

Kinetics of field oxidation of elemental sulfur in New Zealand pastoral soils and the effects of soil temperature and moisture

J.H. Watkinson¹ and A. Lee²

¹*New Zealand Pastoral Agriculture Research Institute, Ruakura Agricultural Centre, Private Bag 3123, Hamilton, New Zealand* and ²*35 Tramway Road, Hamilton, New Zealand*

Received 11 June 1993; accepted in revised form 29 October 1993

Key words: elemental sulfur, mean annual oxidation rate constant, pastoral soil, slow release, soil moisture, soil temperature

Abstract

The effectiveness of elemental sulfur (S°) as a fertilizer is governed by its rate of microbial oxidation in soil to the sulfate form for absorption by plants. Some 80 field oxidation rate experiments were conducted under grazing throughout New Zealand for one year by measuring the residual S° in soil at approximately two-month intervals. The S° was applied as particles 75 to 150 μm in diameter at the rate of 30 kg ha^{-1} . The simple cubic oxidation rate model (no allowance for temperature or moisture changes) accounted for more than 80% of the variance at nearly 70% of sites.

The mean annual soil temperature (10-cm depth) was the most important factor found affecting the mean annual oxidation rate constants, accounting for 38% of the variance through the Arrhenius equation. Other factors, including rainfall, soil moisture, pH and soil groups accounted for only a further 2% of variance. The factor most likely to account for the balance of variance among the sites is the oxidizing efficiency of the associated microorganisms.

The rate constant versus temperature relationship for field oxidation in the five New Zealand climate regions was consistent with mean rate constants of soil groups from a similar set of 47 soils incubated at 25°C and field capacity moisture for 10 weeks or more. Field soils, therefore, had an average moisture for the oxidation rate equivalent to that at field capacity. This would explain the lack of contribution of soil moisture to the variance, and would support the use of the mean annual oxidation rate constant (from the mean annual soil temperature) for calculating the optimum particle size range of S° fertilizer. In confirmation, S° particle size recommendations from field rate constants for pastoral fertilizer were consistent with those from earlier agronomic experiments.

Introduction

Large areas of New Zealand are deficient in S for pastoral agriculture, and S° is increasingly used in place of sulfate fertilizers to reduce transport costs in both low and high rainfall areas (Boswell and Swanney, 1988) and to reduce amounts of S applied in areas of high sulfate leaching.

S° as a fertilizer

S° is the most concentrated form of S possible (100%), minimizing transport and distribution costs (Boswell and Swanney, 1988). It is highly insoluble in water (Meyer, 1977) and only slowly oxidized to sulfate by atmospheric oxygen (Chapman, 1989; Wainwright, 1984) so the

product does not need careful protection from air or rain, and residual S° in soil is not leached by rain. In soil it is rapidly oxidized to sulfate by S° -oxidizing microbes under conditions favourable for plant growth (Sinclair and Boswell, 1983). In New Zealand thiobacilli are ubiquitous (Lee *et al.*, 1987; A. Lee, unpublished), and, although present in low numbers, they rapidly multiply and oxidize on addition of S° (Lee *et al.*, 1987; 1988). The system can, therefore, be partly self-regulating since the oxidation rate would also become slower under conditions unfavourable to plant growth, i.e. low moisture, temperature or nutrients (Sinclair and Boswell, 1983).

S° can pose an explosion hazard if the particles are extremely fine and undiluted with inert material. In New Zealand, molten S° added to single superphosphate during manufacture crystallizes giving 70 to 80% of the incorporated S° $<150 \mu\text{m}$ dispersed safely throughout the product (Boswell and Swanney, 1986; Sinclair and Enright, 1983). Heterotrophs oxidize at only about 10% of the rate of S° -oxidizing autotrophs (Watkinson and Blair, 1993) and this may be inadequate under low temperatures. For example, in Western Canada where S° is oxidized by heterotrophs (Germida *et al.*, 1984) and is of limited effectiveness (Janzen and Bettany, 1987b) the soil temperatures are below 15°C for most of the year (Janzen and Bettany, 1987b). The ineffectiveness may, however, have resulted from inadequate dispersion and incorporation of the S° particles into the topsoil (Solberg *et al.*, 1992).

