MINERALISATION OF SOIL ORGANIC SULPHUR

IN THE TOKOMARU SILT LOAM

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ABSTRACT

Using recently published data, a model of the sulphur (S) cycle for an established pasture, grazed by dairy cattle on Tokomaru silt loam, was constructed by assuming that organic S had reached an equilibrium level. The annual rate of net mineralisation, calculated in the model as 19 kgS ha^{-1}, was the single most important contribution to the plant-available pool of S.

In a field pot experiment involving growing plants under natural rainfall and temperature conditions, the amounts of S mineralised from 6 Tokomaru silt loam soils, differing in their organic matter contents, ranged from 10.9 kgS ha^{-1} to 22.9 kgS ha^{-1}. The relatively high rates of S mineralisation in 2 of the soils collected from the most well-developed pastures suggested that these soils may be approaching the organic matter equilibrium assumed in the model. Such models may therefore be useful in predicting fertiliser inputs to these soils. In contrast, other soils under less well-developed pastures had very much lower mineralisation rates and are apparently still far from equilibrium.

Highly significant relationships were obtained between the amounts of S mineralised in the field and the total S content of the soils. The accumulation of soil organic S within a soil type as indicated by the total S content may be a useful indicator of the approach to equilibrium and hence the extent of net S mineralisation.

The presence of growing plants significantly enhanced S mineralisation in the field in most soils and reduced leaching losses

of S from all soils.

In conjunction with the field pot experiment, a long term field incubation and a series of shorter term incubations (both in the field and laboratory) were conducted to investigate the effects of temperature, moisture content, pH and soil pretreatments on S mineralisation. The amounts of S mineralised in the long term field incubation were found to vary markedly with time. In contrast, the actual levels of soil sulphate during the incubation period were less variable and were highly correlated with the amounts of S mineralised in the field pot experiment. If such incubation techniques are to be used, the amounts of sulphate at the end of the incubation may be a better indication of the ability of a soil to mineralise S in the field than the actual amounts of S released during the incubation.

There were significant relationships between the final levels of sulphate at the end of all the incubation experiments and the total S content, again suggesting that within a soil type, total S content may be used to indicate the ability of the soil to mineralise S.

In all incubation experiments there were negative relationships, for each soil, between the levels of sulphate initially present at the start of the incubation period and the amounts of S mineralised during that period. This indicates some type of 'end product regulation' which may involve sulphatase enzymes.

No significant effects of temperature or moisture content were observed on the rate of mineralisation of soil organic S under the conditions of these incubations.

The addition of lime was found to increase S mineralisation in all soils. The amounts of S mineralised after liming were significantly related to the pH attained in all soils, although in 2 soils they were better related to the amounts of lime added.

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CHAPTER 1

CHAPTER 1 INTRODUCTION

In recent years the escalating costs of superphosphate and sulphur (S) have focussed attention on the efficiency of use of these fertilisers in New Zealand. Many farmers are already being forced to consider a reduction in the use of superphosphate, and in the future it has been suggested that phosphate rock, which contains very little S, may become more widely used. Since the S requirements of New Zealand pastures in the past have generally been satisfied through the use of superphosphate, this new trend may lead to an increase in the incidence of S deficiencies. In order to avoid this, a sound knowledge of the S cycle in the soil-plant-animal system will be required.

Recent work by Smith (1979), in which the major inputs and outputs of S in a grazed pasture system were measured, has enabled a simple S cycle to be constructed (figure 1.1). The model pertains to an established pasture, grazed by dairy cattle, on Tokomaru silt loam. The following assumptions apply:

(i) The pasture has been established for a large number of years and has received regular topdressing such that the accumulation of organic S has now reached an equilibrium plateau.

(ii) There is no significant pool of adsorbed S in Tokomaru silt loam soils.

(iii) The pasture is a ryegrass-clover mixture producing 10,000 kg ha^{-1} of dry matter annually, with an average S concentration of 0.3 per cent (Metson, 1973). Thus there will be 30 kgS $ha^{-1}year^{-1}$ incorporated in plant tops. Assuming a top-root

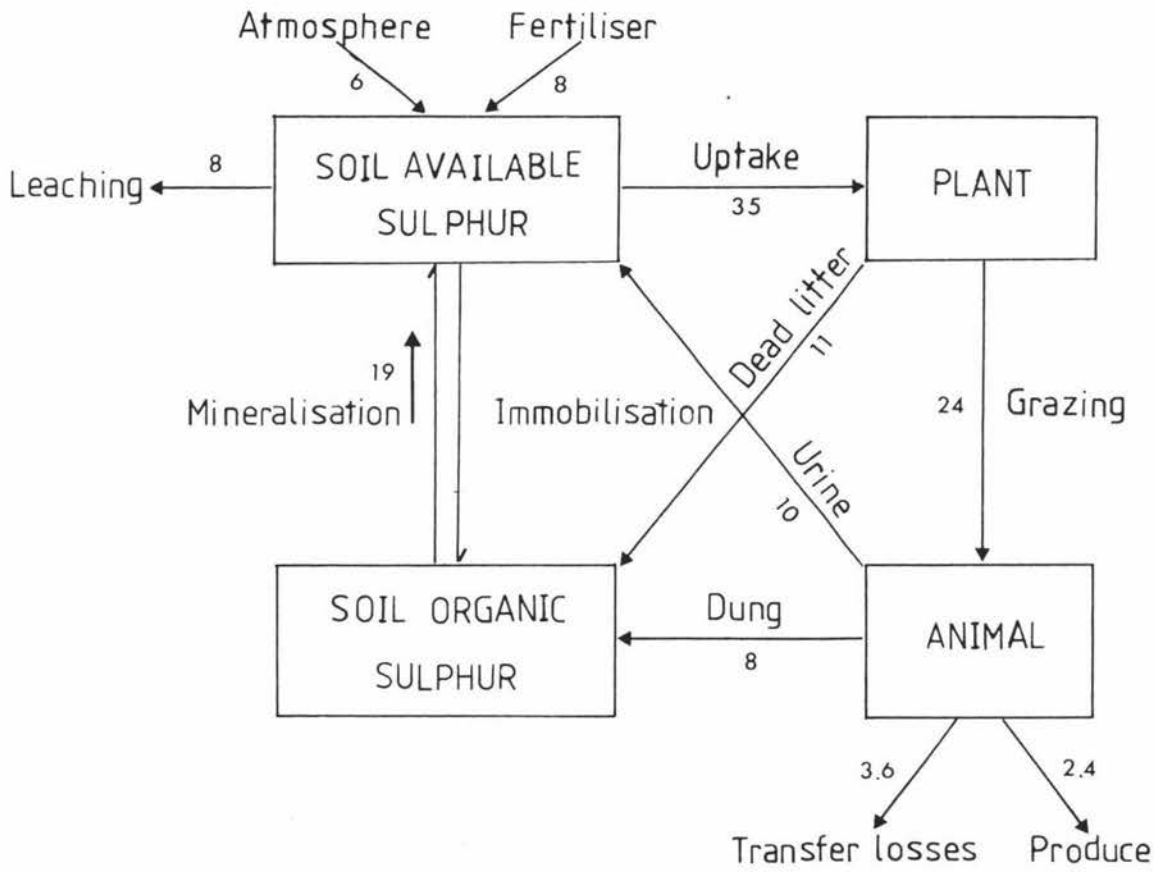

Figure 1.1 Model of a sulphur cycle for an established pasture grazed by dairy cattle on Tokomaru silt loam. (Transfer rates between pools are expressed as kgS $ha^{-1}year^{-1}$).

production of 3:1 and a root S content of 0.15 per cent (Gregg, 1976), another 5 kgS ha^{-1} will be incorporated annually in roots. The total plant uptake is therefore estimated to be 35 kgS $ha^{-1}year^{-1}$.

(iv) The pasture utilisation is assumed to be 80 per cent thus giving 24 kgS ha^{-1} consumed by animals and the remainder (11 kgS ha^{-1} including root material) returned as dead litter. The S in dead plant residues is assumed to be mostly in organic combination.

(v) Of the herbage S consumed by the dairy cattle (24 kgS $ha^{-1}year^{-1}$), 10 per cent is retained in animal products (During, 1972) and the remainder (21.6 kgS $ha^{-1}year^{-1}$) excreted. A proportion (15 per cent, During, 1972) of excreta is returned to non-grazing areas and is thus lost from the cycle.

(vi) Of the S returned in excreta to productive areas (18 kgS $ha^{-1}year^{-1}$), 60 per cent is in urine (Till, 1975). Approximately 90 per cent of the urinary S is in the form of sulphate which is considered readily available (Walker, 1957). The S in urine returned to the available pool is thus 10 kgS $ha^{-1}year^{-1}$ leaving 8 kgS $ha^{-1}year^{-1}$ in dung and urine returned to the organic pool.

(vii) Leaching losses amount to 8 kgS $ha^{-1}year^{-1}$ (Smith, 1979). These losses could be higher if fertiliser S is applied immediately prior to a prolonged period of rain.

(viii) The annual input of S in rainfall is 6 kgS ha^{-1}. This estimate is based on the amount of S (3 kgS ha^{-1}) deposited in rainfall at the site over 5 months during the winter (Smith, 1979).

(ix) Since soil organic S is assumed to have reached equilibrium, the annual inputs to the organic S pool from dead plant

material (11 kgS ha^{-1}) and dung (8 kgS ha^{-1}) must be balanced by loss through mineralisation. The net mineralisation of soil organic S should therefore amount to 19 kgS $ha^{-1}year^{-1}$.

If these assumptions are made, a balance sheet showing the inputs to, and outputs from the available S pool (table 1.1) indicates that without fertiliser addition, there is a net loss of 8 kgS ha^{-1} $year^{-1}$ from the available pool. In order to maintain a constant level of available S, this 8 kgS must be supplied by fertilisers.

It can be seen that mineralisation of organic S contributes to the available pool more than twice as much S as fertiliser and represents about 55 per cent of the total plant requirement. This clearly illustrates the significance of the mineralisation process in a situation where the conditions and assumptions mentioned above apply. Any appreciable variation, in the amounts of S mineralised, from the amount calculated in the model, will have significant consequences on the amounts of fertiliser S required.

It will be reported later in this study that Tokomaru silt loams under established pasture typically have organic S contents of 400 to 500 $\mu g\ g^{-1}$ in the top 8 cm. Since organic S contents generally decrease with the depth of soil (Whitehead, 1964), it is estimated that the top 15 cm of a well-developed Tokomaru soil may contain about 450 $\mu g\ g^{-1}$ of organic S. The annual rate of mineralisation calculated in the model (19 kgS $ha^{-1}year^{-1}$) therefore corresponds to an annual turnover rate of soil organic S of 2.4 per cent. This is in contrast to an annual rate of mineralisation of 1.25 per cent estimated by Walker (1957) and recently repeated by other workers (Tan, 1967; Gregg, 1976; Metson, 1979). Walker (1957) based his calculation upon an assessment of mineral nitrogen (N)

Table 1.1 A balance sheet showing inputs to and outputs from the available S pool in soil (kgS $ha^{-1}year^{-1}$)

INPUTS			OUTPUTS	
Net mineralisation	19		Plant uptake	35
Atmosphere	6		Leaching	8
Urine	10		Total	43
	35	(Deficit = -8)		
Fertiliser	8			
Total	43			

production (Walker et al., 1954) in normal soils of humid temperate climates and their relatively constant N:S (10:1) relationship. According to Walker's (1957) estimate, the annual rate of S mineralisation in Tokomaru silt loams under established pasture would be between 9 and 11 kgS ha^{-1} which is appreciably smaller than the annual turnover rate calculated in the model (19 kgS ha^{-1}).

This large discrepancy may be related to the variation in the equilibrium level of soil organic S. Walker (1957) suggested that the equilibrium level of total soil S under the "best New Zealand conditions" would be 0.12 per cent (or 1200 $\mu g\ g^{-1}$) and that it would take at least 50 years to attain such a level. In this study the relatively low organic S content (400-500 $\mu g\ g^{-1}$) in Tokomaru silt loams under established pasture would indicate that the soils are far from approaching such an equilibrium level. However, recent work by Quin (pers. comm.) on regularly topdressed pastures in Canterbury has shown that soil organic S reached an equilibrium plateau at 400 $\mu g\ g^{-1}$, and this within 25 years. This conflict clearly suggests that there is a need for a knowledge of the actual rate of mineralisation of soil organic S under developed pastures. More investigations are also required to establish any relationships between mineralisation and soil properties so that such properties can be used to predict the rate of mineralisation of soil organic S.

The objectives of this study are:

(i) to determine, under field conditions, the rate of S mineralisation in a number of Tokomaru silt loam soils differing in their organic matter contents;

(ii) to establish the relationships between mineralisation of soil organic S and soil S characteristics in order

to use such characteristics to predict the rate of mineralisation; and

(iii) to examine the influence of soil temperature, soil pH and growing plants on the mineralisation of soil organic S.

CHAPTER 2

CHAPTER 2 REVIEW OF LITERATURE

2.1 The role of mineralisation of soil organic sulphur in grazed pastures

The S cycle in grazed pastures is an interactive system comprised of various pools of S in the soil, plants, and animals. Soil S can be regarded as the most important pool in the cycle since plants derive most of their S from the soil. Plant available S consists of water-soluble sulphate and adsorbed sulphate both of which have been shown to be highly available (Williams, 1975). Losses from the available pool include plant uptake, leaching and immobilisation into organic matter, while additions come from fertilisers, mineralisation of soil organic S, atmospheric S and return in animal excreta.

In order to prevent S deficiency in pastures, the S in the available pool must be maintained at an adequate level. The input from fertilisers, particularly in New Zealand, has been through the widespread use of superphosphate, which has primarily been used to correct phosphorus deficiency, but at the same time has supplied S to pastures. There is however a trend towards a reduction in the use of superphosphate due to its increasingly high cost and the more developed state of pastures which means that less S may be supplied by this fertiliser in the future. The addition of S from atmospheric sources is also decreasing due to the measures taken to minimise atmospheric pollution from industrial and domestic sources. As a result plants are having to rely more and more on soil S to replenish the pool of available S.

In the surface horizons of well-drained non-calcareous soils

of the humid regions, organic S is the predominant form of S, and the inorganic forms account for only a small fraction of the total S (Freney and Swaby, 1975). Organic S must be mineralised to sulphate in order to become available for plant uptake. The rate of this mineralisation is therefore important in the replenishment of S in the available pool under grazed pastures when other inputs from fertilisers and atmospheric sources are decreasing. It has been demonstrated that the rate of mineralisation of organic S is the rate-limiting step in the S cycle and possibly the key factor in determing production in grazed pastures in Australia (Till and May, 1970).

The S cycle in a grazed pasture is represented diagrammatically in figure 1.1. The inputs to and outputs from the system will be discussed in relation to their overall influence on grazed pastures in New Zealand.

2.1.1 Inputs of sulphur

The additions of S to the grazing system arise from atmospheric sources, fertilisers, and the weathering of primary minerals. In New Zealand contributions from weathering are considered relatively insignificant (Walker and Gregg, 1975).

Atmospheric S can be derived from industrial sources and aerosols from the sea. It is precipitated onto the land in rain or as dry fall, and then enters the S cycle in a similar manner to fertiliser S. In coastal areas, thermally active regions, and large industrial sites, atmospheric S may be an important source of S to the available pool (Whitehead, 1964). It has been suggested that atmospheric returns of S form a small proportion of S in grazing systems over most of New Zealand particularly in inland areas

(Walker and Adams, 1958). Few investigations have actually been made on S inputs from the atmosphere in New Zealand. Walker et al. (1956) suggested an estimate of 1 kgS $ha^{-1}year^{-1}$ in much of inland South Island, and a figure as low as 0.5 kgS $ha^{-1}year^{-1}$ has been recorded at Tara Hills, a remote site with low annual rainfall in Central Otago (Anon., 1960). In coastal areas, higher values are expected and in fact 9.7 kgS $ha^{-1}year^{-1}$ was measured at Haast (1.5 km from the west coast of the South Island) (Walker and Gregg, 1975).

Figures obtained in the North Island have been, on average, higher than those from the South Island. At Rukuhia in the Waikato, a sulphur input of 3 kg $ha^{-1}year^{-1}$ was reported (Anon. 1960). Blakemore (1973) reported a mean figure of 7.7 kgS $ha^{-1}year^{-1}$ in rainfall at Taita, near Wellington. Miller (1968) also recorded 10 kgS $ha^{-1}year^{-1}$ of S inputs including dust near Wellington, while Muller (1975) observed an average input of 13.2 kgS $ha^{-1}year^{-1}$ at Otara near Auckland, at an urban site close to industrial areas and rather polluted tidal waters. It seems likely that the latter figure would be close to the maximum to be expected on agricultural land in New Zealand with the possible exception of some coastal sites in the path of prevailing on-shore winds (Metson, 1979). In Manawatu, Smith (1979) recorded 3 kgS ha^{-1} received in the rainfall over a five-month period. Although evaluation of direct plant and soil absorption of SO_2 has not been reported in New Zealand, the amount of S entering the S cycle in this manner is likely to be related to returns in precipitation and therefore generally small (Walker and Gregg, 1975).

The main fertiliser source of S in New Zealand is single

superphosphate (During, 1972). Other S fertilisers such as gypsum, S-fortified superphosphate and elemental S are less frequently used. In most areas of New Zealand, even on improved pastures, fertiliser S applications are necessary because of the continuing losses by leaching, accumulation in organic matter, and removal in animal products (Walker and Gregg, 1975). This is confirmed by a number of responses observed in field trials throughout New Zealand (Metson, 1979). It has been suggested that an annual application of 25 kgS ha^{-1} is generally required to maintain high pasture production level (Toxopeus, 1965). There is however evidence from field trials that some soils require less than 25 kgS ha^{-1} annually (During, 1972), and that others, for instance, the yellow-brown pumice soils, require more (Hogg and Toxopeus, 1966).

The rate of application of fertiliser S is only one of several factors related to the requirement of fertiliser S. Other equally important factors are the time of application, the type of fertiliser and its rate of release which in turn depends on the form and size of the fertiliser itself as well as the rate of water movement through soil (Barrow, 1975). In low-rainfall districts, gypsum was found to give a quicker response than elemental S (During, 1972) but in higher rainfall areas, elemental S may be preferred because of the rapid leaching of gypsum. It is believed that application of gypsum or superphosphate in autumn often results in a large proportion of S being leached out by winter rain, whereas most of the S applied in the spring is likely to be retained in the root zone and available to plant (Hogg, 1965; Toxopeus, 1965, 1970; During and Cooper, 1974).

2.1.2 Losses of sulphur

Under grazed pastures, S may be lost from the system by leaching, volatilisation, erosion, in animal products and in animal excreta returned to unproductive sites. The S losses due to the volatilisation under the conditions normally encountered in grazing systems are likely to be minimal (Lovelock et al., 1972; Sachdev and Chhabra, 1974; Banwart and Bremner, 1976). Losses of volatile S compounds from animals and excreta represent an extremely small proportion of the S in the cycle (Till, 1975). In the absence of severe overstocking or drought the losses by erosion are relatively small (Young, 1969).

Losses of S in drainage water can arise from water percolating down the profile as well as water moving over the soil surface. There have been few direct measurements of losses of sulphate by leaching in the field in New Zealand. In one of the earliest experiments, Waters (1957) found an average loss of 19 kgS $ha^{-1}year^{-1}$ over 3 years from lysimeters under unfertilised pastures on a yellow-brown loam at Rukuhia. In a lysimeter study at Otara on a yellow-brown loam with moderate sulphate retention, Muller (1975) found much lower losses of S from an unfertilised lysimeter averaging 7.6 kgS $ha^{-1}year^{-1}$. The average figure for a fertilised lysimeter on the same soil type was 32 kgS $ha^{-1}year^{-1}$ during the same period. The soil was fertilised with 272 kgS $ha^{-1}year^{-1}$ as powdered superphosphate. The much higher losses from the fertilised lysimeter were attributed in part by the author to the powdered form of the fertiliser.

Leaching losses of S are also affected by rainfall conditions (During, 1972). By using ^{35}S, Gregg (1976) found that 90 days after

application of fertiliser S (45 kgS ha^{-1}), almost all of the added S remained within the upper 15 cm of the soil. During this period, the soil received 106 mm of rainfall. Over a similar period, a similarly textured soil received 384 mm of rainfall and in this soil the added fertiliser S was distributed evenly to a depth of 60 cm.

The rate of S leaching and the total amount of S leached have been found to be influenced by soil properties (Jones et al., 1968; Gregg, 1976). Water holding capacity of soils is one of the contributing factors (Gregg, 1976). This author reported that on a steepland yellow-brown earth, almost 70 per cent of the applied fertiliser S was lost from the 0-45 cm soil depth 2 months after application. In contrast, it was found that on a recent soil with a much higher water holding capacity, greater amounts of applied S remained within the upper 45 cm over a period of similar rainfall. When interpretation of the results from such leaching studies are made, the depth of plant uptake from the soil must be taken into account. For example, the S leached out of the upper 15 cm may accumulate in the subsoil and if plant roots can penetrate to such depth, then the S leached cannot be considered lost.

Sulphate retention capacities of soils can markedly influence the downward movement of S (Hogg, 1965). On a recent soil with low sulphate retention, Gregg (1976) found that fertiliser S penetrated beyond 60 cm in the winter following the spring application, but under similar rainfall conditions fertiliser S did not move beyond 60 cm on a yellow-brown earth soil with a medium sulphate retention in the subsoil. On another highly sulphate retentive soil (more than 30 per cent), During and Cooper (1974) reported very little leaching of applied S in spite of 3000 mm of excess rainfall.

It is suggested that in highly sulphate retentive soils, the sulphate retention capacity of soil may override the effect of rainfall on the leaching losses of S.

Recently a field study was carried out on a yellow-grey earth soil in Manawatu to investigate the effects of time of fertiliser application on the leaching losses of S (Smith, 1979). The soil used was Tokomaru silt loam which had a low sulphate retention capacity (During, 1972). This heavy silt loam soil received a total of 518 mm of rainfall over a period of 17 weeks from May to September. It was found that 7.5 kgS ha^{-1} was lost from soils to which fertiliser S (45 kgS ha^{-1} superphosphate) had been applied several months earlier in the spring. Leaching losses were increased to 15.2 kgS ha^{-1} from a similar soil when the same amount of fertiliser S was applied in July, 6 weeks after sampling had commenced.

It can be concluded from various studies on the movement of S in soil that leaching losses of S will depend firstly on soil properties such as sulphate retention capacity and internal drainage; secondly on fertiliser factors such as the physical and chemical nature of the fertiliser S and the rate and time of application; and lastly on the extent of water movement, which is related to rainfall and soil properties. The interactions of these factors are probably responsible for the very variable results obtained from the different studies of S movement.

Grazing animals can cause S losses from the cycle through incorporation of S into animal products and transfer in dung and urine away from a large proportion of the grazed area. Transfer losses are variable depending mainly on the type of grazing animal,

stocking rates, and stock movement. It has been estimated that losses can vary from 3 to 7 kgS $ha^{-1}year^{-1}$ (During, 1972). The amounts of S retained by grazing animals and subsequently removed from the cycle as products have not been measured directly. Tracer studies with sheep show that about 10 per cent of the ingested S is retained (Till et al., 1973). The same figure has been estimated to be retained by dairy cattle (During, 1972).

2.1.3 Recycling of sulphur

Plants derive their S in the form of sulphate from the available pool in the soil. Sulphur taken up by plants can be returned directly to the soil as dead litter and roots. Some is consumed by grazing animals and returned as urine to the available pool and as dung to the organic pool in soil (Walker, 1957). The S in the organic pool can enter the available pool via the mineralisation process thus completing the S cycle. The reverse process, immobilisation can occur at the same time and some of the available S will be incorporated directly into organic forms. These two processes are carried out mainly by microorganisms (Freney and Swaby, 1975).

In a steady-state system in which soil organic S levels are constant, the rate of immobilisation will balance the rate of mineralisation. It has been suggested that such an equilibrium exists under well-developed pasture (Jackman, 1964). In support of this, During (1972) has indicated that after a period of years with regular topdressing, the rate of accumulation of organic matter under developed pastures would decrease and the net mineralisation become a more significant supplier of plant available S. However it is generally suggested that mineralisation of S from soil organic matter is inadequate to meet the requirement of high producing crops or even

pastures (Harward et al., 1962). Walker (1957), for example, by assuming that 1.25 per cent of total soil S is mineralised each year, has estimated that mineralisation from a pasture soil with 0.012% total S would provide only 2.5 kg ha^{-1} of S, or about 10% of plant requirements. Many estimates of S mineralisation have been obtained from incubation experiments. Interpretation of such studies in terms of the grazed pasture is frequently difficult because only a net mineralisation or production of sulphate is measured, and this in the absence of competing processes such as plant uptake and grazing. Recent studies on grazed pasture following the application of ^{35}S-labelled fertiliser have shown that mineralisation from the large reserves in various organic forms is essential to maintain production. It has been suggested that the rate of this mineralisation is probably the key factor in determining production in grazed pastures (Till and May, 1970).

2.2 Soil organic sulphur

Despite the general assumption that organic S is an important reserve of soil S in grazed pastures, little is known of the identity of organic S in soil at the present time (Williams, 1975). Now that more attention is being focussed on the availability of this large reserve of organic S in soil, there has been growing interest in the nature and properties of the S-containing components of soil organic matter (Anderson, 1975).

It is known that proteins are the organic S compounds that occur in greatest abundance in plants and microorganisms. Many of the early reports of the identification of organic forms of S in soil were from investigaitons in which amino acids present in acid hydrolysates were isolated and identified. Among amino acids

derivatives identified were cystine, methionine, cysteic acid, methionine sulphoxide and methionine sulphone. The reliability of these early determinations is questionable because of the uncertainties in the extraction and analysis (Freney et al., 1962). The analyses were likely to underestimate the amounts of these forms of soil S due to losses during hydrolysis. For instance, cystine and methionine decompose when subject to the acid hydrolysis treatment required to free tham from organic and mineral complexes (Freney and Stevenson, 1966). The S-containing compound biotin has been detected in some surface soils in New Zealand, particularly those under coniferous forest (Jones et al., 1962).

While much of the organic S in soils remains uncharacterized, some progress has been amde in recent years in subdividing it into three broad categories: hydriodic acid reducible S, carbon-bonded S, and residual S. The differentiation is based purely on the chemical fractionation shown in figure 2.1, and the identities of these fractions have not yet been verified.

