

## The diagnosis and correction of sulfur deficiency and the management of sulfur requirements in New Zealand pastures: a review

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**Abstract.** This review consolidates and updates our understanding of the diagnosis and correction of soil S deficiencies, and the management of S requirements for pastures, using both historical data from field trials and recent developments in the understanding of the sulfur (S) cycle in New Zealand pastoral soils. The basis for, and the practical implications of, a new quasi-equilibrium S model for pastures is discussed in terms of the size and changes in the pools of sulfate S, readily available extractable organic S (EOS) and total organic S over time and with the addition and removal of S through fertiliser and leaching. With this background, the use and interpretation of the 2 S soil tests are discussed. Historical data from field trials and the recent research on nutrient ratios are used to update the use of pasture S concentrations for diagnosing S deficiency. Historical data is also used to examine the distribution and size of pasture responses to S fertiliser and to define the biological S requirements for New Zealand soils. The effects of time, single or split, and annual or triennial applications of sulfate and S<sup>0</sup> are reviewed and the suitability of current S<sup>0</sup> fertilisers is discussed. Generalised fertiliser S strategies are then developed for the major soil groups, climate zones and farm types, based on all this information.

### Introduction

In the early 1980s a steady-state sulfur (S) model was developed as the basis for making fertiliser S recommendations on pastures in New Zealand (Sinclair and Saunders 1984). Subsequently, Sinclair *et al.* (1985) reviewed the available agronomic data from many field trials in New Zealand and concluded that this model predicted the long-term maintenance S requirements with a moderate degree of confidence. Goh and Nguyen (1997) reached the same conclusion based on detailed measurements at 1 site. This steady-state model calculates the long-term maintenance fertiliser S requirements as the sum of the losses of S from the soil–plant–animal system assuming that the accumulation of organic S had reached a steady-state (Sinclair and Saunders 1984; Goh and Nguyen 1997). The contribution that organic S makes to plant-available S was acknowledged and situations that were not at steady state were accommodated using a pasture development index (PDI) (Sinclair and Saunders 1984), but as noted by Goh and Nguyen (1997), this methodology may not be accurate.

Subsequent reviewers (Nguyen and Goh 1994; Sagar *et al.* 1998) have emphasised the need to develop a dynamic S model for pastoral soils and highlighted the limitations in current knowledge preventing this development. Both emphasised the need to better understand the dynamics of organic S mineralisation and immobilisation and particularly, the need to measure and quantify the

contribution that organic S makes towards plant-available S. Addressing these issues, Watkinson and co-workers proposed (Watkinson and Perrott 1990), and subsequently verified (Watkinson and Kear 1996a), a rapid quasi-equilibrium model between soil sulfate S and a pool of readily plant-available organic S in New Zealand pastoral soils. A soil test that measures this pool of readily plant-available organic S has also been developed and calibrated (Watkinson and Kear 1996b). The significance and implications of this body of research appears to have been overlooked in these recent reviews.

Other recent developments in terms of improving the technical basis for making fertiliser recommendations include the development and verification of a model that describes and predicts the rate of oxidation of elemental S (S<sup>0</sup>) based on first principles (Watkinson 1989; Watkinson and Blair 1993; Watkinson and Lee 1994; Ghani *et al.* 1997). This enables the agronomic effectiveness of S<sup>0</sup> fertilisers to be accurately predicted. Furthermore, a database comprising records from over 3500 S field trials on pasture from throughout New Zealand has been compiled by the New Zealand Pastoral Research Institute Ltd (AgResearch) from which information on the size and pattern of pasture S responses can be determined.

All of this new research has been included in the S submodel of the AgResearch PKS Lime Decision Support Software (Overseer 5, 2003, D. M. Wheeler pers. comm.),

developed to assist consultants and advisers to make fertiliser decisions. The biological basis for some of the key components of the S submodel has already been published (Thorrold and Woodward 1995; Wheeler and Thorrold 1997; Ghani *et al.* 1997), but other relevant information remains unpublished.

The purpose of this review is to draw together this disparate information into a coherent review and, using this information, critically examine current fertiliser S practices and recommendations. This review does not attempt to comprehensively review all of the literature relating to the S cycle in pastures in New Zealand — this has been done elsewhere (Nguyen and Goh 1994; Saggar *et al.* 1998). Rather, it draws upon research that impacts upon the practical application of current knowledge.

### Sulfur dynamics in pastoral soils

#### Theoretical considerations

Organic S begins to accumulate in virgin soils when they are sown to legume-based pastures and fertilised. The rate of accumulation varies with soil group, climate and fertiliser S inputs and estimates range accordingly from 2–12 kg S/ha.year (Walker *et al.* 1959; Jackman 1964; Watkinson and Kear 1996a; Nguyen and Goh 1990; Saggar *et al.* 1998).

Given sufficient time (5–50 years), a maximum level of soil organic S is reached that is constant over long periods of time and unaffected by further S inputs. Jackman (1964) referred to this as the steady-state and the total amount of organic S accumulated at this point depends on the soil group, climate, and parent material (Table 1). It is lowest on drier soils (e.g. semi-arid soils), increases with increasing soil moisture conditions, and is highest on soils containing allophane or derived from organic matter (Watkinson and Kear 1996a).

Several workers (Nguyen and Goh 1994; Watkinson and Kear 1996a; Saggar *et al.* 1998) have pointed out that on a fertile soil that has reached its steady-state with respect to organic S accumulation, the annual uptake of S by pasture is

**Table 1. Measured steady-state concentrations of total organic sulfur ( $\mu\text{g/g}$ ) in the topsoil (0–75 mm) for some of the major soils groups in New Zealand**

Soil group <sup>A</sup>	Total organic sulfur <sup>B</sup>	Extractable organic sulfur <sup>C</sup>
Semi-arid	230 (227–235) ( $n = 2$ )	about 7
Pallic	500 (380–630) ( $n = 6$ )	15 (11–19)
Recent	605 (560–650) ( $n = 2$ )	18 (17–20)
Brown	630 (370–1070) ( $n = 6$ )	19 (11–32)
Pumice	900 (630–1180) ( $n = 5$ )	27 (19–35)
Allophane	1330 (1070–1800) ( $n = 7$ )	40 (32–54)
Organic	2900 (2600–3190) ( $n = 2$ )	87 (78–95)

<sup>A</sup>After Hewitt (1993).

<sup>B</sup>Derived from Jackman (1964) and Perrott and Sarathchandra (1987) ( $n =$  number of sites).

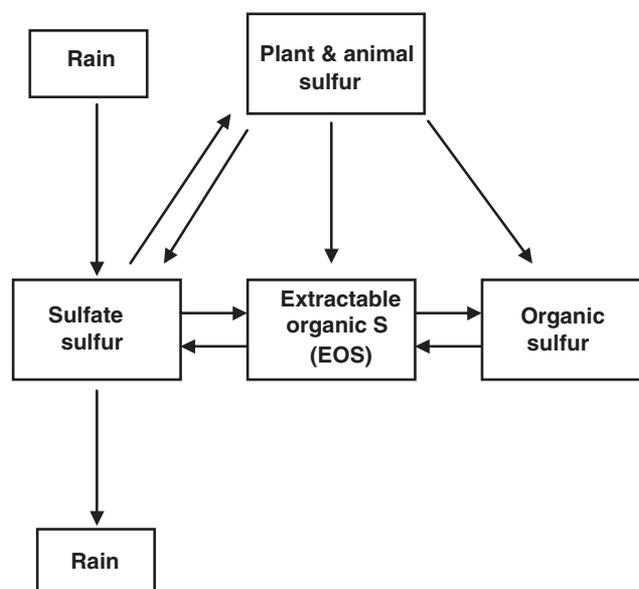
<sup>C</sup>Extractable organic sulfur (EOS) = 3% total organic S (G. S. Rajendram pers. comm.).

much greater than the amount of soil S present as sulfate S. This implies that some of the accumulated total organic S must be mineralised during the year and become plant-available. Sinclair and Saunders (1984) attempted to estimate this contribution to pasture S uptake by including a ‘pasture development index’ (PDI) in their steady-state S model, developed for estimating fertiliser S requirements for pastures.

Building on these ideas, Watkinson and co-workers (Watkinson and Perrott 1990; Watkinson and Kear 1996a) proposed a model to describe the major components of the soil–plant–animal S cycle in pastoral soils. This included a pool of organic S and a smaller pool of mineralisable organic S in quasi-equilibrium with a pool of sulfate S (Fig. 1). They also developed a simple soil test [extractable organic S (EOS)] to measure this pool of mineralisable organic S (Watkinson and Kear 1996b). In principle this is similar to the KCl-40 soil test developed by Blair *et al.* (1991) for Australian pastoral soils.

Watkinson and Kear (1996a) reviewed and discussed all the evidence supporting this quasi-equilibrium model and summarised the key points as follows:

- sulfate S remains constant (*for a given soil and under the conditions of equilibrium, emphasis added*), in spite of continuous removal by plants, and in some soils, leaching of an annual amount several times that present in the soil at any time;
- EOS is virtually constant for periods of up to 2 years (*noting that there is an annual cycle of small amplitude*) and is unaffected by any removal or addition of sulfate S by fertilisers, plants, urine from grazing animals or leaching. Only under animal dung is EOS elevated



**Figure 1.** Diagram of the Watkinson–Perrott quasi-equilibrium sulfur model for pastures (redrawn from Watkinson and Kear 1996a).

- significantly and this may be the mechanism that most contributes to the accumulation the total organic S;
- (iii) following the addition of a large amount of sulfate S (*normal fertiliser rates*), soil sulfate increases rapidly then returns within 2–6 months to a steady level (*specific to a given soil and its equilibrium EOS content*);
  - (iv) sulfate S and EOS are positively correlated with each other (*under equilibrium conditions*) and have a similar relation among all soil groups. There is sufficient variability in this relationship to accommodate other effects, such as small seasonal variations in EOS;
  - (v) sulfate S (*at equilibrium*) and EOS are directly related to the sulfate mineralised during laboratory incubation; and
  - (vi) soil sulfate, EOS and mineralised sulfate are all related to annual plant yield responses to sulfur fertiliser.