Effects of temperature and moisture on oxidation rate

Incubation studies have shown that the S° oxidation rate in soil is related exponentially to soil temperature (Chapman, 1989; Janzen and Bettany, 1987b; A. Lee and J. H. Watkinson, unpublished), and parabolically to soil moisture, with the maximum at approximately the field capacity moisture (Janzen and Bettany, 1987b; Kittams and Attoe, 1965; Moser and Olson, 1953).

Soil moisture has a decreasing effect on oxidation rate (the parabola broadens) as temperature is decreased below 25°C (Janzen and Bet-

tany, 1987b), and as incubation time at 25°C is increased to four weeks or more (Kittams and Attoe, 1965; Moser and Olson, 1953). For the six soils from Western Canada studied by Janzen and Bettany (1987b), there was little change in oxidation rate at less than 23°C for water potentials between -10kPa (field capacity) and -1500kPa (wilting point).

The insular climate of New Zealand means that, at a given site, the maximum change in the average daily soil temperature during the year is only about 10°C (Lee *et al.*, 1988a,b), although for some inland areas it is greater. The average S° oxidation rate would not, therefore, change greatly from one season to another. Furthermore, the increased oxidation rate during the higher summer temperatures would be moderated by the lower moisture. (The New Zealand temperate climate is broadly characterized by warm summers and cool winters, with most rain falling in the winter.) Conversely, the decrease in rate during winter might be buffered to some extent by the increased moisture.

Soil moisture is generally much closer to field capacity than to the wilting point, particularly in soils under a higher rainfall ($>1200 \text{mm}$). For most of the year, therefore, soil moisture values would be such as to give close to the maximum oxidation rate. The exception would be during the lower moisture of the hotter summer period.

Oxidation rate models

A model following the oxidation of S° taking into account the diminution in size of the particles has been developed for soils at constant temperature and moisture (Janzen and Bettany, 1987a; McCaskill and Blair, 1989; Watkinson, 1989). For blocky-shaped particles (which can be treated as "equivalent spheres" (Watkinson, 1989) where the ratio of greatest to least size is no more than two, and where the mass distribution is constant with size, the appropriate equation is (Watkinson, 1989):

$$(m/m_0)^{0.33} = 1 - at/(bc)^{0.5} \quad (1)$$

where m_0 is mass of S° applied originally;
 m is mass of S° remaining at time t ;
 a is the oxidation rate constant in terms
of reduction in diameter per unit time
of the S° particles;
 $(bc)^{0.5}$ is the geometric mean of the
greatest and least sizes.

The rate constant, a , is a property of the site and is a function of the oxidizing organisms, soil temperature and moisture. Since m_0 , b , c are known and m is measured (Watkinson *et al.*, 1987) at a given time, t , " a " can be estimated. (Alternatively, an oxidation rate constant, k , can be defined equal to $1/2 \rho a$, (Watkinson, 1989), where ρ is the S° particle density of 2.07 g cm^{-3} (Meyer, 1977) and k becomes the mass of S° oxidized per unit area per unit time).

Equation (1) for particles of the same size has been modified to include the effects of temperature and moisture (Janzen and Bettany, 1987b; McCaskill and Blair, 1989). However, the modified models are based on only short term incubation experiments (one to three weeks) and have not been tested in the field (Janzen and Bettany, 1987b; McCaskill and Blair, 1989).

In view of the earlier discussion, it seems likely that the effect of moisture under New Zealand field conditions would be of much less importance than in the two proposed models (Janzen and Bettany, 1987b; McCaskill and Blair, 1989); and that the exponential effect of temperature on oxidation rate (Janzen and Bettany, 1987b) would be of far greater importance than moisture.

To measure field oxidation rates and check the applicability of the simple cubic oxidation rate model (uncorrected for moisture or temperature) for a narrow size range of S° (Watkinson, 1989), 75 to 150 μm , field trials were conducted under different climates throughout New Zealand in which residual S° in the soil was measured at regular intervals for at least one year.