A proportion of soil organic S can be reduced to hydrogen sulphide by a reagent containing hydriodic acid (HI), formic acid, and hypophosphorus acid (Johnson and Nishita, 1952). This reagent does not liberate S directly bonded to carbon (C) (Freney, 1961). Much of this so-called 'HI-reducible' S fraction is thought to consist of sulphate esters (i.e. organic sulphates, containing the C-O-S linkage) and ethers in the form of phenolic sulphates, sulphated polysaccharides, choline sulphate, and sulphated lipids (Freney, 1967; Tabatabai and Bremner, 1972b). It is also suggested that this fraction is largely associated with active side chain components of fulvic and humic materials (Bettany et al., 1973). In most mineral soils,

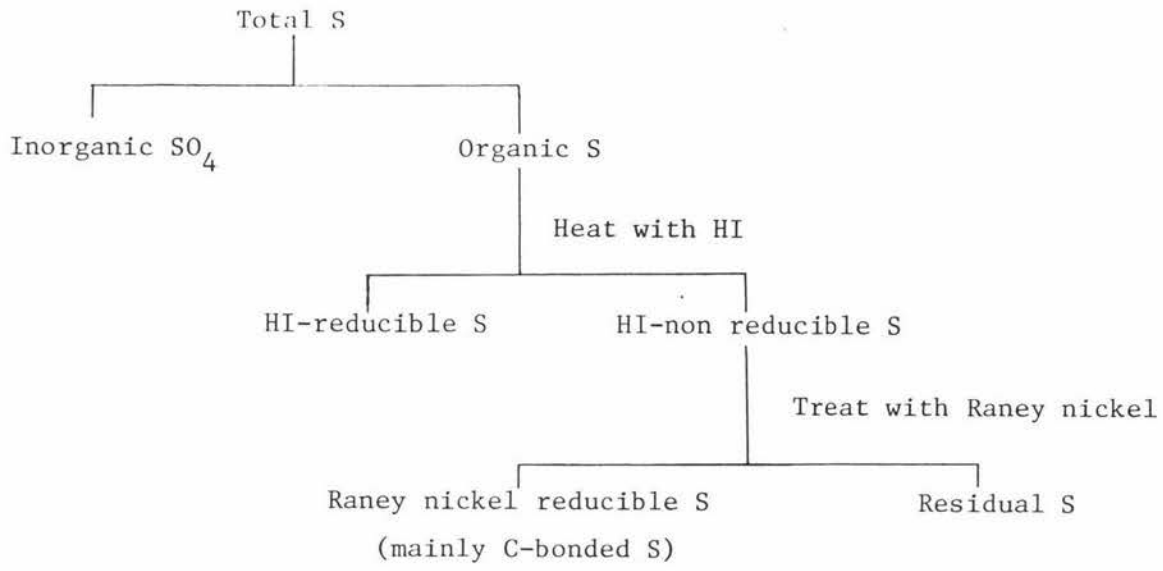

Figure 2.1 The chemical fractionation of soil S

(Adapted from Freney et al., 1975)

HI-reducible S accounts for a considerable proportion of organic S, although results from a number of soils ranged from 25 to 78 per cent (Biederbeck, 1978). Scott and Anderson (1976) found in several Scottish soils that HI-reducible S accounted for an average of 64 per cent of organic S in acid soils, compared with only 23 per cent in calcareous soils.

Treatment of soils with Raney nickel in an alkaline medium causes the C-S bond in many compounds to be broken (Lowe and DeLong, 1963). The types of organic S linkages broken in this way include disulphide, sulphydryl, sulphoxide, sulphinic acid, and some sulphonic acids (Arkley, 1961). The method has been criticised for failing to reduce all C-bonded S compounds and for the possibility of producing artifacts (Freney et al., 1970; Tabatabai and Bremner, 1972b). It is nevertheless considered the best method available for assessing this component (Biederbeck, 1978). Amino acids, proteins and some inorganic S trapped deep within crystal lattices are thought to be reduced by the Raney nickel method (Arkley, 1961). It was estimated that about half of the C-bonded S occurs as amino acids (Freney et al., 1972). The C-bonded S fraction determined by Raney nickel accounts for between 5 and 35 per cent of the organic S in mineral soils (Biederbeck, 1978). A much higher proportion was found in several organic soils where figures of 47-58 per cent were reported (Lowe and DeLong, 1963). It has been postulated that C-bonded S is primarily associated with the strongly bonded aromatic core of humic acids (Bettany et al., 1973).

The presence of a residual fraction of soil organic S was first suggested by Lowe (1964) who found that the HI-reducible and the C-bonded S together accounted for only 57 per cent of the total

organic S in one soil. Because of the presence of this unaccounted fraction, and the fact that Raney nickel does not reduce all C-S linkages, some investigators have assumed that C-bonded S can be estimated as being the difference between total and HI-reducible S (Freney et al., 1970). However, Biederbeck (1978) suggests that the assumption that all non-HI-reducible soil organic S consists of C-bonded S is probably an oversimplification and is not justified in view of the existence in soils of sizeable amounts of inert S with characteristics differing from those of HI-S and C-S fractions (Lowe, 1965).

The agronomic significance of differentiating C-bonded S from the non C-bonded fraction is questionable because there is conflicting evidence with regard to their contribution to the available S pool. As S in the HI-reducible pool can be easily hydrolysed into inorganic sulphate by acid or alkali (Freney, 1961), it is considered to be the most labile fraction of soil organic S (Spencer and Freney, 1960; Lowe, 1965; Freney et al., 1971; Cooper, 1972; Lee and Speir, 1979). In contrast, Freney et al. (1975), using ^{35}S-labelled soil organic matter, showed that most of the available S removed by plants in a pot experiment came from the C-bonded fraction. It was also found that plants derived most of the labelled S from the non C-bonded fraction of the freshly incorporated organic residues. The results therefore indicated that all fractions contributed available S for plant uptake. This is consistent with a study of Widdowson (1970) who found that plant uptake S was not related to either C-bonded or non C-bonded forms.

Freney et al. (1971) found that mineralisation of S resulted in an increase in the HI-reducible fraction and a decrease in C-bonded

S although there was little change in the total amount of S in the two fractions. The authors therefore concluded that there must have been conversion of C-bonded S to HI-reducible form during incubation. McLachlan and DeMarco (1975) and McLaren and Swift (1977) have since used this conclusion to explain the results of their mineralisation studies. McLaren and Swift (1977) found that under cultivation, the mineralisation of organic S resulted in a high proportion (75 per cent) of S being lost from C-bonded S and only 25 per cent from HI-reducible forms. Similarly, in a pot experiment, McLachlan and DeMarco (1975) found that plants derived most of the organic S from the C-bonded fraction. Both authors suggested that C-bonded S was converted to HI-reducible forms which were then mineralised to inorganic sulphate. Such a mechanism would tend to maintain the level of the HI-reducible pool while the C-bonded S diminished.

Although Freney et al. (1971) suggested that C-bonded S must be converted to the HI-reducible fraction before being mineralised to sulphate, there is no direct evidence to prove that such a mechanism exists. It is equally possible that C-bonded S may have been mineralised to sulphate and later incorporated into the HI-reducible fraction. Furthermore the mechanisms proposed for the decomposition of S-containing amino acids (Freney, 1960) do not include ester sulphates or any HI-reducible intermediates in the pathways. It is possible that C-bonded S or S-containing amino acids can be mineralised to give inorganic sulphate without prior conversion to HI-reducible forms.

If there is, however, a ready movement of S between the C-bonded pool and the HI-reducible pool, then any factors affecting

the rate of conversion may be more important in determining the potential availability of soil organic S than the actual quantities found in either fraction at any one time.

2.3 Mineralisation of soil organic sulphur

In the same way as nitrogen, S accumulates in the soil mainly as a constituent of organic matter and does not become available to plants until it has been mineralised to sulphate. Little is known of the individual steps in the conversion of the S compounds in the soil organic matter to sulphate in well-aerated soils. It is believed that organic S compounds are decomposed to simple organic molecules which are later converted to inorganic sulphate (Freney and Stevenson, 1966). The limiting step appears to be the initial decomposition of the organic matter rather than the subsequent conversion of the decomposition products (Burns, 1967).

2.3.1 Initial enzymatic breakdown

A great variety of S compounds have been isolated from plants, animals, and microorganisms (Freney, 1967), but in soils decomposable S derives basically from three sources: (a) fresh plant or animal residues; (b) the soil biomass including cells and by-products of microbial systhesis; and (c) humus (Biederbeck, 1978). Although the three fractions differ in their biological stability, it is expected that most of the S in these fractions occurs in the form of proteins or sulphated esters (Biederbeck, 1978).

The initial decomposition of organic S compounds is carried out by numerous microorganisms and involves a number of reactions necessary to disrupt a variety of linkages. It is known that soil

microorganisms produce extracellular enzymes which can hydrolyse a great variety of peptide and ester bonds in molecules of varying sizes (Alexander, 1977). The proteinaceous components of plant and microbial residues are sequentially broken down into polypeptides, peptides and eventually individual amino acids (Biederbeck, 1978). Similarly, the sulphate esters occurring primarily as macromolecules in the structural components of plants, animals and microbial tissues will require breakdown to low molecular weight compounds before further S hydrolysis by hydrolases and arylsulphatases can occur (Houghton and Rose, 1976). It is suggested that S in these fresh organic residues is readily decomposed (Anderson, 1975).

During the decomposition of large S molecules, there occurs not only an enzymatic breakdown into their basic organic components, but also microbial assimilation of intermediates as well as synthesis and excretion of a wide range of different organic S compounds (Biederbeck, 1978). The concentration of uncombined organic S compounds in soil has been found to be normally low and variable because they are susceptible to decompostion (Starkey, 1950). Thus naturally-occurring low molecular weight sulphate esters or free S-containing amino acids do not accumulate in soils (Houghton and Rose, 1976; Paul and Schmidt, 1961).

During the microbial assimilation of uncombined organic S compounds, the organic S, in excess of that needed for microbial growth, is partly mineralised by intracellular enzymes and released as sulphates (Biederbeck, 1978). It has been estimated that together the bacteria and fungi in the surface of a grassland soil account for 1.3 per cent of total organic S in soil (Kowalenko, 1978). Although the microbial biomass contains only a small proportion of

soil organic S at any one time, this fraction is considered extremely labile and is the driving force for S turnover in soil (Biederbeck, 1978).

In contrast to the relatively rapid decomposition of fresh organic residues in soil, the degradation and release of S from the humus fraction is minimal and very low (Biederbeck, 1978). These humus components are much more stable and very resistant to enzymatic hydrolysis (Anderson, 1975; Houghton and Rose, 1976). This resistance can probably be attributed to a lack of flexibility of the substrate, and to mechanical as well as chemical shielding of localised areas of the substrate surface (Biederbeck, 1978). The degradation of humic acid and other soil organic S compounds does still occur in soil, although slowly, and is certainly carried out by microbial enzyme-catalysed sequences producing low molecular weight intermediates (Mathur, 1971).

2.3.2 Further degradation of sulphur-containing amino acids

As mentioned earlier, uncombined organic S compounds do not accumulate in soil. They are rapidly utilised by microorganisms, and the S in excess of microbial requirements is released in inorganic forms. Many reactions may be involved, and it is believed that the principal end-product is sulphate under aerobic conditions, and sulphide under anaerobic conditions (Alexander, 1977). There have been a number of studies on the pathways and products of aerobic and anaerobic decomposition of various S-containing amino acids with pure cultures of organisms isolated from soils (Freney, 1967). Relatively little is known, however, of the decomposition of these compounds in the soil itself. The soil microflora is considered very heterogeneous,

and consequently the reactions taking place in soil may be different from those with pure cultures because of interaction between species.

It has been shown that the aerobic decomposition of cysteine and cystine usually ends in the formation of sulphate (Alexander, 1977). The conversion is rapid because many organisms attack the two amino acids and the decomposition may proceed by any one of several competing pathways (Freney and Stevenson, 1966). One of the pathways which was proposed by Freney (1960), who identified all the intermediates involved, is as follows:

Cysteine → Cystine → Cystine disulphoxide →

Cysteine sulphinic acids → Cysteic acid → Sulphate

The decomposition of methionine has been suggested to have a different mechanism. It is found that methionine is more resistant to microbial attack and is thus broken down at a slower rate (Alexander, 1977). There are several pathways suggested for methionine decomposition (Freney, 1967). In soil, usually very little or no sulphate is released, and the decomposition produces several volatile S compounds such as methyl mercaptan and dimethyl disulphide (Frederick et al., 1957). Sometimes there is, however, a complete conversion of methionine-S to sulphate as found by Hesse (1957). It appears that the products of decomposition of methionine vary with the soil type and conditions (Whitehead, 1964). Barrow (1959) found that the products obtained depended on the proportion of S which was supplied as methionine as opposed to other S compounds. When the ratio of methionine to cysteine was 40:60, the main product was sulphate which was released in nearly as great quantities as when all the organic S was cysteine. However when the ratio of

methionine to other S compounds was large, very little sulphate was formed.

2.3.3 Hydrolysis of sulphate esters

A substantial proportion of soil organic S is present in the form of sulphate esters. This proportion averages about 40 per cent of total S in soils from Australia, England, Canada, Nigeria, and U.S.A. (Fitzgerald, 1976). It has therefore been suggested that sulphate ester hydrolysis may play some part in the mineralisation process but the magnitude of this contribution is not known.

When a variety of synthetic sulphate esters were incubated with various soils, most of them were readily hydrolysed suggesting that the soils contained sulphatases capable of releasing sulphate from these compounds (Houghton and Rose, 1976). Bacteria and fungi are among the major sources of these enzymes in soil (Fitzgerald, 1976), although plant roots are known to contain some enyzmes that can hydrolyse some sulphate esters (Nissen, 1968).

Arylsulphatases were the first sulphatases detected in soils (Tabatabai and Bremner, 1970b). Arylsulphatase enzymes will catalyse the following reaction (Cooper, 1972):

$$R{\cdot}O{\cdot}SO_3^- + H_2O \longrightarrow R{\cdot}OH + H^+ + SO_4^{2-}$$

R = an aryl group.

The existence of these enzymes has been reported in several African, U.S., Canadian, and New Zealand soils (Tabatabai and Bremner, 1970b; Cooper, 1972; Kowalenko and Lowe, 1975b; Lee and Speir, 1979). Irradiation treatment of soils has indicated that most of this activity is due to extracellular, particle-adsorbed arylsulphatases (Biederbeck, 1978).

Several studies on arylsulphatase activity have indicated that this activity can be influenced by a number of factors. Air-drying moist soils was found to cause a marked increase in arylsulphatase activity, although cycles of drying and wetting reduced the activity (Tabatabai and Bremner, 1970c; Cooper, 1972). The activity decreased with depth in the profile as organic matter decreased and was related to organic C content (Tabatabai and Bremner, 1970b). Cooper (1972) also reported significant correlations between the enzyme activity and total C, organic S and particularly HI-reducible S. It is interesting to note that arylsulphatase activity is strongly related to HI-reducible S or sulphate esters which are the natural substrates for the enzymes. Microbial synthesis of arylsulphatase is found to be subject to 'end product regulation' by sulphate (Fitzgerald, 1976). Thus, high levels of sulphate inhibit the production of this enzyme.

The amounts of S mineralised from a range of Iowa soils were not related to arylsulphatase activity (Tabatabai and Bremner, 1972a). In contrast, Kowalenko and Lowe (1975b) found that soils with the highest initial levels of arylsulphatase released the greatest amounts of sulphate. However, it was observed that the sharp decrease in the enzyme activity during the first period of the incubation did not agree with the increase in the rate of S mineralisation for the remainder of the incubation. The authors then concluded that the presence of this enzyme was not a major factor controlling the release of sulphate in this soil. In a recent study on New Zealand soils, the sulphatase activity was found to be strongly correlated with mineralised S as indicated by uptake of ryegrass from organic sources (Lee and Speir, 1979). The authors

have, however, sugggested that the correlation may not be conclusive, since both sulphatase activity and plant uptake from organic S sources were strongly correlated with the amount of ester sulphate. Furthermore the degree to which mean sulphatase activity increased with increasing temperatures did not correspond to the mean increase in the apparent mineralisation of organic S.

Considering the inconsistency of the results found by various workers, it is concluded that the role of arylsulphatases in S mineralisation in soil remains uncertain and requires further investigation.

2.4 Factors affecting mineralisation of soil organic sulphur

The availability of the large reserves of organic S in soil is governed by the rate of mineralisation into inorganic sulphate. Since the mineralisation process is primarily microbial, environmental factors which influence microbial activity will also influence the rate of conversion of organic S to plant available sulphate. These factors include soil temperature, aeration, moisture, pH, and the effects of plants. In addition to the enviornmental factors, the amount and type of soil organic matter will certainly influence the rate of turnover of organic S since it is the source for the mineralisation process.

2.4.1 Soil organic matter

Attempts to relate the amount and rate of S mineralisation to soil organic matter parameters have had variable results. In Mississippi, Nelson (1964) found significant correlations bweteen the amounts of S mineralised in incubated soils and their organic S and organic C

contents. Comparing pasture and arable soils of the same group, Swift (1977) reported a significant correlation between S mineralised and total soil S. Several other workers however have been unable to demonstrate such relationships in soils from Australia (Freney and Spencer, 1960; Williams, 1967), France (Simon-Sylvestre, 1969), Oregon (Harward et al., 1962), Iowa (Tabatabai and Bremner, 1972a), England (Jones et al., 1972), the West Indies (Haque and Walmsley, 1972), and Canada (Bettany et al., 1974; Kowalenko and Lowe, 1975b). These workers have concluded that the amount of S mineralised does not appear to be directly related to soil type, to total amounts of C, N or S, or to C:S, N:S, or C:N ratios. Nevertheless, the results from several studies seem to suggest that larger amounts of S are generally mineralised from soils with relatively high organic matter contents and in particular from soils with low C:S or N:S ratios (Harward et al., 1962; Nelson, 1964; Stewart and Whitefield, 1965; Haque and Walmsley, 1972; Bettany et al., 1974; Kowalenko and Lowe, 1975b). Thus, it is evident that there exists a rather complex interrelationship among soil organic S, C, and N.

In view of the similarity between microbial transformations of N and S (Starkey, 1966), it has been assumed that the relative rate of mineralisation of N and S from soil organic matter would be similar, and that they will be mineralised in approximately the ratio that they occur in soil organic matter (Walker, 1957; White, 1959). Barrow (1960b) has also concluded that the mineralisation of S from decomposing organic matter added to soil depends on the S content and C:S ratio of the decomposing material in the same way as mineralisation of N depends on the N content and C:N ratio. This hypothesis however fails to explain the results of several studies mentioned

earlier where,no significant relationships between S mineralised and total organic S were found. Recent work has shown that whereas the release of N can sometimes be correlated to total N (Haque and Walmsley, 1972), no such relationship seems to exist for S (Tabatabai and Bremner, 1972a; Kowalenko and Lowe, 1975b). Swift (1977) has concluded that while the mineralisation of N and S are interrelated, they are not analogous.

In conclusion, it would appear that in contrast to the behaviour of N, the rate and extent of the release of plant available S from soil organic matter is not closely governed by the major soil organic matter properties such as C, N, and S contents.

2.4.2 Soil temperature

The influence of soil temperature on the mineralisation of S has been investigated largely under controlled conditions in glasshouse and incubation studies. Williams (1967) found that no sulphate was released from soil organic matter when moist soil was incubated at 10C or below, but that the rate of S release increased with increasing temperatures up to 35C. Chaudhry and Cornfield (1967b) reported an increase in the release of S with increasing temperatures from 20C to 40C but a decrease at 50C. The optimum temperature for most S-oxidising microorganisms is between 27C and 40C (Burns, 1967). Most of the incubation studies on the mineralisation of S have been carried out at 30C, a temperature thought to be optimal for the mineralisation process.

In contrast, the results from a glasshouse experiment where growing plants were involved (Nicolson, 1970) showed that increasing soil temperatures between 10C and 20C increased plant growth but had very little effect on S mineralisation. In a recent pot experiment

in New Zealand, Lee and Speir (1979) observed that mineralisation of organic S as indicated by S uptake increased with temperature. The authors suggested however that other factors such as increased root exploitation of the soil and increased availability of adsorbed sulphate may have been involved. Furthermore it was found that there was only a slight increase in sulphatase activity (less than 2 per cent) between 10C and 18C and a decrease at 25C. The decrease in activity at 25C was attributed to denaturation of the enzyme. This is in contrast to the findings of Tabatabai and Bremner (1970b) in which arylsulphatase was found to function well under adverse temperature conditions and the optimal activity for the enzyme in six different soils was reported at 67C.

Considering the somewhat contradictory findings, it appears that when soils are incubated alone at constant temperature, S mineralisation generally increases with temperature (up to 40C or 50C) but in the field where temperatures fluctuate and external influences such as plant uptake and leaching exist, this general relationship may not apply.

2.4.3 Moisture and aeration

Conditions of moisture and aeration in soil are related since increasing moisture content generally causes decreased aeration in soil and vice versa. Soil moisture influences the form in which S is released from organic matter, the rate of S mineralisation, the activity of sulphatases, and the movement of sulphate in soil (Biederbeck, 1978). When soils were incubated at varying moisture levels, it was found that S mineralisation was sharply retarded at moisture contents appreciably above or below field capacity

(Williams, 1967), and that the optimum moisture level was 60 per cent of the maximum water-holding capacity (Chaudhry and Cornfield, 1967a). The apparent decline in S mineralisation at moisture levels close to saturation is probably due to poor aeration. Under such high moisture conditions, the release of S measured as sulphate tends to underestimate the S mineralisation because S accumulates in the reduced forms (Williams, 1967). In incubation studies of S mineralisation in soil, it is therefore necessary to ensure that the system remains aerobic.

Cooper (1972) reported the influence of moisture on the activity of arylsulphatase in Nigerian soils. It was found that the level of activity of the enzyme was closely related to seasonal changes in moisture under field conditions.

The moisture effects on S mineralisation reported by Chaudhry and Cornfield (1967a) and Williams (1967) are based on laboratory studies where soil moisture and other interrelating factors such as temperature were kept constant. It is therefore difficult to predict the influence of soil moisture on the S mineralisation under natural conditions.

The effect of moisture fluctuations has been investigated in pot experiments (Freney et al., 1975). Their results suggest that gradual moisture fluctuations in the range between field capacity and wilting point have little influence on S mineralisation and that rather drastic changes in soil moisture condition are required to produce a flush in S mineralised. It has been suggested by some workers (Barrow, 1961; Till, 1975) that the S released as a result of wetting and drying is derived primarily from sulphate esters in the soil organic matter. This theory is supported by Cooper's

(1972) finding that the initial release of S upon wetting some Nigerian soils is associated with a decrease in the HI-reducible S fraction.

The rate of S mineralisation has been found to increase immediately after air-dried soils were rewetted (Williams, 1967). Numerous reports show that air-drying releases some sulphate from a wide variety of soils (Freney, 1958; Barrow, 1961; Williams and Steinbergs, 1964; Williams, 1967; Tabatabai and Bremner, 1972a; Walker and Doornenbal, 1972; Kowalenko and Lowe, 1975a). It was found that the release was immediate and that air-drying had little effect on subsequent S mineralisation (Barrow, 1961; Williams, 1967). Little is known about the mechanisms involved, but Williams (1967) has suggested that they are associated with the same processes that bring about the increased solubility of organic matter after drying or heating (Birch, 1959). The amounts of S released upon drying have been shown to be completely unrelated to microbial activity (Kowalenko and Lowe, 1975a), although the sulphate released is readily available to plants (Barrow, 1961). It has been found that the amounts of S released are affected by the manner of drying, period of drying, temperature and period of storage, and soil type (Barrow, 1961; Williams, 1967). Thus Chaudhry and Cornfield (1971) suggest that storage of air-dried samples at -2C will not affect subsequent S mineralisation. The increases due to drying and storage as reported by various workers range from 20 to 80 per cent of the initial sulphate levels (Biederbeck, 1978).

Thus the increased availability of S caused by soil drying may affect the results of S mineralisation studies in which soils are

air-dried initially. It has been recommended that in estimating S mineralised during the incubation, analysis after incubation should be made on moist samples without drying in order to obtain a more reliable index of microbial S mineralisation.

2.4.4 Soil pH

Little is known of the influence of the natural soil pH on the mineralisation of organic S. Most studies have involved the addition of lime (calcium carbonate) or other chemicals such as sodium hydroxide, magnesium carbonate and hydrochloric acid to bring the pH of soils to different levels. Except in Hesse's (1957) study, the addition of calcium carbonate has been found to cause an increase in pH as well as an increase in the production of sulphate upon incubation (Ellet and Hill, 1929; Wiklander et al., 1950; White, 1959; Nelson, 1964; Williams and Steinbergs, 1964; Tan, 1967; Williams, 1967; Probert, 1976). Using a variety of non-calcareous soils from Australia, Williams (1967) found that with three soils the amount of S mineralised upon liming was directly proportional to pH up to pH 7.5. Above that pH, mineralisation increased rapidly, suggesting that possibly chemical hydrolysis was affecting the process. With three other soils, however, mineralisation of S was proportional to the amount of calcium carbonate added and not to the pH attained. The increases were not related to soil type or any single soil property (Williams, 1967). It is possible that pH is not a direct factor influencing the mineralisation of S in some soils.

Probert (1976) found that the increased S mineralisation due to liming was a short-lived effect. Using ^{35}S, the author also found

that, although liming caused an initial increase in adsorbed sulphate extracted, most of the S released in response to liming originated in the organic S fraction. Barrow (1960b) also observed an increase in sulphate mineralised after sodium hydroxide was added, but suggested that the increase was due to the increased alkalinity causing some organic matter to dissolve and thus making it more susceptible to decomposition.

The change in soil pH may influence the mineralisation of organic S by affecting the balance of microflora. Eno and Blue (1954) reported that an increase in pH from 5.5 to 8.5 caused a 6.25-fold increase in the bacterial population in soil but a decrease in the number of fungi. In the presence of toluene and formaldehyde, Williams (1967) found that the enhanced effect of liming on mineralisation of S was not completely eliminated. This seems to suggest that while the main effect of calcium carbonate addition is to stimulate microbial mineralisation, it also promotes chemical hydrolysis of organic S.

Freney and Stevenson (1966) have concluded that the increase in the release of sulphate upon liming may be due to three factors: (a) sulphate mineralised from soil organic matter by bacteria growing better in a more favourable pH environment; (b) sulphate released from soil organic matter by chemical hydrolysis; and (c) adsorbed sulphate released from soil exchange sites because of an increase in pH.

2.4.5 Effect of plants

The presence of growing plants can markedly influence the mineralisation of S from soil organic matter. In a pot experiment,

Freney and Spencer (1960) found that mineralisation of S was more than twice as great in the presence of plants as in the corresponding uncropped soils. They also reported that the addition of S fertilisers decreased the net S mineralisation more in the uncropped soils than in the cropped soils. Using the S balance approach, Cowling and Jones (1970) and Nicolson (1970) also reported a marked increase in S mineralisation in the presence of plants. Barrow (1967) found that the enhancing effect of plants on mineralisation of S was greater in the glasshouse than in the controlled growth cabinet environment and suggested that absorption of atmospheric S by plants in the glasshouse may be reponsible. A recent tracer study also indicated that S mineralisation in soils cropped to Sorghum was several-fold greater than in uncropped soils (Freney et al., 1975).

The increased mineralisation may be due to greater microbial activity in the presence of growing plants. Another possibility is the excretion by plant roots of enzymes which catalyse the decomposition of soil organic matter (Freney, 1967). The marked influence of plants on the mineralisation of soil S means that results obtained from incubation studies in the absence of plants may not accurately represent mineralisation of S in field situations where plants are present.

2.5 Techniques used to study the mineralisation of soil organic sulphur

Organic S in soils can be made available for plant uptake by the mineralisation process, and at the same time inorganic sulphate in the available pool can be immobilised directly into the organic pool by soil microorganisms. The net balance of both mineralisation and

immobilisation will determine whether inorganic sulphate will accumulate or not. Since both processes occur simultaneously in soils, it is difficult to determine their rates individually. The determination of the amount and rate of S mineralisation in soils has therefore usually been based on the measurement of the accumulation of inorganic sulphate, which represents the net mineralisation over a given time period.

As the accumulation of inorganic sulphate is a direct result of the decomposition of organic S, the depletion in the total organic S in soil should also theoretically serve as a measure of the mineralisation of S. Such changes, however, generally account for only a few per cent of total organic S annually and so this approach is not feasible for short term experiments, because the associated analytical errors are too high.

The usual approach is to measure the amounts of inorganic sulphate present in a soil at the beginning and the conclusion of the decomposition period. The change in the amount of inorganic sulphate will indicate the rate and extent of net mineralisation of organic S over that period, if there are no other additions or losses of S to or from the available sulphate pool. Various techniques have been used to investigate mineralisation of S in soils and they can be grouped into 4 types: (i) laboratory incubations; (ii) glasshouse and growth cabinet experiments; (iii) field experiments and (iv) field incubations.