Tan *et al.* (1994a) reported that there was no relationship between sulfate S and EOS on 8 soils from Canterbury. However, it is not clear whether the conditions for the quasi-equilibrium — no recent additions of fertiliser S or leaching events — apply to this data. Certainly, the result from a soil that had been fertilised was an outlier. Leaving this exception aside, the remaining data are consistent with the quasi-equilibrium model noting that the evidence presented by Watkinson and Kear (1996a), in support of condition (iv) above, were from 42 New Zealand soils and 153 soils from the USA.

Tan *et al.* (1994b) also found considerable seasonal variation in carbon-bonded and HI-reducible S suggesting that condition (ii) above may also not apply. Also, Ghani *et al.* (1990) reported a large seasonal variation in biomass S. However, these observations do not necessarily invalidate condition (ii), because what is not known is how EOS is related to these seasonally variable properties. Certainly, the data presented by Watkinson and Kear (1996a) from 7 sites demonstrate that the temporal variability in EOS is very small relative to that of sulfate S, leading them to conclude that the relationship between EOS and sulfate S is sufficiently robust to accommodate small seasonal changes in EOS.

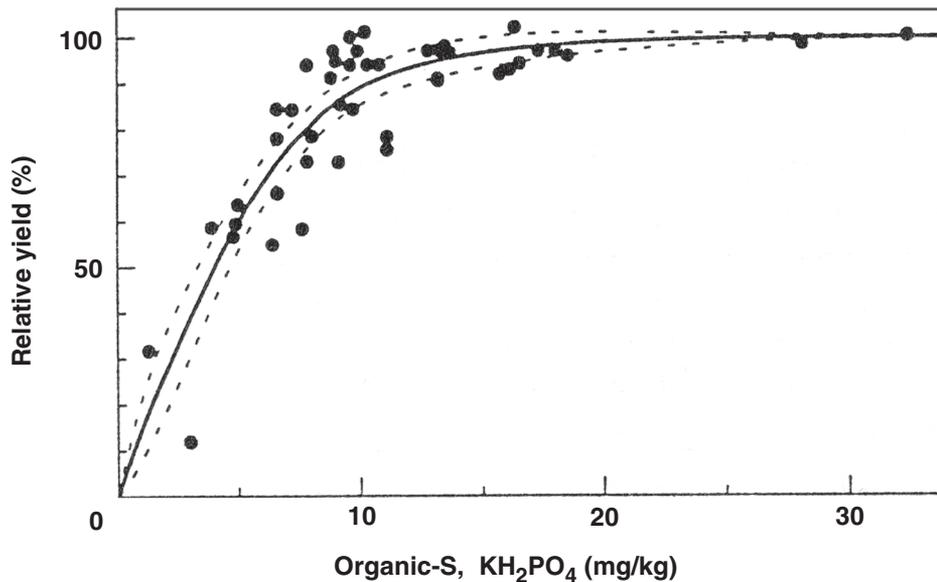
A novel aspect of the model is that it describes what is a microbially mediated process as if it were a chemical-physical process. To account for this, Watkinson and Kear (1996a) proposed that, at any given time, only a small fraction of the total organic S is accessible, on the aggregate surfaces, to the soil microbes and that it is this fraction that is involved in the steady-state equilibrium with sulfate S. This suggestion that the stability of organic S may be related to soil aggregation has been made elsewhere (see Saggar *et al.* 1998) and has been used to explain some of the differences in organic S accumulation between soil groups (Watkinson and Kear 1996a). As suggested by Watkinson and Kear (1996a), over time, soil aggregates are continually breaking down and reforming, providing a continuous supply of accessible

organic S. The factor determining the supply of mineralisable organic S is the rate of formation and deformation of the aggregates, and this is determined by soil physical and chemical processes, including drying, wetting, frost heave and animal treading and pugging. Thus, the size of the EOS pool, and hence the amount of sulfate S at equilibrium, is realistically related to soil chemical and physical properties.

A challenging implication of the model, as noted by Watkinson and Kear (1996a), is that organic S is uniform with respect to its synthesis and degradation by microbes. They reasoned that if a fraction of the organic S was resistant to microbial attack, for whatever reason, the total organic S would increase indefinitely, comprising an increasing proportion of the microbially resistant S. This clearly does not happen, as shown by Jackman (1964). This, they suggest, is evidence that all the various chemical forms of organic S are equally labile with respect to microbial degradation. Further evidence to support this comes from their earlier work (Watkinson and Perrott 1990) in which they showed that the small amounts of EOS are significantly correlated with increasingly alkaline extractants, 0.5 mol/L bicarbonate, 0.1 mol/L caustic soda and finally total S itself.

Both Nguyen and Goh (1994) and Saggar *et al.* (1998) in their reviews of the literature, noted that there is conflicting evidence regarding the chemical composition of organic S and in particular, the proportion, role and lability of HI-reducible and C-bonded S. A difficulty with this body of research is that most data is derived from short-term incubation and/or pot trial experiments. Pamidi *et al.* (2001) demonstrated that the choice of methodology can affect the results and Ghani *et al.* (1992, 1993a, 1993b) reported that the chemical form of S, either immobilised or mineralised, depends on the initial sulfate S concentration, the soil pre-treatment (air-dried, moist), addition of substrates (C, N and S) and, importantly, the duration of the experiments. It appears however that the majority of the evidence is consistent with the conclusion that both forms are involved in mineralisation and immobilisation, with emphasis on HI-reducible S being the more labile (Freney *et al.* 1975; McLachlan and De Marco 1975; McLaren *et al.* 1985; Ghani *et al.* 1993a, 1993b; Blair *et al.* 1994; Goh and Pamidi 2003). Thus, this body of research does not contradict the hypothesis that organic S is functionally uniform with respect to microbial degradation, as implied by the quasi-equilibrium model, noting the annual timescale implicit in the model. Clearly, more work is required on this point. If indeed organic S is functionally uniform, then the significance of chemically defined fractions such as HI-reducible and carbon-bonded may have limited interpretive and diagnostic value.

The quasi-equilibrium model implies that all soils will, broadly speaking, behave similarly, the only differences being in the size of the respective pools of S and the rate of turnover of the aggregates and microbial activity and the rate

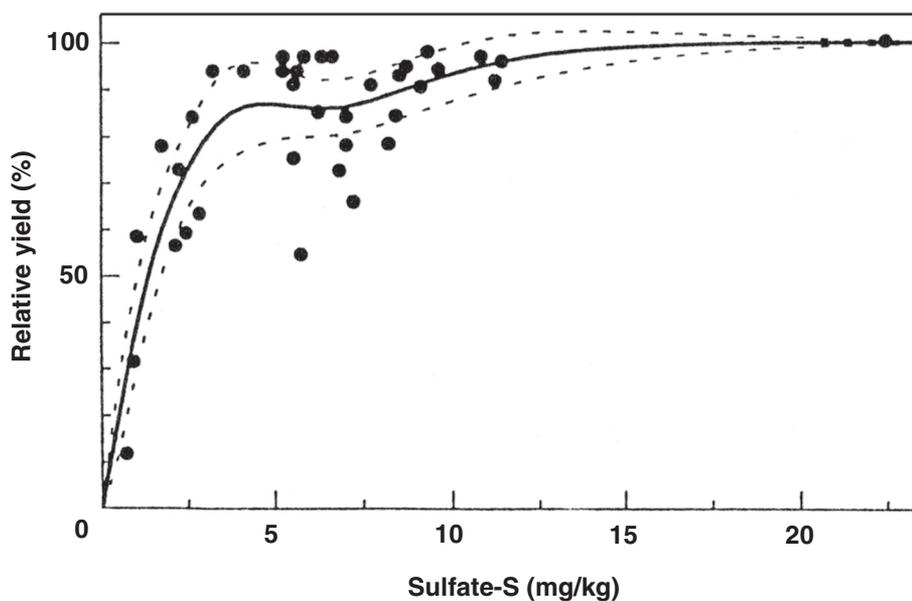


**Figure 2.** The relationship between relative annual pasture production and extractable organic sulfur (EOS) for a range of New Zealand soils (Watkinson and Kear 1996*b*) (dotted lines represent the 95% confidence interval).

of leaching of sulfate S. Indeed, the relationships between pasture response to S fertiliser, and (i) EOS (Fig. 2) and (ii) equilibrium soil sulfate concentration (Fig. 3), across a wide range of soils and soil groups (44 sites) confirms this to be the case.

Finally, the apparent contradiction that organic S accumulates in soils but EOS is relatively constant over time requires comment. As noted earlier the average annual rate of

accumulation of total organic S is between 3–13 mg/kg (assuming a soil bulk density of 0.90). Given that EOS represents about 3% (see discussion) of the total organic S then the maximum expected change in EOS is an increase of about 1 EOS unit every 2–3 years. Such a small change will only be detected in the long-term (5–10 years), against the normal field variation in soil fertility levels. The reverse processes are anticipated when fertiliser S is withheld,



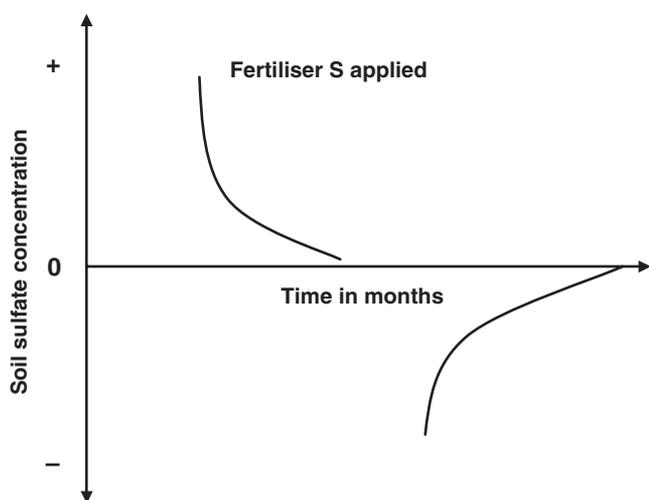
**Figure 3.** The relationship between relative annual pasture production and the equilibrium concentration of sulfate-S for a range of New Zealand soils (Watkinson and Kear 1996*b*) (dotted lines represent the 95% confidence interval).

although there is currently no experimental data to support this expectation.