Experimental

To determine the effects of climate, New Zealand was divided into five regions, based on 30-year

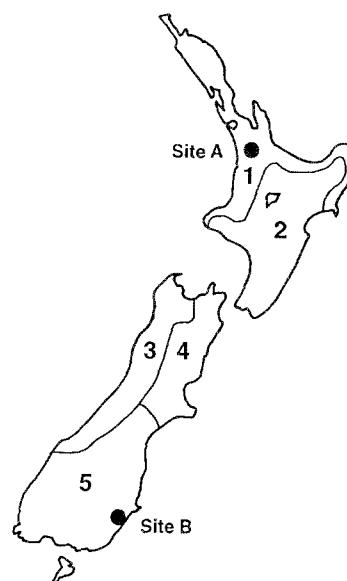


Fig. 1. Map of New Zealand outlining the five climate regions described in Table 1, and position of sites A and B (Table 3).

weather patterns (New Zealand Meteorological Service, 1984a,b) (Table 1, Fig. 1).

Some 80 small-plot field experiments were conducted throughout New Zealand, for one year or more (1989 to 1991) under grazing and over a wide range of soil groups, temperatures and moisture values. Sites with a recent history of applied S° were excluded.

The S° , 75 to 150 μm (Watkinson, 1989), was applied at the rate of 30 kg ha^{-1} on to duplicate, grazed plots of 9 m^2 in fields of dominantly, ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.). Untreated areas adjacent to the treated plots were sampled as control plots.

Eighteen soil cores (Watkinson *et al.*, 1987), 0 to 38 mm depth (and in some experiments 38 to 75 mm), were collected from treated and untreated plots at approximately two-month intervals. They were analyzed for residual S° (either immediately or after storage in a freezer (Watkinson *et al.*, 1987)), pH and gravimetric soil moisture.

Since the amount of S° applied, 27 g plot^{-1} , did not always correspond with the apparent amount applied, m_0 from regression analysis (see under discussion), Equation (1) was rearranged

Table 1. New Zealand climate regions based on temperature and rainfall

Region	Average annual soil temperature range, 10-cm (New Zealand Meteorological Service, 1984a) range (°C)	Annual rainfall (New Zealand Meteorological Service, 1984b) (mm)
1. N North Island	13–15	1000–1500
2. S North Island	12–13	800–1500
3. NW South Island	10–12	1000–3000
4. NE South Island	9.5–11.5	800–1000
5. S South Island	8–10	400–1200

and plotted as:

$$m^{0.33} = m_0^{0.33} - m_0^{0.33} at/(bc)^{0.5} \quad (2)$$

The cube root plot also provided a uniform variance over the wide concentration range of S° in the soil, sometimes down to 1% of applied (Watkinson, 1989) (Fig. 2).

The annual mean soil temperature (10-cm depth) was measured directly at about 10 sites. Values for the others were supplied by the New Zealand Meteorological Services as best estimates from nearby meteorological sites in their national network.

Annual regional soil temperature at 10-cm depth (to nearest 0.5°C), as an estimate for the mean temperature during S° oxidation, and rainfall for the farmed areas were estimated from 30-year averages (1951 to 1980) on isotherm maps and rainfall tables (New Zealand Meteorological Service, 1984 a,b).

Results and discussion

Application of model to field oxidation

The intercept, m_0 , from Equation (2) was, on average, 60% (SD 14%) of the amount applied (27 g plot⁻¹) (Fig. 2). The loss of 40% on average, and its similarity at each site, can be explained in terms of partial retention of S° on the leaves

Table 2. Variances from fitting the simple cubic model, Equation (2)

Variance accounted for (%)	Number of sites (%)
>80	68.7
71–80	8.8
61–70	7.5
51–60	7.5
<51	7.5

of the pasture plants, and its subsequent ingestion by grazing animals and removal from the plots (possibly also by wind) before it could reach the soil. In experiments conducted the following year when more care was taken to recover applied S° , the average recovery increased to 80% (SD 24%)