2.5.1 Laboratory incubations

The incubation technique has been widely used to characterize the S supplying power of soils mainly because it is simple and

convenient to carry out. The general procedure consists of incubating a soil sample under near optimum conditions and evaluating the net amount of sulphate produced during the incubation. Such a procedure, however, has a number of disadvantages. The incubated soil is kept in a very favourable environment which is entirely artificial. The results are, therefore, not expected to represent what actually happens under natural field conditions but may be used to obtain relative results for different soils, since the soils are studied in similarly controlled environments.

Freney and Swaby (1975), reviewing the literature, observed that S mineralisation during incubation can follow one of a number of patterns:

(a) Immobilisation of S during the initial stages of incubation followed by mineralisation of S in the later stages (Barrow, 1961, 1967, 1969; Haque and Walmsley, 1972; Kowalenko and Lowe, 1975b; Nelson, 1964; Nicolson, 1970; Tabatabai and Bremner, 1972a). It was suggested that a low S content and a high C:S ratio in the decomposing organic matter caused the initial immobilisation (Barrow, 1961; Nelson, 1964).

(b) Initial rapid release of sulphate attributed to the remoistening effect of air-dried soils, followed by a slower and steady S mineralisation (Nelson, 1964; Williams, 1967; Kowalenko and Lowe, 1975b).

(c) A steady release over the whole period of incubation (Nelson, 1964; Williams, 1967).

(d) A slow rate of release from the commencement of incubation which decreases further with time (Williams, 1967). In this situation an accumulation of sulphate may have been responsible for the decline

in S mineralisation.

(e) No definite pattern of S release (e.g. Nelson, 1964).

These different patterns of S release can be attributed partly to differences in the chemical nature of the decomposing organic matter and variations in other soil properties such as pH and texture, and partly also to differences in incubation conditions. Thus, although there have been a large number of incubation studies on the mineralisation of soil S, no common standard procedures exist. Temperature, moisture content, sample preparation, period of incubation and methods for the determination of sulphate are among the factors that are likely to affect the results.

Williams (1967), incubating soils at 10C, 20C and 30C for 9 weeks, found that the greatest amounts of S were mineralised at 30C, only 50-70 per cent as much at 20C and little or no release at 10C. Incubation at higher temperatures was studied by Chaudhry and Cornfield (1967b). They found that during 12 weeks of incubation, mineralisation of S increased with increasing temperatures between 20C and 40C but decreased at 50C. The extent of the effect of temperature on S mineralisation was found to vary between soils and it was concluded that the optimum temperature for S mineralisation in these soils was 40C. The temperatures of incubation used in various mineralisation studies range from 20C to 40C with the majority of the incubations carried out at 30C. Although the optimum temperature for the soils used by Chaudhry and Cornfield (1967b) was 40C, it is unlikely that many soils would experience such a high temperature under natural conditions.

Most incubation studies have been carried out under moisture conditions that allow sufficient aeration, since oxygen is normally

required for the production of sulphate (Burns, 1967). When a moist soil was incubated at a wide range of moisture contents (Chaudhry and Cornfield, 1967a), it was found that sulphate was released if the soil water content was within the range of 20-60 per cent of the maximum water-holding capacity (mwhc), and the release increased with moisture contents within this range (Chaudhry and Cornfield, 1967a). The moisture content of 60% mwhc was then considered the optimum level. When the moisture content approached saturation (80% mwhc) or higher, large amounts of S were immobilised. In another study by Williams (1967), it was shown that incubation at moisture levels appreciably above or below field capacity resulted in a marked reduction in the amounts of sulphate produced. The reduced production of sulphate at low moisture levels was probably a result of inhibited microbial activity due to lack of moisture. At high moisture levels, it was suggested that a decreased oxygen supply inhibited the oxidation of reduced forms of S to sulphate which resulted in a decrease in sulphate production (Williams, 1967).

Since the absolute water content at which saturation (and generally an anaerobic condition) occurs, differs between soils, the upper limit of soil moisture in terms of absolute water content will also vary. For this reason, the optimum moisture content for incubation is expressed in terms of field capacity or percentage of the maximum water holding capacity. The soil moisture content at field capacity (as determined at -100cm pressure potential) or at 40-60% mwhc generally represents a moisture level within the optimum range for S mineralisation (Williams, 1967). These moisture conditions have therefore been used in most incubation studies to provide optimum conditions for S mineralisation.

It is generally accepted that an adequate supply of oxygen is essential to optimise mineralisation of S (Burns, 1967). The incubation system is designed to minimise moisture losses without restricting the supply of oxygen. In a closed system, moisture losses are prevented and oxygen can be supplied by chemicals such as barium peroxide (Cornfield, 1961) or by frequently opening the system for aeration (Williams, 1967; Kowalenko and Lowe, 1975a). Plastic film is widely used to seal incubation vessels to prevent moisture losses (e.g. Barrow, 1961). There have been conflicting reports regarding the permeability to oxygen of these plastic films. Bremner and Douglas (1971) concluded that plastic films were not sufficiently permeable to be used for sealing incubation vessels. It has, however, been suggested that the effectiveness of plastic films is also related to other factors such as the size and thickness of the film used, and the size of the incubation vessel (Kowalenko and Lowe, 1975a).

Since the report by Bremner and Douglas (1971) was published, modifications have been made to the use of plastic films in incubation studies. Haque and Walmsley (1972), for example, put small holes in the plastic films to ensure sufficient air movement. Kowalenko and Lowe (1975a) also used polyethylene films, but the incubation jars were aerated frequently and the authors concluded that the system was sufficiently aerobic.

Open incubation systems have also been employed in mineralisation studies (e.g. Williams, 1967; Freney et al., 1971; Kowalenko and Lowe, 1975a). In such systems frequent weighing and water additions are necessary to maintain the moisture level. It was, however, noted that in comparison with a closed system, a greater variability of the

results was obtained from the open system (Kowalenko and Lowe, 1975a). The authors attributed this to greater fluctuations in moisture content in the open system. In an attempt to minimise such fluctuations, Swift (1977) has stoppered the incubation flask with a cotton wool plug. Moisture content was still checked regularly and any losses replenished. Considering the success of the similar closed incubation systems employed by Kowalenko and Lowe (1975a) and Swift (1977), it can be concluded that a closed system (with regular opening for aeration) should be suitable for studies of S mineralisation.

Preparation of soils for incubation studies often involves air-drying, sieving and mixing of soils, all of which have been shown to affect results of S mineralisation investigations (Williams, 1968; Biederbeck, 1978). The effects of air-drying have already been discussed in the previous section (section 2.4.3). In general, it can be concluded that air-drying of soils would have no effect on subsequent mineralisation if the soils are sampled dry in the field and have been dry for some time. Air-drying of moist soils, however, would cause some S release thus affecting results of mineralisation studies (Williams, 1967). After incubation, air-drying of the samples prior to the extraction is, therefore, not recommended (Kowalenko and Lowe, 1975a). Results from the incubation of undisturbed soil cores and mixed, sieved soil samples indicate that mixing of the soil has little effect upon the pattern of mineralisation of S (Williams, 1968). The small effect of mixing is probably more than compensated by the reduced field variation.

Although the incubation technique is usually considered a short term procedure, periods of incubation of up to 6 months have been

reported (Nelson, 1964). It is evident from various incubation studies that the amounts of sulphate released varied with time during the incubation. Results of incubation studies are therefore dependent upon the time of sampling or the period of incubation. In general, greatest changes in the amounts of S mineralised or immobilised occurred during the first few weeks of incubation (e.g. Nelson, 1964; Williams, 1967; Kowalenko and Lowe, 1975b). The reasons suggested for this initial release or fixation have already been mentioned (section 2.4.3). It has also been suggested that this short period at the beginning of an incubation involves adjustment of the microbial population to the incubation conditions imposed, and to the initial levels of readily available substrates (Kowalenko and Lowe, 1975b).

Incubation studies on the mineralisation of soils S generally require the determination of soil sulphate. Numerous extractants are available which will extract variable proportions of soluble, organic and adsorbed sulphate. The most commonly used extractant is either some solution containing phosphate ions or a solution of calcium chloride ($CaCl_2$). The phosphate extractants are known to extract variable proportions of adsorbed and organic sulphate in addition to the readily soluble form extracted by $CaCl_2$ solutions (Ensminger and Freney, 1966). When both extractants are used in incubation studies, the phosphate extractant is generally found to give greater results for S mineralisation than does $CaCl_2$ (Barrow, 1961; Williams, 1967; Kowalenko and Lowe, 1975a).

Kowalenko and Lowe (1975a) have suggested that since phosphate can displace adsorbed sulphate, a phosphate extractant should be better than a solution of $CaCl_2$ for studying mineralised sulphate

particularly in soils with a high sulphate adsorption capacity. The authors, however, found that the $CaCl_2$ extractant gave results which more closely paralleled microbial activity. A possible explanation may be that adsorbed sulphate is not all equally plant available (Metson, 1979). It is likely that a phosphate extractant may be more suitable than a $CaCl_2$ extractant for the study of S mineralisation in soils which have not only high sulphate adsorption capacity but also high amounts of adsorbed sulphate that are available to plants. For soils with very little sulphate adsorption capacity, a $CaCl_2$ extractant as suggested by Kowalenko and Lowe (1975a) may be more suitable.

Since it is clear that temperature, moisture content and aeration during the incubation, together with soil preparation, period of incubation and methods for determining sulphate can influence the results of incubation studies, all such factors must be considered when interpretation or comparisons of results are made.

2.5.2 Glasshouse and growth cabinet experiments

One of the disadvantages of the incubation technique is that the effect of plants is not included. Since it is known that the presence of plants can have a marked influence on the mineralisation of soil S (Freney and Spencer, 1960), glasshouse experiments including growing plants may be more advantageous in the study of S mineralisation in soil. In such glasshouse experiments, determination of S mineralisation is based on the S balance approach. The apparent mineralisation of soil S is estimated by the plant uptake of S, the change in soil sulphate level during the growth period and the amount of S, if any, lost in the leachate as follows:

S mineralised = Final soil sulphate - Initial soil sulphate

+ Plant S uptake + Leached S.

The estimation of S mineralisation in the presence of plants is likely to be subject to large errors unless extreme care is exercised to ensure the complete recovery of roots from soil and to measure S inputs in daily watering and from the atmosphere. Barrow (1967), for example, found no enhancing effect of plants on S mineralisation because of incomplete recovery of the S contained in the plant. In the study by Cowling and Jones (1970), atmospheric S was reported to be the reason for the greater effect of plants on the measured mineralisation of S in a glasshouse than in a controlled growth cabinet enviornment.

The amounts of S mineralised obtained from glasshouse or growth cabinet experiments are expected to be influenced by similar factors to those affecting laboratory incubations. In addition, factors related to plant growth, such as the supply of other nutrients, the type of plant grown and the period of growth must be considered.

The influence of temperature on the mineralisation of S in a glasshouse was studied by Nicolson (1970). Soil temperatures of 10C, 15C and 20C were achieved by placing the pots on frames in thermostatically controlled water tanks which were located in an enclosed glasshouse. The method enabled the soil temperature to be maintained within $\pm$1C. It was found that although increasing temperatures enhanced the growth of subterranean clover (Trifolium subterranean), very little effect of temperature was observed on the mineralisation of S. This may be due to the fact that the rate of mineralisation was so slow that the changes in the amounts of S

mineralised were too small, to be accurately measured.

Lee and Speir (1979) have successfully demonstrated the effect of temperature on S mineralisation in 12 New Zealand soils in controlled environment rooms. The mean increase in mineralisation of S from 10C to 18C was 87 per cent, and from 18C to 25C, 114 per cent. The increases in S mineralisation did not correspond to the sulphatase activity, which was similar at 10C and 18C but much lower at 25C. It was again shown that S uptake increased with temperature. Although the authors have attributed the increase in plant uptake to an increased mineralisation, they pointed out that increased root exploitation of the soil and/or increased availability of adsorbed sulphate are also to be considered.

Most glasshouse and growth cabinet experiments have been carried out at moisture contents at or close to field capacity which is considered to be the optimum level for S mineralisation (Williams, 1967). A constant moisture level is normally maintained by daily weighing and watering and allowance is made for the weight of plant material as the plants grow. Freney et al. (1975) tried to simulate soil moisture fluctuations that occur under field conditions by applying a moisture stress treatment of below wilting point and near field capacity alternately. It was found that the moisture stress treatment decreased dry matter yield of Sorghum slightly but did not stimulate the release of S from soil organic matter as does air-drying (Freney, 1958; Barrow, 1961; Williams, 1967). The authors explained that although the moisture content of the soils under plants reached wilting point, it never reached an air dry state and this was probably the reason for the lack of a drying effect.

A number of glasshouse and growth cabinet experiments carried out on S-deficient soils (e.g. Nicolson, 1970; Cowling and Jones, 1970) have been hampered by poor plant growth. Thus, in an attempt to correct such S-deficiencies, S has been added to soils in several glasshouse and growth cabinet studies investigating S mineralisation (Freney and Spencer, 1960; Cowling and Jones, 1970; Jones et al., 1972; Bettany et al., 1974). Reports on the effect of S addition on the results of such mineralisation studies have been conflicting. For example, in a growth cabinet experiment, Bettany et al. (1974) found that addition of 25 μgSO_4-S g^{-1} of sulphate had no effect on S mineralisation in both S-deficient soils and soils containing adequate amounts of inorganic sulphate.

In contrast, other workers have shown that S addition can affect the mineralisation of S in soils. Freney and Spencer (1960), found under glasshouse conditions, that the addition of S resulted in net immobilisation of S in uncropped soils, but mineralisation of S in the presence of plants was increased by additions of S up to 20 $\mu g\ g^{-1}$ although immobilisation occurred when more than 20 $\mu gS\ g^{-1}$ was added. It was suggested that added sulphate stimulated plant growth, giving a more extensive root system in the soils, but when the added S was more than that required by plants, the excess sulphate would be immobilised. Nicolson (1970) also found that it was necessary to apply S in order to observe the effect of soil temperature on mineralisation, particularly at high temperature. Contrasting effects of S addition were, however, reported by Cowling and Jones (1970). It was found that even when only 20 $\mu gS\ g^{-1}$ was added, the rate of mineralisation of S in the soil under perennial ryegrass was reduced below that in uncropped soils. It would appear

that the effects of S addition on mineralisation of S depends upon the type of plant and the level of sulphate already present in the soil.

2.5.3 Field experiments

Little is known about the mineralisation of soil organic S under field conditions as most investigations have been based on laboratory incubation procedures and glasshouse experiments (Freney et al., 1971; Bettany et al., 1974; Freney et al., 1975). Despite the favourable environments provided in many of these investigations, generally only small amounts of S have been mineralised (McLaren and Swift, 1977).

In field experiments, the mineralisation of S in soils can be studied in the natural environment under the influence of rainfall, leaching, growing plants and fluctuating conditions of temperature and moisture. Theoretically, field studies of S mineralisation involve measurements of the various inputs to and outputs from the available S pool. These include accessions of S in rainfall, plant uptake and leaching losses. As a result, such experiments demand a considerable amount of work, time and money. Furthermore they are subject to uncontrolled influences which may limit the application of the results to a particular situation. Because of these difficulties, little effort has been made to directly measure the mineralisation of S in the field situation although some similar types of studies have been carried out on soil nitrogen (Kowalenko and Cameron, 1978).

Mineralisation of soil S in the field has also been studied using a simpler and more convenient approach based on long term

changes in the total amount of organic S in soil. Williams and Lipsett (1961), for example, studied the changes occuring in New South Wales soils cultivated for wheat. The soils had carried at least 20 crops and had lost an average of 30 per cent of their organic matter duirng that period. McLaren and Swift (1977) studied the long term natural mineralisation process by comparing the level of organic S between soils under pasture and soils from adjacent sites on the same soil series that had been cultivated for many years. The levels of organic S in the arable soils were 16 to 60 per cent lower than in the corresponding pasture soils. The authors assumed that the lower levels of S in the arable soils were due to the mineralisation of organic matter brought about by cultivation.

A few workers have also examined the mineralisation of S under field conditions by studying the changes in soil sulphate concentrations. Seasonal changes in sulphate levels have been studied in a soil under subterranean clover pasture in Australia (Williams, 1968). It was found that sulphate accumulated in summer probably as a result of mineralisation of organic S under favourable moisture and temperature conditions, and the lack of plant uptake. The low levels of sulphate found in winter and spring were probably due to leaching and plant uptake, together with a low rate of mineralisation at the low soil temperature.

2.5.4 Field incubations

In an attempt to find a method which can combine the simplicity and convenience of incubation procedures with the realistic field environment, field incubation techniques have been developed for

studying the mineralisation process. Barrow (1969) used a field incubation method to observe seasonal changes of soil sulphate. The technique involved a series of 2-week incubations of soils at their field moisture content in sealed bottles placed in a louvred box set at ground level in the field. Such a method included the field temperature fluctuations but excluded the influence of plant uptake, rainfall and leaching. It was found that the rate of mineralisation of soil organic S during the winter months was very slow and even became negative because of the lower temperatures (Barrow, 1969).

Another field incubation technique involves incubating soils in polyethylene or plastic bags. This method was first used by Eno (1960) to examine nitrate production in the field. The polyethylene bag was considered to be permeable to oxygen and carbon dioxide but impermeable to water. Its use in such incubation studies has, however, been questioned by Bremner and Douglas (1971). They have shown that although polyethylene was more permeable than other types of plastic films, it was not sufficiently permeable to oxygen and carbon dioxide to permit its use in incubation studies. Their conclusion was based on a study using plastic films to seal incubation jars. In this situation only a small area of plastic films was used and this might restrict the air movement. When plastic bags are used, however, the larger surface area would probably allow sufficient diffusion of oxygen and carbon dioxide through the bags.

Eno (1960) has shown that the rate of nitrification in soil incubated in polyethylene bags for 6 weeks was the same as that in soil contained in ventilated bottles. Aeration in the bags was,

however, reduced when air was trapped in the bag. It was recommended that bags should be closed tightly against the soil to ensure maximum contact of soil with the film and, in turn, to improve aeration. Under a longer incubation period (5½ months), van Schreven (1968) found only a slightly reduced aeration of the soils in plastic bags used to determine nitrification.

The moisture contents of soils incubated in plastic bags have been generally at or near field capacity or 60 to 65 per cent of the maximum water holding capacity (Eno, 1960; Nelson, 1964; van Schreven, 1968; Boswell and Anderson, 1974). Only slight losses of soil moisture occurred during a 6-week incubation period in Eno's (1960) study. Van Schreven (1968) reported a 0.7 per cent loss of moisture when plastic bags were incubated in the laboratory for 5½ months, but a 0.4 per cent gain in the field incubation over the same period. The changes in moisture content were considered insignificant as they had no effect on nitrate production.

Among the literature reviewed, there has only been one study reported to have used polyethylene bags to study the mineralisation of S in soil (Nelson, 1964). The 6-month incubation was, however, carried out under laboratory conditions. No problems concerning aeration or moisture losses were reported.

Since the 'buried polyethylene bag' technique had proved to be sufficiently sensitive for studying the effect of soil temperature on nitrate production (Eno, 1960; van Schreven, 1968), the same technique should also be satisfactory for the study of S mineralisation in the field.

CHAPTER 3

CHAPTER 3 MATERIALS AND ANALYTICAL METHODS

3.1 Introduction

Studies on the mineralisation of S were conducted on 6 Tokomaru silt loam soils which varied in their soil organic matter contents. Bulk samples of these soils were collected in the summer (December, 1979) at the commencement of the studies, air-dried and stored in the laboratory. These bulk air-dried soils were used in the field pot experiment (chapter 4), the long term field incubation (chapter 5), the liming experiment and one of the short term field incubations (chapter 6) and the laboratory incubation (chapter 7). In one of the short term incubation studies (section 6.2.2), fresh samples were collected for each incubation and these field moist samples were incubated without prior drying.

The long term field incubation was carried out for 20 weeks from February to June, 1980. The field pot experiment was started later in mid-February and carried on to the same completion date. The short term (2-week) field incubations of both the bulk air-dried samples and the field moist samples were also started in mid-February and carried out at 2-week intervals over the same period. The liming experiment was carried out for 2 weeks in May, 1980.

3.2 Soils

3.2.1 Description

The soils used were samples of Tokomaru silt loam which is a moderately gleyed, yellow-grey earth derived from loess (New Zealand

Soil Bureau, 1968), and according to U.S.D.A. Soil Taxonomy (Soil Survey Staff, 1975) is classified as a sub-group 'typic fragiaqualf'. Soils were sampled to a depth of 8 cm from 6 different sites (for locations and full site descriptions, see Appendix I). Four of the sites (soils A, B, C, D) were established pastures of ryegrass and clover, which had received regular topdressing. One site (soil E) was a native pasture which had never received any fertilisers. The last site (soil F) was adjacent to one of the developed pastures (soil D) but it had been cultivated for barley for the past 4 years.

3.2.2 Sampling

Bulk samples were collected from the top 8 cm of soil at the end of December, 1979. Soils were passed through a 2 mm sieve, air-dried and stored in the laboratory.

The collection and treatment of fresh soil samples for one of the short term incubation studies will be described in the appropriate chapter (chapter 6).

3.3 Analytical and extraction methods

3.3.1 Sulphur analysis

Sulphur in the samples was analysed by reduction to sulphide and colorimetric determination using a slightly modified method of Johnson and Nishita (1952). Liquid samples were evaporated to dryness before being analysed whereas ground soil and herbage samples were analysed directly after ignition at 550C with a bicarbonate/silver oxide mixture (Steinbergs et al., 1962).

3.3.2 Total carbon and total nitrogen

Soils from the bulk air-dried sample (section 3.2.2) were analysed for total C by a Walkley-Black procedure (Allison, 1965) and total N by a semi-micro Kjeldahl method (Bremner, 1965).

3.3.3 Extraction of sulphate

(a) Phosphate extractable sulphate (Searle, 1979).

Samples (5 g) of sieved, air-dried soil (section 3.2.2) were shaken for 16 hours with 25 ml of 0.04M $Ca(H_2PO_4)_2$ adjusted to pH 4.0 at 20C. The extracts were centrifuged, filtered and analysed for S.

(b) Calcium chloride extractable sulphate (Williams and Steinbergs, 1959).

Samples (5 g) of sieved, air-dried soil (section 3.2.2) or a calculated equivalent weight of moist soil (based on measured moisture content) were shaken for 30 minutes with 25 ml of 0.01M $CaCl_2$. The extracts were centrifuged, filtered and analysed for S.

3.3.4 Soil pH

Samples (10 g) of sieved, air-dried soil (section 3.2.2) or a calculated equivalent weight of moist soil were mixed with 25 ml of distilled water (1:2.5 ratio), and left to equilibrate overnight. The pH was measured with a combined electrode pH meter.

3.3.5 Moisture content

Samples (10-20 g) of moist soil were placed in a pre-weighed tin, the total weight recorded and the tin placed in an oven at

105C overnight. The tin containing the oven-dried sample was weighed and the moisture content calculated using the equation:

$$\% \text{ Moisture content} = \frac{\text{total wet weight} - \text{total dry weight}}{\text{total dry weight} - \text{tin weight}} \times 100$$

CHAPTER 4

CHAPTER 4 FIELD POT EXPERIMENT

4.1 Introduction

Although there have been a number of studies on the mineralisation of S in soils, most of them have been carried out either in the laboratory or glasshouse, and relatively few under natural field conditions. Laboratory or glasshouse incubations are particularly useful for evaluating the effects of various factors such as temperature or moisture on the rate and extent of S mineralisation. Incubation techniques, however, do not include the effect of plants which is a potentially important factor influencing the mineralisation of S, and in the glasshouse and growth cabinet studies, even though plants are generally included, the enviornmental conditions are still artificially controlled. Since the mineralisation of soil organic S is a microbial process, it will be influenced by such enviornmental conditions. There are, therefore, a number of limitations to be considered when results from laboratory or glasshouse studies are applied to the field situation.

Mineralisation studies of S in the natural enviornment must be based on a mass balance approach which requires a knowledge of the inputs and outputs of S in the system under study. The apparent mineralisation over a given time period can be calculated by measuring the size of the available S pool before and after the period of interest and allowing for various inputs and outputs according to the equation:

$$\Delta S = (SO_4\text{-}S_F + S_P + SO_4\text{-}S_L) - (SO_4\text{-}S_I + S_A)$$

where ΔS = mineralised S

$SO_4\text{-}S_F$ = soil sulphate at the end of the experiment

S_P = S taken up by plants

$SO_4\text{-}S_L$ = sulphate in the leachate

$SO_4\text{-}S_I$ = initial soil sulphate

S_A = S in the rainfall.

Although the principle on which this balance approach is based seems relatively simple, it is often difficult to quantitatively determine some of these parameters in the field, particularly the atmospheric inputs and the leaching losses of S. There can also be a large degree of field variability in the two measurements of soil sulphate. These difficulties, together with the fact that the actual amount of S mineralised may be a small number calculated as the difference between relatively much larger numbers can lead to substantial errors. Special techniques must therefore be employed if reliable estimates of mineralisation in the field are to be obtained.

In this experiment, a 'field pot method' was used to study the mineralisation of soil S in the presence of growing plants in the field. The method enabled direct measurements to be made of both the leaching losses and plant uptake of S from the soils in the pots. Field variations were also minimised since the soils were sieved prior to potting. The experiment was conducted on the site where S accessions in the rainfall have previously been measured (Smith, 1979).

4.2 Materials and methods

Tokomaru silt loam soils from 6 sites were used (see section 3.2.1). For a given soil, a sieved, air-dried sample (section 3.2.2) of 300 g was placed in a plastic pot which had drain holes in the bottom. The pot was then watered to bring the soil to 80 per cent field capacity. The field capacity was determined on sieved samples of soil B at -40 cm pressure potential. Thirty five perennial ryegrass seeds (Lolium perenne L.) were sown in each pot and the pots kept in a glasshouse for 10 days until the ryegrass had germinated. Soil moisture was maintained by daily weighing and addition of deionised water. The pots were then placed outside the glasshouse during the day for another 10 days in order to harden the plants. After the hardening period (20 days from sowing), the seedlings were thinned to 15 plants per pot and the pots transferred to the trial area. Plant-free pots of each soil were also included and were treated similarly to the pots containing plants. All treatments were replicated 3 times to give a total of 36 pots (6 soils x 2 treatments x 3 replicates).

