leaching losses of N, S or K from these hill country pastures. This is in contrast to observations made with dairy cow urine in lowland dairy pastures (Williams *et al.*, 1989), where preferential flow has been shown to be a major vector by which N, K and S are lost from the root zone. For the short winter-spring growing season studied, deposition of dung and urine did not increase the leaching losses of S, N or K from these annually topdressed low fertility pasture soils. This aspect remains to be examined in different climatic conditions and for pastures which receive higher fertilizer application rate and have higher stocking rates.

The low amounts of freshly applied excreta S, N and K recovered by pasture and lost by leaching suggested that most of the S and N removed by plants was derived from the mineralization of organic S and N which had accumulated from previous application of fertilizer and excreta return.

The results presented here and those of Chapter-6 further suggest that the majority of excretal and fertilizer S may be immobilized in to soil organic matter in the short-term and not immediately cause accelerated nutrient leaching losses. It is apparent that the input of excretal S into the soil organic matter eventually leads to higher soil S mineralization rates, increased pasture uptake and losses by leaching of soil S.

## CHAPTER-8

### MODELLING THE FATE OF SULPHUR IN THE SOIL-PLANT SYSTEM IN GRAZED PASTURE

#### 8.1 INTRODUCTION

As discussed in Chapter-1, a prerequisite for managing the efficient use of fertilizer S in agricultural systems is a knowledge of the processes and interactions occurring within each system that influence the fate of S. In New Zealand, the Ministry of Agriculture and Fisheries scientists have considered that S requirements of grazed pastures can be maintained if all S losses from the system are replaced. A simple mass balance model has been developed for calculating the maintenance S requirements of such grazed pastures (Sinclair and Saunders, 1982). The model assumes that the fluxes of S between various pools within the pasture system (S-cycle) are in steady state and estimates the balance between gains and losses from the grazing system in order to make fertilizer recommendations.

For most soils the mass balance model does not take into account the losses occurring within the soil system such as immobilization. It is not a dynamic model in the sense, that it deals simply with calculating the annual balance whereas seasonal rainfall, plant growth and organic matter mineralization are not considered and therefore the model cannot be used to predict any seasonal limitations in S availability caused by leaching frequency and/or soil organic matter turnover (Nguyen and Goh, 1990). Such descriptions are useful to identify the time of the year when S fertilizer is best applied to overcome the growth limitations due to the lack of S in the plant available pool or minimize losses of fertilizer S from the system.

Partially dynamic models have been formulated for grazed pastures under Australian conditions in two separate studies using information gained from tracing the fate of radioactively labelled gypsum (Till and May, 1971) and examining the fate of S in a long term grazing study (M<sup>c</sup>Caskill and Blair, 1990). Although the data in both studies suggested that active cycling occurs in nearly all segments of the system,

except for some less labile organic sulphur fractions, no direct measurements of many of the processes were made, particularly the rates of mineralization, immobilization and leaching and their seasonal and climatic dependency. These Australian models cannot be applied to New Zealand situations, because sulphate leaching, an important process in New Zealand was not considered in detail in either of the Australian studies.

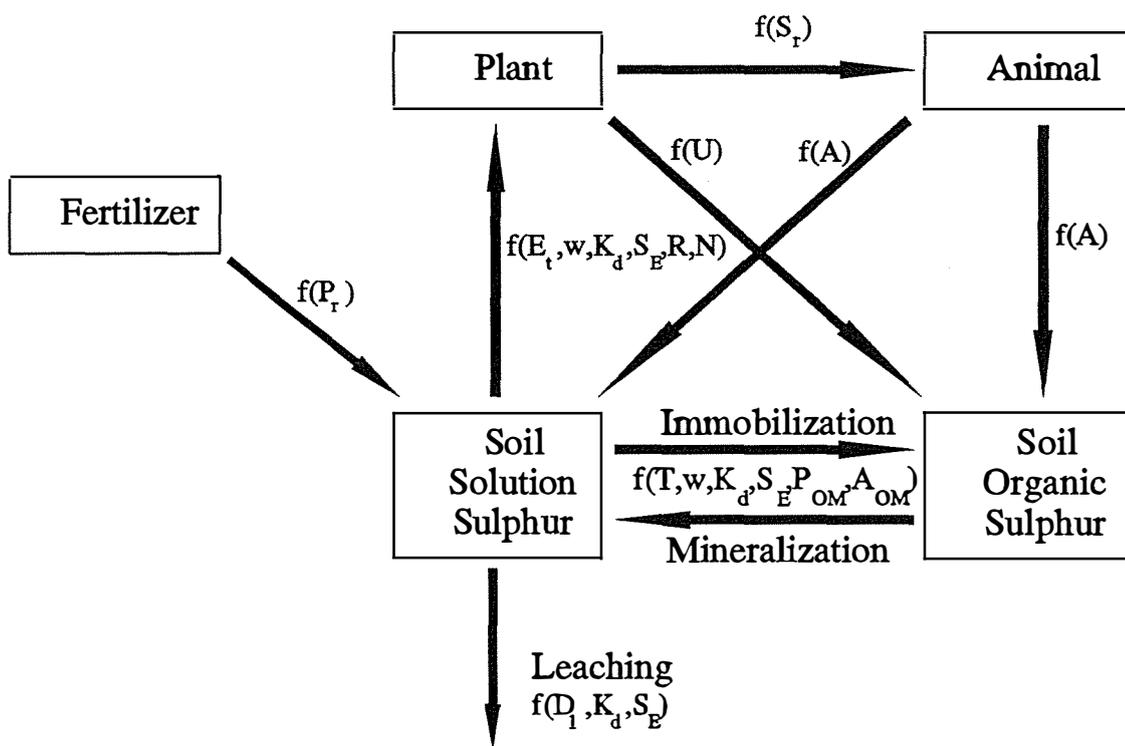
Few (Gregg and Goh, 1978, 1979; Goh and Nguyen, 1991) attempts have been made to quantify the fluxes of S between various soil S pools in New Zealand grazed pasture systems. There is a need therefore to provide information for agronomist on the movement of S within soil-plant-animal system and between plant available and organic pools, and how they influence the fertilizer requirements of New Zealand pasture system. This may be achieved by constructing a mechanistic model that describes the important processes using information gained from field experiments and then evaluating this model by applying it to New Zealand farming systems. A simple, conceptual dynamic model for S cycling that describes the important processes and their major controlling factors would take the form as shown in Fig.8.1. A successful simulation of these processes over time, would provide information about the timing, frequency and rate of S fertilizer application.

In this Chapter a simple computer simulation model was constructed to describe the movement, transformation and losses of S from the soil-plant system only, adhering as closely as possible to the concepts outlined in Fig.8.1. These concepts are explained in more detail in the discussion section (section 8.3). The model output was compared to field observations made in Chapters 5 and 6. This modelling exercise is an attempt to summarise information gained in this thesis on the soil-plant part of S cycle in a form which is useful to agronomists.

## 8.2 MATERIALS AND METHODS

Methods employed in making the field observations were discussed in Chapters 5 and 6.

Fig. 8.1. A Simple Conceptual Dynamic Model Showing the S - Cycle



- |          |   |   |                                 |
|----------|---|---|---------------------------------|
| R        | = Rainfall  | N | = Growth Limiting Nutrient      |
| $K_d$    | = Soil Sulphate Adsorption Coefficient                | U | = Pasture Utilisation           |
| T        | = Temperature   | f | = function of a variable listed |
| $E_t$    | = Transpiration                                       |   |                                 |
| $S_r$    | = Stocking Rate                                       |   |                                 |
| $P_{OM}$ | = Plant Organic Matter, Quality                       |   |                                 |
| $A_{OM}$ | = Animal Organic Matter, Quality                      |   |                                 |
| $P_r$    | = Particle Size plus Oxidation or Solubility Constant |   |                                 |
| $S_E$    | = Extractable Sulphate                                |   |                                 |
| $D_1$    | = Drainage  |   |                                 |
| $A_1$    | = Animal Excretion Patterns                           |   |                                 |
| w        | = Soil Volumetric Water Content                       |   |                                 |

### **8.2.1 Determination of the relationship between extractable and solution sulphate**

The relationship between extractable sulphate and solution sulphate for the yellow brown earth soils from the Ballantrae research farmlets (sections 5.2, 6.2 and 7.2) were determined for three soil depths (0-75mm, 75-150mm and 150-250mm) for two of the four sites, namely, LF-LS and HF-LS. Field moist soil core samples were used for establishing the relationship. Samples of field moist soil (7.5g net, approximately 5g oven dry < 2mm sieve size) sample were weighed into a 10ml plastic centrifuge tube, which had a hole in its base, which was covered with glasswool. This centrifuge tube with the soil was placed inside another centrifuge tube of similar dimensions. Five millilitres of sulphate solution was added. The soil was left (not shaken) overnight in order to attain equilibrium. A range of sulphate solution concentrations were used (e.g. 0, 20, 40, 80, 160 and 320 mg S l<sup>-1</sup>). After 24 hours the soil solution was collected in the outer tube by centrifugation at 15,000 RPM for 15 minutes. After collecting the soil solution the soil (approximately 0.5g water g<sup>-1</sup> soil) was extracted with 0.04M Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> for 16 hours at a soil:solution ratio of 1:5 and the sulphate was determined in the extract by the method described in section 3.2 (Chapter-3). The soil solution sulphate concentration was plotted against 0.04M Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> extractable sulphate (Fig 8.8) rather than adsorbed sulphate because 0.04M Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> can be routinely used to measure adsorbed plus solution sulphate in field soils (see discussion section,8.3.3.1).

## **8.3 MODEL DEVELOPMENT**

### **8.3.1 Water balance**

#### **8.3.1.1 Calculating drainage volumes**

The vector for the movement of plant nutrients in the soil is the soil water. A drainage model is required to predict the movement of water through the soil because loss of sulphate by drainage was a major fate of both applied fertilizer S (Chapter-7) and mineralized soil organic S (Chapter-6). Daily drainage water volumes for a soil

column of known depth were predicted using the following simple balance equations.

$$w_f = w_i + R - E_t \quad (8.1a)$$

where

$w_i$ = the initial depth of water (mm) in a soil column of specified depth.

$w_f$ = the final depth of water (mm) in a soil column of same depth.

$R$ = Daily rainfall (mm).

$E_t$ = Daily potential evapotranspiration (mm) (see section 5.2)

Initially it was assumed that rainfall intensity does not exceed the infiltration rate of water into the soil. This assumption was tested by comparing actual and predicted drainage volumes (Chapter 6, section 6.3.1).

when  $w_f$  is greater than the depth of soil water at field capacity ( $w_{fc}$ ), drainage (Dmm) occurs. The amount of drainage (Dmm) occurring is given by the equation

$$D = w_f - w_{fc} \quad (w_f > w_{fc}) \quad (8.1b)$$

The drainage for the first experimental season (Chapter-5, section 5.3.1) was not measured but for the second experimental season (Chapter-6, section 6.3.1) the drainage was measured and could be predicted well using equation 8.1a and 8.1b (Chapter-6, Fig.6.2) which explained 98% of the variation in the observed data. The close relationship between predicted and measured drainage (description of calculations is given in Chapter-5) indicated that surface runoff during this experimental period was negligible. Thus the simple water mass balance model is adequate for predicting the volume of daily drainage events.

### 8.3.1.2 Estimating actual daily evapotranspiration.

The actual evapotranspiration ( $AE_t$ ) from these pasture soils will be used to estimate the flux of water from the soil through the plant. This will be the vector which carries soil solution sulphate into the plant (Fig.8.1, Section 8.2.3.3). With complete cover of the soil by pasture plants evaporation from the soil surface is negligible and 100% of evapotranspiration ( $E_t$ ) can be considered to occur from leaves of pasture plants (Coulter, 1973; Jensen, 1973; McNaughton *et al.*, 1979; Payne, 1990).

The effect of decreasing soil water content is to decrease the rate of evapotranspiration

(Payne, 1990; Gregory, 1990). This effect can be approximated by the relationship given by Scotter *et al.* (1979) and Rickard *et al.* (1986). Rickard *et al.* (1986) considered that for the Lismore stony silt loam plant growth completely stops (permanent wilting point, PWT) when the soil water deficit was approximately 70% of the maximum soil water deficit and the potential evapotranspiration ( $AE_t/E_t$ ) could be achieved when the soil water deficit was less than 50%. In the absence of data on pasture growth soil water deficit comparisons, for the Ballantrae field site, the relationship derived by Rickard *et al.* (1986) has been applied. The soil water depth ( $w$ , mm) shown in Fig.8.2. are those applicable to the top 75mm of the soil at the LF-LS site where  $w_{fc}$  was measured at 34.7mm and the maximum observed deficit was 26mm (see below). Actual evapotranspiration ( $AE_t$ ) equals the potential evapotranspiration ( $E_t$ ) at soil water contents between  $w_{fc}$  and  $0.5(w_{fc}-PWT)$ . The ratio of  $AE_t/E_t$  decreased linearly, however, when the soil water content declines from  $0.5(w_{fc}-PWT)$  to PWT. The soil water depth at which the soil water deficit is zero ( $w_{fc}$ ) were measured as 34.7mm, 32.7mm and 41.0mm for 0-75mm, 75-150mm and 150-250mm soil depths by measuring the moisture content of field soil cores samples one day after a heavy winter rainfall event during which drainage occurred from LF-LS site. Similar values (g water  $g^{-1}$  soil) for the other three sites were given in Appendix-5.1. The maximum soil water deficit at which plant growth completely stopped (permanent wilting point) for the three layers (increasing depth) were measured at -24.3mm, -22.9mm and -28.7mm in November 1989 after a twenty day period without rain when no significant pasture growth was observed in the last three days of the drought. So applying the relationship of Rickard *et al.* (1986) the reduction of  $E_t$  to  $AE_t$  was predicted to occur when the soil water deficit reached -12.15mm, -11.5mm and -14.4mm for the three layers (increasing depth). Using this relationship the  $AE_t$  was calculated from a knowledge of daily  $E_t$  and the soil water content using the Multiplan spreadsheet version 4.01.

Water leaving the sward as evapotranspiration from the pasture herbage will be drawn from different soil depths and the extent of extraction from each soil depth will depend upon root distribution and the difference in water potential between the soil

Fig.8.2 Effect of increasing soil water deficit on the amount of evapotranspiration for 0-7.5cm soil depth from LF-LS site.



water at the root surface and that within the root and the resistance to flow (resistivity) attributed to the root membrane. The flow of water from the plant root to the leaf will depend upon the difference in water potential between water in the root and the water in the stomatal cells and the length and resistivity of the xylem vessels connecting the two. In turn the water potential in the stomatal cells is determined by the water vapour pressure in the stomatal cavity which itself is determined by the extent of the stomatal pore opening and the atmospheric water vapour pressure (Gregory, 1990). Modelling the above processes to explain the evapotranspiration loss from pastures is beyond the scope of this thesis. However in this simple model it is assumed that the amount of water removed by plant from the soil depends only upon the distribution of root weight in each soil depth. There is some evidence (Payne, 1990) that this method provides a reasonable description of water removal from different soil depths. Barker *et al.* (1988) showed that, the root distribution of a hill country pasture containing browntop, perennial ryegrass and white clover was 65%, 30% and 5% for 0-75mm, 75-150mm and 150-250mm soil depth. The total  $E_t$  was partitioned to draw water from each depth relative to the percentage root distribution in each soil layer.  $E_t$  from  $i^{\text{th}}$  soil layer was calculated as follows

$$E_{t,i} = E_t \left( \frac{r_i}{\sum_{i=1}^3 r_i} \right) \quad (8.2)$$

where  $\sum r_i$  is the total root mass for all the layers ( $i=1$  to 3) and  $r_i$  is the root mass for the  $i^{\text{th}}$  layer.  $E_t$  from each depth was then converted to  $AE_t$  based on the relationship between  $AE_t/E_t$  and soil water deficit in each depth.

### 8.3.2 Testing the concept of single sulphate pool for plant and leached sulphate

The simple configuration in Fig.8.1 assumes that there is one available sulphate pool from which S is taken up by plant and lost by leaching (Syers *et al.*, 1987; McCaskill and Blair, 1988). In the experiment described in Chapter-6,  $^{35}\text{S}$  labelled superphosphate was used to label this sulphate pool and other soil S pools. If the simple concept outlined above is correct, then the specific activity of S ( $^{35}\text{S}$  cpm/mgS)

taken up by plant and lost by leaching (collected on the lysimeter resin traps, Chapter-6) on any one day should be similar since both losses are derived from the same pool. This hypothesis will be tested in this section.

Previous studies on the mineralization and immobilization of S using  $^{35}\text{S}$  labelled S showed that the specific activity of the sulphate pool decreased with time (Freney *et al.*, 1975; McLaren *et al.*, 1985). This is due to the removals of sulphate from the  $^{35}\text{S}$  labelled sulphate pool by plant uptake and immobilization to organic forms as native unlabelled organic S is mineralized into the pool.

The specific activity of the pasture S at each harvest (Appendix 8.1) is the result of the uptake of labelled sulphate from the soil sulphate pool over a period of time (normally one month harvesting interval), during which, the specific activity of the sulphate pool decreases continuously. Thus the specific activity of the pasture represents a growth (rate of S uptake) and time weighted average of the soil solution sulphate specific activity. The specific activity of the leached S collected on the resin trap (Appendix 8.1) however, may have resulted from drainage occurring only on a few days during this period of plant growth. The specific activity of the leached S may be greater or lower than the specific activity of the pasture S, depending on when the leaching occurred during plant growth.

Both the trends in the accumulated activity of  $^{35}\text{S}$  (Fig.8.3a) and the accumulated total S (Fig.8.3b) taken up by plant can be described by the function below

$$Y = A + B \exp(CX) \quad (8.3)$$

where

Y= cumulative uptake of  $^{35}\text{S}$  activity (cpm/core) /or S (mg S/core) for a given period of X days

A, B and C are fitted coefficients.

These Mitscherlich type curves explained a large percentage of the variation (Table 8.1a & 8.1b) in the uptake of radioactive  $^{35}\text{S}$  (Fig.8.3a) and total S by the plant (Fig.8.3b).

Fig.8.3a Cumulative amounts of S-35 activity removed by pasture with time at all four sites from Jan. to Oct. 1990.