The balance of the available evidence therefore supports the existence of the quasi-equilibrium, which in terms of diagnosing S deficiency and determining the need for S fertiliser has several practical implications. Providing that the conditions of the equilibrium apply — no recent leaching events or fertiliser S additions — EOS and soil sulfate represent the same entity and are both related to the degree of S deficiency (Figs 2 and 3). In practice however, leaching events disturb this equilibrium, reducing the concentration of sulfate S, and adding external sources of sulfate increases the concentration. This is the reason why the temporal variation in soil sulfate levels is relatively high, about 20–40% (Edmeades *et al.* 1988, Ghani *et al.* 1990). However, the perturbed soil sulfate concentration returns to the equilibrium concentration, dictated by the amount of EOS, within a short time (2–6 months) as shown by Watkinson and Kear (1996a). These effects are demonstrated pictorially in Figure 4.

In contrast, EOS is unaffected in the short term by these events, and the addition of animal excreta (Watkinson and Kear 1996b), and is relatively constant from year to year (Watkinson and Kear 1996b). For these reasons EOS is a more accurate measure of the soil S supplying capacity and is better correlated with pasture responses fertiliser S than sulfate S (compare Figs 2 and 3).

Since EOS is proportionally related to total organic S (Watkinson and Perrott 1990), the higher the total soil organic S, the higher the amount of EOS and consequently the higher the concentration of sulfate S that can be maintained by that soil. However, the capacity of soils to accumulate organic S varies (Table 1). Because of the climatic factors and soil properties discussed earlier, there are some soils such as the semi-arid and some Pallic soils,



**Figure 4.** Schematic representation of the effects of sulfur inputs from fertiliser and leaching losses on soil sulfate S and extractable organic sulfur (EOS) (zero equals the equilibrium EOS level).

that will never accumulate sufficient organic S such that the amount of organic S mineralised in any one year will be sufficient to supply the annual S requirements for a productive pasture. Consequently, such soils will always require fertiliser S inputs to achieve maximum production.

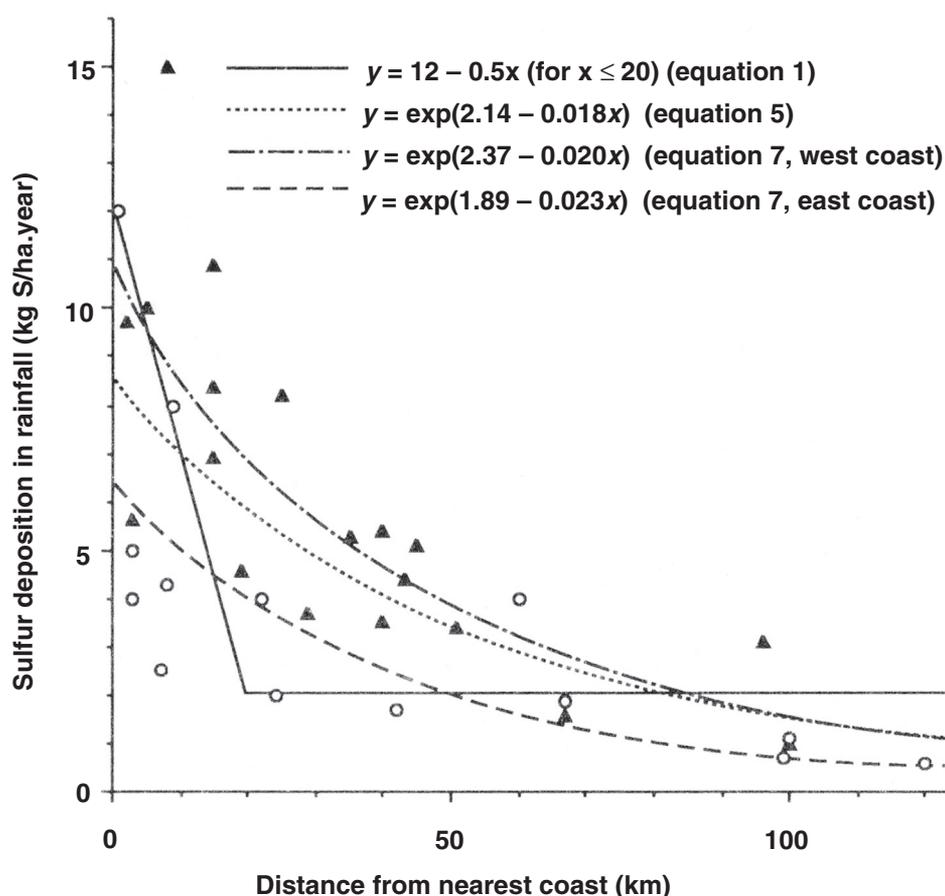
#### *Quantifying the sulfur cycle*

The amount of total organic S present when a soil has reached steady-state is finite and defines the upper limit for the amount of EOS that can accumulate in a given soil (Table 1). Once the steady-state condition is reached, further additions of fertiliser S do not result in further accumulation of organic S. This implies that the net losses of S, from removal of product, transfer to non-productive areas and leaching, will be equal to the net inputs from rainfall, irrigation and fertiliser.

Ledgard and Upsdell (1991) reviewed the available New Zealand data on the amounts of S deposited in rainfall. They found a 25-fold range in the amounts of S deposition ranging from 0.6 (Central Otago) to 15 kg S/ha.year (Helensville, Auckland). The major determinant was the distance from the coast (Fig. 5) but this relationship was different for the east and west coasts. Typically, agronomically significant amounts of S (>5 kg/ha.year) from rainfall only occur within <20–30 km of either coast.

A summary of recent data on leaching losses of sulfate S from intensive pastures is given in Table 2. The losses ranged from 15–89 kg S/ha.year. In their review, Nguyen and Goh (1994) summarised the available data suggesting leaching losses of between 11–43 kg S/ha.year. Most of their data was from less intensive farming operations and the recent data in Table 2 indicate S losses could be higher, at least in some years under intensive grazing as was the case at the Waikato site. Nguyen and Goh (1994) and Saggat *et al.* (1998) reviewed the various factors that affect the rate of S leaching and both emphasised the important effect of drainage. Rajendram *et al.* (1998a, 1998b) reported that the drainage in each of the 3 years of their experiment (Table 2) was 550–600 mm, 670–710 mm and 232–300 mm, respectively, further illustrating the strong relationship between the amount of S leached and the volume of drainage. They also found that the rate of S leaching decreased (from 28 to 15 kg S/ha.year) with increasing fertiliser N (from nil to 400 kg N/ha.year). This effect can be attributed to the decrease in drainage (from 300 to 232 mm) resulting from the increase in fertiliser N inputs.

Nguyen and Goh (1992) and Goh and Nguyen (1997) constructed and quantified the S soil–pasture–animal cycle on a Pallic soil under sheep in Canterbury, based on detailed measurements of the S inputs and some of the outputs. Their key data (rounded up for simplicity) (see also Goh and Williams 1999), for the treatment with 188 kg superphosphate/ha.year, are shown in Figure 6. The total S inputs from fertiliser, rainfall and irrigation were



**Figure 5.** The effect of distance from the coast (km) on annual sulfur inputs to soils from rainfall (Ledgard and Upsdell 1991).

30 kg S/ha.year and plant uptake was 28 kg S/ha.year. Total losses of S as animal product and transfer where 6 kg S/ha.year. It was estimated that a total of 30 kg S/ha.year was returned to the soil, 14 kg S/ha.year as plant litter and 16 kg S/ha.year as animal excreta. [The discrepancy between total plant S uptake and the S returned to the soil suggests that some of the returned S may be overestimated, noting that pasture S uptake is likely to be more accurately measured than the outputs].

Nguyen and Goh (1992) and Goh and Nguyen (1997) partitioned the returned organic S (30 kg S/ha.year) between C-bonded and HI-reducible S (about 80% of the herbage and faecal S was C-bonded and 5% of the urinary S), arguing that the C-bonded S was returned to the organic pool and the latter, being water-soluble was returned to the pool of plant-available S. Consistent with this, Watkinson and Kear (1996b) found that urine had little effect on EOS, 5 days after deposition, but dung increased EOS, albeit slowly. Applying these distributions, Nguyen and Goh (1992); Goh and Nguyen (1997) estimated that of the 14 kg S/ha.year in returned plant litter, 11 kg/ha.year was returned to the organic S pool and 3 kg S/ha.year to the available S pool. Similarly,

the 16 kg S/ha.year returned as excreta was distributed as 6 kg S/ha.year to the organic S pool and 10 kg/ha.year to the plant-available pool. Thus, the annual additions of S to the organic S pool via recycling plant litter and animal excreta are 17 kg S/ha.year with a further 13 kg S/ha.year to the available S pool.