In the field, each pot was placed inside another similar container already set in the ground (figure 4.1). This second pot acted as a leachate receiver and had a plastic tube attached to the bottom to carry the leachate to a collecting bottle. The top of the pot containing the soil under study was at the same level as the surface of the field soil so that temperature fluctuations were as realistic as possible. The pot containing plants and the plant-free pot of the same soil were located in the field so that the leachate drained from each pot into separate bottles in the same hole (figure 4.1). Replicates of all soils (6 soils x 3 replicates)

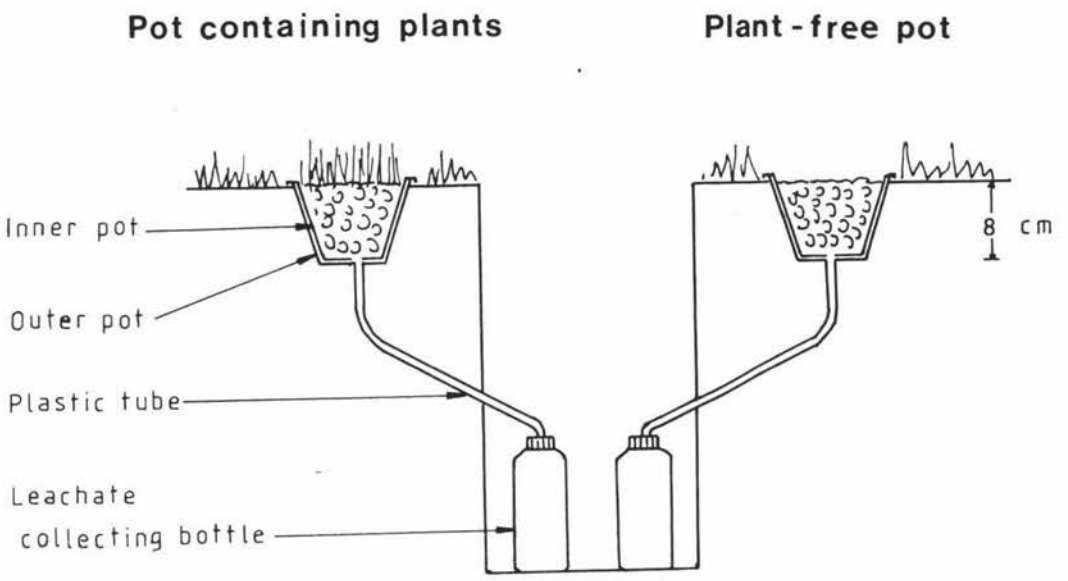

Figure 4.1 Experimental arrangement for a replicate of one soil in the field pot experiment. The pot containing plants and the plant-free pot drain into separate leachate collecting bottles placed in the same hole.

were then completely randomised across 18 holes dug in a grid pattern. Such an arrangement of the pots enabled the results to be statistically analysed according to a split-plot design.

The plants were ready for a harvest at 8 weeks. The herbage was cut, dried at 60C and stored until ready for analysis of total S. When the trial was completed after 13 weeks, plants were again cut and dried at 60C. The herbage was combined with that from the first harvest, weighed, ground and analysed for total S (section 3.3.1). Soils in the pots containing plants were found to be extensively bound by roots which held the soil together forming a solid mass. After weighing, the soils were therefore cut into quarters in order to facilitate the separation and recovery of roots from soils. Diagonal quarters were combined, weighed and roots were separated from the soil by placing the two quarters of soil on a sieve and washing with running water. The washed root material was dried at 60C, ground and analysed for total S (section 3.3.1). The results from these two quarters were then corrected back to a whole pot basis. Soils in the other two quarters were pushed through a sieve to separate the roots. Subsamples were taken without prior drying for the determination of $CaCl_2$-extractable sulphate, pH and water content (sections 3.3.3 - 3.3.5). Soils from plant-free pots were also pushed through a sieve and subsamples were taken for the analyses listed above.

Samples of the leachate in the bottles were taken after 4 weeks when the bottles were almost full, and again at the completion of the trial. At each sampling, the volume of the leachate in each bottle was measured, and a subsample collected, filtered and stored at -1C until ready for analysis of sulphate (see section 3.3.1).

4.3 Results and discussion

4.3.1 Chemical characterization of the soils

The amounts of sulphate extracted from the 6 soils by $CaCl_2$ ranged from 6.4 μgSO_4-S g^{-1} in soil D to 29.5 μgSO_4-S g^{-1} in soil B (table 4.1). The high concentrations of soluble sulphate in soils A and B were probably related to the substantial topdressing history of the well-developed pastures on these soils (see Appendix I). Relatively lower levels of sulphate were found in soils C and D which came from less developed pastures, and also in soil E under unfertilised native pasture. Among the pasture soils (A to E), the amounts of total S ranged from 515 $\mu g\ g^{-1}$ in soil A to 402 $\mu g\ g^{-1}$ in soil D (table 4.1). There was a significant correlation ($r = 0.899^{*}$) between the amounts of sulphate and total S present in the pasture soils suggesting that soils with high total S tend to maintain high levels of soil sulphate.

Soil F is different from the other five soils in that it has been cultivated for 4 years and its total S content is therefore the lowest of all the soils, at 362 $\mu g\ g^{-1}$. Despite this, however, its sulphate level is intermediate in relation to the levels of pasture soils, probably because it has been well topdressed with fertilisers (except for N). It also had the lowest C:S (85) and N:S (6.0) ratios of all the soils.

4.3.2 Field pot experiment

After a plant growth period of 13 weeks, the amounts of sulphate remaining in the soils were remarkably uniform, ranging from 3.2 μgSO_4-S g^{-1} in soil F to 4.6 μgSO_4-S g^{-1} in soil B (table 4.2). The decrease in soil sulphate level varied from only 2.4 μgSO_4-S g^{-1}

Table 4.1 Some chemical and physical properties of the 6 Tokomaru silt loam top soils (0 - 8 cm) used in the study

Soil	Soil sulphate $\mu gSO_4\text{-}S\ g^{-1}$	Total S $\mu gS\ g^{-1}$	Total C %	Total N %	C:S	N:S	C:N	pH	Bulk density $kg\ m^{-3}$
A	26.7	515	4.69	0.324	91	6.3	14.5	6.25	1338
B	29.5	478	4.77	0.352	100	7.4	13.6	6.56	1291
C	12.1	423	4.60	0.360	109	8.5	12.8	5.62	1175
D	6.4	402	4.66	0.314	116	7.8	14.8	5.97	1263
E	10.1	434	6.51	0.405	150	9.3	16.1	5.16	1086
F	19.3	362	3.09	0.216	85	6.0	14.3	5.95	1227

Table 4.2 Changes in levels of soil sulphate, amounts of S removed by plant uptake and leaching, and the calculated mineralisation of S in the presence and absence of plants in a field pot experiment conducted on 6 Tokomaru silt loam soils.

Soil	Initial soil sulphate	Final soil sulphate	Changes in soil sulphate	Plant uptake of S	Leached S	Mineralised S[#]	
	μgSO_4-S g^{-1}			μg S g^{-1}			
(i) With plants							
A	26.7	4.3	22.4	17.3	26.9	21.3	a*
B	29.5	4.6	24.9	16.8	28.2	19.6	a
C	12.1	3.7	8.4	20.8	3.6	15.5	ab
D	6.4	4.0	2.4	11.9	2.4	11.4	b
E	10.1	3.5	6.6	15.0	4.4	12.3	b
F	19.3	3.2	16.1	8.2	19.8	11.4	b
(ii) Without plants							
A	26.7	6.0	20.7	-	35.2	14.0	Aa
B	29.5	6.7	22.8	-	36.0	12.7	ABa
C	12.1	5.1	7.0	-	12.9	5.4	Cb
D	6.4	5.5	0.9	-	7.0	5.6	Cb
E	10.1	4.8	5.3	-	14.2	8.4	BCb
F	19.3	5.8	13.5	-	25.9	11.9	ABa

[#] Mineralised S was calculated from: Plant uptake of S + leached S - changes in soil sulphate - atmospheric S. Addition of atmospheric S is 0.5 $\mu gS\ g^{-1}$ (calculated from Smith, 1979).

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

in soil D to 24.9 μgSO_4-S g^{-1} in soil B and was found to be greater in soils with higher initial sulphate levels. The reduction was more than half of the initial level of sulphate present in all soils except in soil D which had only 6.4 μgSO_4-S g^{-1} of sulphate initially.

The pattern of changes of sulphate in the soils in the fallow pots was similar to those observed in the pots containing plants. The amounts of sulphate remaining in the soils after 13 weeks were slightly higher than when plants were present and they ranged from 4.8 μgSO_4-S g^{-1} in soil E to 6.7 μgSO_4-S g^{-1} in soil B (table 4.2). The decreases in soil sulphate were therefore smaller in the absence of plants, ranging from 0.9 μgSO_4-S g^{-1} in soil D to 22.8 μgSO_4-S g^{-1} in soil B.

The amounts of S taken up by plants from the five pasture soils varied from 11.9 $\mu gS\ g^{-1}$ in soil D to 20.8 $\mu gS\ g^{-1}$ in soil C (table 4.2). The plant uptake of S in the low-sulphate soils (C, D and E) was greater than the initial level of soil sulphate but this was not the case in the other two soils with higher sulphate levels (soils A and B). The amount of S taken up by the plants from the arable soil (F) was only 8.2 $\mu gS\ g^{-1}$, the lowest of all the soils. This relatively low plant uptake was possibly due to an N-deficiency resulting in poor growth, as indicated by an extremely low dry matter yield compared with the other soils (see Appendix II).

It should also be noted that the overall growth of ryegrass on all soils was somewhat poorer than expected. There was a problem of fungus disease in the early stages of growth and it was necessary to apply a S-free fungicide to all pots to overcome the problem. This early check in the growth of ryegrass might have been responsible

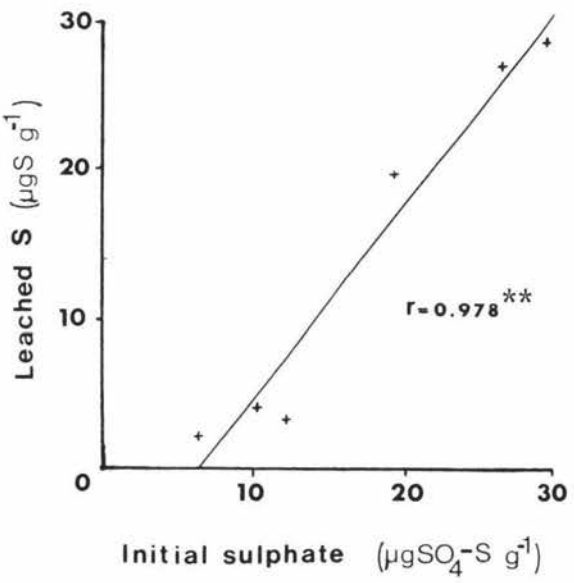

Figure 4.2 Relationship between the amounts of S leached from 6 Tokomaru silt loam soils in the presence of plants and the initial soil sulphate levels.

for the poor dry matter yields overall.

In the presence of plants, the amounts of sulphate leached varied from only 2.4 μgSO_4-S g^{-1} in soil D to 28.2 μgSO_4-S g^{-1} in soil B and were strongly related to the initial levels of soil sulphate (figure 4.2). Leaching losses of S from the high-sulphate soils (A and B) were approximately the same as the initial soil sulphate concentrations, while in the low-sulphate soils (C, D and E), losses were less than half of the initial levels of soil sulphate. In comparison with the plant uptake of S, the amounts of S leached were higher in soils with high sulphate levels (A and B) but lower in the low-sulphate soils (C, D and E). The arable soil (F) behaved similarly to soils A and B in this respect.

Leaching losses of soil sulphate are dependent mainly upon the concentration of soil sulphate present at the time and the quantity of leaching water. During the 13-week growth period, the pots received 275 mm of rainfall which amounted to 2160 ml for each pot. The volumes of leachate were very similar in all soils with an average of 1130 ml or 52 per cent of the rain water received (see Appendix III). The concentration of soil sulphate present at any given time was governed by the amounts initially present in the available pool and the amounts of S taken up by plants and released by mineralisation. Growing plants act as a continuous drain on the available S pool in soil and tend to reduce the amount of available S which is susceptible to leaching. The amounts of S leached are therefore expected to be partly governed by the extent of plant uptake. In other words, the greater the plant uptake, the smaller the available S remaining in the soil, and thus the lower the amounts of S leached. However a direct correlation between leaching

losses and plant uptake of S was not found in this experiment probably because of the different initial levels of soil sulphate and different rates of mineralisation.

In the absence of plants, leaching losses of S varied from 7.0 μgS g^{-1} in soil D to 36.0 μgS g^{-1} in soil B (table 4.2). In all soils leaching losses of S were greater than the losses in the presence of plants and these increases were statistically significant for all soils (see Appendix IV). Leaching losses of S in the absence of plants exceeded the levels of sulphate initially present in soils. This clearly illustrates the influence of growing plants in reducing leaching losses of soil S. Other experimental evidence in support of reduced leaching losses of S in the presence of plants is lacking. There is, however, sufficient evidence from nitrogen studies (Allison, 1959; Raney, 1960) to support this finding of greater S movement in uncropped than in cropped soils. As in the presence of plants, the amounts of S leached were strongly dependent upon the initial concentrations of soil sulphate (figure 4.3).

Leaching losses of S from these soils in terms of kgS ha^{-1} were calculated by assuming a soil depth of 8 cm (the depth of the pots) and using the bulk density of each soil (table 4.1). Losses in the presence of plants ranged from 2.4 kgS ha^{-1} in soil D to 29.1 kgS ha^{-1} in soil B (table 4.3). The average loss was 14.5 kgS ha^{-1} which is relatively large compared to the findings of Smith (1979) who obtained losses of 7.5 kgS ha^{-1} in tile drainage over the winter period from a Tokomaru silt loam which had not been topdressed for 6 months prior to the experiment. This large discrepancy may be attributed to the fact that leaching in this experiment was measured as losses from the top 8 cm of the soil whereas losses in Smith's

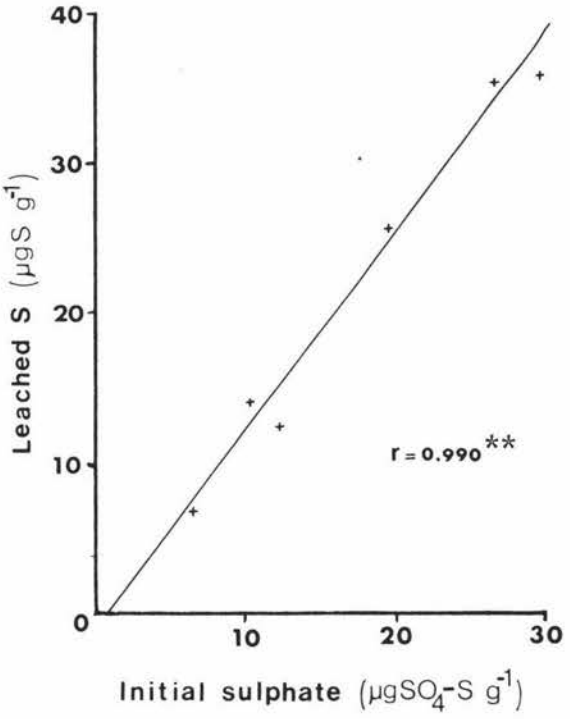

Figure 4.3 Relationship between the amounts of S leached from 6 Tokomaru silt loam soils in the absence of plants and the initial soil sulphate levels.

Table 4.3 Leaching losses of soil S, in the presence of plants, from 6 Tokomaru silt loam soils in a field pot experiment

Soil	Leaching losses kgS ha^{-1}
A	28.8
B	29.2
C	3.4
D	2.4
E	3.8
F	19.4
Average	14.5

(1979) study were taken at 45 cm which was the depth of the mole drains. Sulphate that is leached out of the top soil could be adsorbed in the subsoil because of the likely higher clay content, and less competition from phosphate which is normally present at a lower level than in the top soil (Metson, 1979). If this adsorption does occur in the subsoil it would explain the discrepancy in these findings. Whether this adsorbed sulphate in the subsoil is considered lost from the system or not, depends on its availability to plants, which is influenced by their rooting depth.

It can be concluded that of the two processes removing S from the available pool in soils, leaching losses of S were more significant than plant uptake in soils with high initial sulphate levels (soils A, B and F) and the opposite was true in soils with low sulphate levels (soils C, D and E). However, it should be noted that in this experiment plant growth was not as substantial as expected and if there had been better growth, plant uptake of S might have been more important than leaching.

The amounts of S mineralised from soils under growing plants ranged from 11.4 $\mu gS\ g^{-1}$ in soil D to 21.3 $\mu gS\ g^{-1}$ in soil A (table 4.2). In the low-sulphate soils (C, D and E), more S was mineralised from organic matter than was initially present in the available pool. The reverse was found in the soils with high sulphate levels (A and B).

The amounts of S mineralised were not directly related to either plant uptake or leaching losses of S alone. This is not surprising since both components affect the amounts of available S and they are also interactive. It is shown in figure 4.4 that the amounts of S mineralised from all soils were closely related to the sum of the amounts of S removed by plant uptake and lost by leaching. It is

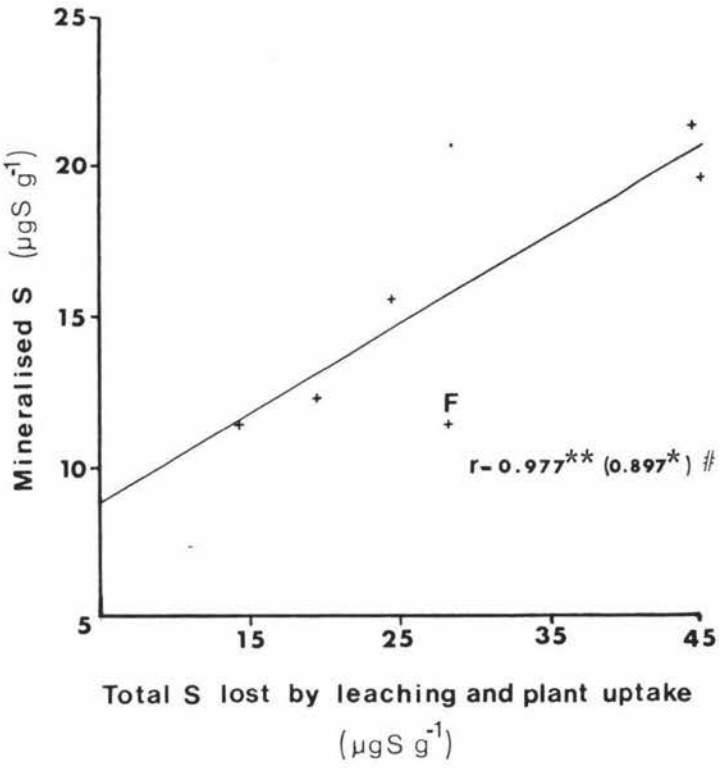

Figure 4.4 Relationship between the amounts of S mineralised from 5 Tokomaru silt loam pasture soils and the total amounts of S lost from the soils by leaching and plant uptake.

(# Correlation coefficient for all 6 soils including the arable soil,F)

not clear whether high leaching losses and plant uptake of S led to high rate of S mineralisation or whether it was the fact of a high rate of mineralisation which encouraged more leaching and plant uptake. By removing S from the available pool in soil, both plant uptake and leaching could be expected to drive the mineralisation-immobilisation balance towards net mineralisation. On the other hand, the greater rate of S mineralisation leading to higher concentrations of available S could result in higher plant uptake and leaching losses of S. It is likely that both mechanisms operate in soils.

Highly significant relationships were found for the amounts of S mineralised with total soil S and with initial sulphate levels in all soils (table 4.4). It should be noted that initial soil sulphate levels were closely related to total amounts of soil S ($r = 0.899^{*}$). It is likely that total S in soil may be more important in governing the amounts of S mineralised than the initial sulphate levels which are merely a consequence of the total S level.

There are no significant correlations between the amounts of S mineralised and other soil properties such as total C, total N, soil pH, C:S and N:S ratios (table 4.4), although the correlations for C:S and N:S ratios did approach significance. These findings are in general agreement with those of several other workers (see section 2.4.1).

It should be noted that the relationships between the amounts of S mineralised and various soil properties (table 4.4) were less apparent when the arable soil (F) was included. Soil F had not only the lowest amount of total S but also a different composition of organic matter in terms of C:S, N:S and C:N ratios (table 4.1).

Table 4.4 Correlation coefficients for relationships between the amounts of S mineralised from 5 Tokomaru silt loam pasture soils and selected soil properties

(Figures in brackets refer to correlations in which the arable soil (F) was included)

Soil properties	With plants		Without plants	
Total S	0.936*	(0.920**)	0.963**	(0.494)
Initial soil sulphate	0.932*	(0.813*)	0.921*	(0.894*)
Total C	-0.428	(0.061)	-0.048	(-0.249)
Total N	-0.275	(-0.254)	-0.118	(-0.312)
C:S ratio	-0.784	(-0.397)	-0.480	(-0.544)
N:S ratio	-0.775	(-0.296)	-0.685	(-0.701)
pH	0.704	(0.619)	0.619	(0.600)

* Significant at 5% level

** Significant at 1% level

In contrast to the pasture soils (A to E), soil F had been cultivated and cropped for 4 years and therefore its forms and amounts of organic S were likely to be different from those in pasture soils. It is differences such as these which have probably been responsible for the failure to obtain significant relationships between total soil S and the amounts of S mineralised in studies covering a wide range of soil types (e.g. Freney and Spencer, 1960; Jones et al., 1972). Nelson (1964) and Swift (1977) were among the few workers who were able to demonstrate such relationships. In this study, differences in total S content alone could account for more than 80 per cent of the variation in the amounts of S mineralised from these soils. This suggests that total S content would provide a good indication of how much mineralisation of S may potentially occur within a soil type.

It has been mentioned that the amounts of S mineralised differed between the 6 soils and that the differences were not strongly related to any individual soil properties except total S and initial sulphate levels. It is likely that, since mineralisation is a microbial process, many factors would interact to influence the rate and amounts of S mineralised from soils. It is therefore difficult to obtain a simple relationship with any one of these properties. However, it is possible to show which soil properties in combination best explain the pattern of S mineralisation by using multiple regression analysis (table 4.5). It was found that almost all of the variation in the amounts of S mineralised could be explained by a combination of total S, C:S ratio and total N.

Assuming a soil depth of 8 cm and the bulk densities presented in table 4.1, the amounts of S mineralised from the pasture soils

Table 4.5 Multiple correlation coefficients (R) for relationships between the amounts of S mineralised from 5 Tokomaru silt loam pasture soils and selected soil properties

(Figures in brackets refer to correlations in which the arable soil (F) was included)

With plants			Without plants		
Soil properties	R		Soil properties	R	
Total S	0.936*	(0.920**)	Total S	0.963**	
C:S ratio	0.980**	(0.984**)	Initial soil sulphate	0.968*	(0.894*)
Total N	0.999**	(0.996**)	C:S ratio	0.984**	(0.985**)

during the 13 weeks of this experiment ranged from 10.1 kgS ha^{-1} in soil E to 22.9 kgS ha^{-1} in soil A and averaged 16 kgS ha^{-1} (table 4.6). It is possible that if the experiment was carried out over a 12-month period, the amounts of S mineralised from these soils would have been even higher. The amounts of S released would also be higher if a soil depth greater than the 8 cm used in this experiment is considered (e.g. a soil depth of 15 cm assumed in the model in chapter 1).

In comparison to the calculated figure of 19 kgS ha^{-1} for the amount of S mineralised (figure 1.1), the average result of 21.5 kgS ha^{-1} obtained in 13 weeks from the soils with high organic S (A and B) was relatively high. The greater rate of mineralisation in the experiment may be due in part to an initial flush of S mineralisation caused by prior air-drying of the soils. There have been a number of workers reporting the increased mineralisation of soil organic S due to drying of soils (Biederbeck, 1978). However, as no other investigations have been reported on S mineralisation in soils involving growing plants as well as leaching, there are no other published results available for comparison.

The percentage of total S mineralised from all soils ranged from 2.8 in soils D and E to 4.1 in soils A and B (table 4.6). It was surprising to find that the percentage of S mineralised was positively related to the total amounts of S in soils. In other words, the higher the total soil S, the greater proportion was mineralised. This is in contrast to Walker's (1957) suggestion that 1.25 per cent of total S would be mineralised each year from most soils regardless of their total S content. If a higher proportion of total S is mineralised as organic S accumulates in

Table 4.6 Amounts of S mineralised from 6 Tokomaru silt loam soils in the presence of growing plants in a field pot experiment expressed as a percentage of total soil S and as kgS ha^{-1}

Soil	Mineralised S	
	% of total S	kgS ha^{-1}
A	4.1	22.9
B	4.1	20.1
C	3.7	14.6
D	2.8	11.6
E	2.8	10.9
F	3.1	11.3
Average of pasture soils (soils A - E)	3.5	16.0

soils, it is likely that the equilibrium plateau will be reached in a shorter time period and at lower total soil S level than those suggested by Walker (1957). This could well be another reason which explains the conflict between the estimates used by Walker (1957) and those in the model in chapter 1.

Among the pasture soils, the average proportion of total S mineralised was 3.5 per cent (table 4.6) which is comparable to the 3.2 per cent obtained by Lee and Speir (1979) from a Marton silt loam, a similar soil to the Tokomaru silt loam used in this study. In their study, the range of percentages of total soil S mineralised from 12 different New Zealand soils during a 21-week growth period at 25C was 0.8 to 3.3 per cent. The percentage figures obtained in this experiment are also within the range of 1 to 6.5 per cent of total S mineralised found in several mineralisation studies involving plants (Freney and Spencer, 1960; Nelson, 1964; Cowling and Jones, 1970; Nicolson, 1970).

In this experiment the mineralisation of soil organic S was also assessed in the absence of growing plants. The amounts of S mineralised from the bare soils ranged from 5.4 $\mu gS\ g^{-1}$ in soil C to 14.0 $\mu gS\ g^{-1}$ in soil A (table 4.2). In all pasture soils (A to E), the presence of plants increased the amounts of S mineralised (table 4.7), and for all but one soil (E) these increases were statistically significant. In relation to the amounts of S mineralised in the absence of plants, the increase due to growing plants varied from just over 50 per cent in soils A, B and E, to 100 per cent in soil D and 200 per cent in soil C. This is consistent with the results of Freney and Spencer (1960), Nicolson (1970), and Freney et al (1975), all of whom obtained several-fold

Table 4.7 Increases in the amounts of S mineralised from 6 Tokomaru silt loam soils due to the presence of growing plants in a field pot experiment

Soil	Increases in mineralised S $\mu gS\ g^{-1}$	Significance
A	7.3	*
B	6.9	*
C	10.1	*
D	5.8	*
E	3.9	N.S.
F	-0.5	N.S.

increases in the mineralisation of S in the presence of plants.

The presence of plants, however, had no effect on the mineralisation of S in the arable soil (F) (table 4.7). This is probably due to the very limited S uptake caused by the poor growth of ryegrass. As mentioned earlier, the dry matter production of ryegrass on soil F was considerably lower than the other soils due possibly to an acute nitrogen deficiency.

In the absence of growing plants, the amounts of S mineralised were closely related to the leaching losses of S (figure 4.5). It is not possible, however, from the evidence available to deduce which component was the dependent variable. High leaching losses reduce the amounts of S remaining in the available pool which, in turn, encourages more mineralisation of S from the organic pool. On the other hand, it is possible that a high rate of S mineralisation would increase the level of sulphate in the available pool, which could then be leached.

There were significant correlations for the amounts of S mineralised with total soil S (figure 4.6) and the initial sulphate levels, as was found in the presence of plants (table 4.4). The same explanation could be applied to this situation as to the case where plants were grown. In other words, total soil S was the major factor influencing mineralisation of soil S and a good correlation was obtained with the initial sulphate level only because the latter was closely related to total S. This relationship between the total soil S and the amounts of S mineralised was found to be insignificant if the arable soil (F) was included with the pasture soils (table 4.4). Soil F was markedly different from the pasture soils (A to E) in the correlation between the amounts of S mineralised and total soil S

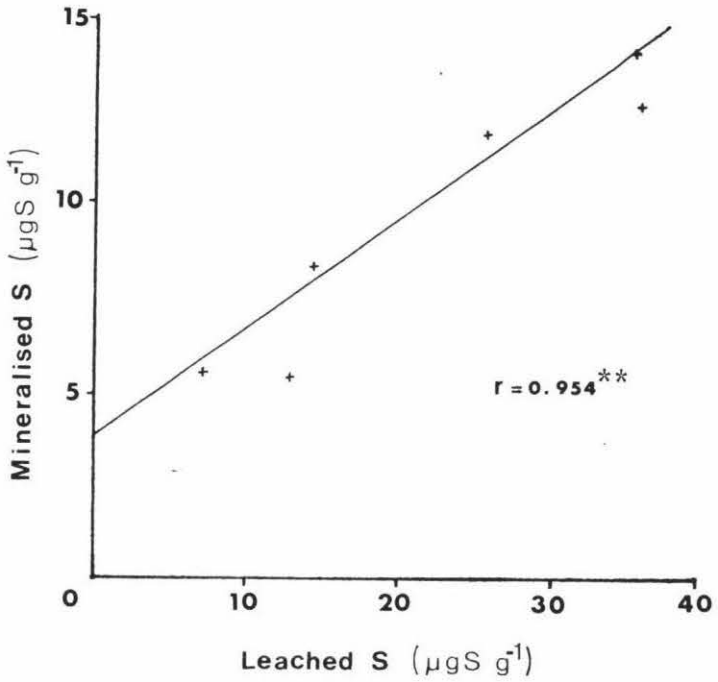

Figure 4.5 Relationship between the amounts of S mineralised from 6 Tokomaru silt loam soils in the absence of plants and the amounts of S leached.