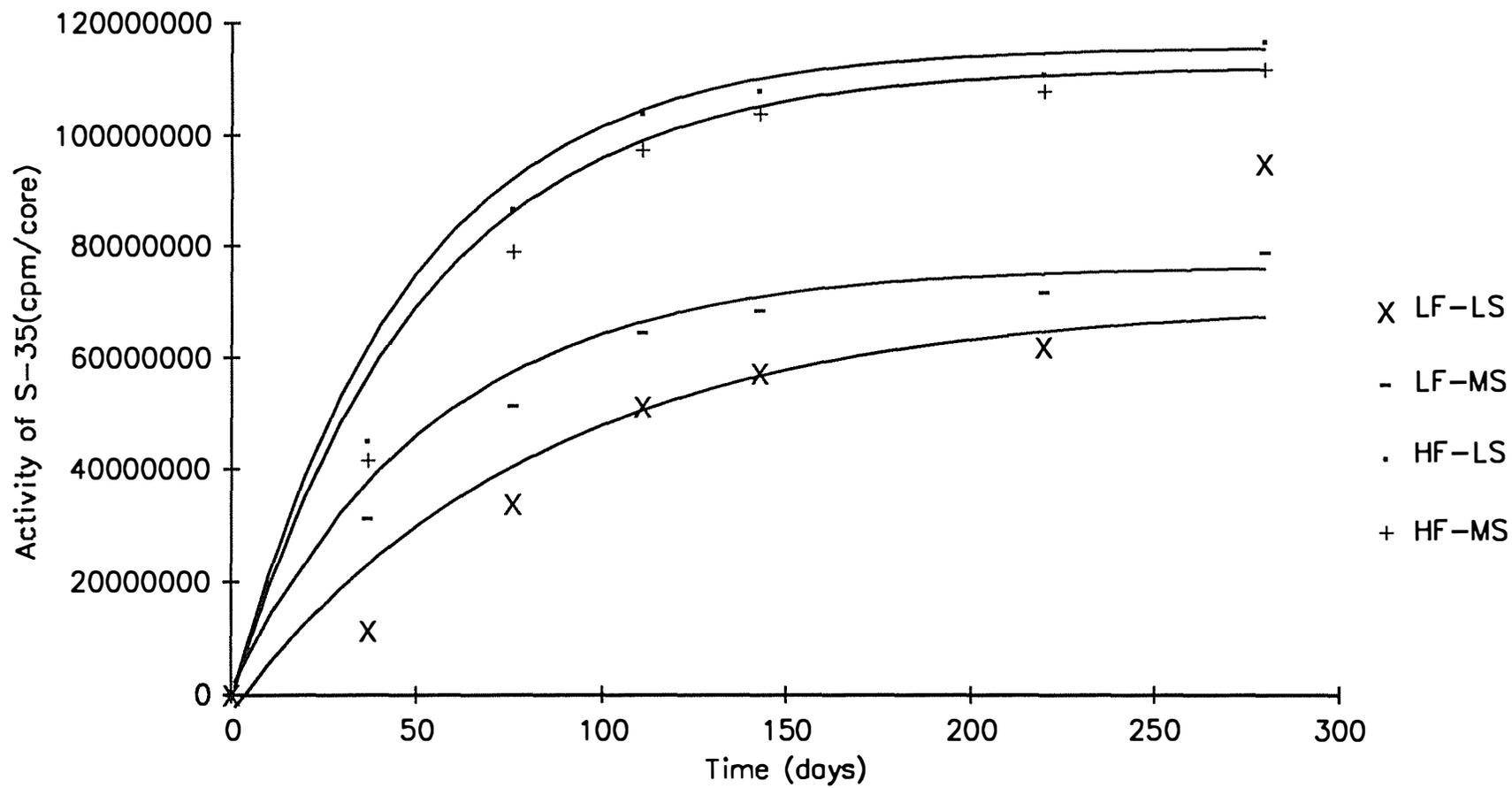
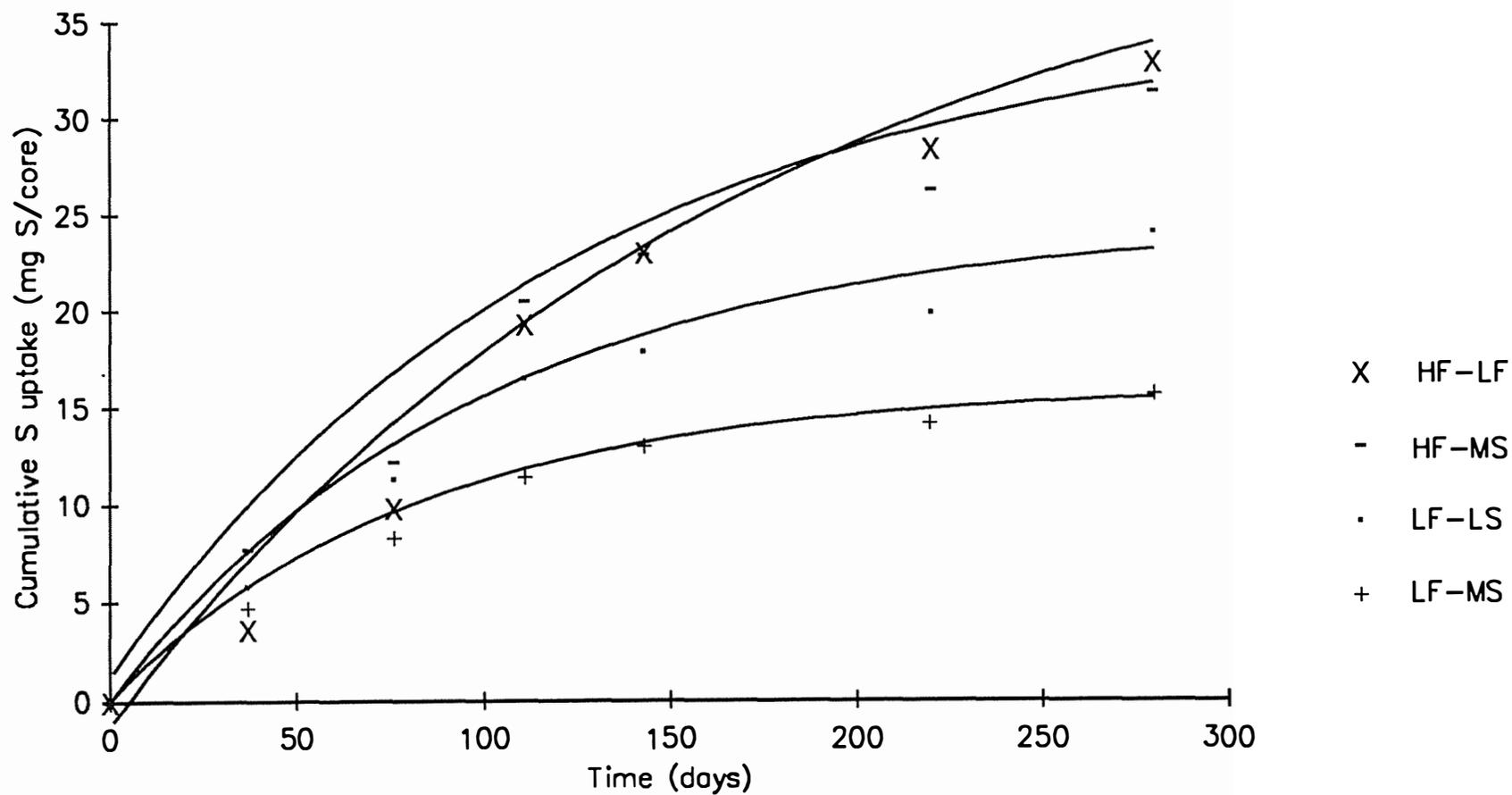


Fig.8.3b Cumulative amounts of S removed by pasture with time at all four sites from Jan. to Oct. 1990.



**Table 8.1a Regressions for the cumulative uptake of  $^{35}\text{S}$  activity (cpm/core) with time for all four sites.**

Farmlet	Regression equation	$R^2$
LF-LS	$y = 11.2-11.3 X \exp(-0.012x)$	99.4
LF-MS	$y = 11.6-11.7 X \exp(-0.012x)$	99.5
HF-LS	$y = 7.7-7.6 X \exp(-0.018x)$	99.2
HF-MS	$y = 7.0-7.3 X \exp(-0.012x)$	97.3

**Table 8.1b Regressions for the cumulative uptake of S (mg S/core) with time for all four sites.**

Farmlet	Regression equation	$R^2$
LF-LS	$y = 16.1-16.0 X \exp(-0.012x)$	99.4
LF-MS	$y = 24.7-24.7 X \exp(-0.010x)$	98.0
HF-LS	$y = 34.5-34.2 X \exp(-0.088x)$	97.7
HF-MS	$y = 43.1-44.3 X \exp(-0.06x)$	96.6

These functions were differentiated to allow uptake of  $^{35}\text{S}$  activity and S to be predicted for each day (equation 8.4). The time dependant differential function for the uptake of  $^{35}\text{S}$  and S is given below

$$\frac{dY}{dX} = BC\exp(CX) \quad (8.4)$$

where Y, X, B and C were described in equation 8.3.

The differential function explaining the rate of  $^{35}\text{S}$  activity uptake was divided by the differential function explaining the rate of S uptake by plants in order to calculate the time dependent function for describing the specific activity of daily plant S uptake. The calculated time dependent specific activities were related well ( $r^2=0.799$ ), but slightly underestimated the observed specific activities of the pasture for all harvests (all six cuts from Jan. to Oct. 1990) from all four sites (Fig.8.4).

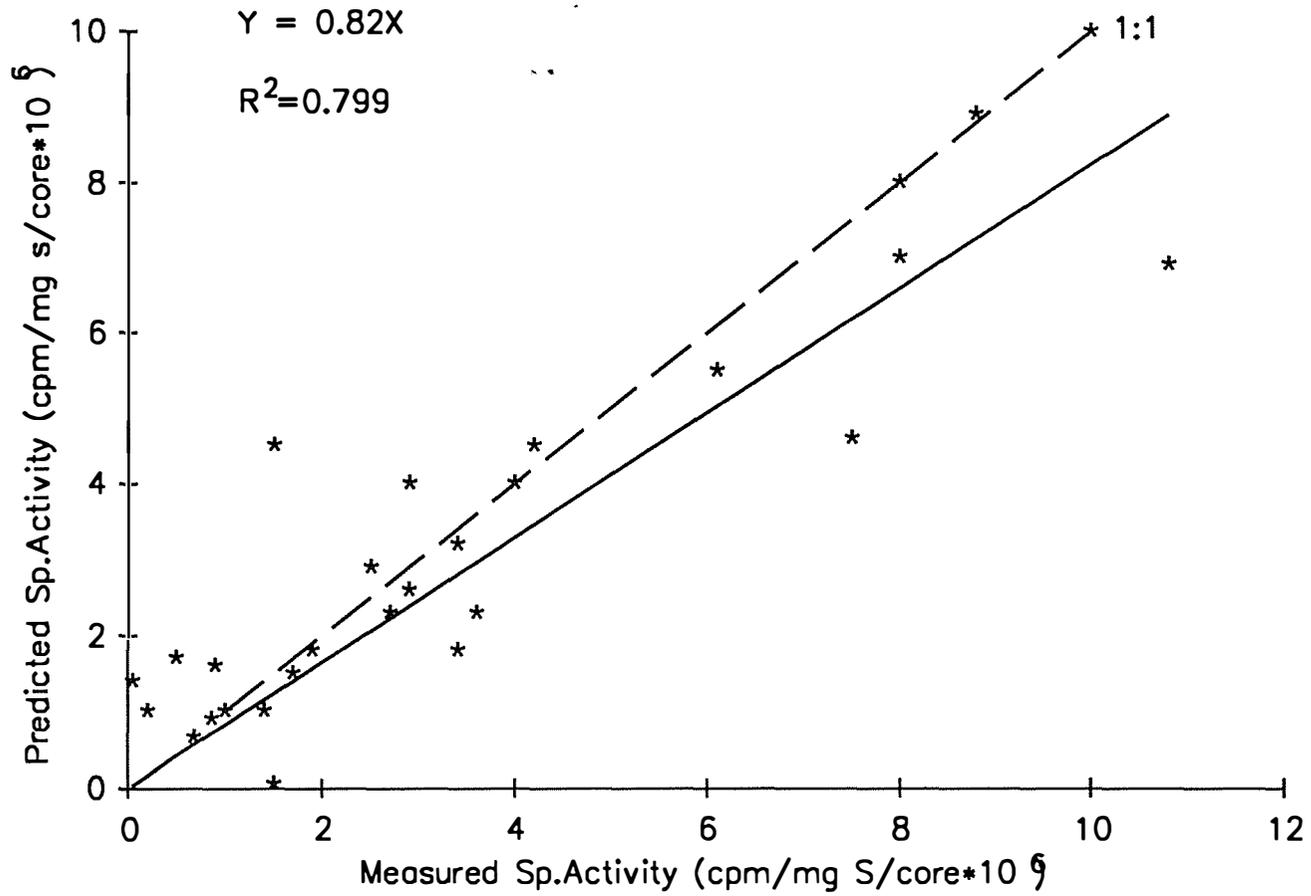
As mentioned earlier, both the resin from the resin trap and pasture from the core were collected at the same time. Leaching might have occurred for only a few days and not continuously during a period plant growth. The amount of sulphate lost by leaching and the specific activity of the leached S on a daily basis was calculated in the following way :

Using the model developed to predict the drainage (Chapter 5 & 6), the days during a growth period in which drainage occurred were identified and the total volume of drainage was calculated between two successive harvests(H), namely  $H_n$  to  $H_{n+1}$ , which is given by the equation

$$D = \sum_{H_n}^{H_{n+1}} D_n \quad (8.5a)$$

where D is the total predicted drainage (mm) between two successive harvests and  $D_n$  is one of a number of daily drainage events (mm) between two successive harvests. From the above equation the fraction ( $\rho$ ) of total drainage for a growth period occurring on a particular day was calculated as

Fig.8.4 Relationship between predicted and measured specific activity of S in pasture for the period from Jan. to Oct. 1990 at all four sites.



$$\rho = \frac{D_n}{D} \quad (8.5b)$$

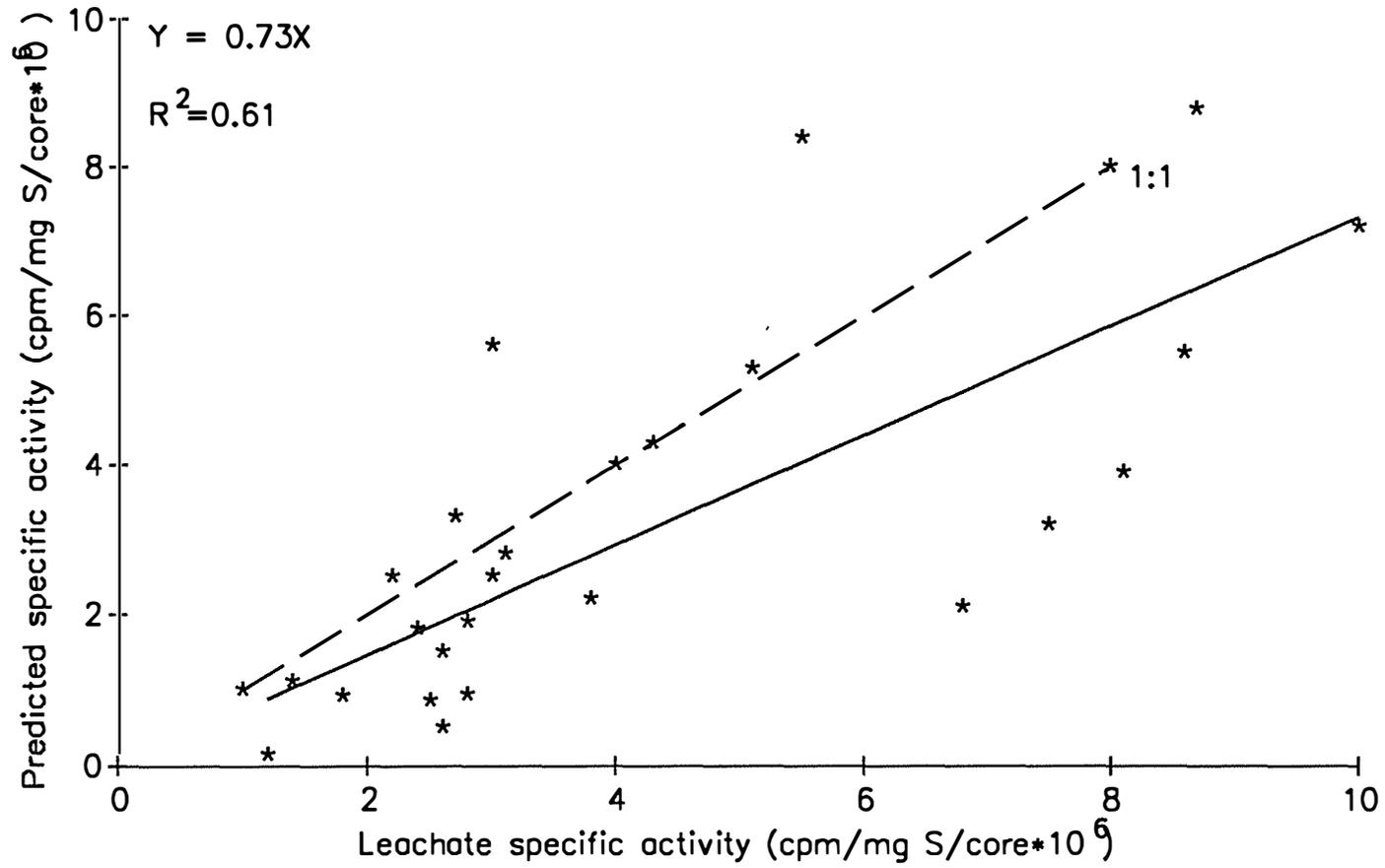
Assuming that the amount of sulphate leached is proportional to the drainage volume, the amount of sulphate leached on a particular day can be calculated as

$$\text{Sulphate leached} = \rho \times \text{Total sulphate leached from } H_N \text{ to } H_{N+1}$$

The specific activity of the leached S on a particular day was considered to be same as that predicted from the time dependent functions describing the specific activity of daily plant S uptake. The amount of  $^{35}\text{S}$  activity leached by a particular rainfall event was estimated by multiplying the amount of S leached on that date by the specific activity of daily plant S. By summing the amounts of  $^{35}\text{S}$  activity leached by each rainfall event (between harvest  $H_n$  to harvest  $H_{n+1}$ ) and dividing this by the amount of sulphate leached, the specific activity of S collected on the resin trap between harvests  $H_n$  and  $H_{n+1}$  could be predicted. The predicted specific activity of the leached sulphate was lower ( $r^2=0.61$ , slope=0.73) than the measured specific activity of leached sulphate collected on the resin (Fig.8.5). The predicted plant specific activity (Fig.8.4), however was also lower (slope=0.82) than the measured specific activity of plant. This suggests that if measured plant specific activities could be used (the intermittent nature of drainage events prevented this) to predict drainage water specific activities the slope of the relationship would be  $0.73/0.82 = 0.9$ . On that basis the specific activity of the plant available sulphate pool is slightly, but consistently lower than that of the pool susceptible to leaching. Reasons for this could include

1. Initial leaching of fertilizer  $^{35}\text{S}$  to depths where root activity (Barker *et al.*, 1988) and sulphate pool turnover rate (Hedley, unpublished) are lower, would lead to less  $^{35}\text{S}$  uptake by the plant and a slower decline in the specific activity of the sulphate pool at depth which remains susceptible to leaching during subsequent rainfall events.

Fig.8.5 Relationship between the predicted (from plant S specific activities) and observed specific activity of the leached S at all four sites from Jan. to Oct. 1990.



2. In the plant rhizosphere which includes micropores exploited by fine roots and root hairs (Barber, 1984), the rate of sulphate turnover may be more rapid than in the bulk soil or in macropores. More leached S may be derived from the larger pores (mobile phase) rather than micropores (immobile phase). Plant root hairs normally derive S from the immobile phase by diffusion (Barber, 1984). The sulphate in the immobile phase may be diluted rapidly because of increased mineralization associated with root activity. Thus in general the specific activity of sulphate in larger pores may be diluted at a slower rate than that in areas of intense root activity.