There is reliable evidence (Nguyen *et al.* 1989; Nguyen and Goh 1990), that this site is at steady-state with respect to

**Table 2.** Recent estimates of leaching losses of sulfate sulfur from pastoral soils (after Rajendram *et al.* 1998a)

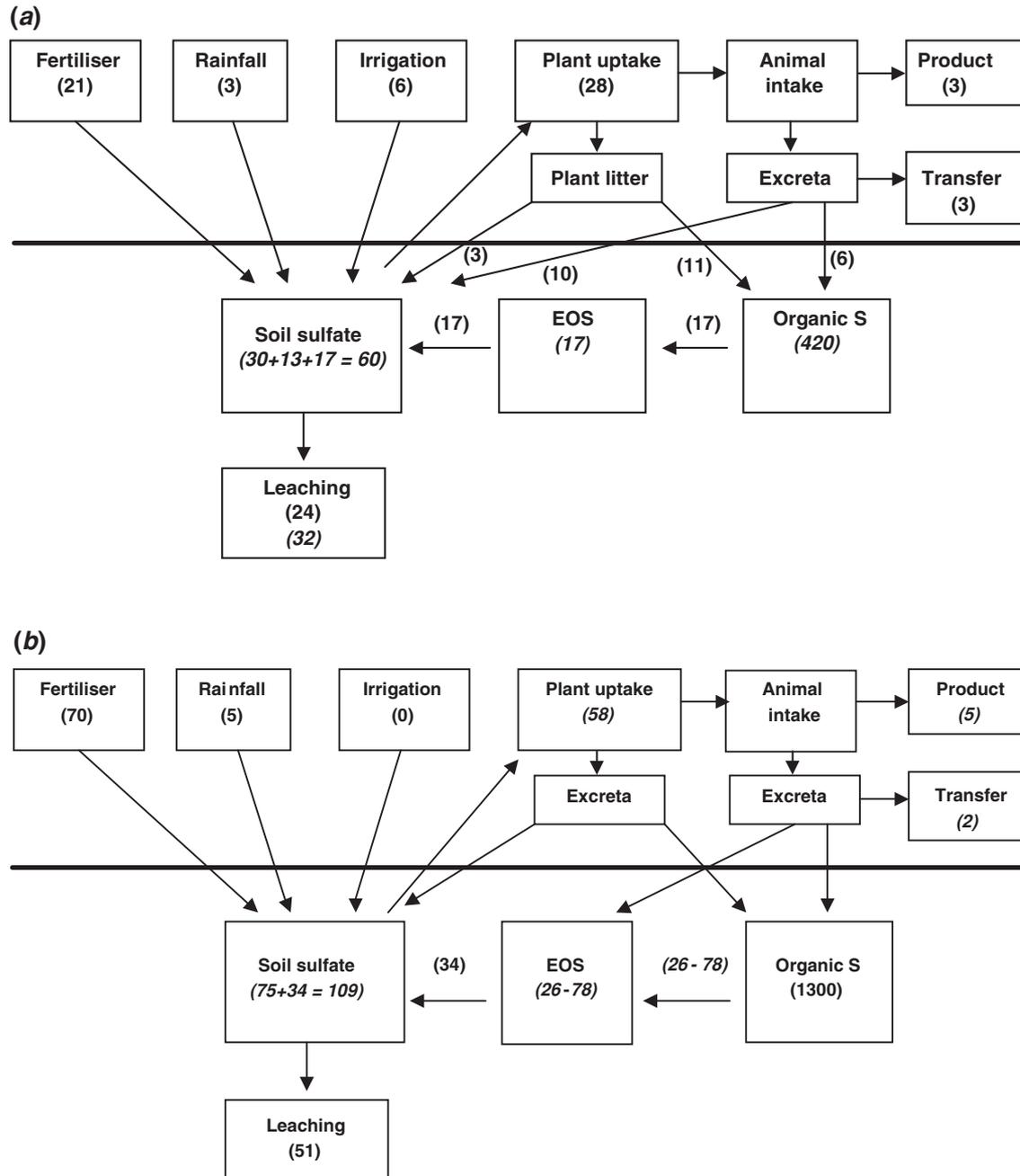
Year	Fertiliser sulfate S (kg S/ha.year)	Sulfate S leached (kg S/ha.year)
<i>Southland</i>		
1	100	42 <sup>A</sup>
2	200	22 <sup>A</sup>
<i>Waikato</i>		
1	84	15–39 <sup>B</sup>
2	84	57–89 <sup>B</sup>
3	84	15–28 <sup>B</sup>

<sup>A</sup>Mean of 4 rates of fertiliser N.

<sup>B</sup>Mean of 3 rates of fertiliser N.

the accumulation of organic matter and in particular organic S. Thus, by definition the net mineralisation of organic S should equal the net additions of organic S. Thus the net mineralisation of organic S on this site is estimated to be 17 kg/ha.year. This is consistent with the value of 19 kg S/ha.year derived from a similar experiment on another Pallic soil in the Manawatu (Tillman 1983; Saggar *et al.* 1998).

The steady-state organic S content of this Pallic soil is about 420 kg S/ha.year (Nguyen and Goh 1990, see also Table 1) and given that EOS is 3% (2–6) of the total S, then the quasi-equilibrium model would predict a net mineralisation of organic S of 13 (9–25) kg S/ha.year. Similarly, based on the organic S content of the soil in the Manawatu experiment (454 kg S/ha.year) (Sorn-srivichai 1980) the predicted rate of net mineralisation is



**Figure 6.** Components of the sulfur cycle in pasture at 2 sites: (a) Winchmore, pallic soil under sheep [values in brackets from Nguyen and Goh (1992) and Goh and Williams (1999)] for the 188 kg superphosphate treatment. Values in italics are derived. (b) Waikato No. 2 Dairy, volcanic soil under dairying [values in brackets from Rajendram *et al.* (1998a, 1998b)]. Values in italics are derived.

14 (9–27) kg S/ha.year. Thus, in both experiments the predicted rates of net S mineralisation of organic S are consistent with the observed rates within the limits of the accuracy of the available data.

Using the data of Rajendram *et al.* (1998a, 1998b), it is possible to calculate some of the components of the S cycle for a high producing dairy farm on a volcanic soil in the Waikato (Fig. 6). This research site has been farmed with regular inputs of fertiliser for over 50 years and is therefore likely to be at steady-state. Averaged over 3 years, the measured inputs of S were 75 kg S/ha.year of which the majority (70 kg S/ha.year) was derived from fertiliser S. The average rate of leaching was 51 kg S/ha.year. The mean pasture production was 16600 kg DM/ha.year (J. Lancaster pers. comm.). Assuming that the mean pasture S concentration was 0.35% then the annual pasture S uptake was about 58 kg S/ha.year. Thus, the total removal of S from the plant-available pool was 109 kg S/ha.year of which 75 kg S/ha.year was replenished via fertiliser and rainfall, suggesting that the amount of available S contributed via net mineralisation of organic S, together with the water soluble S component of excreta and plant litter, was about 34 kg S/ha.year. No soil S measurements (total soil organic S, EOS or sulfate S) were made on this site but if it is assumed to be typical of volcanic soils then a total organic S content can be estimated as 1300 kg S/ha (Table 1). This suggests a net mineralisation of 26–78 kg S/ha.year, consistent with the calculated rate of about 34 kg S/ha.year.

Thus, the available evidence from these 3 field trials is consistent with the predictions from the quasi-equilibrium model, that taken together with the evidence advanced by Watkinson and Kear (1996b), provides robust confirmation of the model. What is required of course is more field information of this type to confirm the application model under other circumstances.

### Measuring soil sulfur status

#### Soil tests

Watkinson and Kear (1996b) provide a useful summary of the historical development of soil tests for S. They noted that there is general agreement that sulfate S is an important source of plant-available S but to determine the total amount of available S in a given soil, the amount of sulfate S needs to be supplemented with some estimate of mineralisable S. Of the various methods that have been suggested for this purpose they argued that laboratory incubation tests were not suitable for routine advisory work and that the test proposed by Blair *et al.* (1991), based on heating the soil with a weak electrolyte (KCl), is limited because it does not measure absorbed sulfate S. For these reasons they investigated the use of both potassium and calcium phosphate (20 mmol/L) as extractants for both sulfate S and organic S. For both extractants, sulfate was measured by HPIC directly on the phosphate extracts (Watkinson and Kear 1994) and total S,

by inductively coupled argon plasma-atomic emission spectrometry (ICAP-AES) (Kear and Sutton 1991). Extractable organic S was calculated as the difference between total S and sulfate S.

They found that the potassium phosphate was superior to calcium phosphate for the following reasons: it extracted the same amount of sulfate but appreciably more organic S; the amounts of organic S extracted increased with increasing soil organic carbon, and presumably increasing organic S content, rather than reaching a plateau at about 5% organic carbon; and there were fewer analytical difficulties with the measurement of sulfate in the extract, using HPLC. For these reasons the potassium sulfate EOS overcame anomalous results on soils with high organic matter, and specifically the allophanic soils, and consequently gave a better correlation with relative pasture responses to applied S over 44 trial sites (Fig. 2).

Watkinson and Kear (1996b) commented that the EOS represents about 1% of the total organic S but it is not clear to which extractant they were referring. Subsequent work (G. S. Rajendram pers. comm.) using the same set of soils has shown that the potassium salt at 20 mmol/L extracts on average 3% (range 2–6%) of the total organic S.

The relationship between potassium phosphate EOS and relative pasture yield derived from 44 sites in New Zealand (25 North Island and 12 South Island) covering a wide range of soil types and groups and hence a range in EOS levels is given in Figure 2. The comparable relationship for sulfate S is given in Figure 3. There is, as is expected in field data such as this [e.g. see Blair *et al.* (1991) for a comparative example from Australia], some uncontrolled variability in these relationships. This is less for EOS than sulfate S as has been discussed. Nevertheless, allowing for this, the data can be interpreted to mean that soil S concentrations for both sulfate S or EOS need to be >10–12 for near maximum production, in the absence of fertiliser S. Sinclair *et al.* (1985) placed a similar interpretation on the relationship between soil sulfate and pasture response for an earlier set of New Zealand soils. Indeed, the data of Blair *et al.* (1991) from Australia using their KCl-40 organic S test can be similarly interpreted.