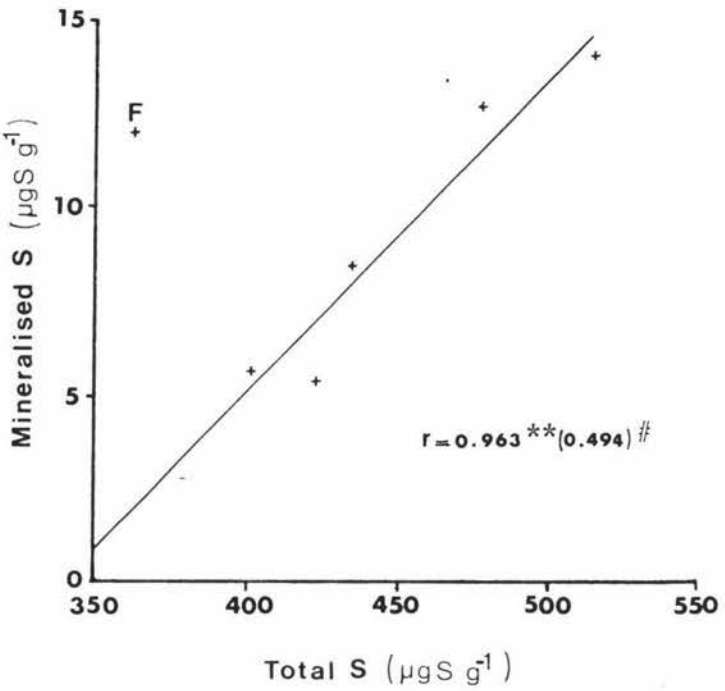

Figure 4.6 Relationship between the amounts of S mineralised from 5 Tokomaru silt loam pasture soils in the absence of plants and the total S content of the soils.

(# Correlation coefficient for all 6 soils including the arable soil, F).

(figure 4.6). Differences in the composition of organic matter as well as forms of organic S may have been responsible, as explained earlier.

The amounts of S mineralised in the absence of plants were not significantly related to other soil properties such as total C, total N, pH, C:S and N:S ratios (table 4.4). Using multiple regression analysis, it was shown that the three most important factors influencing the pattern of mineralisation of S were total S, C:S ratio and initial sulphate concentration (table 4.5).

4.4 Conclusions

The amounts of S mineralised from the 6 soils after a plant-growth period of 13 weeks varied from 10.9 kgS ha^{-1} in soil E to 22.9 kgS ha^{-1} in soil A. The percentage of total S mineralised (2.8 to 4.1) increased with increasing total S contents. Soils A and B were taken from the most well-developed pastures and had the highest levels of total S, suggesting that they were closest to an equilibrium level of organic S. The amounts of S mineralised from these two soils were similar with the average of 21.5 kgS ha^{-1}. This figure would probably be greater if the experiment was carried out over a 12-month period or if a soil depth greater than the 8 cm used in this experiment was considered.

The average mineralisation of 21.5 kgS ha^{-1} (or 4.1 per cent of total S) obtained from soils A and B is relatively high when compared with the calculated annual estimate in the model (19 kgS ha^{-1}) and much higher than the annual estimate (1.25 per cent of total S) suggested by Walker (1957). There are two possible reasons that may explain this discrepancy:

(i) The soils used in this experiment were initially air-dried and this can increase the initial rate of mineralisation (Biederbeck, 1978). The extent of the increase, however, was not likely to be sufficiently substantial or long-lasting to markedly affect the results.

(ii) The estimate of S mineralisation calculated in the model (19 kgS ha^{-1}) may be too low for the highest producing pastures on Tokomaru silt loam. It has been estimated that the maximum pasture production on the No 4 Dairy Farm on a Tokomaru silt loam near Massey University is 12,000 kg dry matter $ha^{-1}year^{-1}$ with an average herbage S content of 0.35 per cent. In an equilibrium situation, such production would indicate that the net annual rate of mineralisation would be 26 kgS ha^{-1} which is more comparable to the findings in this experiment.

The relatively high rates of S mineralisation observed in soils A and B would suggest that some Tokomaru silt loam soils under pastures are approaching the organic matter equilibrium assumed in the model and that such models may therefore be useful in predicting fertiliser inputs. On the other hand, some other soils (e.g. C, D and E) under less well-developed pastures are still further from the equilibrium situation and their rate of mineralisation of S is as low as half of that observed under the more developed situations.

Highly significant correlations were found between the amounts of S mineralised and the total S content in all soils. Differences in the level of total S in soils could account for more than 80 per cent of the variations in the amounts of S mineralised. The accumulation of organic S in soils within a soil type as reflected by total S content may therefore be a useful indicator of whether

the soil is approaching equilibrium or not and also the extent of mineralisation of S.

The presence of plants stimulated the mineralisation of S in all pasture soils (A to E) but this was not the case in the arable soil (F). The increases due to plants ranged from 3.9 kgS ha^{-1} in soil E to 10.1 kgS ha^{-1} in soil C. It has been suggested by several workers (e.g. Freney, 1967) that the increase is due to the rhizosphere effect which involves the excretion by plant roots of enzymes catalyzing the decomposition of soil organic matter. Another possibility is that plants can reduce the level of S in the available pool which is evident in this experiment by the lower final soil sulphate in presence of plants than in their absence. This reduced level of soil sulphate may increase the mineralisation of S in 2 ways:

(i) Less sulphate will be immobilised by soil microorganisms as a result of a lower sulphate level and this would lead to a net increase in mineralisation of S.

(ii) Low levels of soil sulphate may stimulate the synthesis of sulphatase enzymes by soil microorganisms which, in turn, will lead to an increase in the mineralisation of soil organic S.

It was noted that the presence of plants markedly reduced the leaching losses of S from all soils. This is apparently the first experimental evidence with regards to the influence of plants on the leaching of soil S (Gregg, 1976). The S leached from the top 8 cm soil as observed in this experiment may accumulate in the subsoil. The availability of the S accumulated in the subsoil depends on the rooting depth of plants and this will have significant consequences on the amounts of fertiliser S required.

CHAPTER 5

CHAPTER 5 LONG TERM FIELD INCUBATION

5.1 Introduction

In the past, the significance of the mineralisation of soil organic S has usually been evaluated using short term incubation procedures carried out under optimum laboratory conditions (McLaren and Swift, 1977). Such incubation procedures provide a simple and convenient means of assessing and comparing the ability of soils to mineralise organic S. Although the results obtained may indicate the potential capacity of a soil to mineralise organic S, this may bear little relationship to the actual rate and extent of S mineralisation achieved under less favourable environments in the field. Incubation techniques also have value in evaluating the effects of various factors such as temperature or moisture on the rate and extent of S mineralisation in soils. However care must be taken in extrapolating results of incubation studies, carried out under a series of constant temperatures or moisture levels, to the field situation where these parameters can vary markedly over short time periods.

Although field experiments such as that described in chapter 4 enable mineralisation of soil organic S to be studied under more realistic conditions including the influence of plants, rainfall and natural temperature, such experiments are time-consuming, expensive and are subject to uncontrolled variations which may limit the findings to the particular soil and site under study.

In an attempt to find a method which might overcome many of the difficulties listed above, a field incubation technique was used to

examine the mineralisation of soil organic S in 6 Tokomaru silt loam soils and the results obtained were then compared with those from the field experiment described in chapter 4. This technique has been described by Eno (1960) and combines the convenience of incubation techniques with realistic field temperature variations. The 'buried bag technique' has been used to study nitrate production in the field (Eno, 1960. van Schreven, 1968) but has not as yet been used to examine the mineralisation of soil organic S.

5.2 Materials and methods

The plastic bags were made of polyethylene sheet which was sufficiently thin (30 μm) to allow diffusion of oxygen and carbon dioxide (Eno, 1960). Samples (100 g) of sieved, air-dried soil (see section 3.2.2) were placed in the 15 x 25 cm plastic bags and distilled water was added to bring the soil to 'field capacity'. The field capacity was determined on sieved samples of soil B at -40 cm pressure potential and the moisture content was found to be 40 per cent. Although the soils used in this study were all taken from the top 8 cm of Tokomaru silt loams, there were differences in their structure and organic matter contents which resulted in them having slightly different moisture contents at 'field capacity'. It was decided that, to avoid confounding the experiment, all soils would be incubated at the same moisture content of 40 per cent although it is acknowledged that this resulted in some soils being 'wetter' than others. This was considered justified as mineralisation of soil organic S has been shown to be appreciably affected only at moisture levels greatly above or below field capacity (Williams, 1967).

The bag containing the soil sample was then tied so that the soil was spread evenly and there was very little free-space inside the bag. In the field, a turf (20 x 20 x 8 cm deep) was removed, the bag placed horizontally and the turf replaced over the bag. The bags were buried at randomly assigned locations in a grid pattern and those to be removed at each sampling time were randomly selected. Sufficient bags were prepared so that 4 replicates of each soil could be taken out at weeks 2, 4, 6, 8, 12, 16 and 20.

After the bags were brought into the laboratory at each sampling time, the soil in each bag was thoroughly mixed and duplicate samples were taken, without prior drying, for the determination of $CaCl_2$-extractable sulphate and moisture content (sections 3.3.3 and 3.3.5). A standard soil with a known level of $CaCl_2$-extractable sulphate was also analysed each day to check on analytical variability over time. Determination of soil pH was made at weeks 0, 12 and 20. Soil temperatures were recorded daily at 5 and 10 cm depths and weekly at 8 cm.

5.3 Results and discussion

During the 20-week incubation period, the net amounts of S mineralised varied markedly both within and between soils (figure 5.1). Within any one soil, there appeared to be a cyclic pattern of S release. Although there was no moisture loss from the bags, confirming that the polyethylene was impermeable to water, there were some variations in the moisture contents of the soils at analysis. As an extreme example, the moisture content of soil F decreased from 43 per cent to 33 per cent after 20 weeks. The moisture lost from the soil was not lost from the bags but

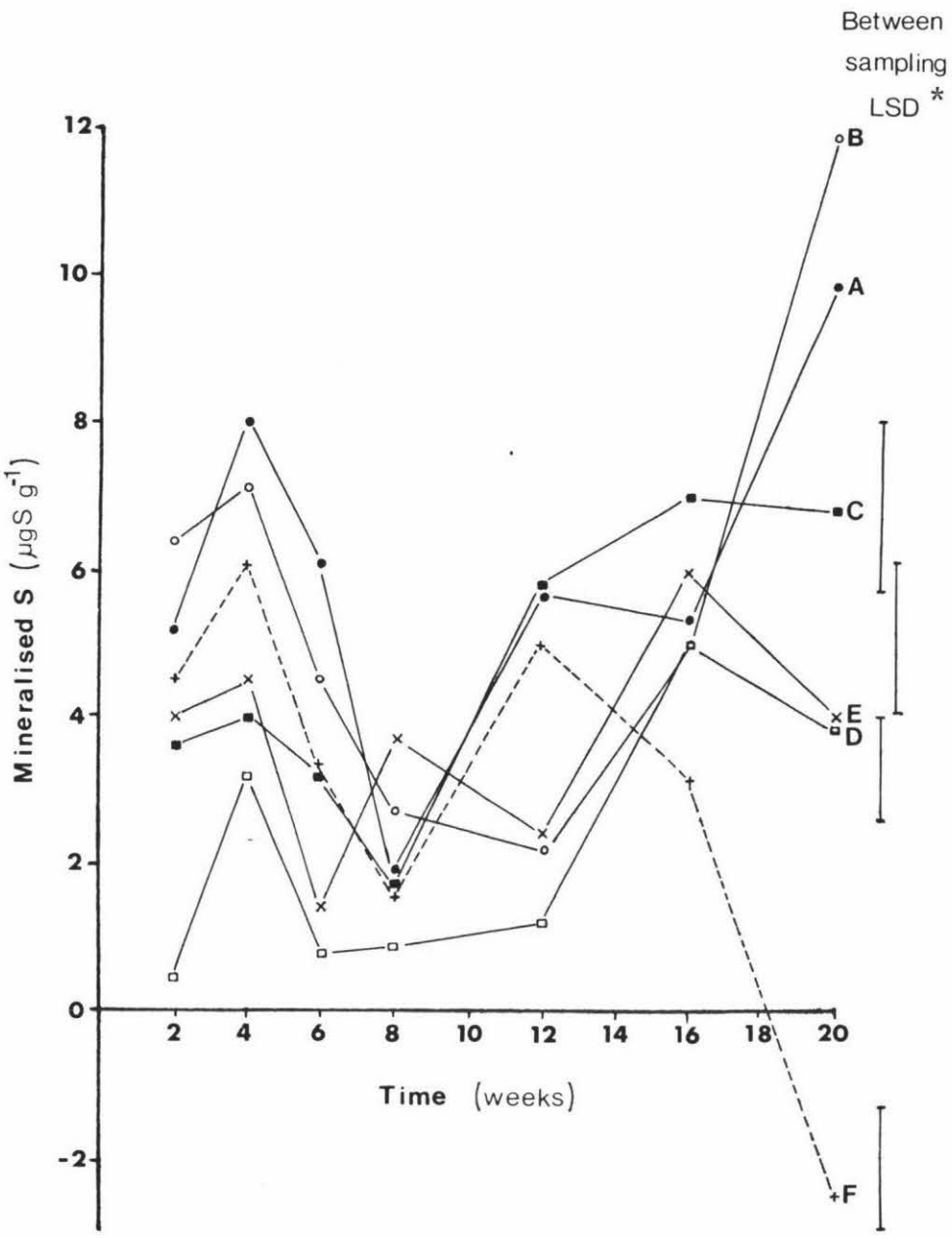

Figure 5.1 Amounts of S mineralised from 6 Tokomaru silt loam soils during a 20-week field incubation.

(* The absence of significant differences between sampling times for soils A and B was due to a large unexplained variation between replicates at one sampling date).

accumulated in the space between the soil and the polyethylene. Soil F was an arable soil having been cultivated for 4 years and was effectively structureless. When the soil was bagged and buried underground, it formed a compact mass inside the bags and gradually forced the water out.

It was found that when the soil in the bag was strongly compacted, there was a thin blue-grey layer in the center indicating a reduced zone. These local anaerobic areas were observed during weeks 8 and 16 in soil A which had the most weakly-developed aggregates among the pasture soils and was therefore easily compacted. The reduced layer was probably caused by restricted aeration in such a compact soil. The bag itself was permeable to oxygen and carbon dioxide since the reduced areas only existed in the center away from the soil-bag interface. It was found that when the samples from these anaerobic areas were analysed, the amounts of sulphate present were the same as those in the aerobic areas. This could be due to the extraction and analytical techniques. Sulphur in reduced forms in these areas was likely to be oxidised while the soil was taken out of the bag and later extracted. Furthermore any dissolved sulphides present in the extract would be measured by the reduction technique of analysis (Johnson and Nishita, 1952).

A few bags were found to have insect damage consisting of small holes apparently caused by grass grub. The extent of the damage was small in most cases and did not seriously affect the results. When relatively large holes were found, however, appreciable amounts of moisture were lost from the soil and the results of the analysis from such bags were not considered. It is suggested that some insect control measures should be considered if the 'buried bag

technique' is to be used in areas where there is an appreciable grass grub problem.

Changes in soil pH, measured at weeks 12 and 20, were very small (less than 0.3 unit) except in soils E and F (table 5.1). There was a decrease of 0.68 pH unit in soil E after 20 weeks but an increase of 0.75 pH unit in soil F. Most of the pH changes occurred during the first 12 weeks of the incubation. No obvious explanation can be given for these different pH changes.

Although mineralisation of soil organic S in a number of incubation studies (e.g. Williams, 1967; Kowalenko and Lowe, 1975b) has been shown to vary with time, Nelson (1964) and Haque and Walmsley (1972) are the only workers who have reported a cyclic pattern of mineralisation of soil S similar to that observed in this experiment (figure 5.1) but they did not offer any explanations.

At the conclusion of the experiment (week 20), the amounts of S mineralised from the pasture soils were at or near the highest level achieved at any prior stage (figure 5.1). The results at week 20 may therefore give an indication of the potential mineralisation of S from the pasture soils. The amounts of S mineralised at week 20 ranged from 3.8 $\mu gS\ g^{-1}$ in soil D to 11.9 $\mu gS\ g^{-1}$ in soil B, while the arable soil (F) showed a net immobilisation of 2.5 $\mu gS\ g^{-1}$ (table 5.2). Although the amounts of S mineralised during the 20 weeks in this experiment were only 30 to 60 per cent of the amounts obtained during the 13 weeks of the field pot experiment (chapter 4), the results from both experiments correlated well ($r = 0.932^{**}$). The greater extent of mineralisation of S in the field pot experiment despite the shorter time period may be attributed to the enhancing effect of plants and the influence

Table 5.1 pH values after 0, 12 and 20 weeks of a field incubation of samples of 6 Tokomaru silt loam soils

Soil	Week		
	0	12	20
A	6.25	6.45	6.47
B	6.56	6.64	6.79
C	5.62	5.40	5.41
D	5.97	5.63	5.85
E	5.16	4.50	4.48
F	5.95	6.79	6.70

Table 5.2 Amounts of S mineralised from samples of 6 Tokomaru silt loam soils in a long term (20 weeks) field incubation and in the presence of growing plants in a field pot experiment

Soil	Mineralised S ($\mu gS\ g^{-1}$)	
	Long term field incubation (20 weeks)	Field pot experiment (13 weeks)
A	9.8	21.4
B	11.9	19.5
C	6.8	15.5
D	3.8	11.5
E	4.0	12.5
F	-2.5	11.5

of leaching.

Since the amounts of S mineralised from all soils fluctuated markedly during the 20-week period, the ranking of a soil relative to others was found to depend upon the time of sampling. For example, the amount of S mineralised from soil C was the lowest of all pasture soils at week 4, but the highest at weeks 16 and 20 (figure 5.1). As a result, any correlations between the amounts of S mineralised and various soil properties also varied with the time of sampling (table 5.3). It is suggested that extreme care would be needed when extrapolating the results obtained by such an incubation technique to the field situation.

In comparison, there were relatively smaller variations in the final levels of soil sulphate during the 20-week period (figure 5.2), and consequently the correlations between the final levels of sulphate and several soil properties were similar at all sampling times (table 5.4). The final levels of sulphate in pasture soils correlated well with the levels of total S, suggesting that soils with high total S content tend to maintain a higher level of sulphate, through greater mineralisation, than soils with lower total S content. It is possible that there may be a certain 'equilibrium' level of sulphate in each soil beyond which no further net mineralisation will occur. If a soil is sampled in the summer when the sulphate level is approaching the 'equilibrium' level, it will mineralise very little S upon subsequent incubation. In comparison, incubation of samples collected in the winter would result in higher S mineralisation in order to bring the amounts of sulphate to the 'equilibrium' level.

Table 5.3 Correlation coefficients for relationships between the amounts of S mineralised from 5 Tokomaru silt loam pasture soils at weeks 4, 8, 16 and 20 of a long term field incubation and selected soil properties

Soil properties	Week			
	4	8	16	20
Total S	0.980**	0.240	0.525	0.810
Initial soil sulphate	0.965**	0.203	-0.439	0.965**
Total C	-0.188	0.827	0.166	-0.463
Total N	-0.157	0.877	0.525	-0.228
C:S ratio	-0.606	0.558	0.282	-0.761
N:S ratio	-0.725	0.447	0.583	-0.674
pH	0.671	-0.360	-0.664	0.805

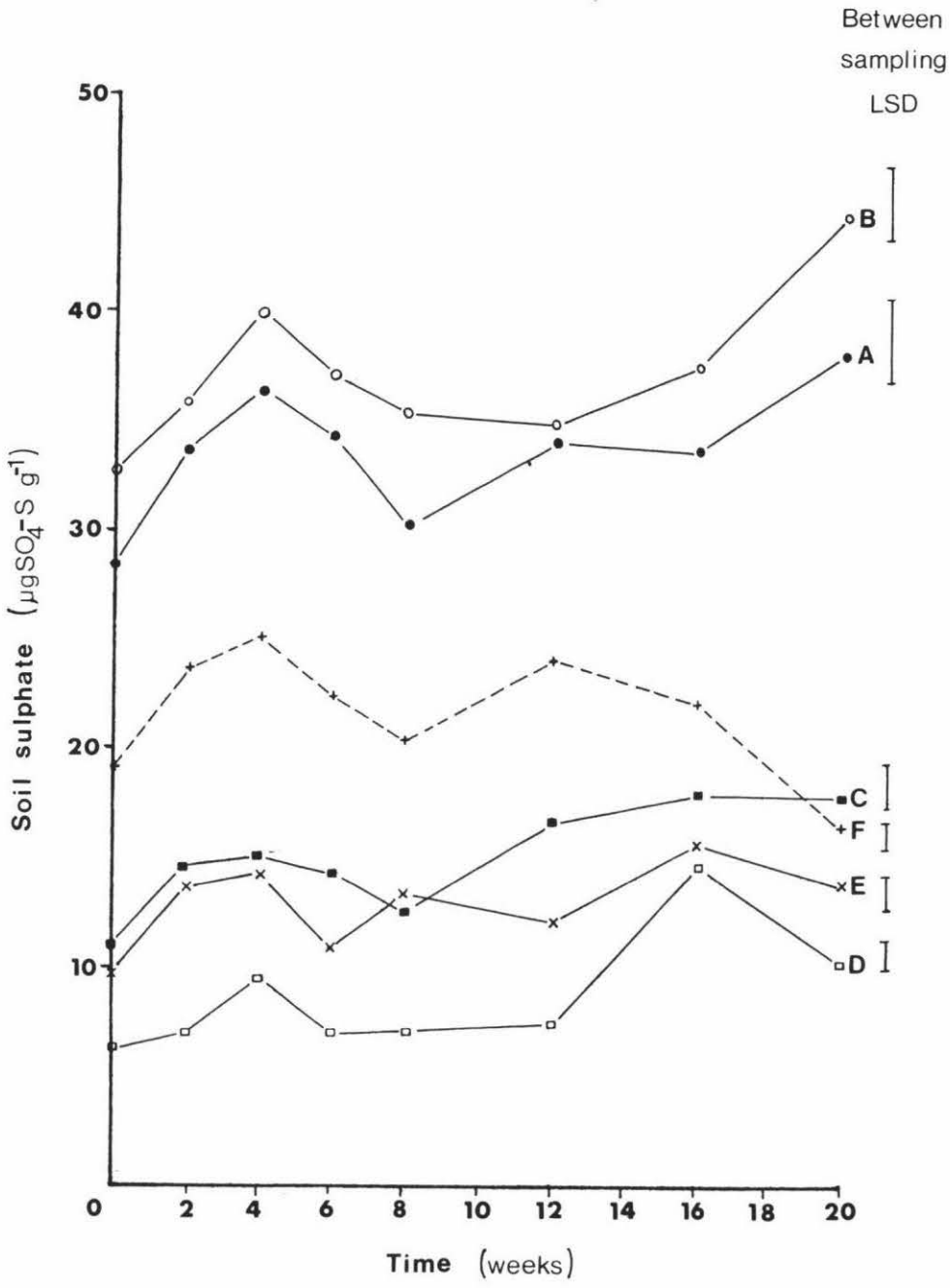

Figure 5.2 Sulphate levels in 6 Tokomaru silt loam soils during a 20-week field incubation.

Table 5.4 Correlation coefficients for relationships between the levels of sulphate in 5 Tokomaru silt loam pasture soils at weeks 4, 8, 16 and 20 of a long term field incubation and selected soil properties

(Figures in brackets refer to correlations in which the arable soil (F) was included)

Soil properties	Week			
	4	8	16	20
Total S	0.916* (0.639)	0.901* (0.654)	0.902* (0.705)	0.884* (0.802)
Total C	-0.298	-0.213	-0.309	-0.349
Total N	-0.197	-0.122	-0.170	-0.210
C:S ratio	-0.668	-0.612	-0.675	-0.699
N:S ratio	-0.717	-0.657	-0.690	-0.707
pH	0.775	0.741	0.764	0.798

'Mineralisation' of S in pasture soils as indicated by the final levels of sulphate after the 20-week incubation correlated well with the results from the field pot experiment (chapter 4) ($r = 0.937^{**}$). It should be noted that when the arable soil (F) was included, this correlation was less significant ($r = 0.853^{*}$). There were also no significant correlations between the final levels of sulphate and total S content when soil F was included (table 5.4). This could be due to differences in the forms of organic S and in the composition of organic matter in soil F as suggested in the previous chapter (section 4.3.2). When all soil properties were considered, it was found that almost all of the variations in the final levels of sulphate after 20 weeks could be explained by a combination of total S, soil pH and N:S ratio (table 5.5).

The cyclical pattern of S mineralisation and immobilisation observed in figure 5.1 suggests that there may be some type of 'end-product regulation' of the amounts of S mineralised during each incubation period. In other words, when the initial level of sulphate present at the beginning of an incubation period is high, the rate of mineralisation of S would be decreased or even become negative during that period. In all soils there were negative relationships between the amounts of S mineralised during each incubation period and the initial levels of sulphate present at the beginning of the period (figure 5.3). The relationships, however, reached significance only in soil E probably because of the small number of data points.

It has been suggested that sulphatase enzymes may play some part in the mineralisation of organic S in soils by hydrolysing organic sulphate esters and releasing sulphates (Freney and Swaby, 1975).