Irrespective of the cause of this small difference in S transformation rates it would be wise to partition the soil into defined zones of differing root activity. In this respect a vertically layered model with root activity and mineralization decreasing down the soil profile would seem acceptable.

### 8.3.3 Modelling the fluxes of S between various pools

The amount of sulphate present in the soil solution for a given layer (i), which is potentially available for plant uptake and loss by leaching at any time 't' is given by the balance equation

$$E_{s,t} = E_{s,t-1} - P_s - L_s + M_s + I_s + F_s \quad (8.6)$$

where

$E_{s,t}$  = sulphate ( $\text{kg S ha}^{-1}$ ) present in the plant available pool at any time t for  $i^{\text{th}}$  layer,

$E_{s,t-1}$  = sulphate ( $\text{kg S ha}^{-1}$ ) present in the plant available solution at time t-1 for  $i^{\text{th}}$  layer,

$P_s$  = sulphate taken up by plant ( $\text{kg S ha}^{-1}$ ) during the period from t-1 to t from the  $i^{\text{th}}$  layer,

$L_s$  = sulphate lost by leaching ( $\text{kg S ha}^{-1}$ ) during the period from the  $i^{\text{th}}$  layer,

$M_s$  = Amount of sulphate ( $\text{kg S ha}^{-1}$ ) mineralized to the sulphate pool from soil organic matter in one day in  $i^{\text{th}}$  layer,

$I_s$ = Amount of sulphur ( $\text{kg S ha}^{-1}$ ) entering the sulphate pool in the  $i^{\text{th}}$  layer from rainfall or other solution inputs,

$F_s$ = Amount of sulphate ( $\text{kg S ha}^{-1}$ ) entering the sulphate pool from fertilizer.

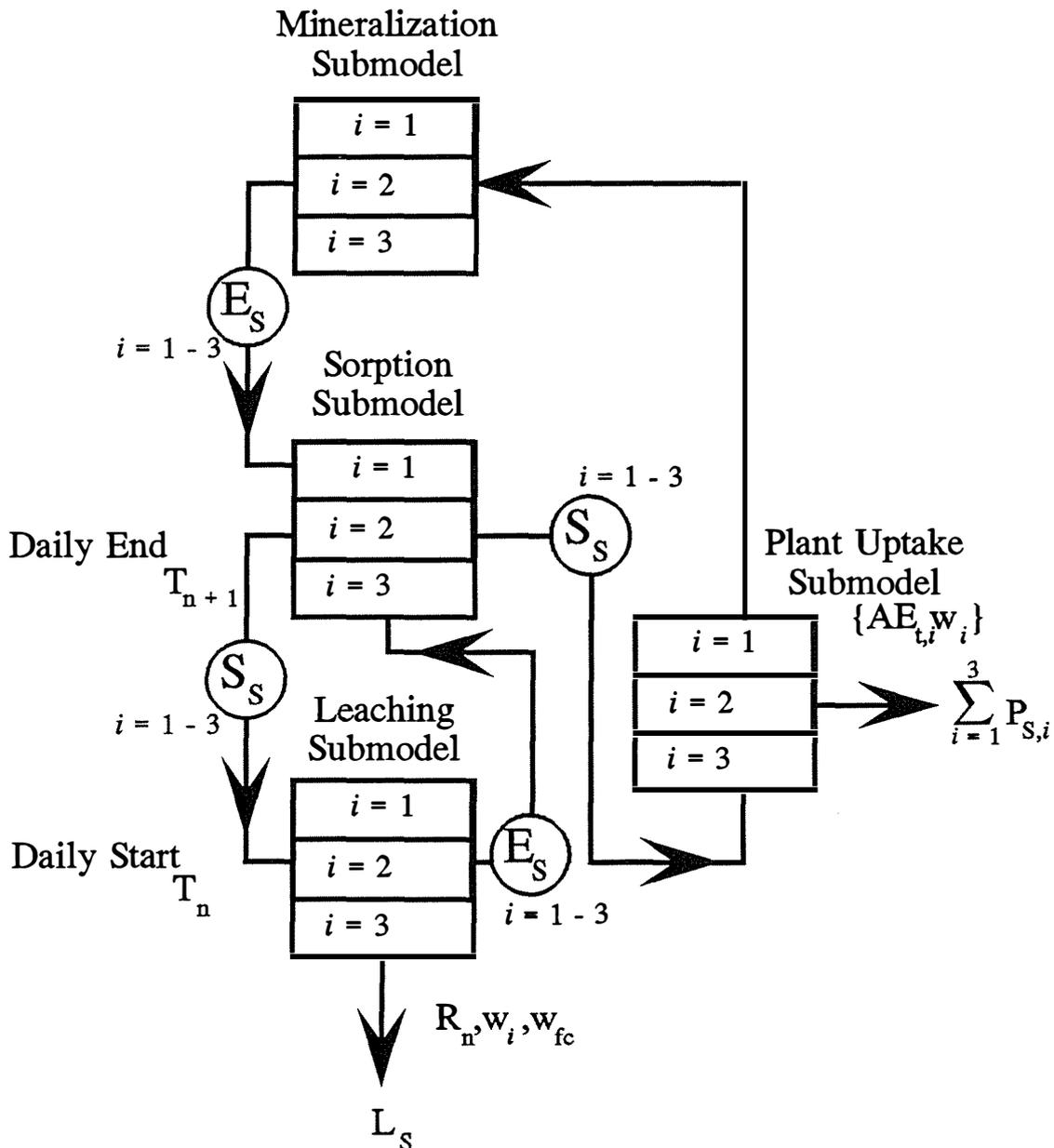
The S input through rainfall is negligible ( $<2 \text{ kg S ha}^{-1} \text{ y}^{-1}$ , see Ledgard and Upsdell, 1991) for the Ballantrae experimental site and no fertilizer was applied during the experimental period to be modelled. The majority of the S input to the sulphate pool is from the mineralization of soil organic matter, which includes the decomposition of animal excreta, plant litter, root and older soil organic matter. In the following discussion the contribution of both fertilizer and rainfall sulphur to sulphate pool were not included. In the model plant S and leached S are derived from solution sulphate and that the order in which the processes occur leaching, plant uptake and mineralization (Fig.8.6). The following sections construct submodels to describe the dynamic features of the components of equation 8.6

### 8.3.3.1 Predicting the soil solution sulphate concentration

For a model to predict the amounts of S taken up by plants or leached (Fig.8.1) the soil solution sulphate must be estimated on a regular basis. To do this ideally functions are required to describe the relationship ( $K_d$ ) between adsorbed and solution sulphate in field soils. The relationships between amounts of adsorbed sulphate and soil S solution concentrations varies from soil to soil depending upon the extent of positively charged soil surfaces (Barrow, 1967b), the past fertilizer history and the present fertilizer application rate (Freney, 1986). Most positive charge in soils is present as protonated hydrous oxide surfaces and organic functional groups or as a layer of cations adsorbed to negatively charged clays and organic matter. The distribution of these components varies with depth for a particular type of soil and with them the ability of the soil to adsorb sulphate (Rhue and Kamprath, 1973).

It is difficult to measure the soil solution sulphate concentrations in field soils, particularly when the soil moisture content is lower than field capacity. In dry periods the soil solution cannot be collected using porous, porcelain cups and suction sampling. It is however, relatively easy to core sample soils and carryout laboratory

Fig. 8.6. Hierarchical Order of the Processes in the S Cycle



$S_S$  = Soil Solution Sulphate

$E_S$  = Extractable Soil Sulphate

Other symbols were described in Fig.8.1.

measurements. The common soil test to measure solution plus adsorbed sulphate in the soil is to extract the soil with 0.01M or 0.04M  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  (Searle, 1979; Saunders *et al.*, 1981). Some of the S extracted from pasture top soils is in organic form (Watkinson and Perrott, 1990). The extractable soil sulphate was measured in this experiment using 0.04M  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  (1:5 soil:solution ratio) (Chapters 5 & 6).

The soil solution sulphate concentration for the 150-250mm soil depth in the field was able to be measured on seven occasions by collecting the soil solution using pre-washed porous ceramic suction cups (Heng *et al.*, 1991) (Table 8.2). The concentration of sulphate in the soil solution (Table 8.2) was related to the soil extractable sulphate (Fig.8.7). This relationship could not be developed for top two soil layers because the soil solution was not collected for those two layers.

A relationship, however, was required between soil solution sulphate and extractable sulphate for the top two soil depths because in the absence of any measurement of soil solution sulphate concentrations such a relationship is required to predict the sulphate concentration in solution present during the experimental period for all soil depths. For sampling purposes the soil profile was divided into three layers, namely 0-75, 75-150 and 150-250mm. For all the three depths the relationship between soil solution sulphate and the 0.04M  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  extractable sulphate was established using 'adsorption isotherms' conducted in the laboratory for soils from both the LF and HF farmlets as mentioned in section 8.2.1. The relationships were not strictly adsorption isotherms, because the extractable sulphate measured using 0.04M  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  contains solution, adsorbed and some organic sulphur (Watkinson and Perrott, 1990). For this reason true adsorption isotherms were not generated using plots of adsorbed sulphate vs solution sulphate. Linear relationships between extractable sulphate and soil solution sulphate however, were established for all the three layers (Fig.8.8). The extractable sulphate concentrations normally found in the field soil throughout the experiment (Table 8.2) were used to limit the range in which the relationships were derived. There was no significant difference between the slopes of the relationships for soils taken from the LF and HF farmlets (data not shown). Data therefore were pooled and combined regression models were generated for each of the three soil depths (Fig.8.8). The relationships show that the soil solution sulphate as a proportion of the extractable sulphate decreased as the soil depth increased (Fig.8.8). The

**Table 8.2 Soil solution sulphate concentrations sampled by suction cup amounts of 0.04M Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> extractable sulphate present in the soil from the 15-25cm depth for LF-LS and HF-LS sites for seven sampling events.**

Farmlet	Suction cup sulphate	
	Extractable mg S kg <sup>-1</sup> soil	Solution mg S l <sup>-1</sup>
LF-LS	9.0	1.3
	8.0	1.0
	6.5	0.9
	9.3	1.0
	8.3	1.0
	9.4	0.8
	10.1	1.0
HF-LS	18.4	8.5
	16.6	7.5
	18.4	9.2
	22.8	9.4
	19.3	8.4
	17.9	8.0
	18.3	8.5

Fig.8.7 Relationship between the soil solution sulphate measured in the laboratory ( - - - ) or in the field ( — ) and 0.04M calcium phosphate extractable sulphate for the 150-250mm soil layer.

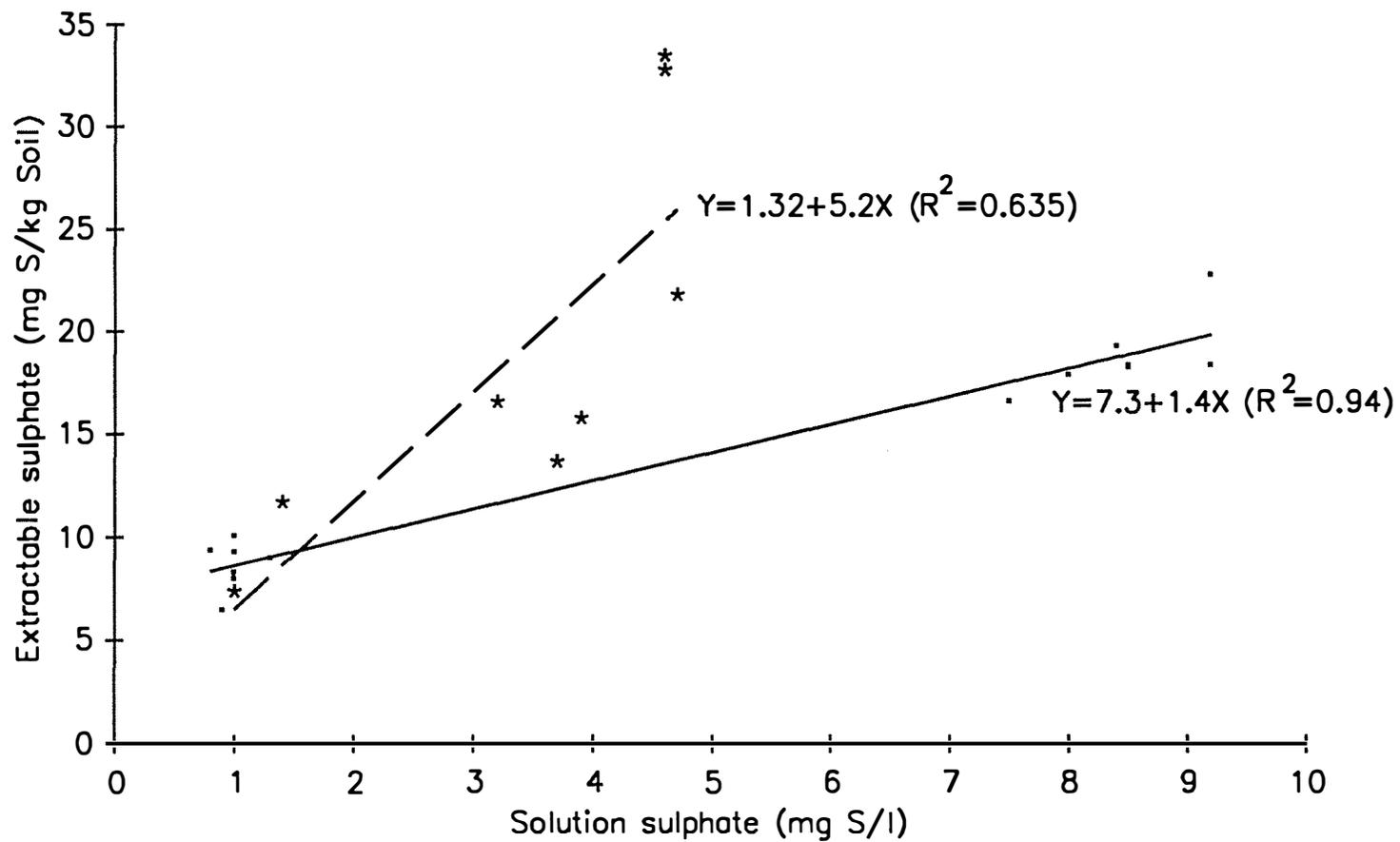
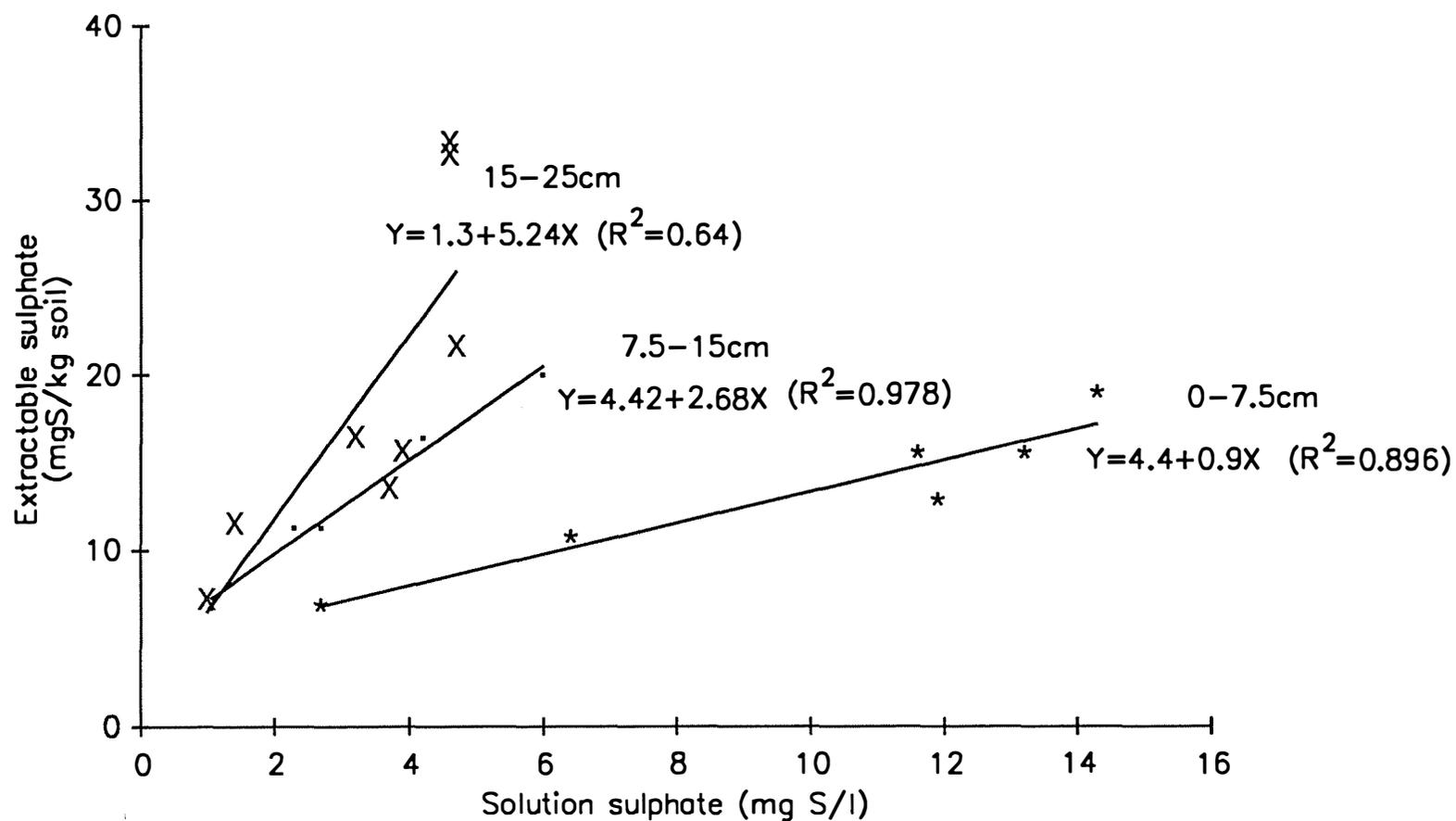


Fig.8.8 Relationship between extractable sulphate and solution sulphate measured in the laboratory for the soils from 0-75, 75-150 and 150-250mm depths for LF and HF farmlets.



functions derived from this relationship were used to calculate the soil solution sulphate for each layer.

For soils from the 150-250mm depth of the low fertility sites (solution sulphate concentrations around  $1\text{mg l}^{-1}$ ) there was little difference between the function derived from the laboratory data and the function derived from the field suction cup data however, for the high fertility sites (solution sulphate concentrations around  $9\text{mg l}^{-1}$ ) these functions are different for 150-250mm depth (Fig.8.7). In the model, the linear function derived from the suction cup data was used to calculate the soil solution sulphate concentration from extractable sulphate data for 150-250mm depth at the high fertility sites only. The laboratory derived relationships were used for all other soil depths. Reasons for this are given in the discussion (section 8.4).