Based on Figure 2, pasture production on soils with EOS >10–12 did not increase with the application of fertiliser S, indicating that for such soils the annual plant S requirement is met entirely from the mineralisation of accumulated organic S. Conversely, soils with EOS <10–12 do not have sufficient reserves of organic S to meet the total S requirement of the pasture via mineralisation.

When fertiliser S is applied to a soil with a low EOS, organic S and hence EOS will increase only if the current level of total organic S is below the steady-state level obtainable for that soil. Thus, for most soil groups under pastoral agriculture in New Zealand the levels of EOS will gradually, given sufficient time and fertiliser S additions, increase to their steady-state determined maxima, as

determined particularly by climate and mineralogy (Table 1). However, the maximum concentration of EOS likely to accumulate in semi-arid and possibly some Pallic soils is less than the 10–12 (Table 1). It is not possible to increase the levels of EOS on these soils above these limits. Such soils will always require some fertiliser S inputs to supplement the amount of organic S mineralised in any one year, in order to maximise production.

In the absence of recent (>6 months) additions or removal of S, sulfate S and EOS are in a quasi-equilibrium and hence measure the same soil property – the ability of the soil to provide plant-available S. Consequently, the concentration of sulfate S at equilibrium is also related to the size of pasture responses to fertiliser S (Fig. 3).

These results are consistent with those obtained from a larger subset of historical trial data from the S database (Fig. 7). The uncontrolled variability in this relationship is larger than in Figures 2 or 6 for reasons to be discussed. Nevertheless, these data suggest that large pasture production responses (>10%) to fertiliser S occurred only when the soil sulfate concentration was <12, as measured using Inductively Coupled Plasma Spectroscopy (ICP) after deducting the organic S in the extract. This introduces a further potential source of variation at the laboratory level. Furthermore, EOS was not measured on these historical sites, and it cannot be known whether the conditions for the quasi-equilibrium apply. Not surprisingly therefore, there are instances in this dataset where no pasture responses to applied S were recorded, even though the soil sulfate concentration was <12. This can arise when a soil has adequate mineralisable organic S (EOS>12) but a recent leaching event has lowered the soil sulfate concentration to below the equilibrium level. Similarly, a high soil sulfate concentration, while indicating that the short-term (<6 months) S supply is adequate, does not necessarily mean that there is adequate available S for the

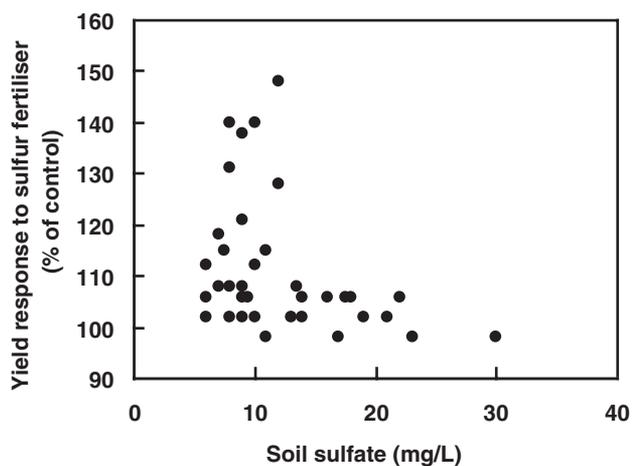
long-term. In other words such a site could still be responsive to fertiliser S applications.

From the discussion above, the following interpretations can be applied to the 2 S soil tests. If the conditions for the quasi-equilibrium apply, then sulfate S and EOS are both measures of the amount of mineralisable S in the soil and hence measure the long-term (1–2 years) S-supplying capacity of the soil. They both measure the severity of S deficiency, and concentrations of <10–12 for both sulfate S and EOS indicate that fertiliser S is required immediately to achieve maximum production. When the equilibrium conditions do not apply, EOS should still be interpreted as above, but under these circumstances the sulfate soil test is only a measure of the short-term supply (<6 months) of S. In practice it does not matter that the conditions for the quasi-equilibrium do not apply, providing the 2 S soil tests are interpreted as above.

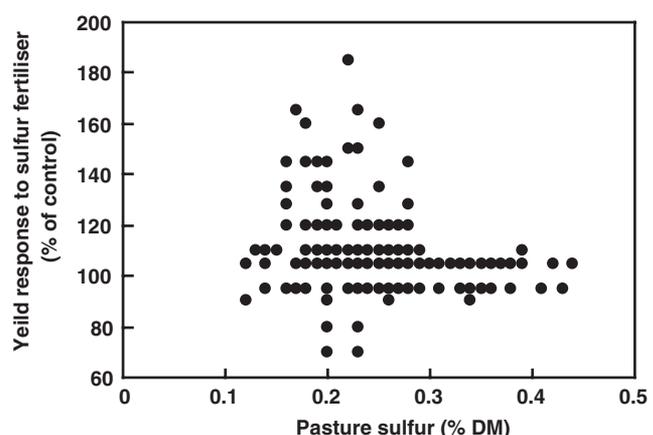
#### Plant analysis

The current criteria for interpreting mixed pasture S concentrations (Cornforth and Sinclair 1984; Roberts and Morton 1999) are as follows: deficient, <0.25%; low, 0.25–0.27%; optimum, 0.28–0.35% and high, >0.35%. These are based largely on the earlier work reported by McNaught (1970) and McNaught and During (1970), modified possibly by more recent trial work. The collective results from the database (Fig. 8) provide more formal evidence for the general validity of these criteria. Allowing for the normal variability associated with such data collected from a variety of sites, season and years, very few pasture responses to fertiliser S occurred if the mixed herbage S concentration, in either spring or summer, was >0.28%. However, no such relationship was apparent from samples collected in autumn and winter; a significant number of pasture responses occurred even though the S concentration were above 0.30% (data not shown). There is some evidence (Metson and Saunders 1978; Edmeades *et al.* 1983) that clover and grass S concentrations are higher in the autumn and winter and lower in the spring and summer. This suggests either that pastures require a higher internal S concentration during periods of slow growth or that the S supply is non-limiting during periods of slow growth. Whatever the explanation, the S content of pasture samples collected in spring and summer are a better guide for diagnostic purposes.

A potential limitation using single nutrient concentrations for diagnostic purposes is that it must be assumed that there is no interaction between the nutrients. Sinclair *et al.* (1996a, 1996b, 1997) initially, and Morton *et al.* (1998) subsequently, have explored this assumption by determining the relationships between various nutrient ratios and pasture yield, in factorial trials. Morton and Smith (2000) have recently summarised their findings. ‘Balanced and optimal nutrition’ is defined as occurring when there is sufficient supply of 1 nutrient so as not to limit the pasture yield



**Figure 7.** The relationship between pasture response to sulfate sulfur fertiliser (%) and soil sulfate concentration for trials on the AgResearch S database.



**Figure 8.** The relationship between pasture response to sulfate-S fertiliser (%) and mixed herbage sulfur concentration (% S) measured in spring for trials on the AgResearch S database.

response to another nutrient. Their initial results from a trial in Southland are shown in Table 3. To achieve 95% of the maximum yield, the concentration of S in the clover needed to be >0.23% and the ratio of S to N, and S to P, 0.0048 and 0.7–0.8, respectively. If these criteria were achieved there was sufficient S present not to limit the response to applied N or P.

Subsequently (Morton and Smith 2000) used these criteria to predict pasture responses to P, K and S at 8 other sites throughout New Zealand. These results confirmed their validity across a range of environments. Interestingly however, the absolute concentrations of P, K and S were as good as their respective ratios at predicting nutrient deficiencies. This suggests that over the range of soil nutrient levels covered in these trials, interactions between the nutrients are of little practical consequence.

From a practical perspective it is easier and less costly to collect a mixed herbage sample and Morton and Smith (2000) examined their data and found high correlations ( $R^2 > 0.70$ ) between the concentrations of P, K and S in samples of clover alone and in mixed herbage samples. Applying this information to the critical mixed herbage concentration of 0.28%, derived from the database (Fig. 8)

**Table 3. Nutrient concentrations and ratios required for adequate and balanced nutrition (after Morton and Smith 2000)**

Nutrient or nutrient ratio	Requirement for 95% relative pasture yield (% DM)
N	4.84
P	0.34
S	0.23
P/N ( $\times 100$ )	7.00
S/N ( $\times 100$ )	4.80
S/P	0.70–0.80

suggests a critical level for clover-only samples of 0.23% similar to that defined as deficient by Cornforth and Sinclair (1984) and Morton and Smith (2000) (Table 4).

#### Distribution and size of pasture responses to sulfur

Wheeler and Thorrold (1997) have described a database of pasture S trials, initially established to determine the effects of rates and types of S fertilisers on pasture production. The frequencies of responses to fertiliser S from these trials are summarised in Table 4, for the North and South Island, according to soil group.

This historical data reflects the S status of individual sites at the time the trials were undertaken; a combination of their initial organic S status together with their ability to accumulate organic S from any subsequent additions of fertiliser S. It is likely however that the majority of these trials would have been established on undeveloped or poorly developed pastures to which little fertiliser had been applied, and therefore reflect the native S status of the soils.

Generally there is a greater frequency of S responses in the South Island, indicating the widespread nature of S deficiency on these soils. The soil groups with the greatest frequency and/or degree of responsiveness are the organic soils, podzols and pumice soils in the North Island and the brown, pallic, melanic and semi-arid soils of the South Island. These observations are consistent with the relative amounts of organic S present in these soils in their undeveloped state. For example, the results of Blakemore

**Table 4. The frequency and size of pasture responses to fertiliser sulfur**

Soil group	Number of measurements <sup>A</sup>	Proportion (%) of measurements with responses >5%	Proportion (%) of measurements with responses >50%
<i>North Island</i>			
Allophane	216	34	1
Brown	174	33	0
Gley	74	26	0
Organic	18	39	17
Pallic	175	21	0
Podzols	27	63	17
Pumice	543	53	5
Recent	12	42	0
<i>South Island</i>			
Brown	373	56	19
Gley	33	46	0
Melanic	17	100	6
Pallic	384	58	11
Recent	33	50	0
Semi-arid	141	54	4

<sup>A</sup>The number of measurements refers to the product of the number of trials  $\times$  years  $\times$  rates of S fertiliser treatment. Technically the number of years in a pasture trial and the number of S treatments are not statistically independent. This will inflate the numbers but is unlikely to change their relativity.