Table 5.5 Multiple correlation coefficients (R) for the relationship between the final levels of sulphate in 5 Tokomaru silt loam pasture soils at week 20 of a long term field incubation and selected soil properties

Soil properties	R
Total S	0.884*
Soil pH	0.952*
N:S ratio	0.996**

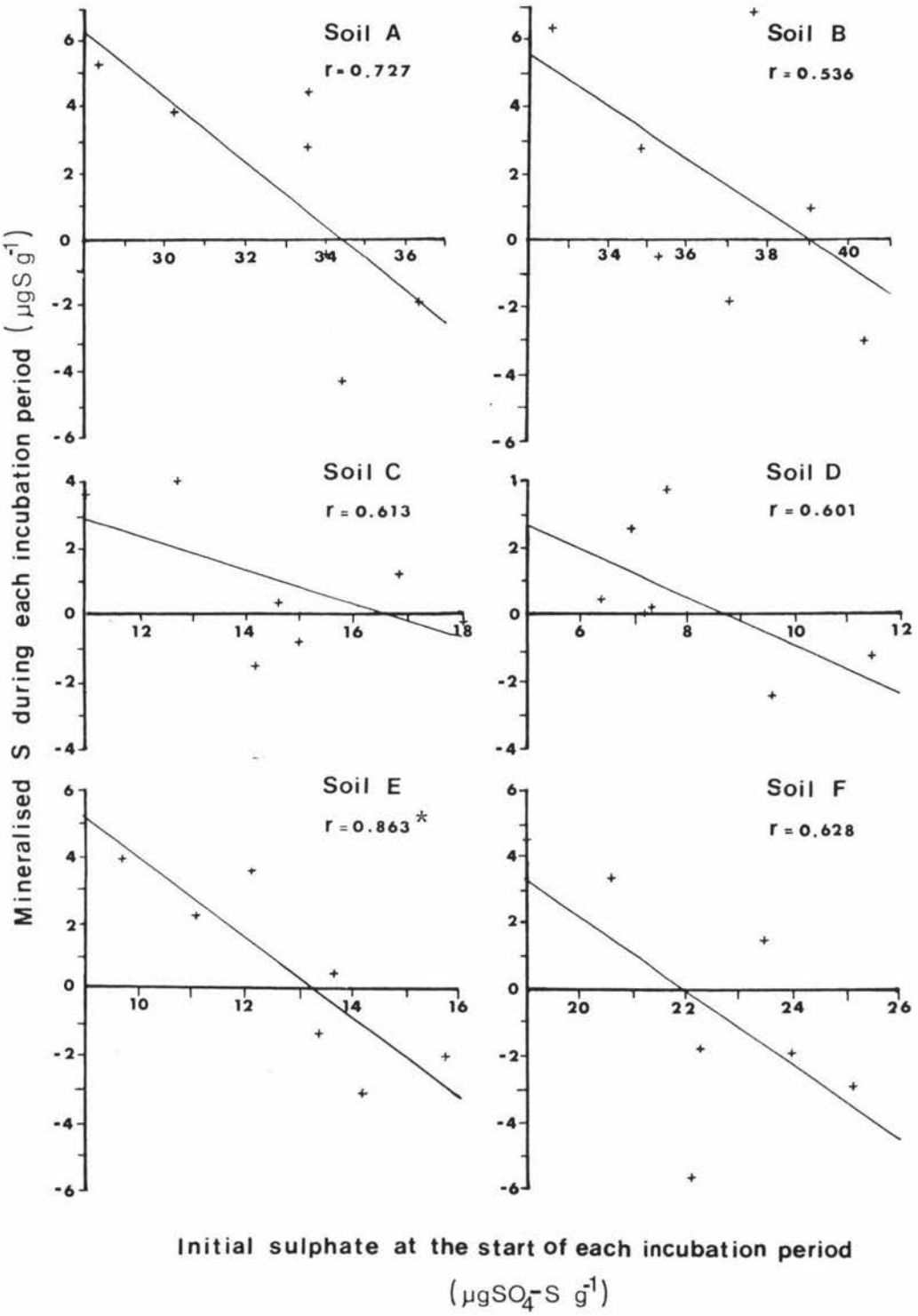

Figure 5.3 Relationships between the amounts of S mineralised during 7 successive 2-week incubation periods and the initial sulphate levels at the start of each period for 6 Tokomaru silt loam soils.

The microbial synthesis of these sulphatase enzymes has been reported to be subject to end-product regulation by sulphate (Fitzgerald, 1976). It is therefore possible that the sulphatase activity may be responsible in part for the decline in the rate of S mineralisation following the build-up of a high level of sulphate. However the significance of the contribution of soil sulphatases in mineralisation of soil S is still not fully understood (Lee and Speir, 1979). It is suggested that sulphatase enzyme activities should be determined during any future incubation studies.

When all pasture soils were considered together, the negative relationship between the amounts of S mineralised during each incubation period and the initial levels of sulphate present at the beginning of the period was absent (table 5.6). Its disappearance may be due to the differences in other properties between soils which could have some influence on the mineralisation process. In fact no significant relationships were found between the amounts of S mineralised between each sampling date and any individual soil properties (table 5.6). It is likely that since mineralisation of soil S is a microbial process, it would be affected by all soil properties acting together and, as a result, no simple or direct relationships between the amounts of S mineralised and individual soil properties can be established. This lack of direct relationships between S mineralised and various soil properties is consistent with several other incubation studies (Freney and Spencer, 1960; Williams, 1967; Kowalenko and Lowe, 1975b). It is, however, possible to show which soil properties in combination best explain the pattern of S mineralisation by using multiple regression analysis. It was found that a significant but relatively low proportion (53 per cent)

Table 5.6 Single and multiple correlation coefficients for relationships between the amounts of S mineralised from 5 Tokomaru silt loam pasture soils in the periods between each sampling date in a long term field incubation and selected soil properties

Soil properties	Single r	Multiple R
Initial soil sulphate		
- at the start of the experiment	0.156	
- at the start of each incubation period	0.036	0.639**
Soil temperature	0.092	0.691**
Soil pH	0.130	0.708**
Total C	-0.075	0.730**
Total S	0.131	
Total N	-0.037	
C:S ratio	0.123	
N:S ratio	-0.109	

of the variation in the amounts of S mineralised could be explained by a combination of the factors: initial levels of sulphate at the beginning of each incubation period, and at the start of the experiment, soil temperature, soil pH and total C content (table 5.6).

5.4 Conclusions

During the 20-week field incubation, the relative amounts of S mineralised from the 6 soils varied markedly with time. As a result any correlations between the amounts of S mineralised and various soil properties were also found to vary with the sampling time. Such variations cast doubts on the usefulness of such a technique in predicting what will happen in a field situation. There were, however, relatively smaller variations in the actual levels of sulphate during the incubation period and it was found that at all times the levels of sulphate were highly correlated with the amounts of S mineralised in the field pot experiment (chapter 4), and with the total S content of the soils. This would suggest that if an incubation technique is to be used, the amount of sulphate at the end of the incubation may be a better indication as to the ability of a soil to mineralise S in the field than is the actual amount released during the conduct of the incubation.

This may be explained as follows. The measured amounts of S mineralised in soils are the net result of both mineralisation and immobilisation processes which occur simultaneously. During an incubation, a soil will mineralise S until the level of sulphate reaches an 'equilibrium' at which, the rate of mineralisation

balances the rate of immobilisation. If this 'equilibrium' position is a characteristic of a soil under given environmental conditions, then the amounts of S mineralised during an incubation will depend on the initial level of sulphate relative to the 'equilibrium' level of sulphate for that soil under those conditions. This initial level of sulphate will vary according to what time of the year the sample is taken. A similar idea has been proposed by Barrow (1969). This author collected a soil at the end of summer, incubated it in the laboratory for 60 days, and suggested that the laboratory incubation may be thought of as a continuation of the mineralisation occurring in the field during summer. Consequently, the final level of sulphate at the end of laboratory incubation would give an indication of the mineralisation during summer plus that during laboratory incubation.

Thus it appears that the final 'equilibrium' level of sulphate may be more important in assessing the mineralisation potential of S in soils than the actual amounts of S mineralised as obtained from laboratory incubations.

The cyclical nature of the amounts of S mineralised also suggests that some type of 'end-product' regulation may be involved. In other words, within a soil, when the level of sulphate is high the rate of mineralisation is decreased. Support for this idea is given by negative relationships observed for each of the 6 soils between the amounts of S mineralised during an incubation period and the level of sulphate initially present at the beginning of that period. Since the enzyme sulphatases have been suggested to play some part in mineralisation of soil organic S and their microbial synthesis has been known to be subject to end-product regulation by

sulphate, it is possible that a decline in the rate of S mineralisation following the build-up of sulphate levels is due to a reduction in sulphatase enzyme production. It is suggested that sulphatase enzyme activities should be determined during any future incubation studies.

The 'buried bag' technique was satisfactory as a method for assessing the S mineralisation under field situations for these soils. It is however suggested that soils should be incubated at a lower moisture content, perhaps at 80 per cent of field capacity, in order to prevent anaerobic conditions from developing. Care must also be taken to avoid excessive compaction and therefore anaerobic areas in soils with poorly-developed structure.

CHAPTER 6

CHAPTER 6 SHORT TERM FIELD INCUBATIONS

6.1 Introduction

In general, the rate and extent of mineralisation of soil organic S determined by any procedure, whether in the laboratory, glasshouse or field, applies only to the particular soil being studied and to the environmental conditions at that time. To extrapolate the results to different soils, or even to the same soil under different conditions, requires detailed knowledge of the effects of such variables as pH, temperature, moisture and soil pretreatments (eg. air-drying), on the measurement of S mineralisation.

Many studies have been conducted examining the influence of soil moisture, pH, temperature and soil pretreatments on the mineralisation of S under laboratory conditions (eg. Williams, 1967; Chaudhry and Cornfield, 1967a, b). It is however likely that the influence of these factors on mineralisation may be different in a field situation in which moisture and temperature and thus microbial activity may fluctuate widely within short time periods. In this study, short term field incubations using the 'buried bag' technique, described in the previous chapter, were used to investigate the effects of temperature, moisture, pH, prior air-drying and time of sampling on the measurement of S mineralisation.

6.2 Materials and methods

6.2.1 Bulk sample incubation

Air-dried samples (< 2mm) of all 6 soils (see section 3.2.2)

were incubated for 2-week periods using the same 'buried bag' procedure as that in the long term incubation (section 5.2). Six such 2-weekly incubations were conducted in the period from the end of February 1980 to June 1980.

In each incubation there were 4 replicates (or bags) for each soil. Before and after incubation, duplicate subsamples were taken from each bag for the determination of $CaCl_2$-extractable sulphate and water content (sections 3.3.3 and 3.3.5). The soil used in this study were the bulk air-dried samples used in the experiments described in chapters 4 and 5. Thus the soils at the start of each incubation were always the same, and as the moisture content was held constant, the only difference between succesive incubations of a given soil should have been field temperature.

6.2.2 Incubation of field moist soils

At 2-week intervals fresh samples (0-8 cm) of soils A, D, and E were taken from the field, passed through a 2 mm sieve, and 100g placed in a polyethylene bag without prior drying and then incubated at field moisture content for 2 weeks. The 'buried bag' procedure was the same as that used in the long term incubation (section 5.2). Duplicate subsamples were taken for the determination of $CaCl_2$-extractable sulphate and water content (sections 3.3.3 and 3.3.5) before and after each incubation. There were 4 replicates (or bags) for each soil. This procedure was repeated 6 times such that the incubation periods coincided with the incubations of the bulk air-dried samples (section 6.2.1). By comparison with results of the previous experiment (section 6.2.1), the combined effects of the differing soil moisture and initial level of sulphate could be evaluated.

6.2.3 Liming experiment

Air-dried samples of all 6 soils (see section 3.2.2) were mixed with 5 different rates of lime and incubated for 2 weeks using the same 'buried bag' procedure described previously. The 5 rates of lime were 0, 0.1, 0.2, 0.4 and 0.8g $CaCO_3$ per 100g soil which corresponded to 0, 2, 4, 8 and 16 me% respectively. All treatments were replicated 4 times. Soil pH, $CaCl_2$-extractable sulphate and water content of each replicate were determined before lime addition and after the incubation (sections 3.3.3 - 3.3.5). Subsamples were also taken immediately after the lime was mixed with the soil, for the determination of $CaCl_2$-extractable sulphate (section 3.3.3).

6.3 Results and discussion

6.3.1 Bulk sample incubation

Since the samples of each soil had the same initial sulphate level and the same moisture content prior to each incubation period, any differences in the amounts of S mineralised within a soil (figure 6.1) should be solely due to the temperature in the field. Although soil temperature (5 cm depth) fluctuated widely from day to day, there was a gradual decrease with time (figure 6.2a), but, with one exception, there were no significant relationships between the amounts of S mineralised and any temperature parameters (table 6.1). The significant negative correlations found for soil C surprisingly implied that more S was mineralised when the average temperatures during the incubation period decreased. This anomaly could be due to the use of average temperature which did not reflect any diurnal or daily fluctuations during the incubation period.

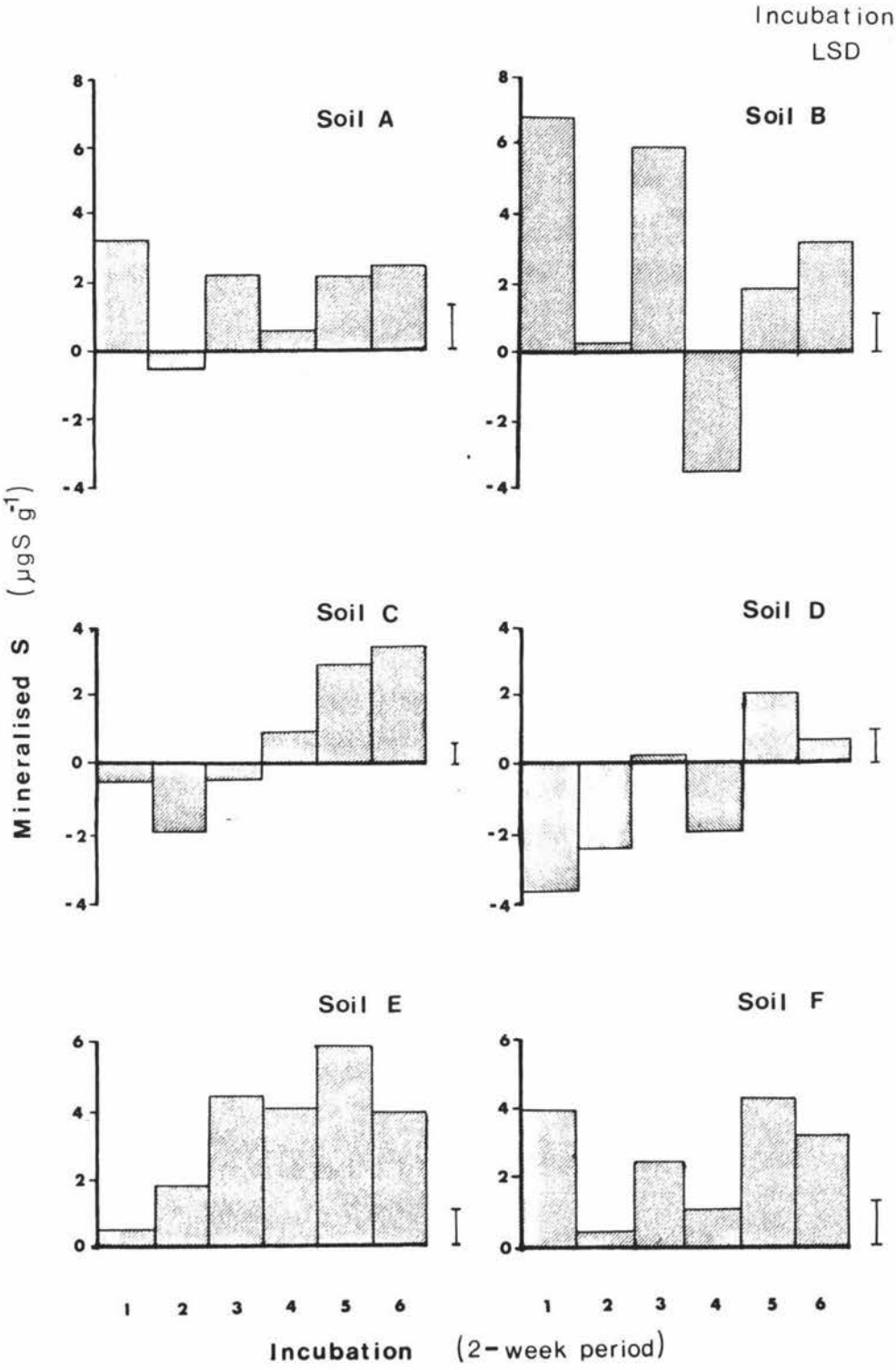

Figure 6.1 Amounts of S mineralised during 6 consecutive 2-week field incubations of air-dried samples of 6 Tokomaru silt loam soils.

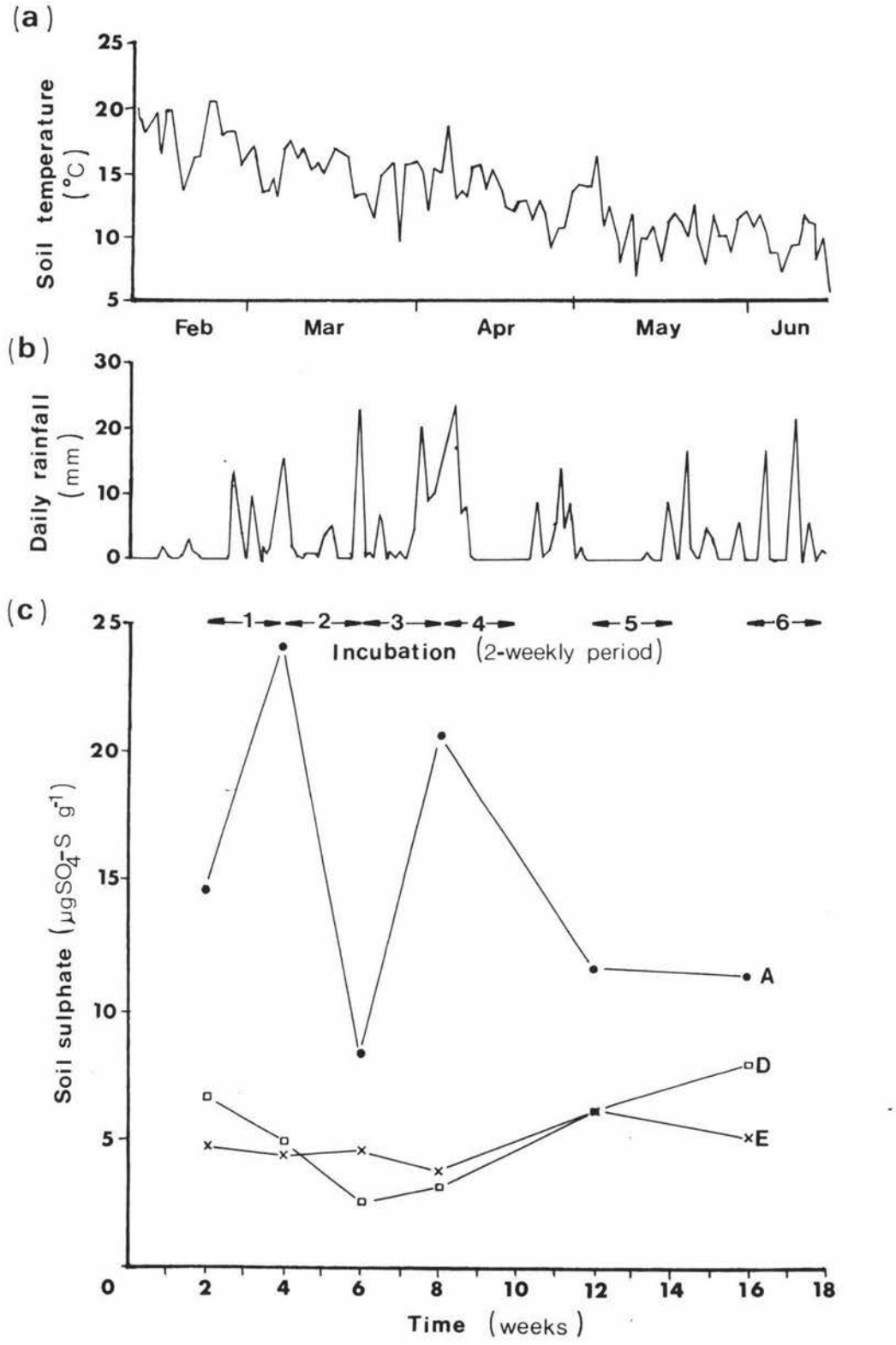

Figure 6.2 Sulphate levels (c) in 3 Tokomaru silt loam soils collected from the field at intervals during the period from February to June, 1980, together with soil temperature (a) and rainfall data (b) for the same period.

Table 6.1 Correlation coefficients for relationships between the amounts of S mineralised in a series of 2-week field incubations, each involving similar air-dried samples of 6 Tokomaru silt loam soils, and selected temperature parameters

Soil	Soil temperature (5 cm)	Minimum air temperature	Maximum air temperature
A	-0.262	-0.166	-0.295
B	0.168	0.210	0.204
C	-0.960**	-0.902*	-0.952**
D	-0.768	-0.794	-0.725
E	-0.672	-0.724	-0.710
F	-0.413	-0.319	-0.555

A similar anomalous pattern of mineralisation of S during incubation in the field was reported by Barrow (1969). In his study, the amounts of S mineralised during the 2-week incubation in the field were variable and they declined during the period in which weekly average maximum soil temperature (2.5 cm depth) showed an increase.

A few other studies have been conducted on the effect of temperatures on the mineralisation of soil organic S and significant increases in mineralisation rate with increasing temperature have been reported (Chaudhry and Cornfield, 1967b; Williams, 1967; Lee and Speir, 1979). These investigations were, however, carried out in the laboratory where constant temperatures were imposed throughout the incubation period. In the field, where temperatures fluctuate markedly, a simple relationship between the temperature and amounts of S mineralised might not be expected.

If the mineralisation data from all five pasture soils were considered together, no significant individual relationships could be found with temperature or any of the measured soil parameters (table 6.2). A multiple correlation (table 6.2) did however achieve significance although it explained only 40 per cent of the variation in mineralisation. This inability to explain variations in the mineralisation of S on the basis of soil properties is similar to that obtained in the long term field incubation (chapter 5). As was the case in that experiment, however, the final levels of sulphate in pasture soils after each incubation were significantly correlated with total S content and better correlations were also obtained with some soil properties such as C:S and N:S ratio and pH (table 6.3). It should be noted that most correlations were similar between incubation periods despite the different soil

Table 6.2 Single and multiple correlation coefficients for relationships between the amounts of S mineralised in a series of 2-week field incubations, each involving similar air-dried samples of 5 Tokomaru silt loam pasture soils, and selected soil properties

Soil properties	Multiple R	Single r
Soil temperature	0.316	-0.316
Initial soil sulphate	0.376	0.192
Soil pH	0.567	-0.096
Total S	0.622	0.014
Total C	0.626	0.059
N:S ratio	0.636	-0.055
C:S ratio		0.032
Total N		-0.018

Table 6.3 Correlation coefficients for relationships between the final levels of sulphate in 5 Tokomaru silt loam soils after each of a series of 2-week field incubations and selected soil properties

(Figures in brackets refer to correlations in which the arable soil (F) was included)

Soil properties	Incubation					
	1	2	3	4	5	6
Total S	0.900* (0.613)	0.910* (0.613)	0.856* (0.629)	0.923* (0.612)	0.943* (0.581)	0.888* (0.626)
Total C	-0.271	-0.188	-0.209	-0.133	-0.152	-0.258
Total N	-0.135	-0.110	-0.094	-0.028	-0.083	-0.151
C:S ratio	-0.643	-0.578	-0.572	-0.539	-0.562	-0.627
N:S ratio	-0.665	-0.655	-0.612	-0.605	-0.654	-0.670
Soil pH	0.747	0.726	0.747	0.656	0.678	0.737

temperature conditions (table 6.3). Almost 100 per cent of the variation in the final sulphate levels of the pasture soils was accounted for by a combination of total S content, pH and N:S ratio (table 6.4). The inclusion of the arable soil (F) was found to result in poorer relationships bweteen the final levels of sulphate and various soil properties. As a result, the correlations between the final sulphate levels and total S content were no longer significant (table 6.3). The reasons for the poorer correlations resulting from the inclusion of the arable soil (F) have already been discussed in chapter 4.

6.3.2 Incubation of field moist soils

The amounts of S mineralised in the 2-week incubation differed markedly between the six incubation periods (figure 6.3). Both net mineralisation and immobilisation were observed in all soils at different times. The pattern of S release was,however, similar between the three soils studied (A, D and E). Since, for each soil, samples were collected from the field at 2-week intervals and then immediately incubated without air-drying, the pattern of mineralisation or immobilisation was likely to be influenced by several factors such as soil moisture, sulphate levels and temperature.

The initial sulphate levels in the soils fluctuated considerably, particularly in soil A (figure 6.2c). The sulphate concentrations in two of the three soils were lowest at week 6. It is interesting to note that on this occasion there was heavy rainfall (21 mm) on the day immediately prior to sampling (figure 6.2b), suggesting that rainfall has a considerable influence on the soil sulphate level in the field.

Table 6.4 Multiple correlation coefficients (R) for the relationship between the final levels of sulphate in 5 Tokomaru silt loam pasture soils after a 2-week field incubation[#] and selected soil properties

Soil properties	R
Total S	0.900*
Soil pH	0.942*
N:S ratio	0.997**

[#] Incubation 1 in the series of field incubations of similar air-dried samples.

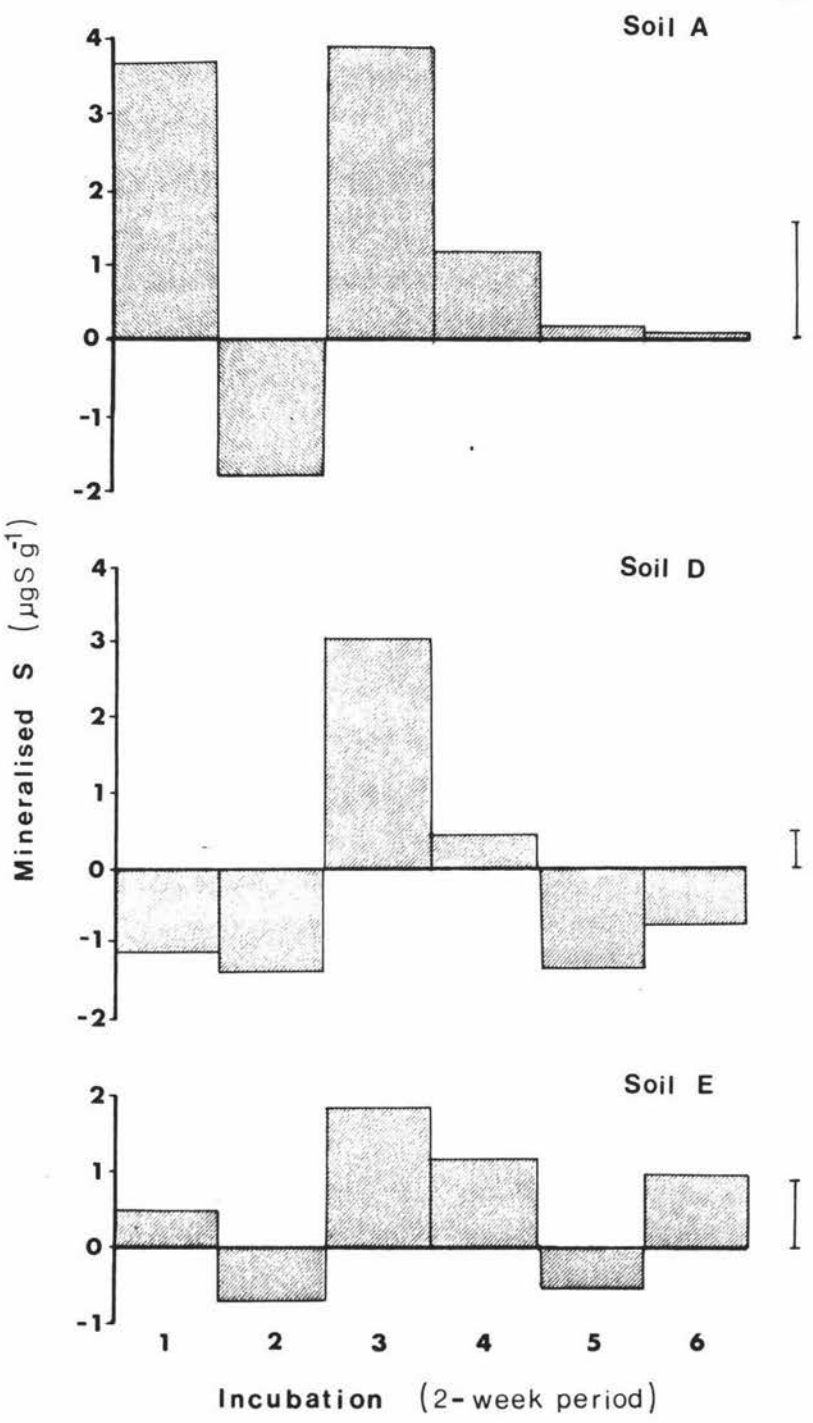

Figure 6.3 Amounts of S mineralised from field moist samples of 3 Tokomaru silt loam soils during 6 consecutive 2-week field incubations.