### 8.3.3.2 Accounting for Leaching of Sulphate

#### 8.3.3.2.1 A layered drainage model with mobile and immobile water phases.

Few mechanistic models have been published describing sulphate leaching from grazed pastures (Heng *et al.*,1991). As the sulphate adsorption capacities for each soil depth were widely different (see Section 8.3.3.1), decreasing with depth, it was considered that a three layered (0-75mm, 75-150mm and 150-250mm) leaching model may be an appropriate way of dealing with these differences.

The main assumption in this three layer model is that an input of water, either rainfall or drainage, from the layer above  $(i-1)(R, \text{mm})$  moves into a layer  $i$  of the soil profile, once the soil water depth ( $w_i, \text{mm}$ ) is equal to soil water depth at field capacity ( $w_{fc}, \text{mm}$ ) the incoming water displaces an unknown proportion of native soil water in relation to the input volume (the condition when  $R$  exceeds  $w_{fc}$  is discussed later). This assumption simulates the condition where some of the input water,  $R\alpha \text{mm}$  (a fraction  $\alpha$ ) will move through larger pores interacting little with the native soil water, while in smaller capillaries native soil water will be displaced ahead of the incoming water,  $R(1-\alpha) \text{mm}$ .

The soil solution sulphate concentration ( $C_{s,i}$ , kg S mm<sup>-1</sup>, per ha slice) for a given amount of extractable sulphate for  $i^{\text{th}}$  layer before input water passes through the layer is given by the equation

$$C_{s,i} = K_{d,i} \times E_{s,i} \quad (8.7a)$$

where

$E_{s,i}$  is the amount of extractable sulphate (kg S ha<sup>-1</sup>) present in  $i^{\text{th}}$  layer and  $K_{d,i}$  is the function explaining the relationship between extractable sulphate and the soil solution sulphate for the  $i^{\text{th}}$  layer. The functions for all the three layers were given in Fig.8.7 and 8.8. Prior to reaching field capacity ( $w_{fc}$ , mm) for the layer  $i=1$  i.e.  $R_i + w_i \leq w_{fc}$  then the new soil solution concentration for layer  $i=1$  is given by the equation

$$C_{s,i} = K_{d,i} [E_{s,i} + I_{s,i}R_i] \quad (8.7b)$$

where  $I_{s,i}$  is the concentration of sulphate (kg S mm<sup>-1</sup>) in the incoming water and  $R_i$  is the amount of input water to the  $i=1$  layer and the remaining parameters have been described earlier. In the case of surface layer the incoming water is rainfall and the concentration of S is negligible. Under such conditions the concentration of sulphate in the soil solution is the one given in equation 8.7a i.e. the change in concentration of sulphate in the soil solution of layer  $i=1$  due to incoming rainwater is assumed to be negligible unless leaching occurs.

When the soil water depth of the  $i^{\text{th}}$  layer ( $w_i$ , mm) has reached  $w_{fc}$ , then the drainage volume ( $D_i$ , mm) is equal to the input water volume ( $R_i$ , mm) and the total amount of sulphur lost by leaching ( $L_{s,i}$ , kg S ha<sup>-1</sup>) from the  $i^{\text{th}}$  layer is sum of two components.

1. The amount of native soil solution sulphate displaced by the slow moving input volume water ( $D_i(1-\alpha)$ ) entering the layer ( $L_{d,i}$ , kg S ha<sup>-1</sup>) which is given by the equation

$$L_{d,i} = K_{d,i} E_{s,i} D_i (1-\alpha) \quad (8.8a)$$

and 2. the mobile fraction ( $L_{m,i}$ ) of the incoming water ( $D_i\alpha$ ) which passes directly through the soil layer. When the input water passes rapidly through the surface layer without interacting with the native soil water its drainage path to lower soil depths is presumed to be un-impeded. Therefore this water will pass through the rest of the layers without any interaction with the native soil water. For the purposes of the model  $w_i$  for the layers  $i=2$  and  $3$  is only increased by the water volume  $D(1-\alpha)$  displaced from the  $i-1$  layer. Also this means that drainage  $D_{i=1}\alpha$  occurs from the whole soil profile as soon as  $R_{i=1} + w_{i=1} > w_{fc,i=1}$ , irrespective of the  $w_{i=2}$  and  $w_{i=3}$ . The input water sulphate concentration ( $I_{s,i}$ ) must now have two distinct components 1. the fast moving drainage water volume  $D_i\alpha$  with S concentration  $I_{s,\alpha}$ , and 2. the slow moving drainage water  $D_i(1-\alpha)$  with S concentration  $I_{s,1-\alpha}$ . The amounts of S in the mobile leached volume would be given by the equation

$$L_{m,i} = I_{s,i} \alpha D_i \quad (8.8b)$$

Therefore

$$L_{s,i} = L_{d,i} + L_{m,i} \quad (8.8c)$$

In the case of rainwater at the Ballantrae site, which contains negligible sulphate  $I_{s,i}$  is zero then  $L_{m,i}$  is equal to zero. At other sites closer to coast  $I_{s,i}$  would require a positive value.

If the displaced drainage water volume ( $D(1-\alpha)_{i-1} + w_i - w_{fc}$ ) is negative then  $D(1-\alpha)_i=0$  and no leaching occurs. i.e.  $L_{s,i}$  is zero in equation 8.8c. After leaching reequilibrium between adsorbed and solution sulphate occurred prior to plant uptake.

The amount of extractable sulphate (kg S ha<sup>-1</sup>) remaining in the  $i^{\text{th}}$  soil layer after an input event or a drainage event is given by the size of initial extractable sulphate pool,  $E_{s,i}$ , plus the amount of sulphate leached from the layer above ( $L_{s,i-1}$ ) minus the sulphate leached from that layer ( $L_{s,i}$ ).

$$E_{s,i,(t+1)} = E_{s,i,t} - L_{s,i} + L_{s,i-1} \quad (8.9)$$

where  $E_{s,i,(t+1)}$  is the amount of extractable sulphate ( $\text{kg S ha}^{-1}$ ) present after leaching. The new concentration of sulphate in the solution is

$$C_{s,i,(t+1)} = K_{d,i} [ E_{s,i} - L_{s,i} + I_{s,1-\alpha,i} D_{i-1} (1-\alpha) ] \quad (8.10)$$

where  $t$  is a time or volume step (see discussion later). This is the solution concentration that is used to calculate plant uptake on a day when leaching occurs (section 8.3.3.3).

### 8.3.3.2 Estimating the mobile volume ( $\alpha$ )

Having constructed this simple drainage model it was necessary to obtain by iterative procedures the value for  $\alpha$ . The value of  $\alpha$  was estimated in the laboratory using intact soil cores collected from the same Ballantrae LF-LS and HF-LS farmlets (Chapter-4). The initial soil solution sulphate concentration for all the three depths and for both the cores were calculated using the relationship between extractable sulphate and the solution sulphate determined in the laboratory measurements (Fig.8.8) and the measured extractable sulphate of the soil for the three depths (Chapter-4). The soil cores were leached with simulated rainfall at a rate of 0.23mm per minute for seven hours (a total of 99mm rainfall was applied) and 85 mm of drainage was collected from each core for the first leaching event. The amount of sulphate leached for both cores were 1.14 and 5.04  $\text{kg S ha}^{-1}$  for LF-LS and HF-LS sites (Chapter-4). It was assumed that sulphate leached from each layer depends upon the earlier model description. The value of  $\alpha$  was adjusted to predict the amounts of measured sulphate leached. The best fit  $\alpha$  values were 0.250 for the soil from LF-LS and 0.3 for HF-LS sites respectively. But in the field this value may change slightly due to seasonal soil compaction and swelling. An  $\alpha$  value of 0.3 was used in the subsequent model.

### 8.3.3.3 Plant Uptake of Sulphur

The second step in the process is the plant uptake of S from the soil solution. The amount of any nutrient taken up by plant for a particular period of time is a function of the amount of water removed by the plant (Scotter et al., 1979; Hayman and

Stocker, 1982; McAneney and Judd, 1983; Rickard et al., 1986; Martin, 1990) and the soils ability to supply nutrient to the soil solution. The amount of water removed by plant can be considered to be the actual evapotranspiration ( $AE_t$ ) from pasture soils (see discussion 8.3.1.2). So, assuming that most sulphate moves to plant roots by mass flow (Barber, 1984) the amount of sulphur removed by plant is proportional to the  $AE_t$  (mm) multiplied by the soil solution sulphate concentration ( $\text{kg S mm}^{-1}$ ).

The amount of water removed from each layer was calculated from daily  $E_t$  and that multiplied by the soil solution sulphate concentration (calculated from equations 8.7a and 8.7b and 8.10 in each layer) to give the amount of sulphur removed from each layer was calculated. Initially it has been assumed in this model that all of the sulphur removed by the plant was moved to the root zone by mass flow. The limitations of this assumptions are explained in the discussion section. The amount of sulphur removed from each of the three layers depends upon the rainfall and drainage. Drainage was considered to be immediate (instantaneous) relative to plant uptake and mineralization (a continuous process). Therefore in this model leaching of S followed by the reestablishment of the equilibrium between adsorbed and solution S occurred prior to plant uptake and mineralization. Thus when drainage occurs from the soil, the amount of sulphur removed from the particular layer by plant uptake will be lower than that removed without drainage.

Mathematically, the amount of sulphur removed by plant from  $i^{\text{th}}$  layer is given by the equation

$$P_{s,i} = C_{s,i} AE_{t,i} \quad (8.11)$$

Where  $P_{s,i}$  is the amount of S ( $\text{kg S ha}^{-1}$ ) removed by plant from the  $i^{\text{th}}$  layer,  $AE_{t,i}$  is the proportion of  $AE_t$  removed from the  $i^{\text{th}}$  layer and  $C_{s,i}$  was discussed earlier. As mentioned in section 8.3.3.2. there exist an equilibrium between the soil solution sulphate and adsorbed sulphate. As the soil solution sulphate decreased by plant uptake, sulphate will be removed to soil solution depending upon the amount of sulphate on the surface of the soil.

A fraction of the total S taken up by plant was considered to be accumulated in the root because for every unit of shoot growth a small amount (8-10% of shoot growth depending upon season) of root growth also occur (Mathew *et al.*, 1989). It was

assumed that the distribution of S between root and shoot and shoot was similar to the distribution of dry matter production measured by Mathew *et al.* (1989) (Appendix-8.2).

#### 8.3.3.4 Accounting for mineralization of soil organic Sulphur

At the outset of planning this study it was hoped that isotopic dilution data in Chapter 6 could be used to calculate the actual mineralization and immobilization rates for these soils. This has not been achieved due to lack of time and therefore the rates of S mineralization used in the model are the net values measured in Chapter 5 by S balance studies using the lysimeters.

In the model, it was assumed that all of the S mineralized from the soil organic matter, plant litter, root and animal excreta are considered to enter into the soil solution sulphate pool (Fig.8.1). The amount of sulphate mineralized to solution sulphate of each soil layer was predicted from the knowledge of the measured amount of S net mineralized under field conditions (chapter-5, section.5.3, Table 5.9). The amount of S mineralized in each soil layer was predicted on the basis of the distribution of root in each layer. The limitations of this assumption are discussed in the discussion section. The amount of S mineralized ( $M_i$ ) for layer  $i$  was predicted using the following equation

$$M_i = \left( \frac{r_{T,i}}{\sum_{i=1}^n r_T} \right) M_T \quad (8.12)$$

where  $r_{T,i}$  is the root distribution for the  $i$ th layer and  $\sum r_T$  is the total root mass for the profile and  $M_T$  is the measured amount of S mineralized per day in  $\sum$  soil layers.

#### 8.3.3.5 Executing the Model

The whole model was executed by entering all calculations and input data into a Multiplan spreadsheet version 4.01. A separate spreadsheet was used for data for each of the four field study sites, namely, LF-LS, LF-MS, HF-LS and HF-MS. Plant uptake of S, leaching losses, mineralization to sulphate pool and extractable soil

for all the four sites on a daily basis for 220 days from June 1989 to Jan. 1990. The model was initiated with the measured values for the amounts of soil extractable sulphate ( $\text{kg S ha}^{-1}$ ) for all the three layers from at all four sites day 1, June 1989. The amount of extractable sulphate ( $E_{s,f,i}$   $\text{kg S ha}^{-1}$ ) present in the soil at the end of each day (after leaching, plant uptake and mineralization) was calculated using the equation given below

$$E_{s,f,i} = E_{s,i} - L_{s,i} - P_{s,i} + M_{s,i} \quad (8.13)$$

where  $M_{s,i}$  is the amount of sulphur mineralized to sulphate pool and the remaining parameters were discussed in earlier sections. The other main inputs to the model were daily rainfall (Appendix-8.3a), evapotranspiration (Appendix-8.3b), initial soil moisture content (Appendix-5.1) and the seasonal pattern of S distribution between shoots and roots.

## 8.4 RESULTS AND DISCUSSION

### 8.4.1 Comparison of model output with field measurements

The predicted and measured S uptake by pasture for 220 days are given in Fig.8.9 and Fig.8.10 for all the four sites. The model predicted the amounts of sulphur removed by pasture tops for all four sites reasonably well. After allowing for the uptake of sulphur by root the total accumulated amounts of sulphur removed by pasture were slightly under estimated (approximately 1 and 3 kg in low and high fertility sites).

Initially the amounts of sulphate lost by leaching were under estimated (17.3 vs 7.4  $\text{kg S ha}^{-1}$  at the HF-LS and 13.3 vs 6.2  $\text{kg S ha}^{-1}$  at the HF-MS site) at high fertility sites when the function derived under laboratory conditions to explain the relationship between extractable sulphate and the soil solution sulphate were used for the 150-250mm soil depths. However, when this function was replaced with the function derived from field data (Fig.8.7) the model predicted the leaching of sulphate at both

Fig.8.9 Predicted (---+---) and measured (—•—) cumulative amounts of sulphur taken up by pasture at LF-LS and LF-MS sites.

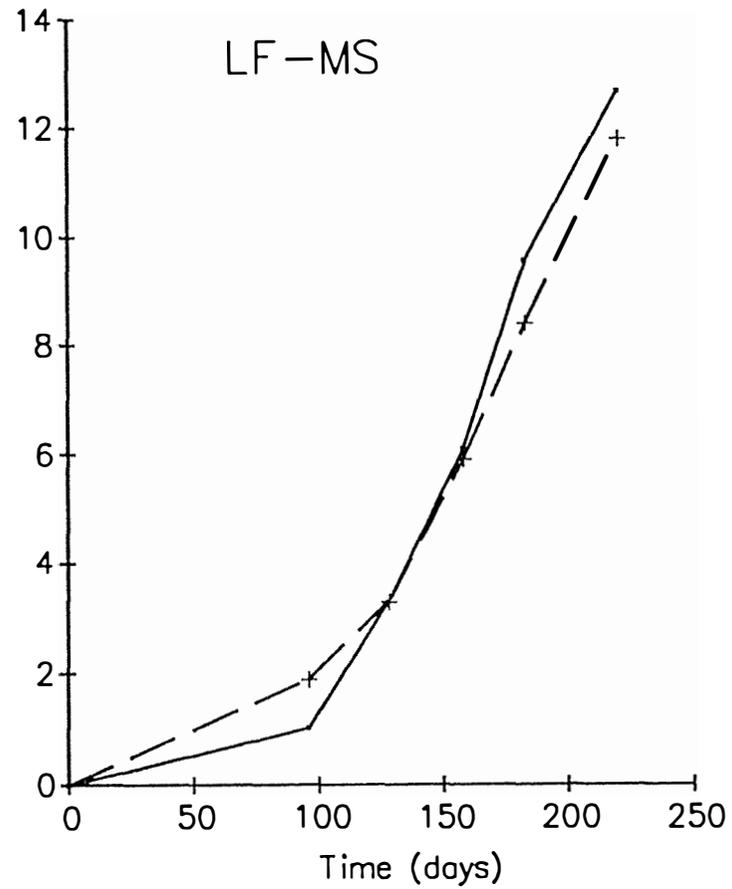
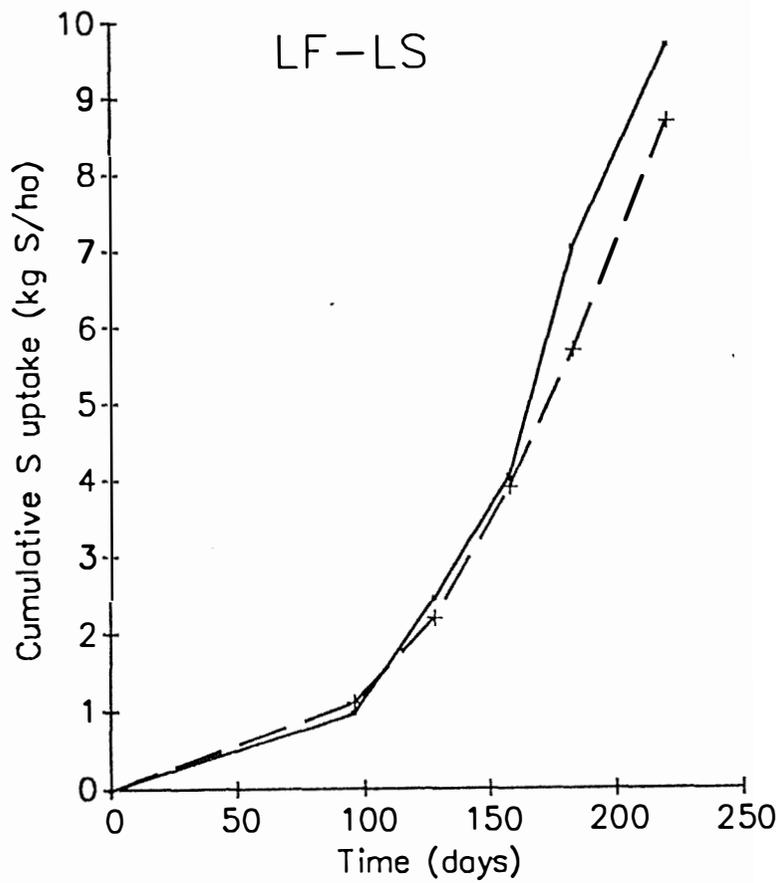
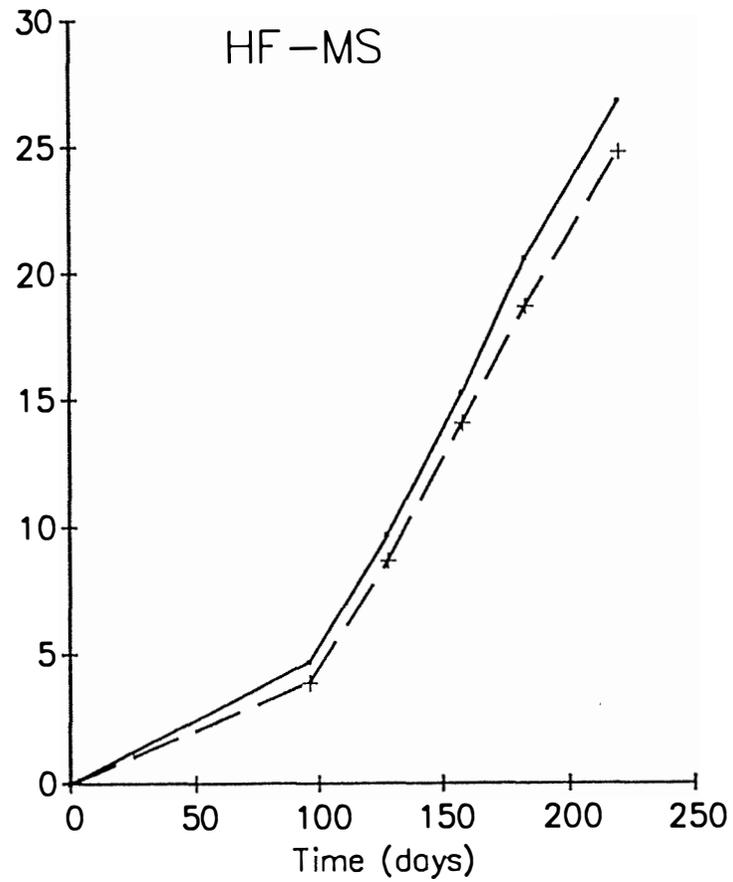
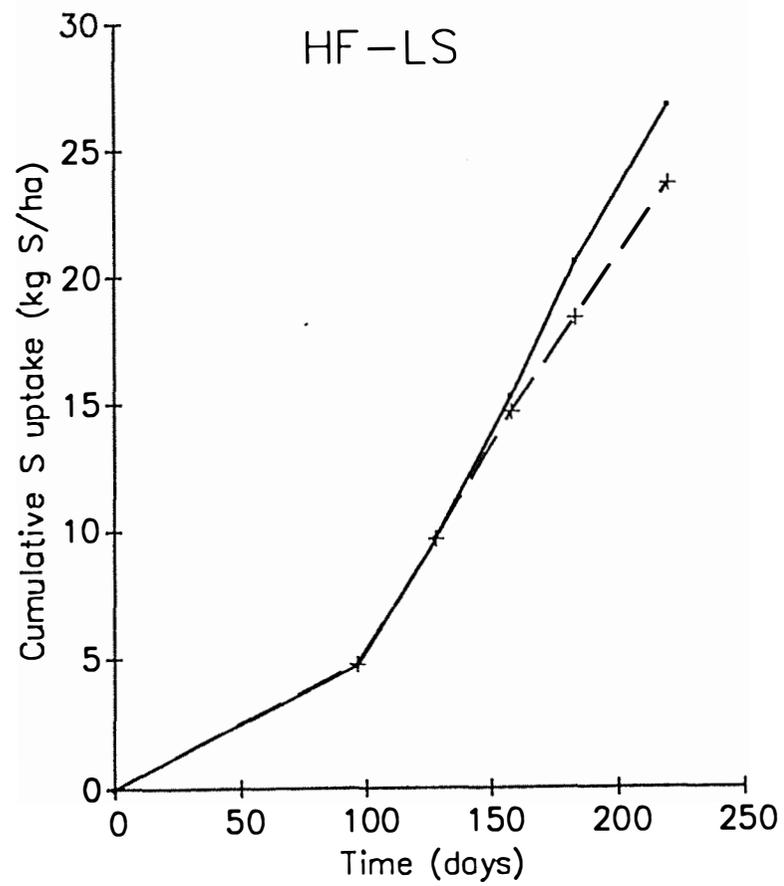