*et al.* (1968) suggest the following order, in terms of the initial amount of total organic S: semi-arid < recent < pallic < brown = podzols = pumice soils < allophanic soils < organic soils, noting that for any given group, organic S decreases with increasing weathering and leaching.

From this database information a generalised map of New Zealand indicating the distribution and severity of S deficiency in pasture has been produced (Fig. 9) (S. F. Ledgard pers. comm.).

### Biological sulfur requirements

#### *Sulfur requirements for pasture development*

Using only those trials in the database that had at least 3 rates of S application, the amount of fertiliser S required initially (most of the trials were 1–3 years of duration) to completely eliminate S deficiency was determined from the shape of the response curve. Sufficient data were available to identify 2 sets of soil groups in terms of the amount of sulfate S fertiliser required for maximum production. For the South Island brown soils and the North Island allophanic soils, near maximum production was obtained with applications of 20–25 kg S/ha annually. In other words, for these soils, even the largest S deficiencies were completely eliminated with the input of 20–25 kg S/ha. However, the North Island pumice soils and the South Island recent soils required 40–50 kg S/ha (as sulfate) to achieve maximum production. [It is noted that the South Island recent soils cover a wide range of soil properties and it is not possible from this dataset to separate these soils further. It is probable however that the majority of this subset are from the coarse recent soils on the West Coast under high rainfall >1500 mm].

With reference to Figure 3, there are 3 factors that determine how much, and for how long, fertiliser S must be applied before no further S is required, except for maintenance. These are the initial amount of organic S present, the steady-state level of organic S and the rate at which fertiliser S is converted into organic S. Jackman (1964) found that the half-life to reach the steady-state was typically 20 years for soils containing allophane (2 pumice soils and 3 allophanic soils) compared with about 2–3 years for non-allophanic soils (2 pallic and 1 melanic soil). Significantly, the annual fertiliser S inputs on these sites were 35 kg S/ha (allophane containing soils), 12.5 kg S/ha (pallic soils) and 25 kg S/ha on the melanic soil. This implies that soil groups, such as the pallic soils, are more efficient in terms of converting fertiliser S into organic S and it is reasonable to suggest that this is related to the competition for S, between uptake by plants and microbes and losses due to leaching. These results, when considered together with those of Blakemore *et al.* (1968) discussed earlier, suggest a reason for the greater initial fertiliser S requirements on pumice and recent soils relative to the brown and allophanic soils.

The brown soils, and soils like them such as the semi-arid and pallic soils, have low initial and steady-state levels of

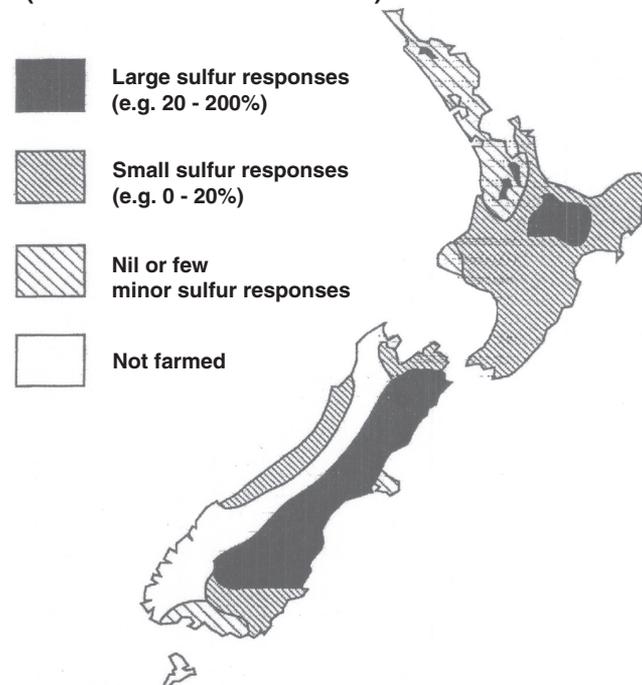
organic S but can rapidly convert fertiliser S into organic S until the steady-state is achieved, because leaching losses are low. In contrast, the pumice soils, and soils like them in terms of their susceptibility to leaching such as the podzols and recent soils, have low initial organic S levels and are less efficient at converting fertiliser S into organic S. Therefore their initial fertiliser S requirements are much higher (about 40–50 kg S/ha.year). Two groups of soils fall outside this generalisation. The allophanic soils behave like the pumice soils in terms of ability to accumulate organic S but they have high initial organic S levels and thus lower initial S requirements than the pumice soils. The organic soils also appear anomalous — they have high initial organic S levels and fertiliser S requirements. It is suggested that for these soils the total organic S does not reflect the pool of plant-available S levels because of their wide C/N/S ratio (Perrott and Sarathchandra 1987).

For these reasons it is proposed (Table 5) that the initial (1–3 years) S requirements for maximum pasture production can be summarised based on the initial organic S status of soils, and, particularly, their susceptibility to leaching.

#### *Maintenance requirements*

Overseer 5 (2003), the AgResearch PKS Lime decision support system for making fertiliser recommendations, uses the relationship between EOS and relative yield (Fig. 2) to

### Sulfur responsive zones (based on recent field trials)



**Figure 9.** A generalised map of New Zealand showing the degree and extent of pasture responses to fertiliser sulfur (S. F. Ledgard pers. comm.).

**Table 5. Inputs of fertiliser sulfur required to achieve maximum production for pasture development**

Soil loss category	Soil groups	Typical soil properties	Fertiliser S category for maximum production (kg S/ha.year)
High loss	Pumice, Podzols, Organic, South Island Recent	Low EOS, low ASC (<60), high rainfall (>1500 mm), high permeability, coarse texture	40–50
Low loss	All other soil groups	Low to high EOS, ASC >60, low rainfall, low permeability	20–25

predict the degree by which S is limiting pasture growth in the absence of fertiliser S. This relationship, as discussed by Watkinson and Kear (1996a) applies to all soils. The fertiliser S requirement for a specific site is then calculated as the amount of S required to achieve maximum production, after taking into account the likely net mineralisation and leaching losses, that in turn are predicted from the rainfall, drainage, soil type and anion storage capacity (ASC, formerly phosphate retention) (D. M. Wheeler pers. comm.).

The outputs from Overseer 5, for the 2 experimental sites previously discussed (Fig. 6), are given in Table 6 (Winchmore and Waikato) for increasing inputs of fertiliser S. In both cases an EOS of 12 is assumed and the stocking rates and production levels are as reported. In both cases the net mineralisation of organic S decreases with increasing inputs of fertiliser S, consistent with experimental observations (Thorrold 1994) and the quasi-equilibrium model, and if sufficient fertiliser S is applied, organic S begins to accumulate, depending on the site.

On the Winchmore site, the predicted losses of S as product and transfer are 6 kg S/ha.year, similar to that observed (Fig. 6), although the partitioning of this loss

between animal and excreta is very different. The predicted rate of S leaching is 26 kg S/ha.year, at a fertiliser S input of 20 kg/ha.year, consistent with the rate predicted by Nguyen and Goh (1992) and Goh and Williams (1999) of 24 kg S/ha.year from this site at the same fertiliser S input.

In the absence of fertiliser S, significant mineralisation of organic S is predicted. Obviously, the productivity of the site could not be sustained in the absence of fertiliser S. Defining maintenance as the input of fertiliser S required, such that the organic S pool neither increases nor decreases, and allowing for some variability in the output, suggests a maintenance input of about 20–30 kg S/ha.year consistent with the agronomic data for this soil group (Nguyen and Goh 1990).

For the Waikato site, in the absence of fertiliser S, the predicted net mineralisation of organic S is 19 kg S/ha.year and leaching losses are 14 kg S/ha.year. With a fertiliser input of 30 kg S/ha.year there is no net increase or decrease in the organic S pool and the leaching loss is predicted to be about 25 kg. As fertiliser inputs increase above 30 kg S/ha.year the leaching losses increase and organic S accumulates. Importantly, the predicted leaching loss with a fertiliser S input of 70 kg/ha.year is 58 kg S/ha.year, consistent with the measured loss of 51 kg/ha.year (Fig. 6).

**Table 6. Sulfur nutrient budgets derived from Overseer 5 for increasing inputs of fertiliser S (as sulfate) on two sites: Winchmore (sheep, stocking rate 19 SU/ha, EOS 12) and No. 2 Dairy (dairy, stocking rate 3.2 cows/ha, 1040 kg MS/ha, EOS 12)**

		Annual fertiliser S input (kg S/ha.year)					
		0	10	20	30	40	50
		<i>Winchmore site</i>					
Inputs	Fertiliser	0	10	20	30	40	50
	Rainfall	3	3	3	3	3	3
	Irrigation	6	6	6	6	6	6
Outputs	Product	6	6	6	6	6	6
	Transfer	0	0	0	0	0	0
	Leaching	15	17	26	35	44	54
S mineralisation (–) or immobilisation (+)		–12	–4	–3	–2	–1	0
		<i>No. 2 Dairy site</i>					
Inputs	Fertiliser	0	10	20	30	40	50
	Rainfall	2	2	2	2	2	2
	Irrigation	0	0	0	0	0	0
Outputs	Product	5	5	5	5	5	5
	Transfer	1	2	2	2	2	2
	Leaching	15	14	16	25	34	43
S mineralisation (–) or immobilisation (+)		–19	–9	–1	0	+1	+2

**Table 7. Effect of time of application of sulfur fertilisers on pasture production (after Wheeler and Thorrold 1997)**

Form of S	Trials	Number of trials	Ratio of annual yield (spring or autumn application)	Annual response to autumn application (%)	Annual response to spring application (%)
Sulfate S	All trials	17	1.01	21	21
	Pumice soils	7	1.06	23	24
	Other North Island	4	0.99	8	8
	South Island	6	0.96	28	27
Sulfate elemental S mixes <sup>A</sup>	All trials	3 <sup>B</sup>	1.08	46	50
Elemental S	All trials	8	0.96	12	12

<sup>A</sup>55% sulfate S.<sup>B</sup>All free-draining permeable soils.**Effects of S fertilisers***Time of application*

Wheeler and Thorrold (1997) have analysed the results from a subset of trials on the database that compared the effects of applying the annual S requirement either all in the spring or all in the autumn (Table 7). A ratio of >1 indicates that pasture production was greater from spring-applied S.