It was found that the amounts of S mineralised were highest during the third incubation period (figure 6.3) when the initial levels of sulphate were lowest (week 6, figure 6.2c). This is consistent with the results obtained from the long term field incubation (chapter 5) which showed, for any given soil, a negative relationship between the amounts of S mineralised and the initial soil sulphate levels. In this experiment, similarly good relationships were also present in all soils (table 6.5) although none of them reached significance mainly due to the relatively small numbers of observations.

Since the experiment was carried out during the autumn-winter period (February to June), when rainfalls were heavy, the moisture contents of the soils were relatively high (table 6.6). For most incubation periods, the moisture contents were between 33 and 40 per cent which were very close to field capacity. This range of soil moisture has been considered an optimum condition for mineralisation of soil organic S under laboratory conditions (Williams, 1967). These near optimum moisture contents probably contributed in part to the lack of significant correlations between the amounts of S mineralised and soil moisture contents (table 6.5).

Although, when each soil is considered separately, the amounts of S mineralised during the six incubation periods were not significantly related to the initial sulphate level or any environmental parameters individually, a multiple correlation including these variables could explain almost 100 per cent of the variations in S mineralisation in soils A and D, and 68 per cent in soil E (table 6.5).

As in previous experiments, when all soils were considered together, the amounts of S mineralised were not significantly related

Table 6.5 Single and multiple correlation coefficients for relationships between the amounts of S mineralised in a series of 2-week field incubations of freshly collected field moist samples of 3 Tokomaru silt loam soils and selected parameters

Parameters	Multiple R	Single r
Soil A		
Moisture content	0.615	-0.615
Initial soil sulphate	0.824	-0.579
Soil temperature	0.862	0.275
Minimum air temperature	0.997**	0.128
Maximum air temperature		0.292
Soil D		
Initial soil sulphate	0.729	-0.729
Minimum air temperature	0.776	-0.047
Moisture content	0.806	-0.098
Maximum air temperature	0.994**	-0.032
Soil temperature		0.096
Soil E		
Initial soil sulphate	0.483	-0.483
Minimum air temperature	0.665	-0.296
Soil temperature	0.795	-0.135
Maximum air temperature	0.826	-0.211
Moisture content		-0.034

Table 6.6 Initial moisture contents of field moist samples of 3 Tokomaru silt loam soils prior to incubation

Soil	Initial moisture content (%)					
	Incubation					
	1	2	3	4	5	6
A	16.8	35.6	33.0	37.3	38.9	37.3
D	18.8	35.0	35.0	37.3	39.8	42.7
E	21.4	33.1	37.0	39.9	49.0	44.7

to any individual soil properties, although a multiple correlation explained more than 70 per cent of the variations in the S mineralisation in these soils (table 6.7).

The amounts of S mineralised from the field moist soils were not related to the amounts obtained from the bulk, air-dried samples during the corresponding incubation periods ($r = 0.347$). The differences between the amounts of S mineralised from a given soil in these two experiments should be related to the different initial levels of sulphate and moisture content. However such relationships were found to be significant only in one soil (E), although a multiple correlation showed that more than 75 per cent of the variations for all the soils could be explained by such differences (table 6.8).

In contrast, there was a highly significant relationship between the final sulphate levels in the two experiments after each incubation period ($r = 0.820^{*}$). This finding, together with the negative correlation between the amounts of S mineralised and the initial levels of sulphate, supports the concept of an 'equilibrium' level of sulphate for a given soil which was suggested in chapter 5 (section 5.3). In order to maintain this 'equilibrium' level of sulphate, samples with low sulphate initially should mineralise more S during the incubation. The final levels of sulphate for a given soil after each incubation were not all the same (figure 6.4), as should have been the case if an 'equilibrium' level was attained. This may be due to the differences in environmental conditions between the incubations and also their relatively short duration. It was, however, found that the final levels of sulphate in soils A, D and E after each incubation showed very good relationships with total S,

Table 6.7 Single and multiple correlation coefficients for relationships between the amounts of S mineralised in a series of 2-week field incubations of freshly collected, field moist samples of 3 Tokomaru silt loam soils and selected parameters

Parameters	Multiple R	Single r
Total S	0.321	0.321
Initial soil sulphate	0.610*	-0.082
Moisture content	0.645**	-0.240
Soil temperature	0.806**	0.117
N:S ratio	0.846**	-0.158
C:S ratio		-0.132
Total C		0.014
Total N		0.043

Table 6.8 Single and multiple correlation coefficients for relationships between the differences in the amounts of S mineralised during a series of 2-week field imcubations of field moist and similar air-dried samples of 3 Tokomaru silt soils and the initial sulphate levels and moisture contents of the field moist soils

Soil properties	Single r	Multiple R
Soil A		
Initial soil sulphate	-0.436	0.436
Moisture content	-0.075	
Soil D		
Initial soil sulphate	-0.618	0.618
Moisture content	-0.574	0.864
Soil E		
Moisture content	-0.891*	0.891*
Initial soil sulphate	-0.618	0.933*

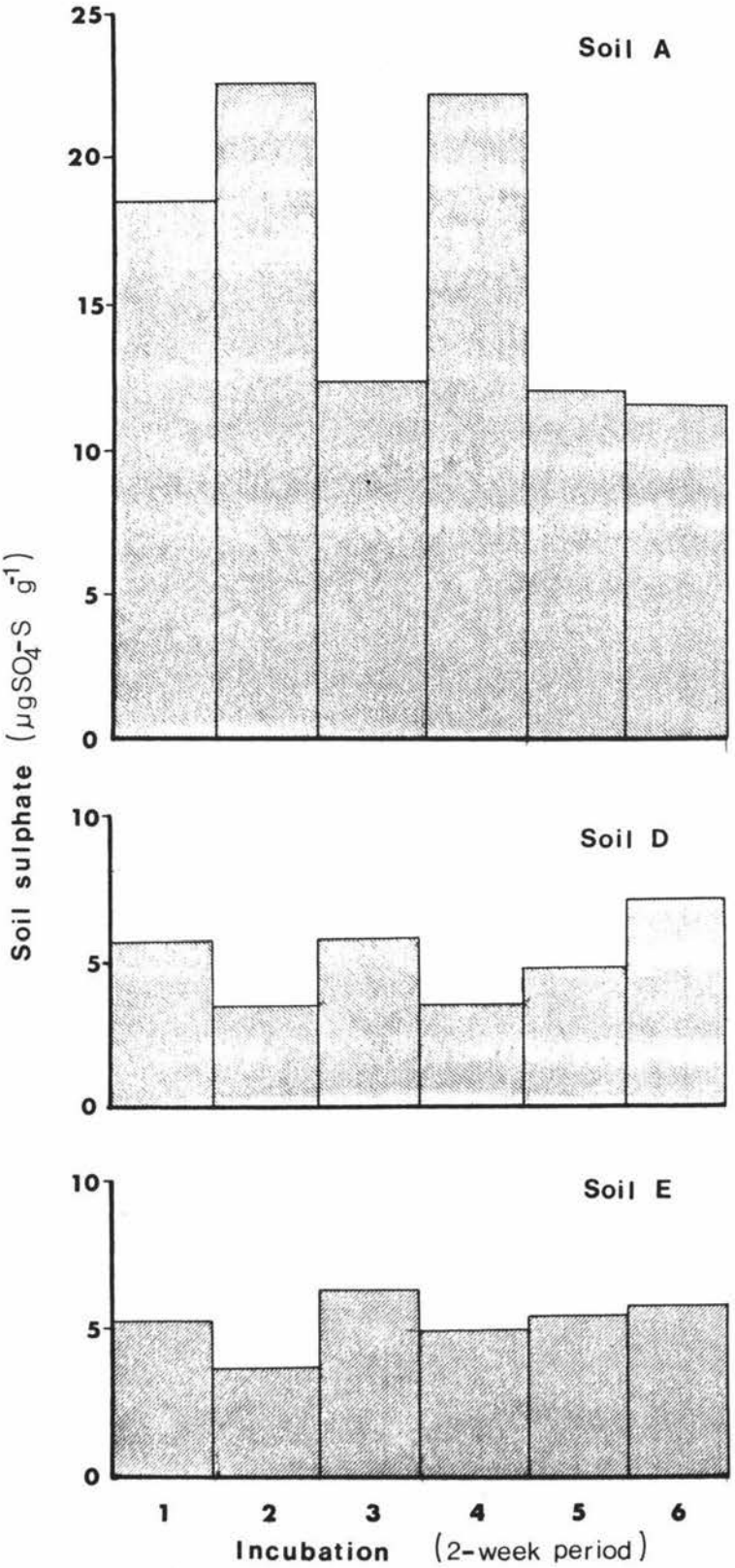

Figure 6.4 Final levels of sulphate after 6 consecutive 2-week field incubations of field moist samples of 3 Tokomaru silt loam soils.

pH, C:S and N:S ratios (table 6.9). A multiple correlation also showed that more than 90 per cent of the variations in the final levels of sulphate could be explained by total S and total C contents (table 6.9). The significant relationships obtained between the final levels of sulphate and total S content were in agreement with the results of the long term field incubation (chapter 5) and the series of incubations of identical soil samples (section 6.3.1).

6.3.3 Liming experiment

The addition of lime caused increases in pH in all soils and the final pH attained after the highest amount of lime (16 me%) was added was remarkably similar (7.2 - 7.4) in all soils (table 6.10 and figure 6.5). The increase in pH was greatest in soil C which had the lowest pH initially while the smallest increase in pH was found in soil B which had the highest initial pH (table 6.10).

In all soils the amounts of S mineralised were also increased by the addition of lime (table 6.11), although significant correlations between the amounts of S mineralised and the rates of lime added were found only in soils B and D (figure 6.6). In contrast, all six soils exhibited significant correlations between final pH and the amounts of S mineralised, although the correlations for the soils B and D, mentioned above, were weaker than for the others (figure 6.7). These results are remarkably similar to those of Williams (1967), who found in some soils, that the amounts of S mineralised were proportional to the amounts of calcium carbonate added, and that in others, there was a direct relationship between final pH and the amounts of S mineralised up to pH 7.5, and a rapid

Table 6.9 Single and multiple correlation coefficients for relationships between the final levels of sulphate in a series of 2-week field incubations of freshly collected, field moist samples of 3 Tokomaru silt loam soils and selected soil properties

Soil properties	Multiple R	Single r
Total S	0.849**	0.849**
Total C	0.878**	-0.413
Total N		-0.345
C:S ratio		-0.709*
N:S ratio		-0.752
Soil pH		0.601

Table 6.10 Soil pH values and the maximum pH increases in 6 Tokomaru silt loam soils after a 2-week field incubation with 5 rates of added lime

Soil	Rate of lime added (me%)					Maximum pH increases
	0	2	4	8	16	
A	6.08	6.78	7.15	7.24	7.27	1.19
B	6.36	7.04	7.20	7.24	7.30	0.94
C	5.06	6.35	6.87	7.15	7.21	2.15
D	5.54	6.34	6.98	7.20	7.27	1.73
E	5.64	6.34	6.74	7.31	7.39	1.75
F	6.12	6.71	7.10	7.26	7.33	1.21

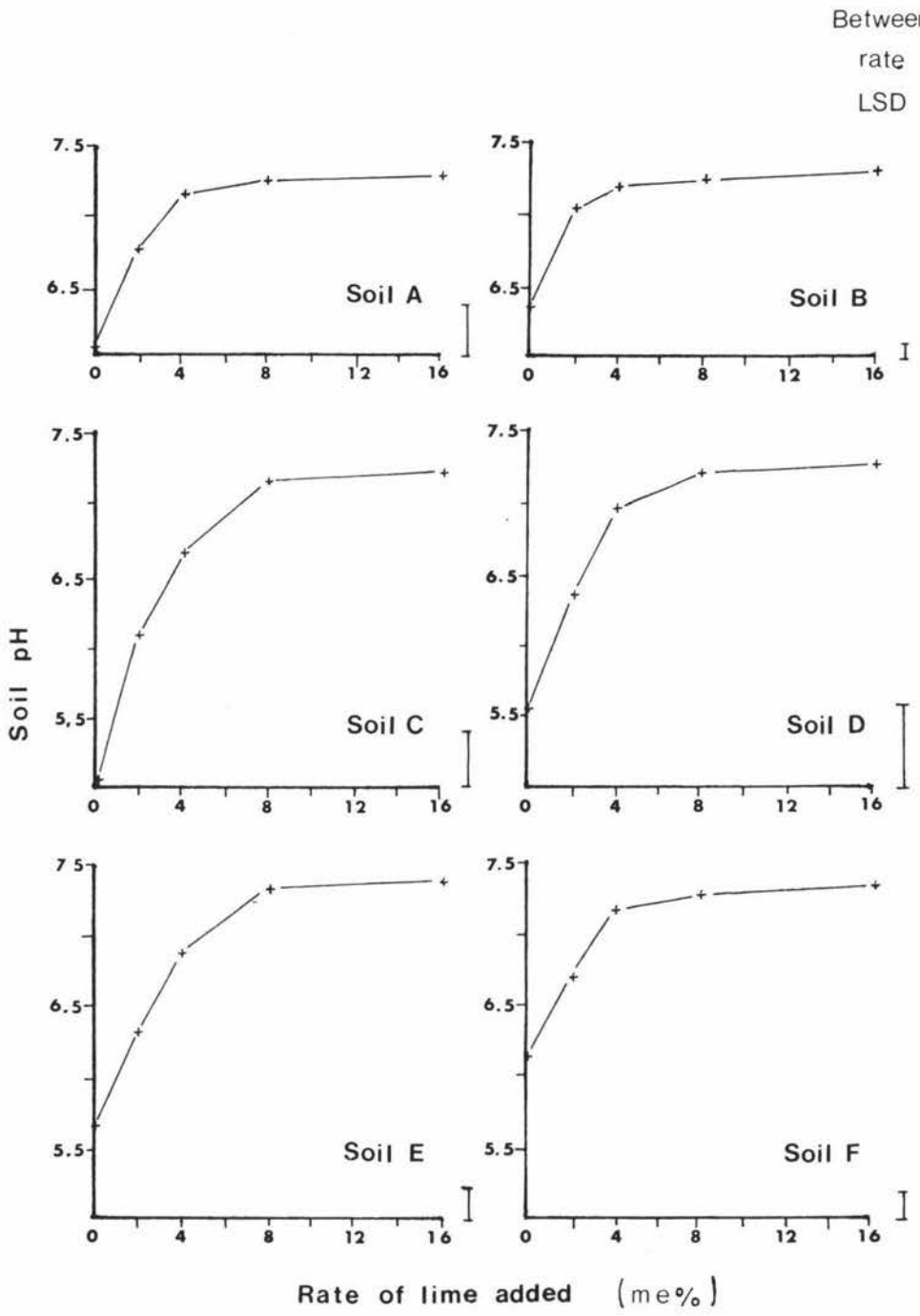

Figure 6.5 Relationships between soil pH after incubation and the amounts of lime added to 6 Tokomaru silt loam soils.

Table 6.11 Amounts of S mineralised ($\mu gS\ g^{-1}$) from 6 Tokomaru silt loam soils after a 2-week field incubation with 5 rates of added lime

Soil	Rate of lime added (me%)					LSD 5%
	0	2	4	8	16	
A	5.7	6.7	7.7	7.9	7.4	0.06
B	4.3	5.7	5.9	7.3	8.0	0.89
C	2.6	4.4	4.4	6.0	5.6	0.77
D	2.0	2.2	2.4	2.6	3.0	0.16
E	2.3	4.8	6.2	8.1	8.1	0.58
F	2.2	4.8	6.6	6.5	6.5	0.28

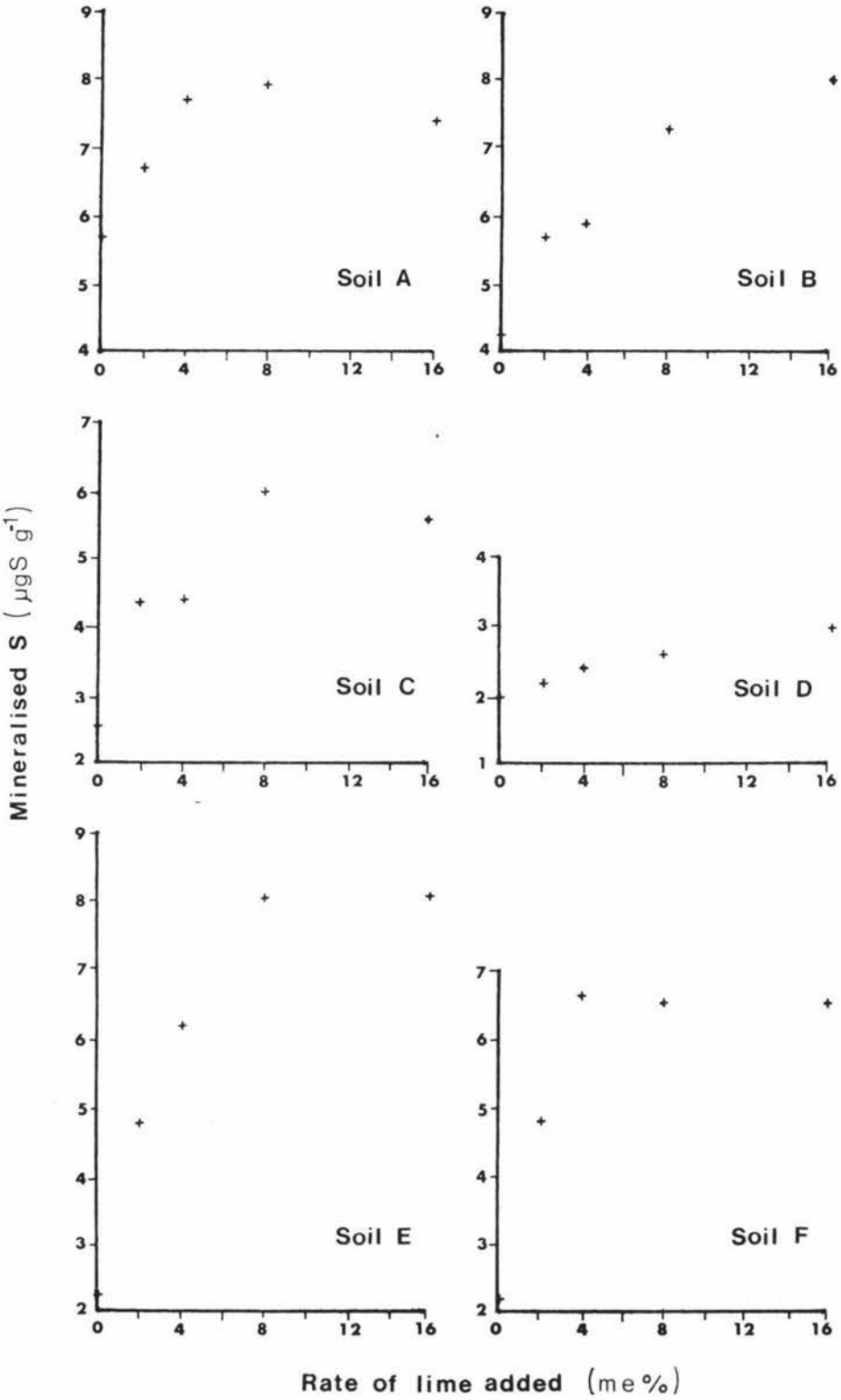

Figure 6.6 Relationships between the amounts of S mineralised from 6 Tokomaru silt loam soils and the amounts of lime added prior to incubation.

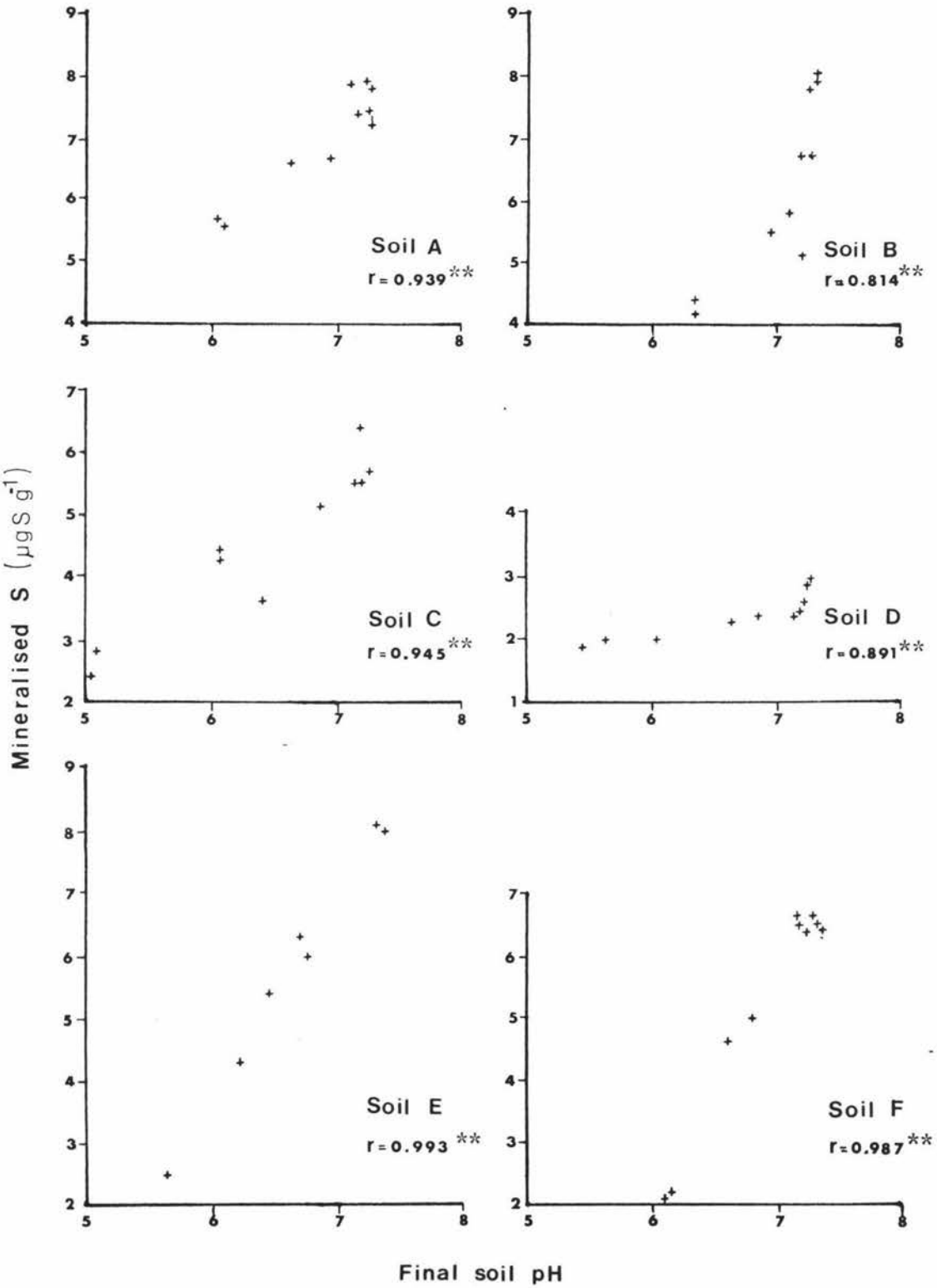

Figure 6.7 Relationships between the amounts of S mineralised from 6 Tokomaru silt loam soils and the final soil pH values attained after incubation with various amounts of lime.

release of S beyond that pH.

The amounts of S released and the increases due to liming differed between soils, but although several soil parameters were correlated significantly with either of these two quantities, this was probably due to the large number of data points, as only a small fraction of the variability in S mineralised could be explained by any one variable (table 6.11). The amounts of S mineralised were, nevertheless, significantly related to a combination of some soil properties (as shown in table 6.12) which could explain more than 80 per cent of the variation.

Some of the release of S was found to take place within 3 hours of the addition of lime. This rapid release of S was different between soils (table 6.13). The amounts of S initially released in soils C, E and F increased with increasing rates of lime added, while the reverse was found in soil A. Constant amounts of S were released from soils B and D. Since this release of S took place within a few hours of the addition of lime, it is unlikely that microbial activity would be responsible. A possible explanation is the effect of a different pH during the extraction causing the desorption of adsorbed sulphate and/or chemical hydrolysis of some organic sulphate esters at the more alkaline pH (Williams, 1967). It has been suggested that adsorbed sulphate can be released from soil exchange sites because of an increase in pH (Freney and Stevenson, 1966).

In this study, the amounts of 'adsorbed' sulphate as determined by the difference between phosphate-extractable and $CaCl_2$-extractable sulphate ranged from 3.0 μgSO_4-S g^{-1} in soil D to 9.7 μgSO_4-S g^{-1} in soil F (table 6.14). The soils used in this study were samples

Table 6.12 Single and multiple correlation coefficients for relationships between the amounts of S mineralised from 6 Tokomaru silt loam soils, in a 2-week field incubation, after addition of various rates of lime, and selected soil properties

Soil properties	Mineralised S		Increases in mineralised S #
	Multiple R	Single r	Single r
Final soil pH	0.664**	0.664**	0.448*
Total S	0.775**	0.464**	0.190
'Adsorbed sulphate'	0.821**	0.526**	0.144
Initial soil pH	0.882**	0.145	0.084
Initial soil sulphate	0.911**	0.543**	0.604**
C:S ratio	0.919**	-0.138	0.494**
Increases in pH		0.514**	0.232
Total C		0.108	0.398**
Total N		0.110	0.261
N:S ratio		0.543**	0.389**

Differences in the amounts of S mineralised with and without the addition of various rates of lime.

Table 6.13 Amounts of S mineralised ($\mu gS\ g^{-1}$) from samples of 6 Tokomaru silt loam soils within 3 hours of the addition of 4 rates of lime

Soil	Rate of lime added (me%)			
	2	4	8	16
A	1.8	1.6	1.3	0.5
B	0.9	0.7	0.7	0.9
C	2.2	2.8	2.8	3.1
D	2.7	2.9	2.7	2.7
E	2.9	2.8	5.2	5.3
F	4.3	4.4	5.4	5.3

Table 6.14 Amounts of sulphate extracted by 0.04M $Ca(H_2PO_4)_2$, 0.01M $CaCl_2$, and the calculated amounts of 'adsorbed' sulphate in 6 Tokomaru silt loam soils

Soil	Phosphate-extractable sulphate	$CaCl_2$-extractable sulphate	'Adsorbed' sulphate
		μgSO_4-S g^{-1}	
A	37.8	28.4	9.5
B	40.1	32.6	7.5
C	14.1	11.0	3.1
D	9.4	6.4	3.0
E	14.8	9.7	5.1
F	28.7	19.0	9.7

of Tokomaru silt loam collected from the top 8 cm. As this soil has a low ability to retain anions as indicated by the phosphate retention test, the levels of adsorbed S in the top soil would be expected to be very low (Metson, 1979). Phosphate solutions are known to extract some organic sulphate as well as adsorbed sulphate (Ensminger and Freney, 1966). It is probable, therefore, that most of the additional sulphate extracted by a phosphate solution from these soils originated from organic S not adsorbed S and that the rapid release of S in the short time period following liming is caused by a chemical hydrolysis of organic sulphate esters in soils at the more alkaline pH. This hypothesis is supported by the observation that there was no correlation between the quantities of possibly 'adsorbed S' and the amounts released in the short term by lime addition.