On the assumption of a loss of some of the applied S° before reaching the soil surface, the data from the field experiments were in good agreement with the simple cubic model of Equation (1), rearranged as Equation (2) (Table 2, Fig. 2). The model accounted for over 80% of the variance at 55 sites, indicating that field oxidation was taking place under conditions of apparent constant temperature and moisture, as in laboratory incubation (Watkinson, 1989; Watkinson and Lee, 1992). The effect of short-term variations in temperature and/or moisture on the rate appeared

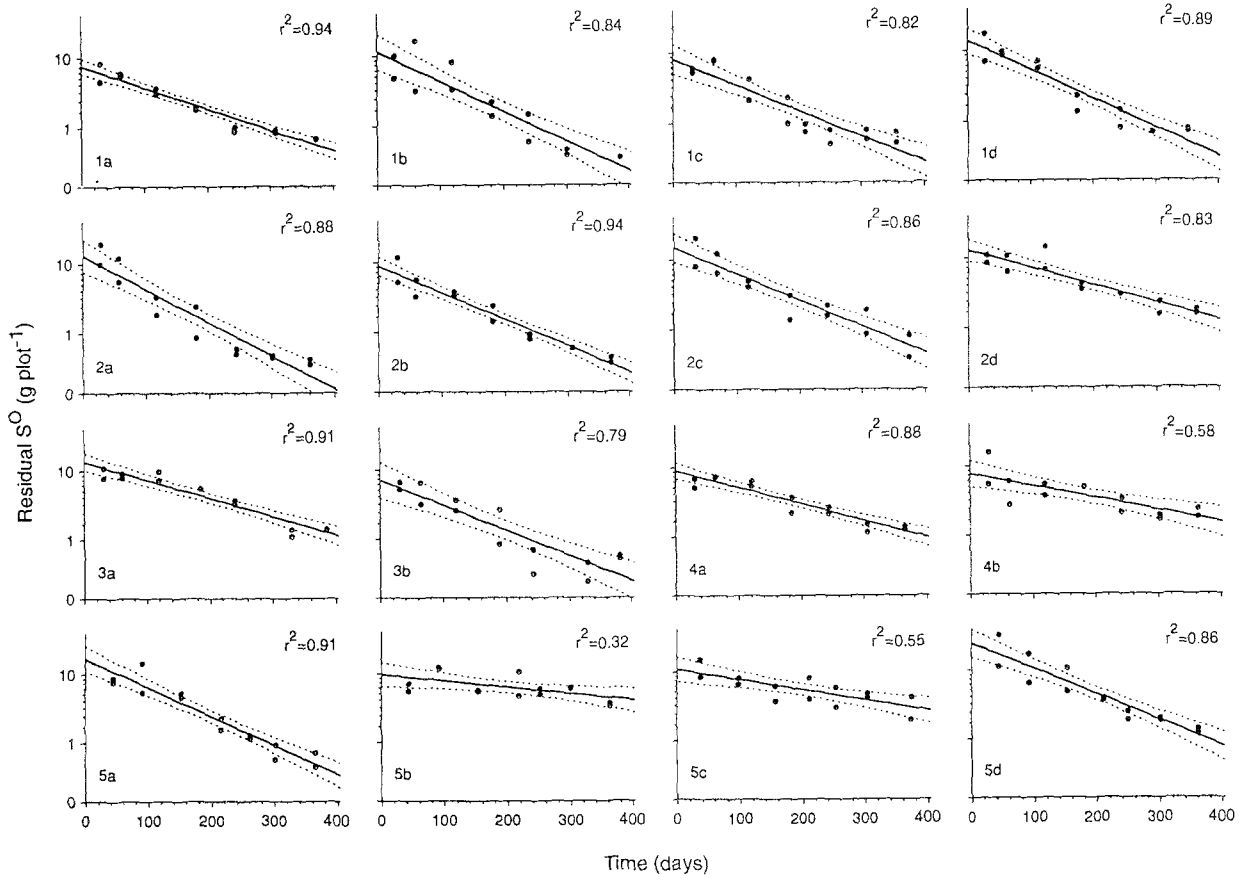


Fig. 2. Plots of the cube root of residual S° against time after application (Equation (2)) for 16 representative sites, showing regression lines, values for r^2 and 95 % confidence intervals (dashed curves). Four sites (a, b, c, d) are taken from the climate regions 1, 2, 5 in Fig. 1, and two (a, b) from each of regions 3 and 4.

to be within the experimental error of values estimated from the mean annual oxidation rate constant. Representative results from 16 experiments showing values for duplicate plots are illustrated in Figure 2. In a total of six sites (<8%) (Table 2) the model accounted for <50% of the variance, but sometimes this was because of the slow oxidation rate and not any poorer precision, e.g. Figure 2(5b) where $r^2=0.32$.