For both sulfate and S<sup>0</sup>, the differences between spring and autumn applications, in terms of total annual pasture production, are very small, indicating that in general, it does not matter when S fertiliser is applied.

There appears to be a small pasture production benefit (6–8% on an annual basis, data not shown) in favour of spring sulfate S applications on the pumice soils and the 3 other free-draining soils, supplied with a mixture of forms of S. This was expressed in greater summer production (16–17%) but poorer winter production (13–15%, data not shown). These data suggest that where leaching of sulfate is high, spring sulfate applications may be an advantage.

However, on all other soils in both Islands where sulfate S was applied, there was a slight pasture production advantage (4% on an annual basis, data not shown) to autumn applications, suggesting that where S leaching is less severe there maybe a small advantage to applying sulfate S in the autumn.

Time of application of S<sup>0</sup> also had very little effect on annual production but there was a slight advantage favouring autumn applications. This result applies only when the S<sup>0</sup> has an appropriately small particle size (see section below on S<sup>0</sup> as fertiliser).

*Single or split applications of sulfate S*

A similar methodology was used by Wheeler and Thorrold (1997) to examine the effects of the same amount of fertiliser sulfate applied in either a single annual application or split into 2 equal applications in autumn and spring (Table 8).

Once again, large responses occurred irrespective of the frequency of application. On an annual production basis, the frequency of application of fertiliser sulfate on most S deficient sites, including those in the South Island, had little effect. However, for the free-draining pumice soils and especially the organic soils, annual production was greater (9–17%) when sulfate S was applied as multiple applications. This benefit was apparent in all seasons (data not shown).

*Annual or triennial applications*

In extensive pastoral agriculture where annual nutrient inputs are low it is advantageous to apply fertiliser infrequently. This can be done for an immobile nutrient such as P without any loss in production (Morton *et al.* 1995). For a mobile nutrient such as sulfate S the trade off between the frequency and cost of application is more relevant.

The results (Table 9) show that for sulfate S, triennial applications — that is 3 times the annual application all applied in year 1 — are inferior to annual applications in all but the first year of the 3 year cycle. With S<sup>0</sup> however, infrequent triennial applications were superior to annual applications. The difference in the form of S in this case is due to the longer residual effect of S<sup>0</sup> relative to sulfate S.

**Table 8. Effects of single vs split applications of sulfate S on pasture production (after Wheeler and Thorrold 1997)**

Trials	No. of trials	Ratio of annual yield (single/split)	Response to annual application (%)	Response to split application (%)
All trials	21	1.06	42	45
Pumice soils	9	1.09	25	27
Organic soils	2	1.17	165	193
South Island	9	1.03	34	35

**Table 9. The effect of annual or triennial applications of sulfur fertilisers on pasture production (after Wheeler and Thorrold 1997)**

Form of S	No. of trials	Pasture production relative to annual S applications				Annual pasture response to annual application
		Year of measurement				
		1	2	3	4	
Sulfate S	8	1.03	0.98	0.96	1.05	26
Elemental S	4	1.06	1.06	1.00	1.05	17

*Elemental S as a fertiliser*

Sinclair *et al.* (1985) summarised much of the earlier work examining the effect of particle size on the agronomic effectiveness of S<sup>0</sup>. They recommended that for annual fertiliser application, S<sup>0</sup> should be <150 microns for cool-temperate regions and <250 micron (50% <150 microns) for warm-temperate regions.

In this earlier research the effectiveness of S<sup>0</sup> was measured indirectly by measuring pasture growth and or soil sulfate concentrations. To obviate the need for further agronomic trials, Watkinson and co-workers developed the methodology to measure small amounts of S<sup>0</sup> residues in soils and used this to develop and test a model that describes and predicts the rate of oxidation of elemental S (Watkinson 1989; Watkinson and Blair 1993; Watkinson and Lee 1994).

The 2 factors that had most influence on the rate of oxidation were particle size and climatic zone (Table 10), the latter reflecting the net result of the opposing effects of soil moisture and temperature on S<sup>0</sup> oxidation. Given the suggestion of Goh and Nguyen (1990) that the presence of grazing animals may also affect the rate of oxidation of elemental S it is noted that oxidation model developed and substantiated by Watkinson and co-workers is based on measurements made under a grazing influence.

From this information it can be predicted that S<sup>0</sup> must be at least <150 microns to be completely oxidised in the year of application in cooler regions and <250 micron in warmer, moister regions (Table 11). These results substantiate the earlier conclusions of Sinclair *et al.* (1985).

The particle size analysis of some commonly used S<sup>0</sup> fertilisers in New Zealand are given in Table 12. Applying the S oxidation model to these data it can be calculated that the proportion of the elemental S oxidised in the year of application for the various products is: screened elemental S (31–43%), Durasul (30–40%), S super 50 (39–47% or 49–65% depending on which analysis is applied) and S super

**Table 10. Effect of particle size on the proportion of elemental S oxidised in the year of application in two climate zones**

Particle size (microns)	Proportion (%) oxidised in 1 year	
	Warm temperate	Cool temperate
1000–2000	15	10
500–1000	30	20
250–500	50	30
150–250	75	55
75–150	95	80
38–75	100	100

30 (70–80%). The difference between the 2 S-fortified superphosphates results from an interaction between the proportion of elemental S added and the final particle size (Boswell and Friesen 1993). It is also noted that there is recent evidence (M. B. O'Connor pers. comm.) suggesting that Durasul may be more effective than indicated by its particle size and may be as effective as the elemental S in S super 30 in Northland.

From this information, the amounts of the various products required to provide either 50 or 25 kg available S/ha in the year of application, can be calculated (Table 13). S super 30 is agronomically equivalent to superphosphate if it is applied at 1.2 times the rate of total S, and S super 50 would need to be applied at 1.8 times the rate of total S to be agronomically equivalent to super.

*Sulfate S v. S<sup>0</sup>*

Only a few trials have compared these 2 forms of S at several different rates of application. McNaught and During (1970) found that S<sup>0</sup> (particle size not given) was superior to sulfate S over a range of S inputs, 2 years after the initial applications on a podzol on the West Coast. Williams and Morton (1985) reported similar results on 3 low ASC soils. They found that a single application of sulfate S, irrespective

**Table 11. The effect of climatic zone on the oxidation of elemental S**

Region	Particle size for 100% application to be oxidised in the year of application (microns)
Warm temperate: Northland, Waikato, BOP, King Country, Taranaki, Northern East Coast	<250
Cool temperate: Taupo, Hawkes Bay, Wairarapa, Wanganui, Marlborough, Caterbury	<150
Cool temperate high rainfall: West Coast	<250
Cold temperate: Otago, Southland	<75

**Table 12. The particle size distribution of elemental S (S<sup>0</sup>) in some common New Zealand sulfur fertilisers**

Sieve size (microns)	Screened	Percentage passing sieve size		
		Sulfur super 30	Sulfur super 50	Durasul
2000	90	—	99 <sup>A</sup> (90) <sup>B</sup>	—
1000	67	100	98 (68)	90
500	42	97	90 (45)	55
250	26	75	54 (30)	13
150	17	59	22 (28)	3
75	9	—	7 (18)	—

<sup>A</sup>From Boswell and Friesen (1993).

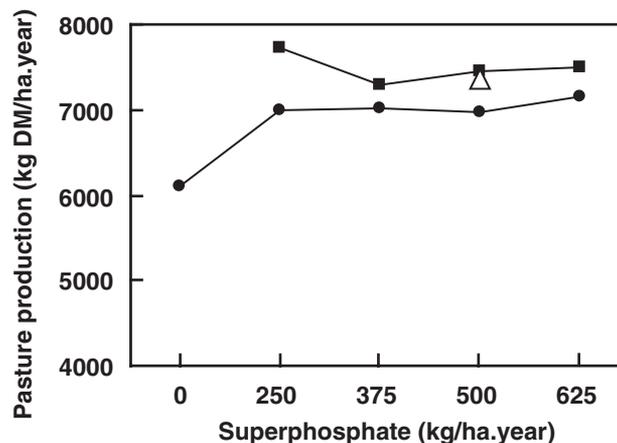
<sup>B</sup>From Sinclair *et al.* (1997).

of the rate of application, was insufficient to achieve maximum production (Fig. 10) which was achieved either by adding S<sup>0</sup> (50 kg S/ha.year) to the application of sulfate S (25 kg/ha) or splitting the sulfate S application into 2 equal applications in spring and autumn. But even in this extreme situation, the advantage of doing this, relative to a single application of sulfate S, was only about 6% of the annual pasture production.

Ledgard *et al.* (1993) compared the effectiveness of different rates of sulfate S and S<sup>0</sup> (as measured by pasture S recovery) on a pumice soil (free draining) and an allophanic soil (slow draining). On the pumice soil, autumn-applied S<sup>0</sup> was superior to autumn-applied sulfate, but there was little difference when they were applied in the spring. On the allophanic soil, spring sulfate was superior to spring S<sup>0</sup> and there was little difference when applied in the autumn (Fig. 11).