Fig.8.10 Predicted (---+---) and measured (—•—) cumulative amounts of sulphur taken up by pasture at HF-LS and HF-MS sites.



**Table 8.3 Measured and predicted leaching losses of sulphate during the experimental period at all four sites.**

Leaching Event	Sulphate Leached (kg S ha <sup>-1</sup> )							
	LF-LS		LF-MS		HF-LS		HF-MS	
	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured
1	0.65	0.66	0.87	0.53	4.8	3.6	4.2	4.1
2	0.67	0.55	0.81	0.74	3.7	3	2.2	1.5
3	0.27	0.20	0.34	0.25	1.4	0.5	0.8	0.4
4	1.00	0.78	0.79	0.93	7.2	10.7	6.1	6.0
5	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0
<b>Total</b>	2.6	2.0	2.8	2.1	17.1	17.3	13.3	11.6

Fig.8.11 Predicted (---+---) and measured (—•—) extractable soil sulphate present in the profile (0-25cm) at LF-LS and LF-MS sites.

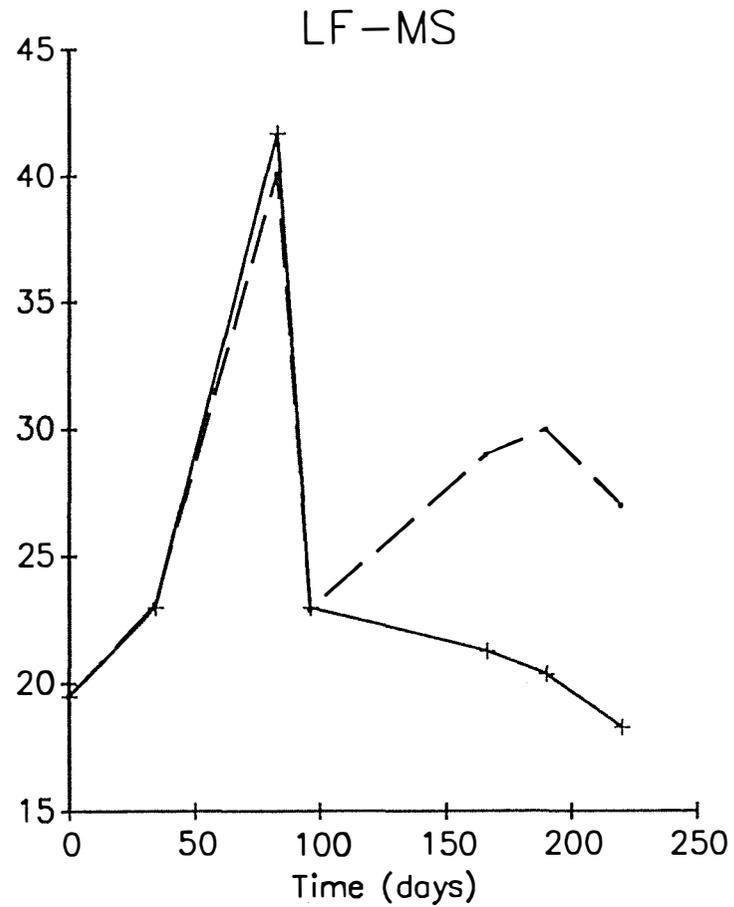
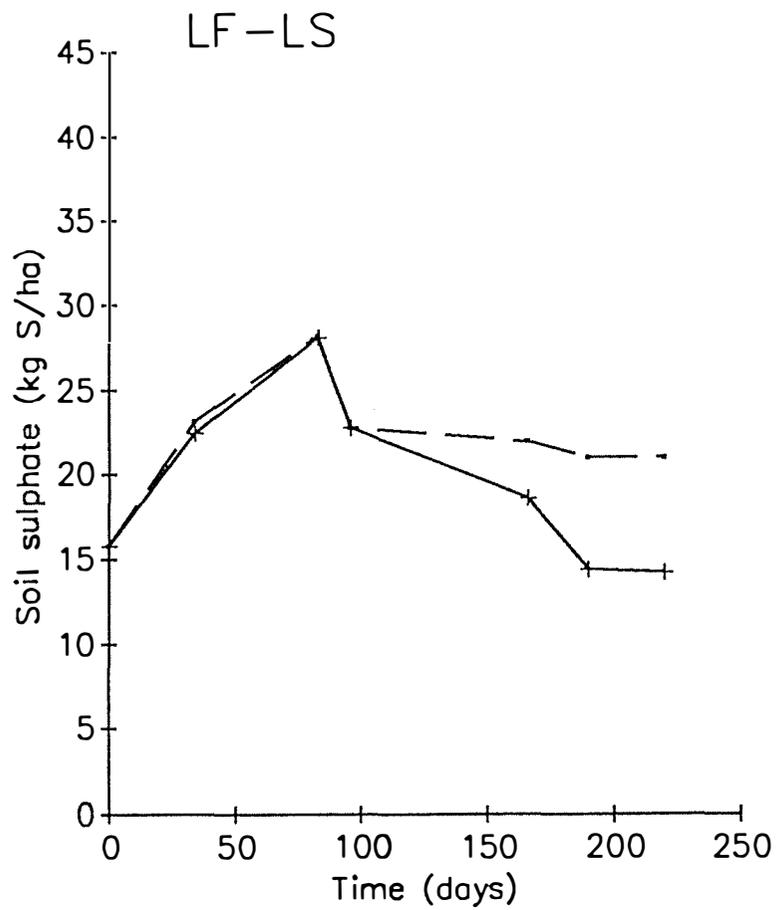
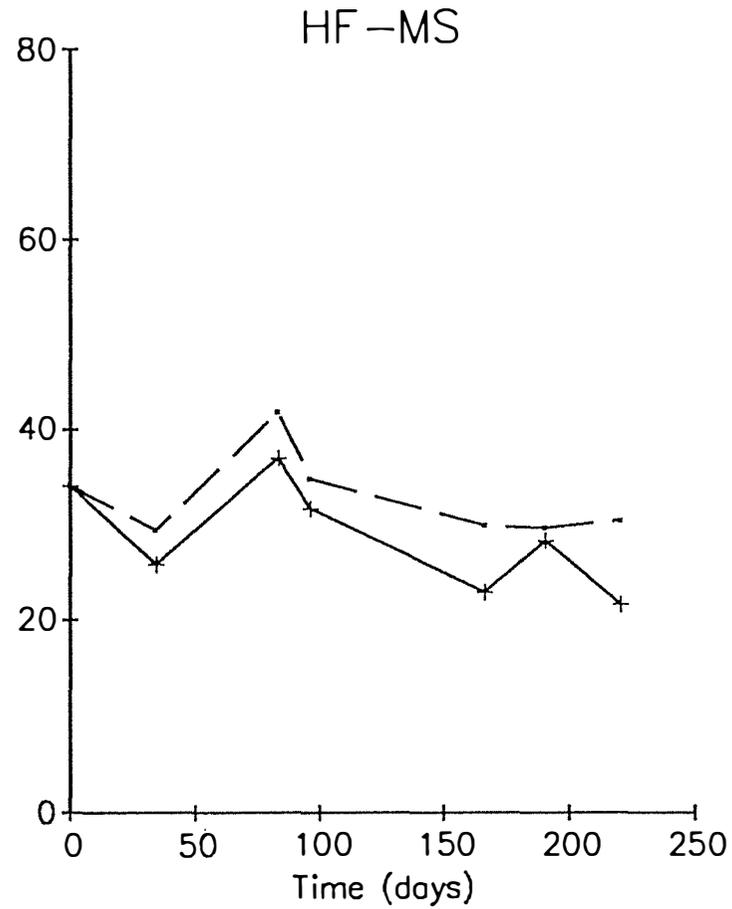
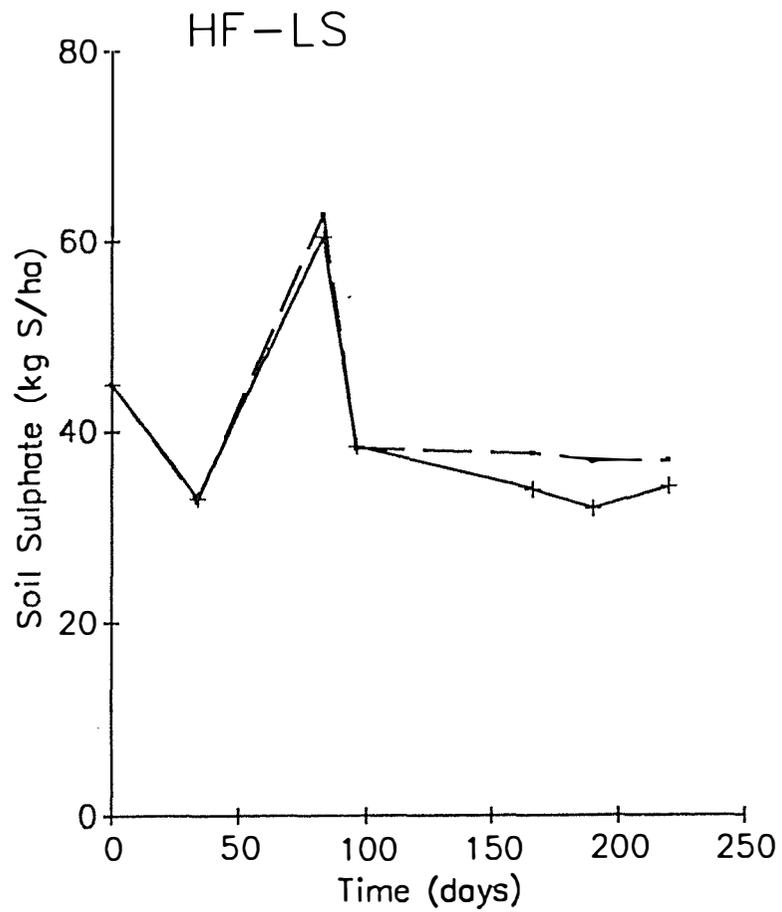


Fig.8.12 Predicted (---+---) and measured (—•—) extractable soil sulphate present in the profile (0-25cm) at HF-LS and HF-MS sites.



the high fertility sites reasonably well. In the low fertility sites the model slightly over estimated the leaching losses (Table 8.3).

The model was able to predict the amount of extractable sulphate present in the soil for the whole profile (Fig.8.11 and 8.12) for most of the experimental period, but it failed to predict the amount of extractable sulphate present in the individual layers (Appendix 8.4).

Plant uptake, mineralization rate, leaching losses and the amounts of extractable soil sulphate are interrelated in all layers thus incorrect estimates of a single factor in an upper layer would lead to incorrect rates of S accumulation or depletion in the layers below.

#### 8.4.2 Sensitivity analysis of $K_d$ and $\alpha$ values

Of the measured parameters required to run this model the  $K_d$  functions which relate the amount of extractable sulphate  $S$  with soil solution  $S$  concentrations and  $\alpha$  value which measures the volume of input water that passes directly through the soil without interacting with the native soil water for field conditions must either be assumed or estimated from measurements made under laboratory conditions. It is useful to know whether errors in obtaining these values cause major changes to the model outputs such as plant uptake or leaching. Using data for the HF-LS site a simple sensitivity analysis of the model was carried out by varying separately the value of  $\alpha$  and the  $K_d$  functions for each soil layer by  $\pm 10\%$ .

An increase in the value of  $\alpha$  (by 10%) simulates a larger mobile water fraction and thus decreased the leaching of sulphate by 15% (Fig.8.13). A decrease in the value of  $\alpha$  (by 10%) which simulates larger native soil water displacement increased the leaching of sulphate by 15% (Fig.8.13).

An increase in the slope (by 10%) of the function of each layer ( $K_d$  function) which simulates greater adsorption of sulphate decreased sulphate leaching by 5%, while a

Fig.8.13 Effect of changing the value of  $\alpha$  (by 10%) on the cumulative amount of sulphate leached at HF-LS site during the period from Jun. 1989 to Oct. 1989. No leaching occurred from Oct. 1989. to Jan. 1990.

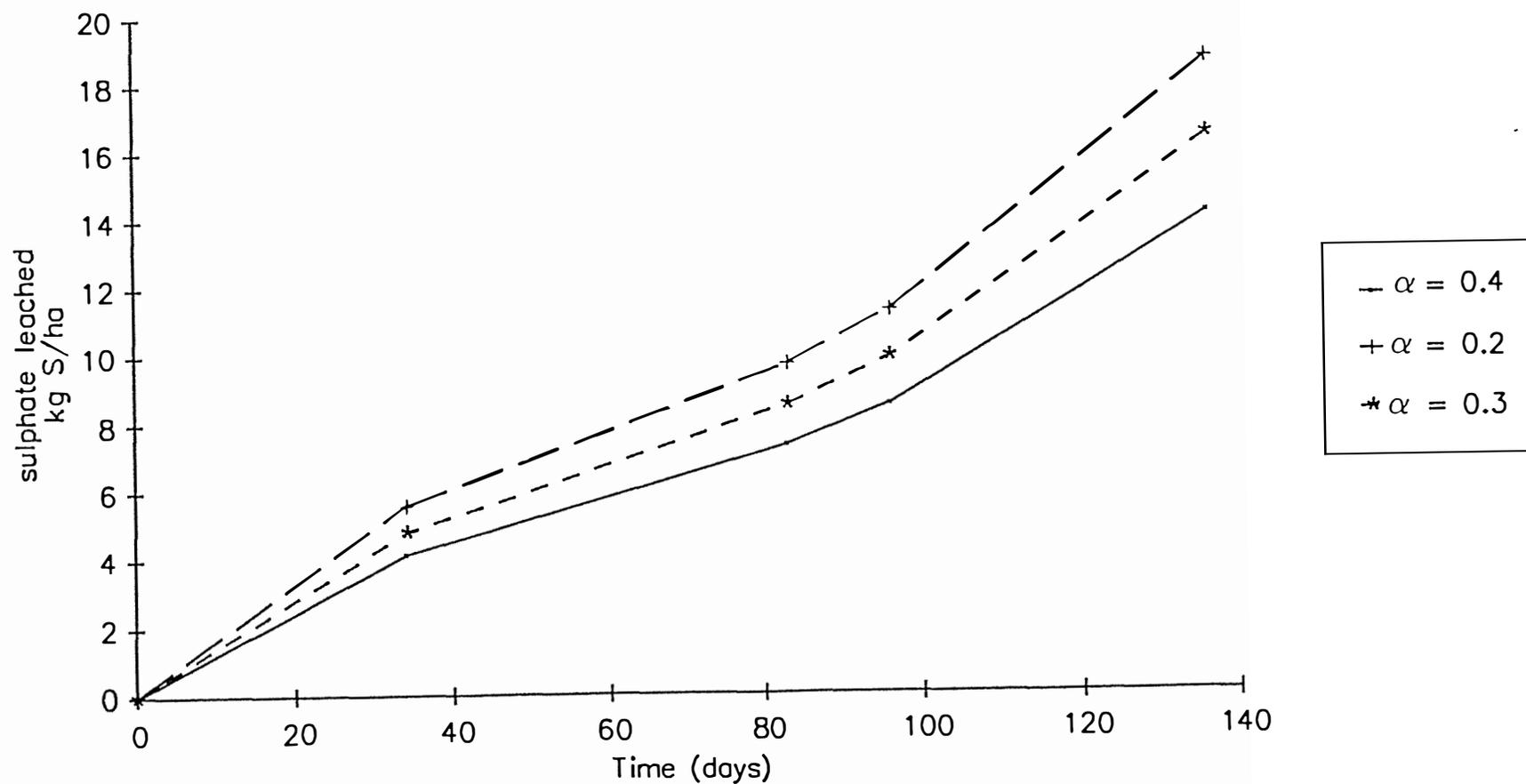


Fig.8.14 Effect of changing the values of  $K_d$  (by 10%) for each soil layer on the cumulative amount of sulphate leached at HF-LS site during the period from Jun. 1989 to Oct. 1989. No leaching occurred from Oct. 1989 to Jan. 1991.