Because of the uncertainty in the amount of S° actually reaching the soil surface, as distinct from the amount of 27 g applied on to the grassed plot, it was not possible to estimate any value for the delay time, t_d (Watkinson and Lee, 1992). This was defined as the apparent time to achieve maximum oxidation rate (Watkinson and Lee, 1992). It included time for colonization of S° and multiplication of thiobacilli from numbers of 10 g^{-1}

soil, or less, to over 10^6 g^{-1} , so t in Equations (1) and (2) would otherwise have been replaced by $t - t_d$.

Analysis (Watkinson, 1993) of the field oxidation of S° in South Western Australia (Barrow, 1971) also showed that the data, covering 500 days, could be described using a mean annual oxidation rate constant. The model accounted for 89, 92, 98% of the variance at each of the three sites (Watkinson, 1993), respectively. Only at the Darkan site was there any evidence of an appreciable delay time, approximately 50 days (Watkinson, 1993).

Effect of soil temperature (10-cm depth) on the rate constant

Mean annual soil temperature. The mean annual

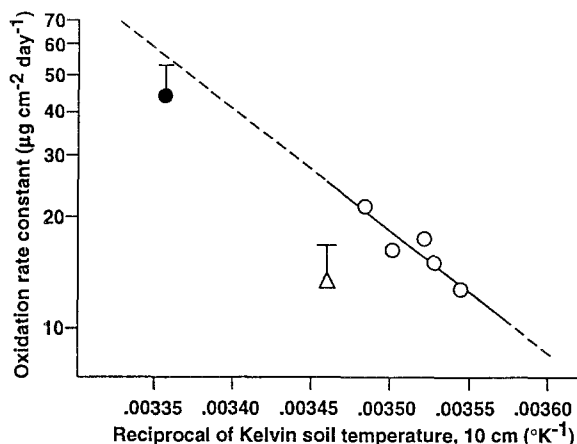


Fig. 3. Effects of soil temperature on the oxidation rate constant (a) for field oxidation in the five New Zealand climate zones (○), and at three sites in South West Australia (Δ) (Barrow, 1971; Watkinson and Blair, 1993) (assuming a soil temperature of 16°C); and (b) for laboratory incubation (at 25°C and field capacity moisture for 10 weeks or more), the mean of 45 soils distributed throughout New Zealand (●) (Lee *et al.*, 1987; Watkinson, 1993; A. Lee and J. H. Watkinson, unpublished).

oxidation rate constant may be used to summarise the effects of mean soil temperature and moisture. Since the oxidation rate will be determined more by soil temperature than moisture, by an activation energy in either a diffusion- or chemical reaction-controlled process, the Arrhenius equation is appropriate to relate the rate constant and temperature (Watkinson and Blair, 1993):

$$\log_e k = \log_e A - E_a/RT \quad (3)$$

where k is the oxidation rate constant ($\mu\text{g cm}^{-2} \text{day}^{-1}$);
 T is the Kelvin temperature ($^{\circ}\text{K}$);
 E_a is the activation energy (kJ mol^{-1});
 R is $8.31(\text{J } ^{\circ}\text{K}^{-1} \text{mol}^{-1})$;
 A is a constant.