From these results and those discussed previously the following principles emerge with respect to the use of sulfate S or S<sup>0</sup>:

- for extensive farming operations where fertiliser is applied for economic reasons either bi- and triennially, S<sup>0</sup> is superior to sulfate S because of its longer residual effect;
- for high leaching soils (rainfall > 1500 mm, coarse textured and with ASC < 60) and where fertiliser is normally applied in a single application annually, S<sup>0</sup> applied in the autumn is the least risk strategy;
- for high leaching soils (rainfall > 1500 mm, coarse textured and with ASC < 60) and where fertiliser is



**Figure 10.** The effect of superphosphate (●) and superphosphate plus elemental S (50 kg S/ha) (■) and a split application (50:50 spring and autumn) of superphosphate (Δ) on pasture production on 3 soils on the West Coast (Williams and Morton 1985).

normally applied in spring and autumn for other reasons, such as reducing luxury uptake of K to minimise animal health problems, then sulfate S is as effective as S<sup>0</sup> but the least risk strategy is to apply some of the S in an S<sup>0</sup> form; and

- for all other soils and situations, sulfate S is as effective as S<sup>0</sup> providing the later is < 250 micron (warm regions) and < 150 micron (cool regions). If the S<sup>0</sup> is coarser than this, then sulfate S will be superior initially.

#### Implications for fertiliser S strategies

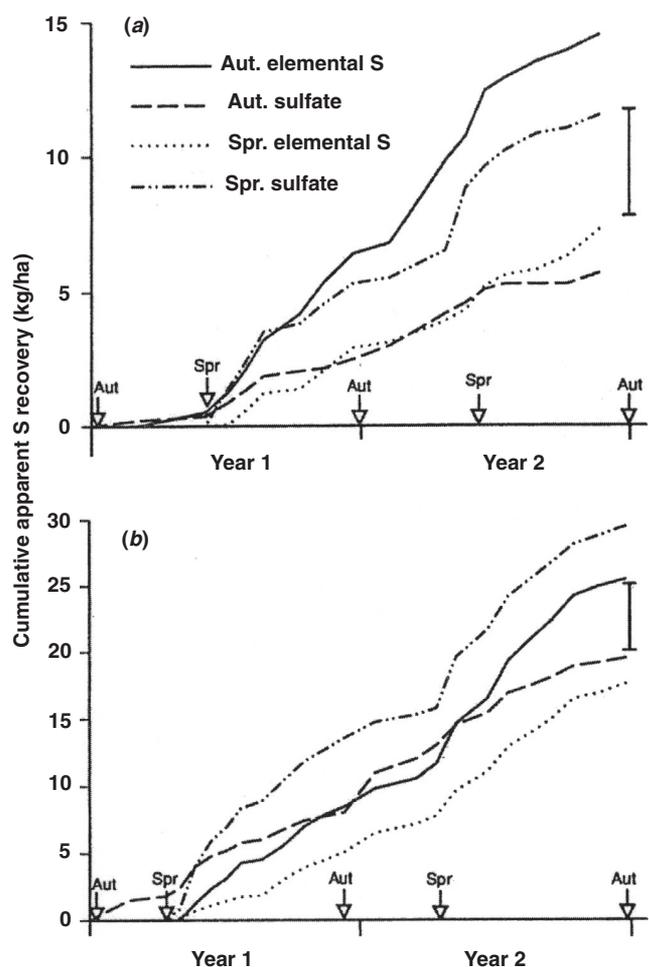
Using a combination of soil testing and plant analysis it is now possible to determine with some confidence the short- (< 6 months) and long-term (1–2 years) S status of most pastoral soils and to develop a fertiliser S strategy accordingly (Table 14).

If there have been no recent (< 6 months) additions of fertiliser S or leaching events and the sulfate and EOS tests are < 10–12 respectively, this is a good indication that the soil is S deficient in an absolute sense. It is likely that the mixed herbage S concentrations will be < 0.28%. Fertiliser S in an available sulfate form is required immediately to maximise production. Sulfate S concentrations can be > 10 even though the EOS level is < 10. This combination indicates that there is sufficient available S in the short term (< 6 months) but that

**Table 13. Inputs of various sulfur fertiliser required on high and low loss soils**

Soil loss category	Annual S requirement (kg S/ha.year)	Climate zone	Fertiliser input to supply annual S requirement in the year of application		
			Screened elemental S	Sulfur super 50 <sup>A</sup>	Superphosphate
High loss	50	Warm	116	190	454
		Cool	161	215	454
Low loss	25	Warm	58	95	227
		Cool	81	107	227

<sup>A</sup>Assuming the particle size of Sinclair *et al.* (1997).



**Figure 11.** The effect of form and time of application of sulfur fertilisers on the uptake of sulfur by pasture on (a) a Pumice soil and (b) an Allophanic soil (Ledgard *et al.* 1993).

this cannot be sustained through the mineralisation of organic S alone. Fertiliser S is required within 6 months — or perhaps longer if the sulfate concentration is  $>20$  — to maximise production.

The amount of fertiliser S required in either case will depend on the current level of EOS and whether it is intended to maintain or increase it. It will also be affected by the type of farm (dairy, sheep and beef) and the topography (Overseer 5, 2003; D. M. Wheeler pers. comm.).

Note that the semi-arid soils and some pallic soils will always have EOS levels of  $<10$ – $12$  indicating that fertiliser S will always be required on an annual basis on these soils to achieve maximum production.

For the allophanic and organic soils and some of the brown and pumice soils, EOS will slowly increase (5–10 years) if the fertiliser S input is greater than maintenance and once an EOS level of  $10$ – $12$  is achieved there will be sufficient organic S mineralised annually to meet the pasture S requirement to maximise production. Maintenance fertiliser S inputs are required in these circumstances to make good the S losses and maintain the soil S status. Either form of S can be used. If the EOS level is  $>15$ – $20$  fertiliser S could be withheld for some time (1–2 years) without any loss in production.

For the high loss soils several equally effective strategies can be adopted to apply the maintenance fertiliser S inputs. Split applications spring and autumn are desirable and this is feasible on most intensive farming operations where other nutrients, and particularly K, are also applied in split applications. However, if fertiliser is to be applied only once annually, as is the case for most extensive operations, the best options are to use sulfate S in the spring or appropriately fine  $S^0$  in the autumn (Table 15). For maintenance applications to low loss soils it does not matter when or in what form the S is applied, providing that the  $S^0$  is suitably fine.

#### Further research

The plea of earlier reviewers (Nguyen and Goh 1994; Saggarr *et al.* 1998) for the development of a dynamic model for S on pastoral soils and for a soil test that measures the contribution that mineralisable organic S makes to plant growth appears to have been headed. The available evidence confirms the validity of the quasi-equilibrium model but

**Table 14.** Interpretation of soil tests for sulfur and pasture analysis

Soil sulfate S (quick test sulfate)	Extractable organic S (EOS)		
	$<10$	$10$ – $20$	$>20$
$<10$	Soluble S required immediately followed by annual maintenance, pasture S $>0.28\%$ <sup>A</sup>	Annual maintenance (either sulfate or elemental S), pasture S may be $<0.28\%$	No fertiliser S required, pasture S $>0.28\%$
$10$ – $20$	Soluble S required within 6–12 months followed by annual maintenance, pasture S may be $<0.28\%$	Annual maintenance (sulfate or elemental S), pasture S $>0.28\%$	No fertiliser S required, pasture S $>0.28\%$
$<20$	Annual maintenance (sulfate or elemental S) <sup>B</sup> , pasture S $>0.28\%$	No fertiliser S required pasture S $>0.28\%$	No fertiliser S required, pasture S $<0.28\%$

<sup>A</sup>Mixed herbage was sampled in spring.

<sup>B</sup>Elemental S should be  $<250$  microns (warm regions) or  $<150$  microns (cool regions).

**Table 15. Strategies for single and multiple applications of fertiliser sulfate**

Soil loss category	Single or split applications	Time of application if single application made
High	Advantage to split application (spring and autumn)	Spring for sulfate S but may lose some winter production. Autumn for elemental S
Low	Split applications generally of no advantage	No difference in terms of annual production

further research should be undertaken to validate (or otherwise) the model across a wider range of conditions.

Further areas of research:

- (i) the model could have wider application to pastoral soils throughout the world. This could be investigated and future research internationally directed towards testing the 6 key principles (listed in the previous section) implicit in the model. Some of this information may already be in existence without the need for further experimentation;
- (ii) the model places emphasis on the amount of organic S present at steady-state. This is also an essential parameter for interpreting the soil EOS and sulfate S tests. However, the data in New Zealand are incomplete and further information is required to accurately define the amounts of organic S present at steady-state effect on the various soil groups and types in New Zealand;
- (iii) there is no information at present on the effect of withholding fertiliser S on the rate of decline of EOS over time. At present it is assumed that this is similar to the rate of increase in the presence of fertiliser S and assuming the soil is currently below steady-state. This assumption needs testing. If, for example, the rate of decrease of EOS is more rapid than expected, there would be a need for greater caution when advising farmers to withhold S inputs;
- (iv) the chemical form of S in EOS needs to be defined. This could be readily done. Such information is unlikely to impact on practical fertiliser decisions but may enhance our understanding of organic S;
- (v) the relationship between relative pasture production and EOS has been defined in New Zealand across 44 sites. It is unlikely that further series of field trials will be conducted or indeed are necessary, but this database could be expanded over time by individual researchers testing the relationship in other as yet untested situations; and
- (vi) finally, it has been suggested (by J. H. Watkinson pers. comm.) that the principles of the quasi-equilibrium model may also apply to nitrogen cycling in pastures, which like S, is dominated by organic forms. If this were so it may be possible to develop and calibrate a soil test for mineralisable N.

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