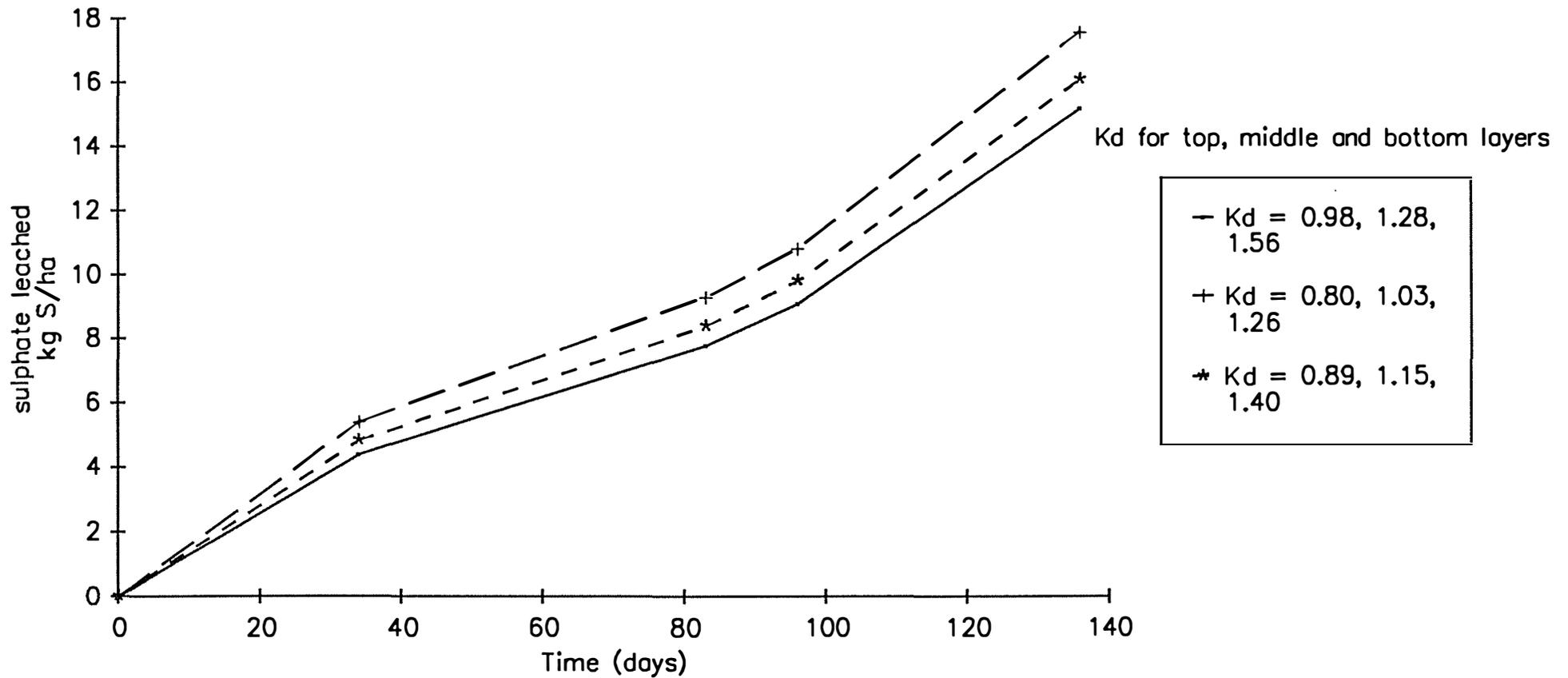


Fig.8.15 Effect of changing the value of  $\alpha$  (by 10%) on the cumulative amount of sulphur removed by pasture at HF-LS site during the period from Jun. 1989 to Jan. 1990.

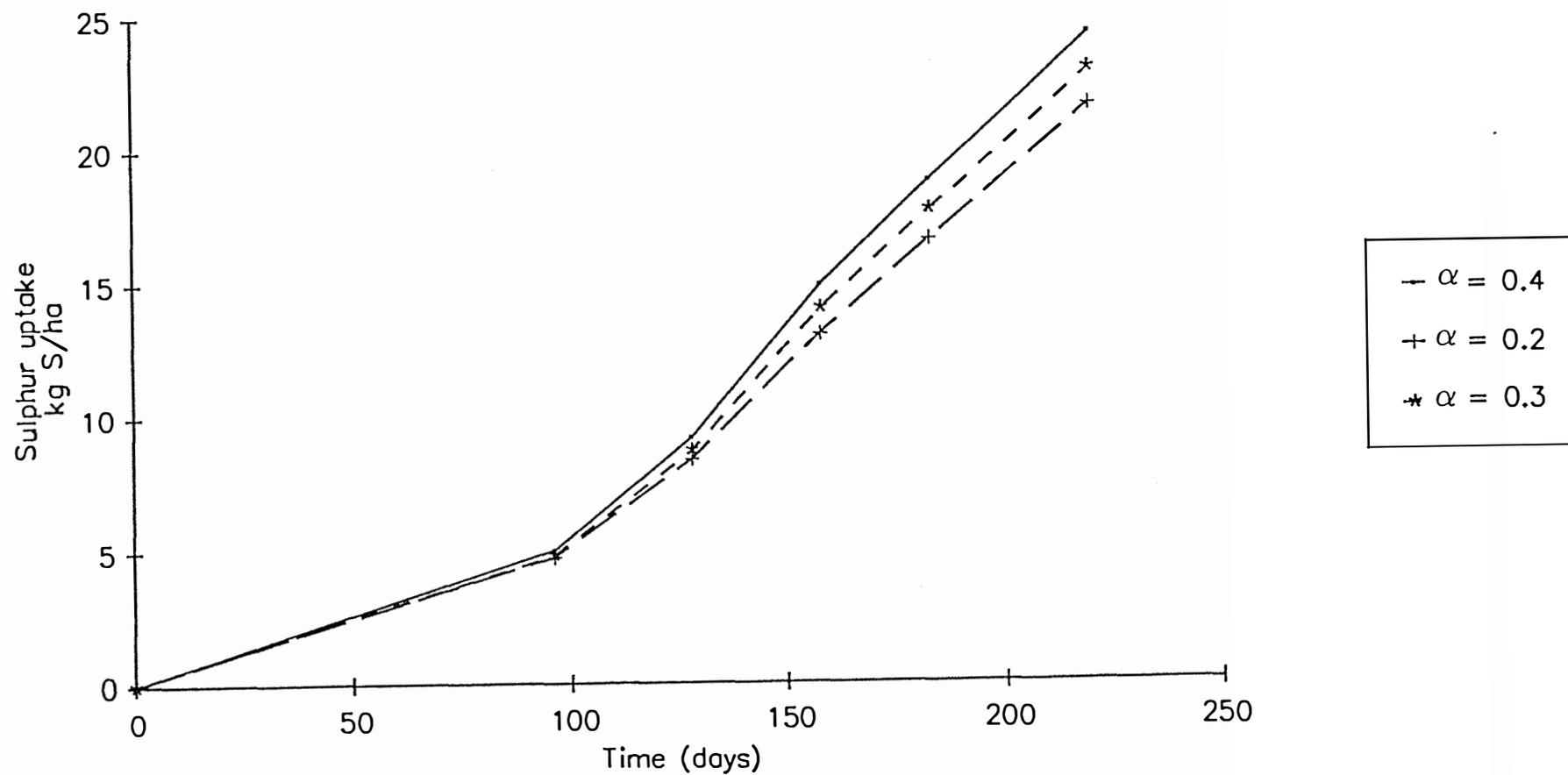
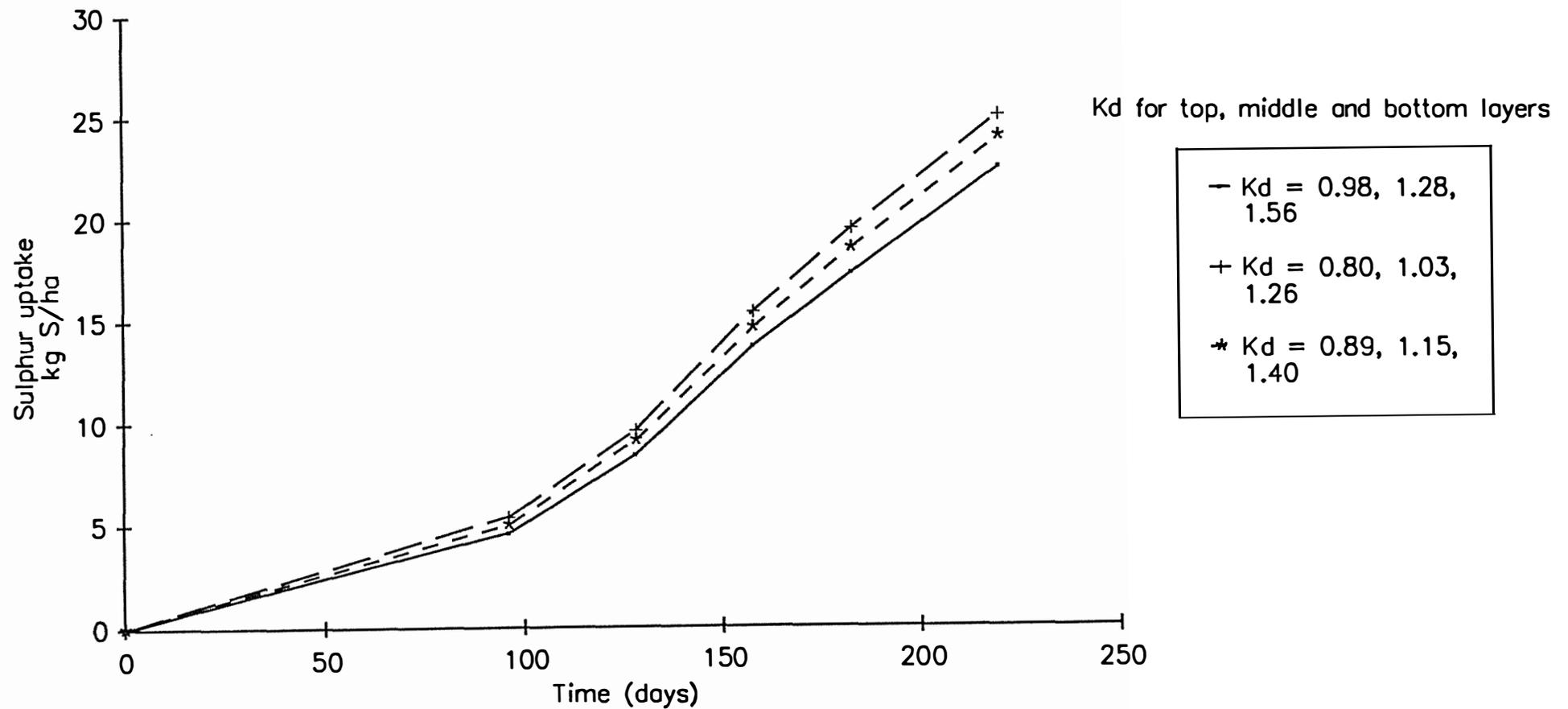


Fig.8.16 Effect of changing the value of  $K_d$  (by 10%) on the cumulative amount of S removed by pasture at the HF-LF site during the period from Jun. 1989 to Jan. 1990.



decrease in the values of the slope of the function ( $K_d$ ) which simulates less adsorption of sulphate increases the leaching of sulphate by 9% (Fig.8.14).

Changing either  $K_d$  or  $\alpha$  values by 10%, only had a small effect on the amount of S removed by pasture (Fig.8.15 & Fig.8.16). This suggests that pasture uptake of S is less sensitive to changes in  $K_d$  and  $\alpha$  values than the amounts of S leached. The greater effect of  $K_d$  change on leaching rather than plant uptake occurs because most of the leached sulphate originated from the 15-25 soil layer where the slope of the  $K_d$  function was much steeper than the slope of the  $K_d$  function for the soil layer 0-75mm from which 65% of the plant uptake occurs. Compared with the changes in  $K_d$  changes in  $\alpha$  value had a much greater effect on leaching, indicating that if leaching of S is to be modelled an accurate measure of the fraction of input water that moves through the soil layer interacting little with the native soil water should be developed.

In general the model has given very good predictions of all outputs but users of the model should be aware of limitations that may show up when used on other sites or for extended periods of time.

1. The major limitation is that the current form of the model requires measured mineralization rates. Future work on the isotopic dilution data from this thesis may resolve this. Also in the model it was assumed that the mineralization and immobilization rates are constant throughout each growth period. In practice this may not occur for the whole period, because mineralization and immobilization rates depends upon soil temperature, moisture and the sulphate concentration in the soil solution as explained in Chapter 2.

2. In the model it was assumed that at a given  $AE_t$  value the amount of S removed by pasture was linearly related to the sulphate concentration in the soil solution (equations 8.16 and 8.17). In practice it is not true because plant growth may be limited by the availability of other nutrients particularly nitrogen. Evidence provided in Chapter 5 indicates that these hill country pastures are nitrogen limited. In particular the ratio of N/S mineralized from soil organic matter at the low fertility farmlet was low

(average of 10.0 kg N ha<sup>-1</sup> and 7.7 kg S ha<sup>-1</sup> for first 35 days) compared to the high fertility farmlet (an average of 25 kg N ha<sup>-1</sup> mineralized while 6.6 kg S ha<sup>-1</sup> was immobilized for first 35 days). This indicated that N was limiting plant growth and S uptake in LF farmlet. This however does not appear to have affected the prediction of plant S uptake at these sites, but such mechanisms may be one of the reasons for the slight overprediction of plant S uptake on the LF-LS and LF-MS sites (Fig.8.9) during winter (first 96 days).

3. If ground cover of the pasture was sparse this would also affect the amount of sulphate uptake by plant. During winter, particularly in low fertility areas the rate of pasture growth may be low. With low ground cover  $E_t$  will not be completely derived from the pasture and soil will also contribute to the  $E_t$ . The model assumes that all  $E_t$  is derived from the pasture. The effect of a proportion of  $E_t$  coming from the soil would be to decrease plant S uptake and increase the concentration of extractable S in the top 75mm of the soil. In this case plant uptake would be overpredicted and the amounts of extractable soil S underpredicted.

4. The fraction of the input water ( $\alpha$ ) that passes directly through the larger pores (mobile phase) without interacting with the native soil water may also change under field conditions. However, this concept is an over simplification. In the model it was assumed only two phases may exist in a layer namely macropores (rapidly mobile water) and micropores (immobile). In practice a range of pore sizes exists giving a continuous spectrum of soil water from rapidly mobile to completely immobile. If the input water which enters the soil matrix does not mix or displace all the micropore water then this would lead to overprediction of S leaching. This would be corrected by increasing the value of  $\alpha$ , but a more sophisticated drainage model may be more appropriate.

5. In the model it was assumed that re-equilibrium between the less mobile and mobile phases established immediately after leaching. The time taken for this equilibration depends upon the diffusion coefficient of the sulphate ion in the soil, the diffusion path length and the soil sulphate buffer power (Barber, 1984). Assuming that the

diffusion coefficient of sulphate is approximately  $10^{-7}$  mm<sup>2</sup> s<sup>-1</sup> in soil water and there is no concentration gradient between the mobile and less mobile phases the distance moved (self diffusion) by sulphate ion in one day is given by  $(2Dt)^{1/2}$ , where  $D$  is the diffusion coefficient (mm<sup>2</sup> s<sup>-1</sup>) and  $t$  is time (days), which is equal to 0.13mm day<sup>-1</sup>. However a concentration gradient between mobile and less mobile phases will exist after drainage. For example the amount of S in soil solution in the top 75 mm of the soil were calculated to be 3.0 and 8.0 kg S ha<sup>-1</sup> for low and high fertility farmlets respectively. After drainage the concentration gradient between mobile and immobile phases in the HF farmlet would be greater than the concentration gradient of LF farmlet. This indicates that the time taken for re-equilibrium to establish in the low fertility farmlet would be approximately three times greater than that for the high fertility farmlet. The model may be improved by accounting for slower equilibration time for lower sulphate concentrations in the soil solution. This may be necessary to explain S leaching behaviour in different textured soils.

## 8.5 CONCLUSION

The ratio of the specific activities of the plant S and leached S from the lysimeters which were fertilized with <sup>35</sup>S labelled superphosphate indicated that the specific activity of the pool of sulphate-S taken up by pasture plants was slightly, but consistently lower than that of the pool of sulphate-S lost by leaching. The explanation for this is that initial leaching of fertilizer <sup>35</sup>S to depths where root activity and sulphate pool turn over rate are lower leading to less <sup>35</sup>S uptake and a slower decline in the specific activity of the sulphate pool at depths which remains susceptible to leaching during subsequent leaching events. There are also spatial differences between the soil zones exploited by roots and those zones from where major drainage flow passes in the soil.

Therefore in attempting to model of sulphate movement in soils, root distribution and the differences in the movement of water the larger soil pores and the interaction with less mobile water in the smaller pores should be considered. It is the water in the larger soil pores which may be displaced and move downwards while water in the smaller soil pores is likely to supply plants with water.

A mechanistic computer simulation model, in which daily evapotranspiration, drainage in conjunction with soil solution sulphate concentration, which was predicted from knowing the soil sulphate retention characteristics, predicted reasonably well the plant uptake and leaching losses of S from four field sites, differing in their soil fertility status.

The simple sensitivity analysis of the model showed that it is important to accurately measure the value of  $\alpha$ , the fraction of the input water that moves through the larger pores interacting little with native soil water. A 10% change in this parameter resulted in a 15% change in the amount of S leached.

Some suggestions have been made for making the model portable to other field sites. In particular it is important that the mineralization rates of soil organic matter and its spatial and temporal variation in the soils are known. Further research is required before the short term fluctuations in net S mineralization rates can be accurately modelled.

In general the model was able to predict S uptake and losses by leaching well at the Ballantrae farmlets. It should be possible to complete the modelling of the full S cycle in these farmlets by adding to this model the above ground nutrient transfer model for S developed by Saggart *et al.* (1990a). The rates of return of plant litter and animal excreta and their rates of decomposition may help predict S mineralization rates in the top soil.

## CHAPTER-9

### SUMMARY

#### 9.1 REVIEW OF LITERATURE

A review of literature (Chapter-2) revealed that in legume based grazed pastures quantitative information on the possible sources of leached sulphate is scarce, in particular the effect of previous fertilizer history on the rate of mineralization of S and its losses by leaching and plant uptake is lacking. Further, quantitative relationships between the mineralization of S and N in grazed pasture were poorly understood both in New Zealand and overseas. In hill country pastures the effect of land slope on the camping behaviour of the grazing animals and subsequently this influence on the rate of mineralization of both S and N and their losses by leaching and plant uptake was also poorly understood.

This study was conducted with the general objectives of identifying and quantifying the main origins of leached sulphate in grazed hill country pastures. As part of the study a preliminary laboratory study investigated the potential of hill country pasture soils to mineralize organic S and N. This was followed by a series of field studies in hill country. These included a study to measure the net mineralization of organic S and N and their relative contribution to S leaching losses and pasture S uptake. The fate of fertilizer and dung and urine S in grazed pastures and the effect of these inputs on the mineralization of soil organic S and N and its contribution to pasture uptake and losses by leaching were also studied. Finally a simple computer simulation model was constructed to predict the fate of S in grazed hill country pastures.