The average values for the five climate regions are plotted in Figure 3, where the log of the average rate constant is plotted against the reciprocal of the mean annual soil temperature on the Kelvin scale (Equation (3)). From the slope of the regression line ($r^2 = 0.86$) the value of the activation energy can be calculated at 63 kJ mol^{-1} . This is lower than the values found from incubation studies of 70 to 90 kJ mol^{-1} (Watkinson

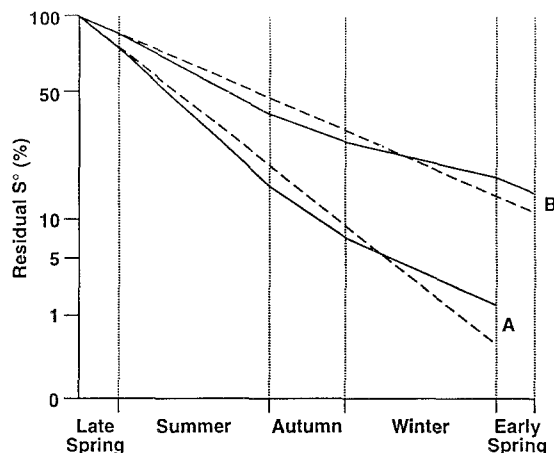


Fig. 4. Calculated effect of seasonal temperature variation on residual S° (solid lines —) for two sites representing the extreme climate zones, N North Island, site A (Lee *et al.*, 1988b) and S South Island, site B (Lee *et al.*, 1988a). The seasonal oxidation rates were calculated from the average seasonal temperatures, Table 3, and equation (2). The effect of using an annual oxidation rate is given by the dashed line (---). (Compare Fig. 2).

and Blair, 1993), but still indicates control by a chemical reaction rather than diffusion (10 to 40 kJ mol^{-1}).

In addition, the regression line extrapolates to within experimental error (SD presented as a vertical bar) of the mean of 45 soils from throughout New Zealand incubated at 25°C for 10 weeks or more (Lee *et al.*, 1987; Watkinson, 1989; A. Lee and J. H. Watkinson, unpublished). Since the soil moisture during the incubations was close to field capacity (Lee *et al.*, 1987) i.e., moisture was non-limiting, this suggests that soil moisture during field oxidation was also not seriously limiting the rate.

Seasonal mean soil temperature. The effect of seasonal changes in temperature on the S° oxidation rate have been calculated for two sites, A and B, that are representative of the northern (Region 1) and southern (Region 5) climate regions (Table 1), respectively, (Fig. 4) (solid lines). It assumes the temperature-rate constant relationship of Figure 3 (Equation (3)), constant soil moisture, and the oxidation rate Equation (2). The seasonal soil temperatures (at 10-cm depth) are estimated (Table 3) from published data (Lee

et al., 1988a,b) At both sites, mean monthly soil temperatures range over 10°C , with mean annual values of 15° and 9°C , respectively. The field experiments were started in late spring, so the calculations start and finish in mid spring. Spring and autumn follow an average rate of S° oxidation, while summer and winter rates are greater and lesser, respectively. Regression lines representing an annual average rate of oxidation could be fitted to the data for the two sites such that all points on Figure 4 would be within 5% of the regression line (dashed). This would be within experimental error (Fig. 2).

Effect of soil moisture on the rate constant

Incubation experiments have shown that changes in moisture values near the field capacity, especially at temperatures $<23^{\circ}\text{C}$ (Janzen and Bettany, 1987b) and for times of four weeks or more (Kittams and Attoe, 1965), have only a minor effect on the rate constant. Consistent with this, the generally good fit of Equation (2) to the data in Figure 2 implies the rates are little affected by changes in soil moisture. In Figure 3, soils from the 11 soil groups incubated at 25°C and at field capacity moisture for 10 weeks or more (Lee *et al.*, 1987; Watkinson, 1989; A. Lee and J. H. Watkinson, unpublished) show the same temperature dependence as the field sites, i.e., the average moisture values of the field soils are equivalent to the field capacity moisture of the incubated soils.