6.4 Conclusions

When samples of six Tokomaru silt loam soils were taken from the field, sieved, air-dried and later incubated for 2-week periods using the 'buried bag' technique, the amounts of S mineralised from any given soil varied considerably depending on when the incubations were conducted. Since the samples of any one soil at the start of each incubation period came from the same source (i.e. the bulk, air-dried sample) and the moisture content was adjusted to the same level, the variation in the amounts of S mineralised should have been solely due to differences in field temperature during the incubation. The variations obtained, however, were not consistent between soils and no significant relationships with any of the temperature parameters measured could be found.

This inability to demonstrate the influence of temperature has two implications. Firstly, the usefulness of such incubation studies in predicting the mineralisation of S in soils is questionable because the answer obtained will vary unpredictably depending on when the incubation is carried out. Secondly, the results of laboratory incubation studies investigating the effect of temperature on mineralisation appear not to be applicable to a field situation. It would appear that in the field, where the temperature fluctuates markedly over short time periods, the relationship between the S mineralisation and temperature is much less apparent than under laboratory conditions where several workers (e.g. Williams, 1967; Chaudhry and Cornfield, 1967b) have noted significant relationships between the rate of mineralisation and temperature.

In comparison with the actual amounts of S mineralised during the incubations, the variation in the final levels of sulphate at the end of the incubations was relatively smaller. A significant relationship was found between these final levels of sulphate and the total S content of the soils. These results were similar to those of the long term field incubation (chapter 5) suggesting again that the sulphate level at the end of the incubation may be a better indication of the rate and extent of mineralisation of soil organic S than the actual amount of S mineralised during the incubation.

When soils were collected from the field at 2-weekly intervals during the autumn-winter period, the concentrations of sulphate within each soil fluctuated markedly between samplings depending largely on the rainfall immediately prior to sampling. The amounts of S mineralised during 2-week incubations of these field moist samples also varied and, for a given soil, were found to be inversely

proportional to the initial levels of sulphate. This supports the earlier suggestion from the long term field incubation (chapter 5) that the amounts of S released by mineralisation in a given soil are inversely dependent upon the level of sulphate present initially.

As the 2-week incubation of freshly collected soils were conducted at the same times as the incubations of the previously air-dried, bulk samples which were discussed earlier, the field temperatures during incubation would have been identical for both. Thus, any differences in the amounts of S mineralised in the two incubations for any one soil should have been due solely to differences in initial moisture level and initial sulphate content. No clear relationship between the differences in the amounts of S mineralised and either or both of these parameters could however be found.

As noted in the bulk sample incubation, the final levels of sulphate after the incubations of field moist soils were well correlated with total S content. Better correlations were also obtained between the final levels of sulphate in the two experiments than between the actual amounts of S mineralised.

When 5 different rates of lime were added to the soils, there were increases in the amounts of S mineralised during 2-week incubations of all six soils. For any given soil, the amounts of S mineralised after liming were directly proportional to the final pH attained, although in two soils (B and D) they were better related to the amounts of lime added. It was noted that part of the increased release of sulphate occurred very rapidly (less than 3 hours) after the addition of lime. It was suggested that this was due to chemical hydrolysis of organic sulphate esters rather than increased microbial breakdown.

CHAPTER 7

CHAPTER 7 LABORATORY INCUBATION

7.1 Introduction

Most studies on the mineralisation of soil S in the past have consisted of laboratory incubations (Biederbeck, 1978) which, although offering the advantages of convenience and environmental control, may be difficult to relate to the field situation. As information was available on the amounts of S mineralised from the six samples of Tokomaru silt loam in a field pot experiment (chapter 4), and in a field incubation study (chapter 5), it was decided to investigate the relationship between a laboratory incubation study under optimum conditions of moisture and temperature and the earlier results.

7.2 Materials and methods

Air-dried samples of all six soils (see section 3.2.2) were prepared and placed in polyethylene bags using the same procedures as those in the long term field incubation (section 5.2). The bags were arranged in layers on racks in an incubator to provide sufficient aeration around each bag. The soils were incubated at 30C for 4 weeks. It was difficult to maintain a constant temperature of 30C on all bags during the incubation and the temperatures were found to fluctuate within 3C of the set temperature. This variation resulted from the arrangement of bags on the racks which did not allow sufficient air circulation inside the incubator. As a result there was a slight vertical temperature gradient with higher temperatures at the lower racks than at the top racks.

Sufficient bags were prepared so that 3 bags (or replicates) of each soil could be taken out at weekly intervals during the 4-week period. Duplicate samples of each bag were taken without prior drying for the determination of $CaCl_2$-extractable sulphate and moisture content (sections 3.3.3 and 3.3.5).

7.3 Results and discussion

During the 4-week incubation period, there were moisture losses from the bags resulting in a decrease in moisture content from 40 to 33 per cent. It appears that at the temperature of 30C, evaporation was appreciable and water vapour could escape from the bags.

The amounts of S mineralised after 4 weeks of laboratory incubation were similar in all soils except soil D (figure 7.1), ranging from 2.8 μgSO_4-S g^{-1} in soil D to 9.4 μgSO_4-S g^{-1} in soil B (table 7.1). They also correlated well with the total S content and the initial levels of sulphate (table 7.2). This is in agreement with the results of the field pot experiment (chapter 4) and the long term field incubation (chapter 5). The significant correlation with the initial sulphate level was probably due to its close relationship with total S content as explained in chapter 5. This again emphasizes the strong influence of the total S content in soil on S mineralisation within a soil type.

There were no significant relationships between the amounts of S mineralised and other soil properties (table 7.2), again supporting similar results reported by other workers (eg. Williams, 1967) as mentioned in chapter 5. The amounts of S mineralised in this experiment agreed only moderately with the results of the field pot

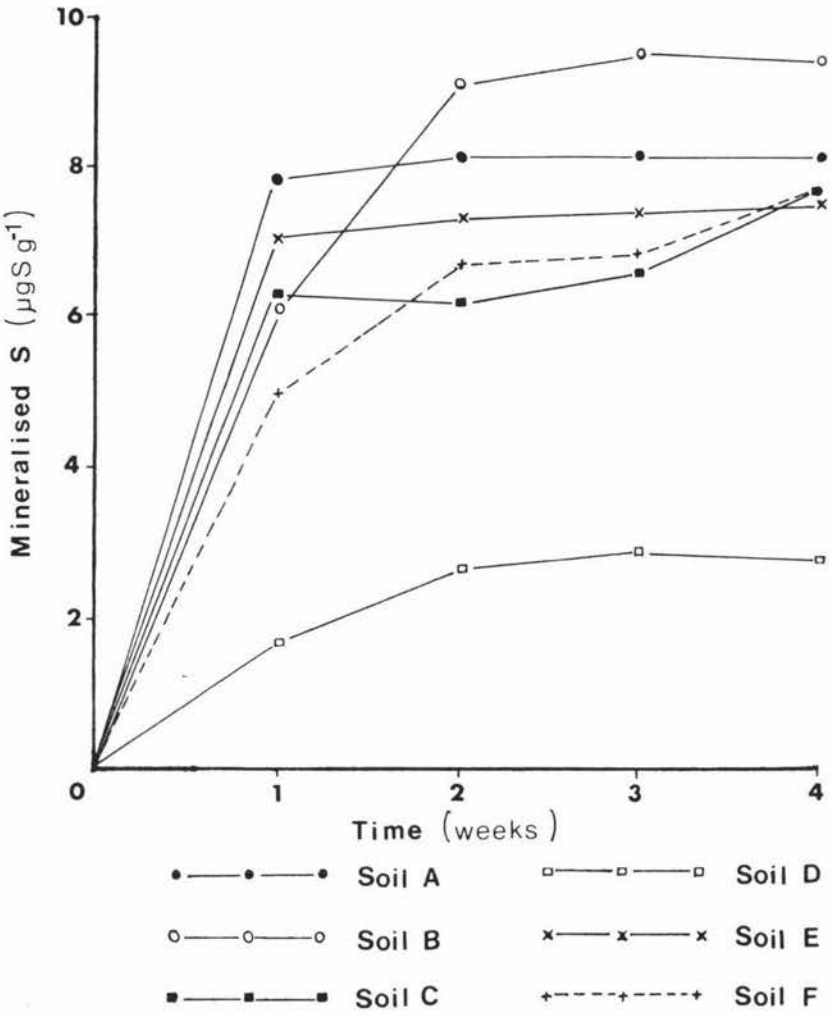

Figure 7.1 Amounts of S mineralised from 6 Tokomaru silt loam soils during a 4-week laboratory incubation.

Table 7.1 Amounts of S mineralised from 6 Tokomaru silt loam soils in a 4-week laboratory incubation

Soil	Mineralised S $\mu gS\ g^{-1}$
A	8.1
B	9.4
C	7.7
D	2.8
E	7.5
F	7.7

Table 7.2 Correlation coefficients for relationships between the amounts of S mineralised from 6 Tokomaru silt loam soils during a 4-week laboratory incubation and selected soil properties

Soil properties	r
Total S	0.541**
Initial soil sulphate	0.689**
Total C	0.133
Total N	0.209
C:S ratio	-0.133
N:S ratio	-0.157
Soil pH	0.181

experiment (r = 0.718).

The pattern of S mineralisation within a soil at 30C under the controlled environment (figure 7.1) was different from that observed under fluctuating field temperatures (chapter 5). In the laboratory incubation, most of the S was released during the first week and after that there was relatively little mineralisation. It is suggested that the high level of sulphate attained as a result of the large release of S during the first week might be responsible for the subsequent decline in the rate of S mineralisation. This is supported by the highly significant negative relationships between the amounts of S mineralised from each soil during each week and the levels of sulphate present at the start of that week (figure 7.2). This is again consistent with the results of the long term field incubation (chapter 5) and the incubation of field moist soils (chapter 6).

As in the long term field incubation (chapter 5), final 'equilibrium' levels at the end of the incubation (figure 7.3) were well correlated with the amounts of S mineralised in the field pot experiment ($r = 0.934^{*}$). There was also a highly significant relationship between the final level of sulphate and the total S content in all pasture soils (table 7.3). Poorer correlations were again obtained when the arable soil (F) was included (table 7.3), indicating the different forms of organic S in soil F as discussed in chapter 5.

7.4 Conclusions

During a 4-week laboratory incubation of six Tokomaru silt loam soils, most of the S was mineralised in the first week, after which there was relatively little mineralisation. It would appear that

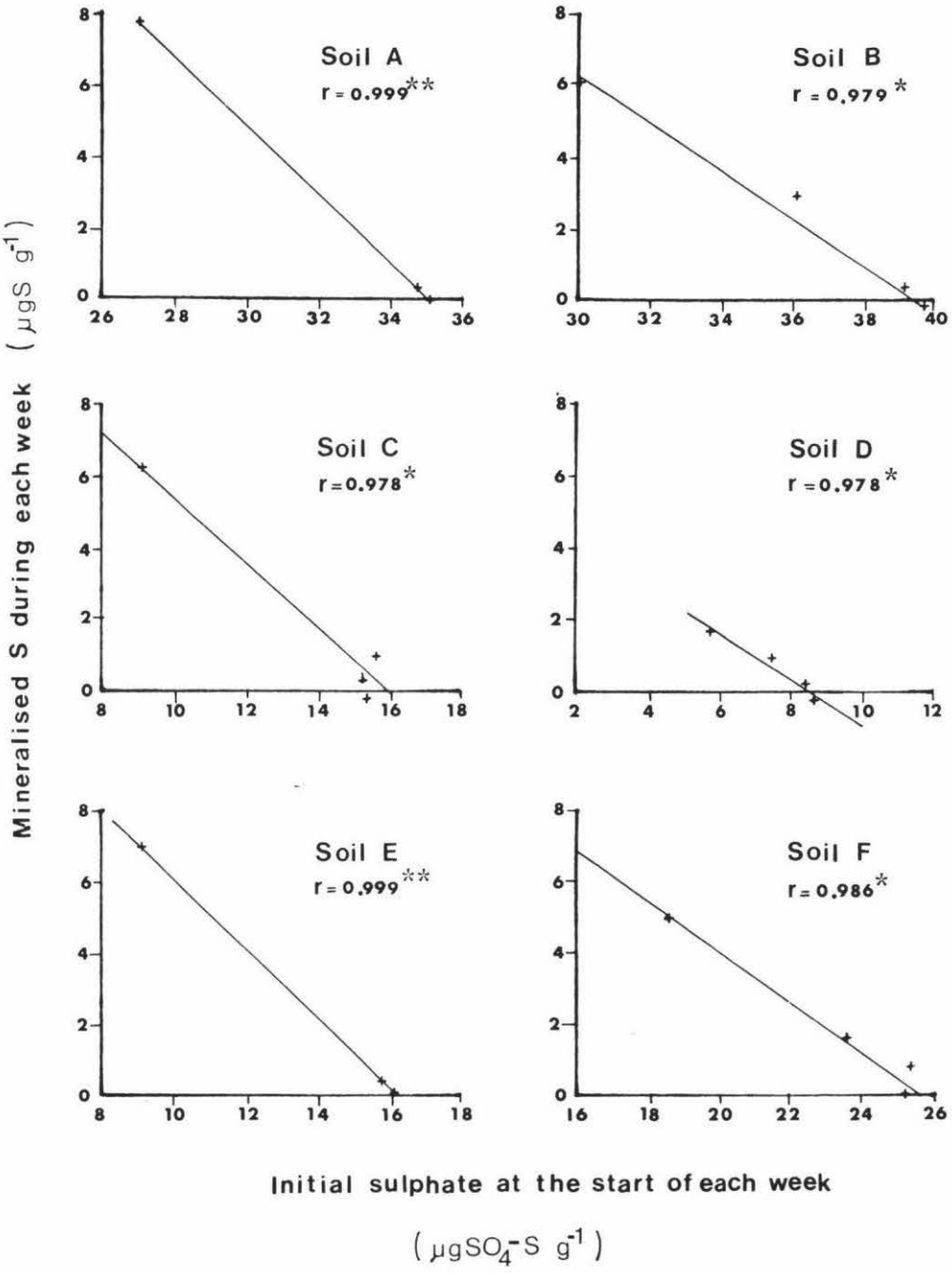

Figure 7.2 Relationships between the amounts of S mineralised from 6 Tokomaru silt loam soils during each of 4 weeks and the level of sulphate initially present at the start of that week.

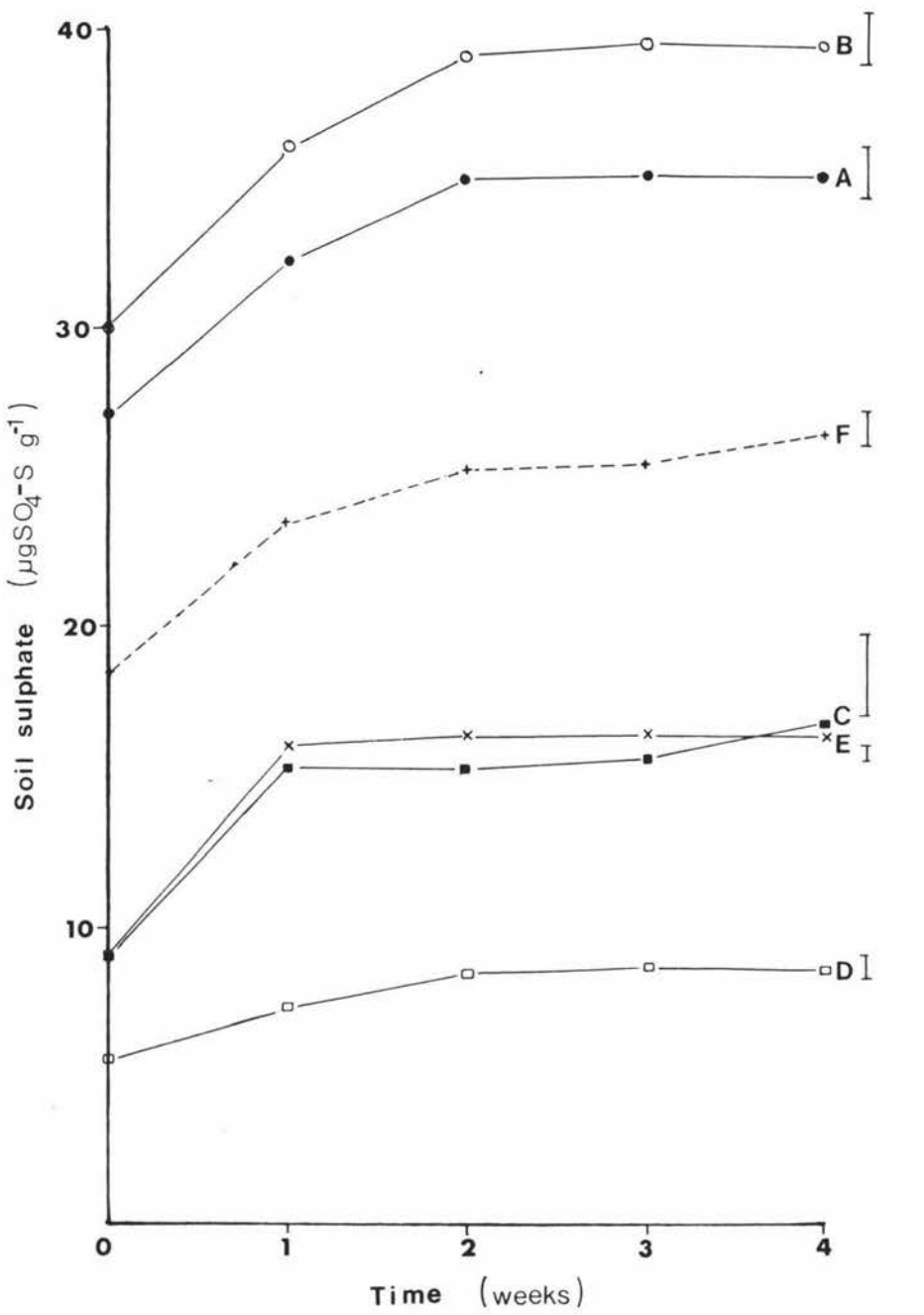

Figure 7.3 Sulphate levels in 6 Tokomaru silt loam soils during a 4-week laboratory incubation.

Table 7.3 Correlation coefficients for relationships between the final levels of sulphate in 5 Tokomaru silt loam pasture soils in a 4-week laboratory incubation and selected soil properties

(Figure in bracket refers to the correlation in which the arable soil (F) was included)

Soil properties	r
Total S	0.915* (0.614)
Total C	-0.196
Total N	-0.046
C:S ratio	-0.589
N:S ratio	-0.612
Soil pH	-0.671

the soils may have reached an 'equilibrium' level of sulphate after the first week and as a result, no net mineralisation or immobilisation was achieved afterwards. Although the cyclical pattern of sulphate release observed in the long term field incubation (chapter 5) was not observed in this shorter laboratory experiment, similar inverse relationships existed within each soil between the amounts of S mineralised during a given period and the level of sulphate present at the start of that period.

The amounts of S mineralised during this incubation were not significantly related to the amounts released in the field pot experiment (chapter 4). In contrast, the final levels of sulphate after the 4-week incubation were well correlated with the calculated mineralisation in the presence of plants and leaching. There was also a highly significant relationship between the final levels of sulphate in this incubation and the total S content. This is in general agreement with the findings of the previous experiments (chapters 4 and 5), suggesting that the final level of sulphate at the end of an incubation may be a better indication of the ability of soils to mineralise S than the actual amounts of S released during the incubation.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

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

1. A model of an S cycle was constructed for an established pasture, grazed by dairy cattle, on Tokomaru silt loam, in which the level of organic S was assumed to have reached an equilibrium. The model indicated that the annual rate of net mineralisation of soil organic S in this situation would be 19 kgS ha^{-1}. This contribution to the available S pool was more than twice as great as the calculated requirement for fertiliser S. Thus any appreciable variation, in the amount of S mineralised, from that calculated in the model, would have very significant consequences on the requirements for fertiliser S. This emphasised the need to know the accuracy with which the assumptions made in the model, regarding the rate of S mineralisation, reflected the actual field situation.

2. A review of literature indicated that a large proportion of soil S is present in organic forms, which must be mineralised to sulphate in order to become plant available. Despite a number of studies on the mineralisation of soil organic S, the process of S mineralisation is not yet fully understood. Furthermore, most of these investigations have been conducted under laboratory or glasshouse conditions and very few under more realistic field invironments. As a result very little

is known about the actual rate of mineralisation of soil organic S in a field situation.

3. In a field pot experiment, involving growing plants under natural rainfall and temperature conditions, the amounts of S mineralised in 13 weeks, from samples of 6 Tokomaru silt loam soils ranged from 10.9 kgS ha^{-1} to 22.9 kgS ha^{-1}. The average S mineralisation from the 2 soils collected from the most well-developed pastures was 21.5 kgS ha^{-1}. Although this figure may be a slight overestimate, it suggests that these soils are approaching the organic matter equilibrium assumed in the model. Such a model may therefore be useful in predicting fertiliser inputs. In contrast, other soils studied, mineralised much smaller quantities of S and are apparently much further from the equilibrium assumed in the model.

4. Highly significant relationships were obtained between the amounts of S mineralised and the total S content in the soils studied. This suggests that the accumulation of organic S in soils within a soil type, as indicated by total S content, may be a useful indicator of the approach to organic matter equilibrium, and hence the extent of net mineralisation of S.

5. The presence of growing plants stimulated the mineralisation of S in all 5 pasture soils. The absence of this effect in the only arable soil studied was attributed to poor growth caused by an N deficiency.

6. The presence of plants markedly reduced the leaching losses of S from all soils.

7. During a 20-week field incubation, the relative amounts of S mineralised from air-dried samples of 6 Tokomaru silt loam soils varied markedly with time. As a result, any correlations between the amounts of S mineralised and soil properties were also found to vary with the sampling time. These variations would appear to limit the usefulness of such an incubation technique for predicting the S mineralisation in the field.

8. The actual levels of sulphate in the 6 soils duirng the period of the long term field incubation showed relatively smaller variations and they were highly correlated with the amounts of S mineralised in the field pot experiment, and with the total S content of the soils. It is suggested that, if an incubation technique is to be used, the amounts of sulphate present in the soil at the end of the incubation may be a better indication of the ability of a soil to mineralise S in the field than is the actual amount released during the incubation. It is possible that there is an equilibrium level of sulphate, characteristic of each soil under given environmental conditions, and the soil will mineralise S until that equilibrium is reached. At this point, the rate of S mineralisation balances the rate of immobilisation. If this is so, the amounts of S mineralised during an incubation will depend on the initial level of

sulphate relative to the equilibrium level for that soil. This initial level of sulphate will vary according to the time of sampling.

9. The cyclical nature of the pattern of S mineralisation in the long term field incubation suggests that some type of 'end-product regulation' of sulphate production may be involved. Sulphatase enzymes are thought to play some part in S mineralisation in soils and their microbial synthesis has been shown to be subject to end-product regulation by sulphate. It is therefore possible that the decline in the rate of S mineralisation, following the build-up of sulphate levels, is due to a reduction in sulphatase enzyme activity.

10. During a series of short term (2-week) field incubations of air-dried samples of the 6 soils, no significant relationships between the amounts of S mineralised and any temperature parameters were found. It is suggested that the effects of long term temperature trends on the rate of S mineralisation in soils may be masked by the relatively large diurnal and daily fluctuations of temperature.

11. In a similar series of concurrent short term field incubations of fresh soil samples, the amounts of S mineralised were different from those obtained from the corresponding air-dried samples but the differences could not be related to differences in either, their initial moisture contents or their initial sulphate levels.

12. The final sulphate levels at the end of the short term incubations of both air-dried and field moist samples were highly correlated with the total S content and the amounts of S mineralised in the field pot experiment.

13. Addition of lime enhanced S mineralisation in all soils. The amounts of S mineralised in a given soil were directly proportional to the final pH, although in two soils, they were better related to the amounts of lime added.

14. The amounts of S mineralised from samples of 6 Tokomaru silt loam soils in a 4-week laboratory incubation at 30C were not significantly related to the amounts mineralised in the field pot experiment. There was however a highly significant relationship between the final levels of sulphate attained in the incubation and the amounts of S mineralised in the field. This suggests once again that in incubation experiments of soils within the same soil type, it is the final level of sulphate, rather than the amounts of S mineralised that is the better indicator of subsequent mineralisation in the field.

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APPENDICES

Appendix I Description and location of soil sampling sites

Soil	Site description	Location (Grid reference)
A	The site was under a predominantly ryegrass-clover pasture which was regularly grazed by dairy cattle. This pasture was 2 years old, the site having been cultivated for maize in 1977. Some incompletely decomposed stubble was still present in parts of soil surface. The soil had received regular applications of fertilisers for the past 10 years. At the time of sampling there was very little pasture cover.	N149/109298(1975)
B	The site was under a predominantly ryegrass-clover pasture which was regularly grazed by dairy cattle. This pasture was 7 years old and had received regular applications of fertilisers. At the time of sampling the pasture had not been grazed for some time and there was abundant growth of ryegrass, clover, dock, dandelion and buttercup.	N149/105309(1975)
C	The site was under a predominantly ryegrass-clover pasture which was regularly grazed by sheep. This pasture was 10 years old and had	N149/101302(1975)

Appendix I (continued)

Soil	Site description	Location (Grid reference)
	received moderate amounts of fertilisers. At the time of sampling there was good pasture cover.	
D	The site was under a predominantly ryegrass-clover pasture which was regularly grazed by sheep. This pasture was 6 years old and had received very small amounts of fertilisers. At the time of sampling there was very little pasture cover.	N149/122298(1975)
E	The site was under a native pasture which was occasionally grazed by sheep and horses. It had never been cultivated or received any applications of fertilisers. At the time of sampling a thick root mat was present in the top soil and there was abundant growth of cocksfoot, browntop, ryegrass and dock.	N149/119317(1975)
F	The site was adjacent to soil D. It had been cultivated for barley for 4 years and had received regular applications of fertilisers supplying all major nutrients except nitrogen.	N149/121299(1975)

Appendix II Dry matter yields of ryegrass after a 13-week growth period on 6 Tokomaru silt loam soils in a field pot experiment

	Dry matter (g per pot)			
	Replicate			
Soil	1	2	3	Average
A	2.06	2.86	2.22	2.38
B	2.56	3.06	2.11	2.58
C	4.17	4.20	2.92	3.76
D	1.90	2.12	1.75	1.92
E	3.05	2.75	3.15	2.98
F	1.18	1.19	1.19	1.19

Appendix III Total volumes of leachate collected from 6 Tokomaru silt loam soils in a field pot experiment after 13 weeks

Soil	Volumes of leachate (ml per pot)	
	With plants	Without plants
A	1169	1224
B	1026	1108
C	1177	1091
D	1074	1119
E	1064	980
F	1268	1140
Average	1130	1120

Appendix IV Leaching losses of S from 6 Tokomaru silt loam soils in the presence and absence of plants in a field pot experiment

Soil	Leached S ($\mu gS\ g^{-1}$)			Significance
	With plants	Without plants	Difference	
A	26.9	35.2	-8.3	*
B	28.2	36.0	-7.8	**
C	3.6	12.9	-9.3	**
D	2.4	7.0	-4.6	**
E	4.4	14.2	-9.8	*
F	19.8	25.9	-6.1	*