#### 9.2 LABORATORY MINERALIZATION STUDIES

In the preliminary laboratory study (Chapter-3), in which both open and closed incubation systems were used to measure the net mineralization of S, N and C, greater amounts of S and N were net mineralized in the open system. In contrast more C was mineralized and released as CO<sub>2</sub> in the closed system, suggesting that microbial

activity is greater in the closed system than in the open system and the S and N mineralized were reimmobilized into organic S and N in the closed system. The closed system is not suitable for measuring accumulated net mineralization of nutrients other than carbon.

In the open incubation system, the amount of S and N mineralized were greater in soils taken from sites that had received high amounts of single superphosphate (SSP) in the past than in soils taken from sites that had received small amounts of SSP in the previous years. This indicated that the accumulation of soil organic matter by regular application of SSP to legume based pastures increased the mineralization of both S and N. In addition soils collected from low slope (0-12°) sites, where a greater proportion of animal excreta is returned, mineralized more S and N than soils taken from medium slope (12-25°) sites. In contrast the amount of C mineralized and respired was greater in soils taken from medium slope sites than in soils taken from low slope sites. The greater amounts of excreta returned to low slope sites decreased the C to N and C to S ratios and thus per unit of CO<sub>2</sub> respired more N and S were mineralized, but in medium slope sites due to the small amount of excreta returned the C to N and C to S ratios were greater than the low slope sites and less N and S were mineralized per unit of CO<sub>2</sub> respired. The ratio of N to S mineralized was narrower than the N to S ratio of the bulk soil suggesting that relative to N more S is available in the soil solution and susceptible to leaching, while N is conserved in the soil. From this preliminary laboratory study it became clear that the mineralization of S from soil organic matter could be an important source of leached sulphate.

### **9.3 DEVELOPMENT OF A TECHNIQUE TO MEASURE MINERALIZATION RATES IN FIELD SOILS**

Cylindrical, mini-lysimeters with ion exchange resin traps for collecting solutes from drainage water were developed to measure the net mineralization of S and N in hill country pastures. Pasture uptake of S and N, leaching losses of S and N and the changes in mineral S and N pools in the soil at the same site were measured

simultaneously and used to calculate mineralization rates. An evaluation of the lysimeter in the laboratory (Chapter-4) showed that the resin trap was capable of removing all the sulphate from drainage water at several different flow rates. The main advantage of the lysimeters over the conventional methods of measuring the leaching losses of anions and cations in the field is that regular drainage collection was not necessary. By introducing mixtures of both anion and cation exchange resins in the trap in the lysimeter, it was possible to monitor the amounts of anions and cations in field drainage over long periods of time before it was necessary to change the resin mixture.

#### 9.4 MEASURING MINERALIZATION RATES IN FIELD SOILS

In a preliminary field study (Chapter-5) using the lysimeters developed in Chapter-4, the net mineralization of S and N was measured at four sites from June 1989 to January 1990 by simultaneously measuring the leaching losses of S and N, the pasture uptake of S and N and the extractable sulphate and mineral N pools in the soil. In addition the leaching losses of cations such as Ca, Mg, K, Fe and Al were also measured (Chapter-5). While, approximately 10 times more N than S was mineralized from soil organic matter, removed by pasture and recycled back to soil through animal excreta, sulphate was the dominant anion found in the drainage water. Approximately ten times more sulphate (2.1 and 15.2 kg S ha<sup>-1</sup> for low and high fertility farmlets, respectively) than mineral nitrogen (0.25 and 1.3 kg N ha<sup>-1</sup> for low and high fertility farmlets) was lost by leaching. Previous fertilizer history had a marked effect on the leaching losses of sulphate with seven times more S lost in the high fertility farmlet which received 375 kg SSP ha<sup>-1</sup> y<sup>-1</sup> with a stocking rate of 16 SU ha<sup>-1</sup> than the low fertility farmlet which received 125 kg SSP ha<sup>-1</sup> y<sup>-1</sup> with a stocking rate of 10 SU ha<sup>-1</sup>. While a three fold increase in fertilizer application doubled pasture production the associated losses of S by leaching increased approximately seven fold.

The lack of any change in sulphate level below the 15cm soil depth during the active growth period suggests that any sulphate that moved below the 15cm soil depth could be considered to be effectively lost from the system. The amounts of S and N net

mineralized were greater in soils from the high fertility farmlet (27.5 and 251 kg S and N ha<sup>-1</sup>) than in the soils from low fertility farmlet (12 and 119 kg S and N ha<sup>-1</sup>), which leads to greater leaching losses of S from the high fertility farmlet than from the low fertility farmlet. This suggests that when the mineralization rate was greater a greater proportion of the mineralized S was lost by leaching while at lower mineralization rate a greater proportion of the mineralized S was removed by pasture.

Associated with the losses by leaching of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were losses of cations. Of the basic cations, Ca was the dominant cation found in the drainage water followed by Mg and K. Despite the fact that the amount of K cycled in the soil-plant-animal system was greater than amounts of both Ca and Mg, less K was lost by leaching. This suggests that in sheep grazed pastures the K returned in excreta is mainly exchanged with soil Ca and Mg and enhances the leaching losses of both Ca and Mg. The amounts of Ca, Mg and K lost by leaching from the high fertility sites (9.5, 1.6 and 3.4 kg of Ca, Mg and K ha<sup>-1</sup>) was greater than those lost from low fertility sites (4.8, 0.6 and 1.0 kg of Ca, Mg and K ha<sup>-1</sup>). The higher stocking rates at the high fertility sites resulted in greater amounts of excretal return to these sites. This increased the mineralization of S and N which increased the leaching losses of S and N causing the greater losses of basic cations by leaching from these high fertility sites. The summed amounts of anion charge lost by leaching could not be balanced with the summed amounts of cation charge lost by leaching. This was partly because some of the main anions such as Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and OH<sup>-</sup> and cations such as Na<sup>+</sup> and H<sup>+</sup> could not be measured from the resin eluate. The oxidation states of Fe and Al species appearing in the leachate was also unknown. In general as the amount of anions lost by leaching increased the associated losses of cations also increased.

## 9.5 THE FATE OF FRESHLY APPLIED SUPERPHOSPHATE SULPHUR

In a second series of field studies,  $^{35}\text{S}$  labelled SSP was applied to lysimeters (Chapter-6) to study the fate of freshly applied fertilizer S and the effect of freshly applied fertilizer on the mineralization of S and N from the soil organic matter.

For a 9 month period from Jan. to Oct. 1990 about 19% and 26% of the fertilizer S was recovered by pasture and lost by leaching at the low and high fertility farmlets, respectively. Of this 61% was taken up by pasture at the low fertility farmlet, while at high fertility farmlet only 24% was taken up by pasture. The remaining S (39% at low fertility farmlet and 76% at high fertility farmlet) were lost by leaching at both farmlets. The amounts of S removed by pasture and lost by leaching clearly showed that pasture at low fertility farmlet removed a greater percentage of the fertilizer S than the pasture at high fertility farmlet. At both the low and high fertility farmlets S derived from the mineralization of soil organic matter contributed more to pasture S uptake and losses by leaching than the fertilizer S. The study further showed that the amounts of both S and N mineralized (40 and 204 kg S and N  $\text{ha}^{-1}$  at the high fertility farmlet and 22 and 125 kg S and N  $\text{ha}^{-1}$  at the low fertility farmlet) were strongly influenced by the current fertilizer application, the rate of application and the past fertilizer history. In particular, the amount of N mineralized and removed by pasture was strongly influenced by current fertilizer application and the rate of application (375 and 125 kg SSP  $\text{ha}^{-1}$  for high and low fertility farmlet). The total losses of S by leaching observed in the study were approximately 48% to 78% of the annual fertilizer application.

## 9.6 THE FATE AND INFLUENCE OF DUNG AND URINE

In order to quantify the effect of excreta on the pasture uptake and losses by leaching of S and N, a field experiment was conducted by applying sheep dung and urine to the lysimeters (Chapter-7).

Application of both dung and urine boosted pasture production and increased the uptake of both S and N. Even though large amounts of K were returned in excreta (376 kg K ha<sup>-1</sup> in dung and 146 kg K ha<sup>-1</sup> in urine) along with S and N, the amount of K removed by pasture was not increased by the application of dung and urine. The percent of excretal S, N and K (either dung or urine) that was taken up by pasture was very small, suggesting that nutrients returned in excreta are, initially at least, an input of nutrient into the soil organic S and N or mineral K pool in the soil and not directly available for pasture uptake. The amounts of S, N and K lost by leaching were not increased by the application of either dung or urine suggesting that in sheep grazed pastures leaching losses of nutrients directly from excreta patches were far less important than the subsequent losses that can occur once it has been incorporated into soil organic matter and then remineralized. Further investigations under different climatic conditions are necessary before the general applicability of these observations can be confirmed. During periods of low temperatures, slow pasture growth and high rainfall more S, N and K may be leached from urine spots.

## 9.7            **MODELLING THE FATE OF SULPHUR IN GRAZED PASTURES**

A preliminary computer simulation model describing the mineralization of soil organic S, pasture uptake and losses by leaching in grazed pasture was developed using the <sup>35</sup>S specific activity, and the soil sulphate data generated in Chapters 5 and 6.

The ratio of the specific activities of the plant S and leached S from the lysimeters fertilized with <sup>35</sup>S SSP indicated that the pool of sulphate-S that was taken up by the pasture plants was slightly but consistently lower than the pool of sulphate-S that was lost by leaching. The explanation for this is that there are spatial differences between the soil zones exploited by roots and those zones from where major drainage flow passes in the soil. Therefore in computer simulations of sulphate movement in soils root distribution and the differences in the movement of water between mobile water in the larger soil pores and less mobile water in the smaller pores should be considered. It is the water in the larger soil pores which may be displaced and move

downwards while water in the smaller soil micropores is likely to supply plants with water and nutrients. The study further showed that in modelling sulphate leaching it is important to measure accurately the fraction of input water that moves through the larger soil pores interacting little with native soil water.

The preliminary model gave reasonable predictions of the changes in soil sulphate concentrations in the soil upto a depth of 25cm, pasture uptake of S and losses of S leaching at four pasture sites varying in their fertilizer history. Further refinement of the model is necessary before it can provide the basis for predicting fertilizer S requirements for hill country pastures.

#### **9.10 APPLICATION OF CONCLUSIONS TO FUTURE RESEARCH**

By developing a new drainage lysimeter technique and field studies using the technique have shown conclusively that the mineralization of soil organic S was the main origin of the leached sulphate in grazed hill country pastures even though direct leaching of fertilizer S also occurred. The low N availability in the soil was a major factor limiting S uptake by plants and the formation of organic S in these pastures. When the N status of the soil was increased greater uptake of N by pasture occurred, which leads to a greater S uptake and reduced the leaching losses. Increasing the N status of the soil increased the plant production and therefore fixed more carbon which increased the immobilization of sulphur.

Manipulating the N supply by applying small amounts of N with fertilizer S may offer one option for making better use of not only applied S but S made available to the plant by the mineralization of soil organic matter. Alternatively, S fertilizers should be applied during the periods when carbon fixation rates are high. Less than 30% of the loss was directly from the applied superphosphate, this portion has the potential to be reduced by the use of elemental S based fertilizers or decreasing the S:P ratio in fertilizers. Further research is required to investigate the effect of N availability on the leaching losses of S by investigating the use of fertilizers containing not only S and P in different forms but also N, at different N:S:P ratios.

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### APPENDIX-5.1

Soil Moisture content for the period from Jun. 1989 to Jan. 1990 (seven sampling occasions) for three depths at all four sites.

Farmlet	Depth	1	2	3	4	5	6	7
	(cm)	g water g <sup>-1</sup> soil						
LF-LS	0-7.5	0.50	0.54	0.55	0.5	0.60	0.38	0.40
	7.5-15	0.36	0.44	0.43	0.44	0.43	0.38	0.36
	15-25	0.35	0.40	0.38	0.34	0.39	0.34	0.36
LF-MS	0-7.5	0.51	0.59	0.63	0.55	0.64	0.44	0.46
	7.5-15	0.41	0.47	0.49	0.48	0.52	0.41	0.37
	15-25	0.39	0.52	0.42	0.38	0.45	0.35	0.38
HF-LS	0-7.5	0.61	0.51	0.59	0.64	0.68	0.37	0.41
	7.5-15	0.42	0.37	0.45	0.44	0.42	0.34	0.35
	15-25	0.39	0.33	0.38	0.37	0.39	0.33	0.33
HF-MS	0-7.5	0.49	0.54	0.49	0.52	0.53	0.28	0.31
	7.5-15	0.32	0.35	0.37	0.41	0.39	0.23	0.27
	15-25	0.29	0.33	0.32	0.37	0.34	0.24	0.38

**APPENDIX-5.2**

**Soil bulk densities for the depths 0-7.5, 7.5-15 and 15-25cm at all four sites measured during July 1989.**

Farmlet	Bulk Density (kg dm <sup>-3</sup> )		
	0-7.5cm	7.5-15cm	15-25cm
LF-LS	0.77	0.97	1.18
LF-MS	0.75	0.95	1.16
HF-LS	0.79	0.99	1.20
HF-MS	0.77	0.97	1.18

Appendix-5.3

Sulphate (kg/ha) present in the soil for three depths during the experimental period.

Farmlet	Depth(mm)	From 31-5-1989 to 8-1-1990						
		31/5	4/7	24/8	5/9	6/11	30/11	8/1/91
LF-LS	0-75	3.8	5.5	8.0	6.1	4.3	3.1	2.9
	75-150	4.2	6.1	7.2	6.1	4.8	3.7	3.6
	150-250	7.8	10.9	13.0	10.6	9.5	7.6	7.7
LF-MS	0-75	3.9	4.7	14.4	5.3	4.2	3.4	3.3
	75-150	4.9	6.1	9.9	5.9	6.7	3.1	4.6
	150-250	10.7	12.2	19.4	12.3	10.6	12.0	10.4
HF-LS	0-75	8.7	8.2	14.4	7.2	5.7	3.5	4.7
	75-150	15.2	10.0	15.3	9.3	8.3	3.2	8.0
	150-250	21.1	14.8	30.5	22.0	20.0	19.4	21.6
HF-MS	0-75	7.7	6.0	6.7	4.4	3.7	2.8	2.8
	75-150	9.9	7.4	9.2	7.7	5.5	3.2	2.1
	150-250	16.5	12.4	21.1	19.6	16.6	16.9	16.1
<sup>*</sup> L S D <sub>p&lt;0.01</sub>		0.9	0.7	2.3	1.3	0.9	1.2	1.7

\* For comparisons of means between sites and depths.

### Appendix-5.4

Mineral nitrogen (kg/ha) present in the soil for three depths during the experimental period.

Farmlet	Depth(mm)	From 31-5-1989 to 8-1-1990						
		31/5	4/7	24/8	5/9	6/11	30/11	8/1/91
LF-LS	0-75	4.3	6.5	11.1	4.1	3.7	2.9	2.1
	75-150	2.6	5.1	8.9	3.5	3.1	2.8	1.6
	150-250	4.5	6.0	8.9	4.5	4.8	3.9	2.4
LF-MS	0-75	3.3	7.4	29.9	5.8	4.6	3.1	1.7
	75-150	1.9	6.3	19.6	3.6	3.7	3.1	3.0
	150-250	4.1	6.6	20.2	6.1	6.1	4.6	2.2
HF-LS	0-75	4.4	7.4	20.8	14.0	7.8	3.5	2.1
	75-150	3.2	5.1	7.2	9.6	5.9	3.2	2.4
	150-250	2.4	5.0	8.9	7.2	8.8	4.1	2.2
HF-MS	0-75	4.1	7.9	7.0	6.3	5.9	2.8	2.0
	75-150	2.9	5.8	5.6	5.0	5.3	3.2	1.5
	150-250	2.1	5.6	7.1	8.2	6.3	5.1	2.3
L S D <sub>p&lt;0.01</sub>		0.6	0.6	4.3	2.1	0.7	0.5	0.7

\* For comparisons of means between sites and depths.

## Appendix-5.5

### Sulphur and nitrogen returned in excreta

The amount of S and N returned in animal excreta and taken up by pasture was calculated as follows

Readily plant available sulphur returned for the period 31-5-1989 to 10-1-1990

#### Low fertility farmlet

#### Dry matter produced(31-5-1989 to 10-1-1990)

LF-LS =3774 kg dm ha<sup>-1</sup>-----1

LF-MS =5189 kg dm ha<sup>-1</sup>-----2

Based on the percentage area of each 10 ha farmlet in a slope category (Saggar *et al.*, 1990a) the total dry matter production for the total low slope (31.5% of the total area) and medium slope (41.5% of the total area) areas were calculated as (expressed for the area)

3774\*0.315 =1185 kg dm for 0.315 ha -----3

5198\*0.415 =2157 kg dm for 0.415 ha -----4

adding 3+4 =3342 kg dm which represents 77% of the total drymatter production and for an area of 0.73 ha in the LF farmlet according to Saggar *et al.* (1990a)

The remaining 27.1% of the farmlet area is occupied by steep slope which produced the remaining 23% of the total dry matter production. The total dry matter produced for all the three slope was

3342/.77 =4340 kg dm ha<sup>-1</sup>

#### Dry matter utilized and S ingested

Of the total dry matter 70% is utilized by sheep

4340\*.7 =3038 kg dm ha<sup>-1</sup>

The weighted mean average S content of the herbage =0.259%

Amount of S ingested =7.9 kg S ha<sup>-1</sup>

85% of the ingested S is returned in excreta (Gillingham *et al.*, 1980)

7.9\*.85 =6.7 kg S ha<sup>-1</sup>

S is partitioned in dung(40%) and urine(60%) (Wilkinson and Lowery, 1973) and dung contains 10% sulphate and urine contains 75% sulphate (Table 1, Chapter-7). Of the total S returned in dung, about 60% and 30% returned to low and medium slopes and of the urine returned about 55% and 31% returned to low and medium slopes (Saggar *et al.*, 1990a). This gives a total return of 6.8 kg SO<sub>4</sub><sup>=</sup>-S ha<sup>-1</sup> to low slope and 2.9 kg SO<sub>4</sub><sup>=</sup> ha<sup>-1</sup> to medium slope. But the amount of SO<sub>4</sub><sup>=</sup>- S taken up plant is only 7% of the total SO<sub>4</sub><sup>=</sup> returned in excreta (discussed in Chapter-7, Goh and Nguyen, 1990) and no excreta SO<sub>4</sub><sup>=S</sup> was lost by leaching (Chapter-7). So the amount of potentially available plant SO<sub>4</sub><sup>=</sup>-S returned were 0.45 and 0.21 kg S ha<sup>-1</sup> for low and medium slopes.

Similarly the amount of potentially available plant S returned in high fertility farmlet is 1.1 and 0.4 kg S ha<sup>-1</sup> for low and medium slopes. The distribution of slope areas in the high fertility farmlet was given in table 1 and stocking rate for this farmlet was described in section 2.

## Readily available nitrogen returned excreta

### Low fertility farmlet

Weighted mean N content of the herbage= 2.97%

Total nitrogen ingested =91 kg N ha<sup>-1</sup>

85% of the ingested N returned in excreta (Wilkinson and Lowery, 1973)

Total N returned in excreta =77 kg N ha<sup>-1</sup>

About 30% of the N returned in dung which is equivalent to 24.3 kg N ha<sup>-1</sup>. The remaining 42.7 kg N (70%) returned in urine. Of the dung N, 60% is returned to low slope and 30% returned to medium slope. In urine 55% returned to low slope and 31% returned to medium slope. About 6% of the dung N readily available form while 70% of the urine N is in readily available form. Again 6% of the readily available N is being taken up by plant and none of

the mineral N was lost by leaching. So the readily available N in the available pool is 3.8 and 2.1 kg N ha<sup>-1</sup> for low and medium slopes. Similarly the amount of N returned in high fertility farmlet was 8.0 and 3.5 kg N ha<sup>-1</sup> for low and medium slopes.

Appendix-6.1

Sulphate (kg/ha) present in the soil for three depths during the experimental period.

Farmlet	Depth(mm)	From 8-1-1990 to 10-10-1990						
		16/2	26/3	30/4	31/5	15/7	23/8	10/10
LF-LS	0-75	4.2	4.4	4.1	4.3	5.3	3.6	3.0
	75-150	4.6	5.2	5.0	6.2	6.3	5.6	6.4
	150-250	8.5	11.0	9.9	11.1	11.9	10.0	10.1
LF-MS	0-75	7.0	5.1	5.5	4.6	6.4	4.1	4.0
	75-150	7.8	8.2	7.8	6.9	8.1	6.0	6.2
	150-250	16.7	17.1	19.5	18.1	20.8	18.9	13.2
HF-LS	0-75	10.8	6.8	5.3	4.9	6.3	4.7	4.9
	75-150	9.4	10.9	8.2	7.2	6.7	7.5	9.2
	150-250	21.6	27.2	23.0	21.6	21.9	23.5	18.1
HF-MS	0-75	24.4	9.0	8.8	3.6	5.1	4.1	4.4
	75-150	13.2	13.1	10.8	7.3	7.5	5.7	6.8
	150-250	22.2	29.0	28.9	20.6	21.8	16.1	16.1
<sup>*</sup> L S D <sub>p&lt;0.01</sub>		2.2	1.4	3.1	2.7	3.4	3.8	4.5

\* For comparisons of means between sites and depths.

Appendix-6.2

Mineral nitrogen (kg/ha) present in the soil for three depths during the experimental period.

Farmlet	Depth(mm)	From 8-1-1990 to 10-10-1990						
		16/2	26/3	30/4	31/5	15/7	23/8	10/10
LF-LS	0-75	6.0	4.9	4.8	5.2	8.7	5.8	12.1
	75-150	5.4	4.9	2.7	4.2	4.1	4.7	5.9
	150-250	7.6	7.7	2.7	4.3	4.0	5.4	6.5
LF-MS	0-75	8.5	5.8	9.3	5.9	10.8	14.0	22.6
	75-150	12.7	5.8	3.1	3.9	6.1	5.3	9.2
	150-250	19.4	8.2	2.7	6.0	4.2	9.7	6.6
HF-LS	0-75	13.2	17.7	19.8	7.8	12.6	16.8	25.9
	75-150	9.7	11.2	9.3	5.9	6.8	1.6	12.8
	150-250	17.6	12.5	7.0	8.5	5.9	13.5	8.3
HF-MS	0-75	12.0	9.8	16.7	5.2	19.7	14.6	10.0
	75-150	11.7	6.5	4.2	3.7	7.6	7.3	8.5
	150-250	21.9	9.5	4.9	5.1	5.6	9.8	10.4
*L S D <sub>p&lt;0.01</sub>		3.3	2.6	2.9	2.5	2.2	4.6	5.6

\* For comparisons of means between sites and depths.

## APPENDIX-7.1

### Distribution of excreta in grazed hill country pastures.

Amount of dung and urine deposited to the low slope and the total area covered on an annual basis (Wilkinson and Lowery, 1973).

Amount of dung deposited and area covered

Stocking rate = 10 SU ha<sup>-1</sup>

Number of defaecation = 6 events day<sup>-1</sup>

Amount of dung excreted per event = 225g defaecation<sup>-1</sup>

Total dung excreted = 225x6x10x365 = 4927 kg FD ha<sup>-1</sup> yr<sup>-1</sup>

Area covered = 176.8x6x10x365 = 0.387 ha

60% returned to low slope = 2956 kg FD

Area covered for 2956 kg dung = 0.387x2956/4927  
= 0.232 ha

Amount of urine returned and area covered

Amount of urine deposited = 1-2 litres day<sup>-1</sup>

On an average it is = 1.2 litres day<sup>-1</sup>

Number of urination events = 8 events day<sup>-1</sup>

Amount of urine voided = 150ml event<sup>-1</sup>

Total urine deposited = 150x8x10x365 = 4380 lit yr<sup>-1</sup>

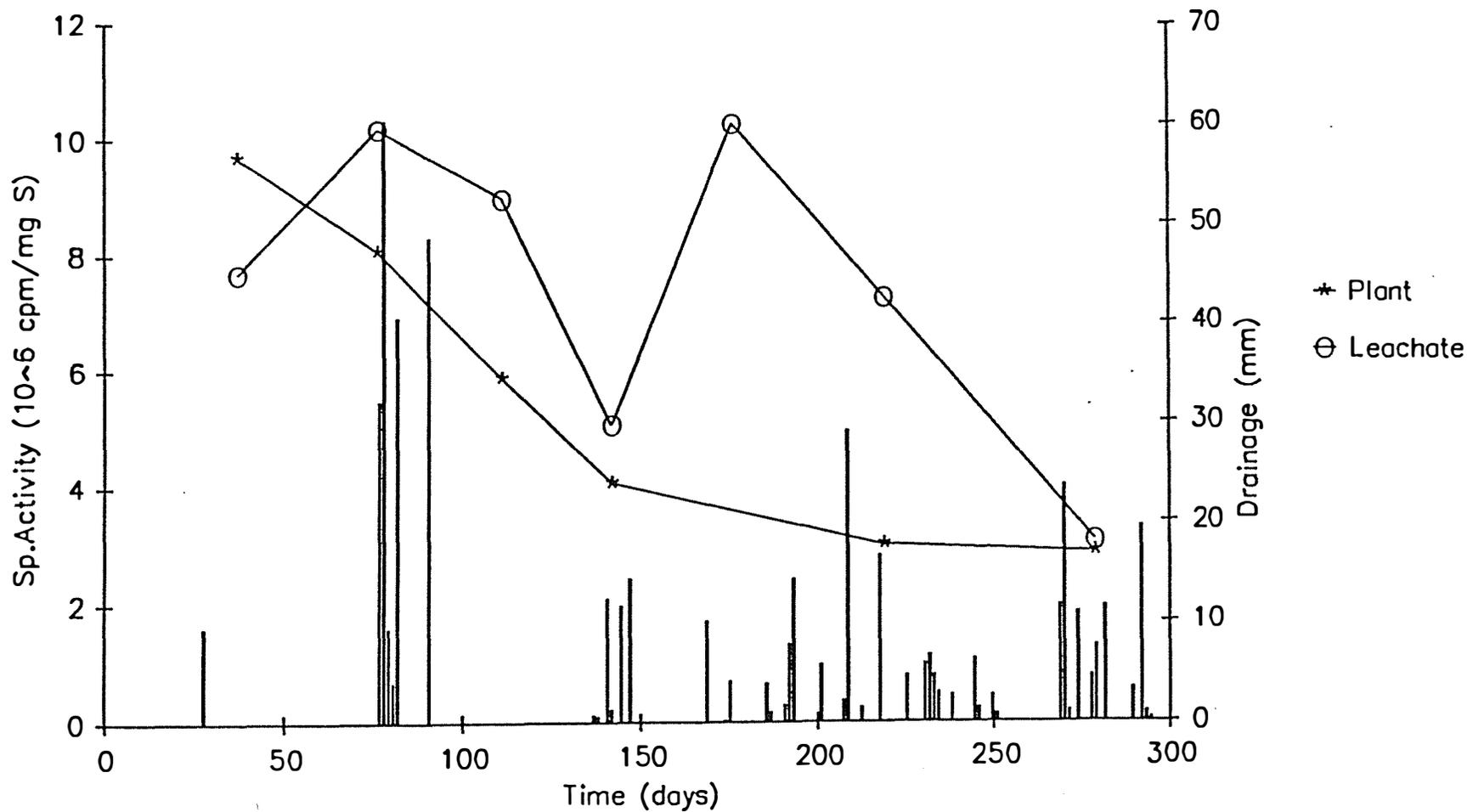
Area covered = 176.8x8x10x365 = 0.516 ha

55% returned to low slope = 2190litres

Which covered an area of = 0.516x2190/4380 = 0.258 ha

Total area of the low slope on a hectare basis = 0.33ha

Appendix 8.1. Change in specific activity of plant and leachate S-35 with time and the days on which drainage (verical bars) occurred for all four sites from Jan. to Oct. 1990.



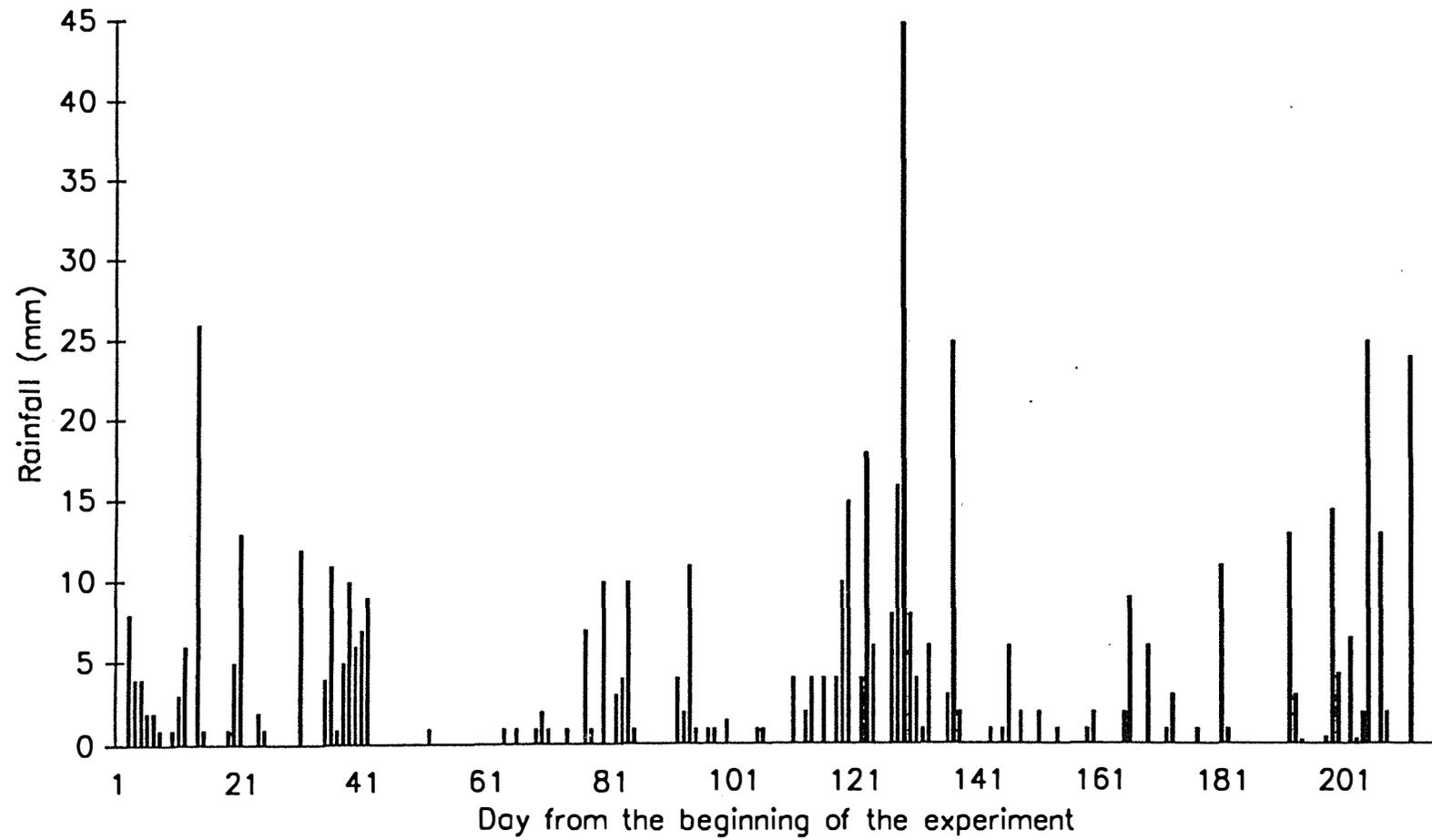
## APPENDIX-8.2

Ratio of shoot and root growth for the experimental period<sup>1</sup>

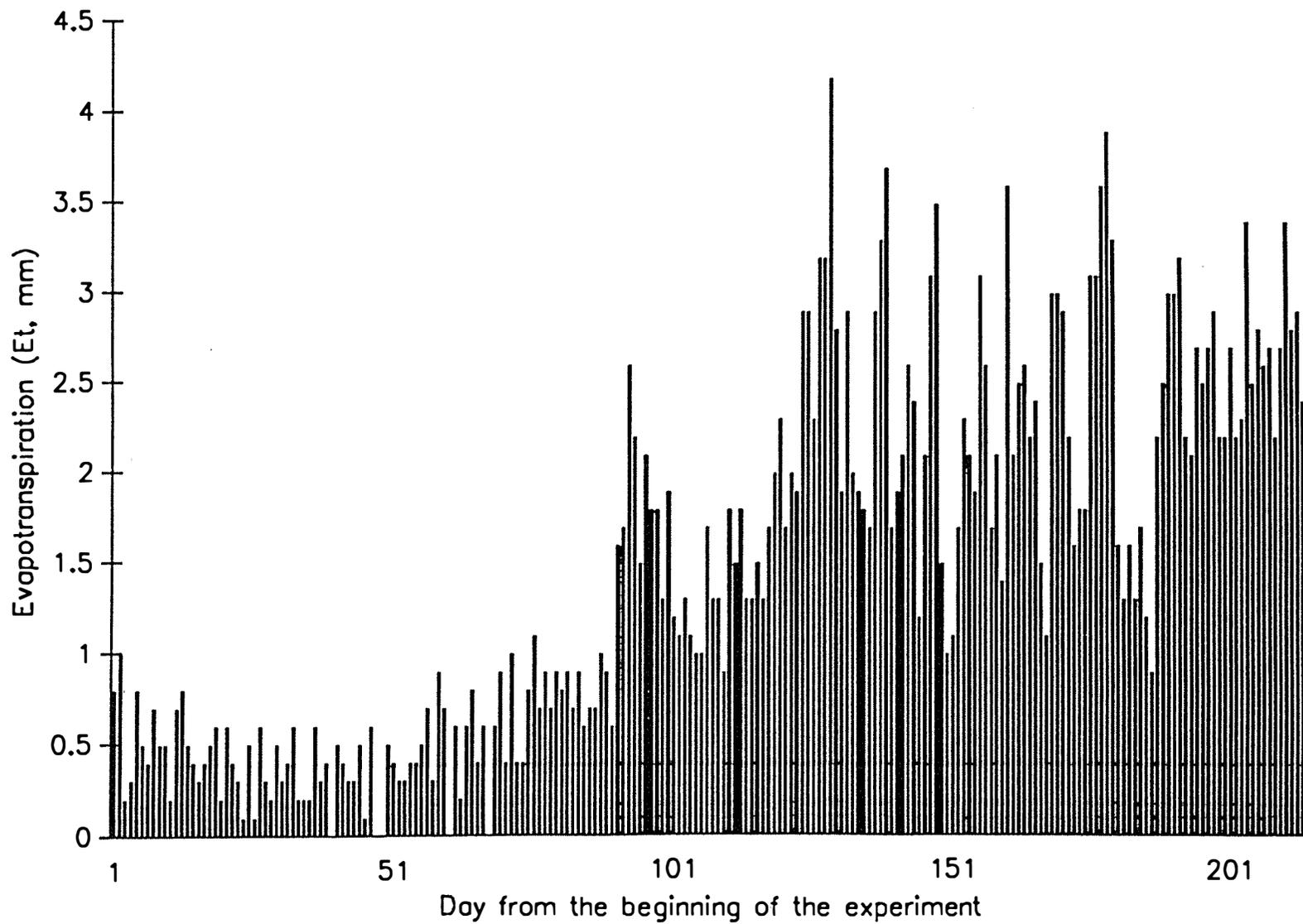
Month	Shoot/Root
June	11.6
July	14
August	10.2
September	12.5
October	15
November	16
December	13
January	17

<sup>1</sup> Calculated using the shoot/root distribution given by Mathew et al. (1989).

Appendix-8.3a Rainfall during the experimental period (Jun. 1989 to Jan. 1990)



Appendix-8.3b Evapotranspiration (Et) during the experimental period (Jun. 1989 to Jan. 1990).



## APPENDIX-8.4

Predicted and measured extractable soil sulphate present in the soil for three depths at all the four sites.

Site	Sampling	Predicted sulphate			Measured sulphate		
		0-7.5	7.5-15	15-25	0-7.5	7.5-15	15-25
kg S ha <sup>-1</sup>							
LF-LS	1	3.8	4.2	7.8	3.8	4.2	7.8
	2	7.9	6.4	8.9	5.5	6.1	10.8
	3	9.5	8.8	10.5	8.0	7.2	12.9
	4	4.8	7.1	10.9	6.1	6.1	10.6
	5	9.2	4.2	8.6	4.3	4.8	9.5
	6	14.4	0	6.8	3.1	3.7	7.6
	7	8.5	4.1	7.6	2.9	3.6	7.7
LF-MS	1	3.9	4.9	10.7	3.9	4.9	10.7
	2	5.4	6.9	10.8	4.7	6.1	12.2
	3	12.3	14.2	13.6	12.4	9.9	19.4
	4	3.4	7.6	11.9	5.3	5.9	12.4
	5	8.4	8.1	12.6	4.2	6.7	10.6
	6	10.7	7.0	12.5	3.4	5	10.2
	7	7	8.2	12.2	3.3	4.6	10.4
HF-LS	1	8.7	15.2	21.1	8.7	15.2	21.1
	2	3.6	9.1	19.9	8.2	10	14.8
	3	27.1	15.6	20.2	14.5	15.3	30.5
	4	7.9	11.3	19.6	7.2	9.3	22
	5	13.1	9.3	15.3	5.7	8.3	21
	6	14.3	7.3	15.3	4.5	8	21.4
	7	9.8	12.9	15.5	4.7	8	21.6
HF-MS	1	7.7	9.9	16.5	7.7	9.9	16.5
	2	6.3	7.9	15.2	6	7.4	17.4
	3	13.4	13.2	15.2	6.7	9.1	21.2
	4	7	12	15.8	4.4	7.7	19.6
	5	13.2	3.9	12.5	3.7	5.5	16.4
	6	12.7	4.4	12.5	4.5	6.9	16.9
	7	8.5	9	12.9	2.8	2.7	16.1