The field soil moisture in New Zealand is close to field capacity, except during periods of higher evapotranspiration under the higher temperatures of summer. Soil moisture is therefore broadly related to soil temperature by being relatively constant at field capacity up to a certain temperature, and then decreasing with increasing temperature. Since the S° oxidation rate is optimum at field capacity and decreases with decreasing moisture (Janzen and Bettany, 1987b; Kittams and Attoe, 1965; Moser and Olson, 1953), the only effect of soil moisture would be to decrease the oxidation rate at the higher soil temperatures which would otherwise have increased the rate. Hence,

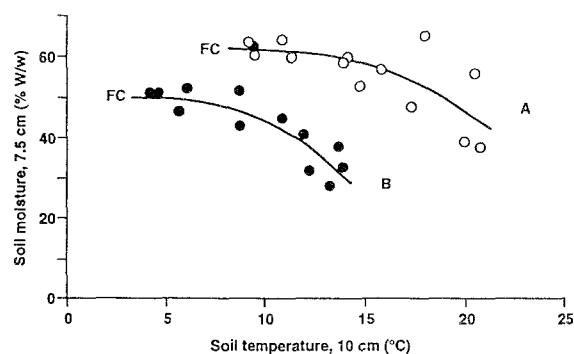


Fig. 5. Relationship between soil temperature (10-cm depth) and gravimetric soil moisture (7.5 cm) over one year for sites A (o) (Lee *et al.*, 1988b) and B (●) (Lee *et al.*, 1988a) (see Fig. 4). FC is field capacity moisture.

in summer, the opposing moisture and temperature effects would tend to cancel each other.

The above relationship between soil moisture and temperature over one year is illustrated in Figure 5 for the two sites used in Figure 4. The published data of soil moisture and of soil temperature (Lee *et al.*, 1988 a,b) were plotted against time, and the data points in Figure 5 were taken from each curve at the same time at one-month intervals. The maximum soil moisture is determined by the field capacity at low soil temperatures. The values are approximately 62% for site A, and 50% for site B. One point is above the rest for each site (Fig. 5), suggesting these moisture values are associated with recent rainfall, and soils had not had time to drain to the field capacity. It can be seen (Fig. 5) that the soil moisture was virtually at field capacity for 10 months out of 13 for site A, but only for 7 months out of 13 for site B. This is in line with the higher rainfall at site A, 1250 mm, compared with only 690 mm at site B. The lowest moistures are well above wilting point, so the relative moisture changes are not large. For example, the lowest moisture recorded at site A over two summers was 20%, corresponding to a water potential of -500 kPa (Lee *et al.*, 1988b).

Since increasing moisture up to field capacity has a positive effect on the rate constant (Janzen and Bettany, 1987b; Kittams and Attoe, 1965; Moser and Olson, 1953) it would tend to negate the effect of the seasonal temperature changes.

Table 3. Estimated seasonal temperatures and rate constants for representative sites A and B

	Late Spring	Summer	Autumn	Winter	Early Spring
Duration (months)	1	4	2	4	1
Site A					
Mean Temp (°C)	16.3	19.2	15.0	10.8	13.8
Rate constant ($\mu\text{g cm}^{-2} \text{ day}^{-1}$)	24.1	29.8	22.0	16.1	20.1
Site B					
Mean Temp (°C)	10.3	13.2	9.0	4.8	7.8
Rate constant ($\mu\text{g cm}^{-2} \text{ day}^{-1}$)	15.4	19.3	14.0	10.1	12.7

Site A is in North Island at Huntly (Lee *et al.*, 1988b);

Site B is in South Island at Mosgiel (Lee *et al.*, 1988a).

However, from the preceding paragraphs, the balancing effect of moisture on temperature is likely to be small at higher moisture, and would probably be of importance only in summer at low moistures (Janzen and Bettany, 1987b; Kittams and Attoe, 1965), particularly under drought conditions approaching the wilting point. Hence the magnitude of the summer deviation is not likely to be as great as that shown in Figure 4 under the assumption of constant moisture. The combined effect of temperature and moisture on the field oxidation rate over the four seasons would therefore result in values for m/m_0 within about 5% of those assuming a mean annual rate constant.

The data of Barrow (1971) under the drier Mediterranean climate of South West Australia, including a site at only 350 mm annual rainfall, also supports the use of Equation (1) and a mean annual oxidation rate constant (Watkinson, 1993).

Assuming a mean annual soil temperature of 16° to 17°C for the three sites in South West Australia of Barrow (1971) allows comparison of the estimated mean annual rate constant of $13.7 \pm 3.1 \mu\text{g cm}^{-2} \text{ day}^{-1}$ (Watkinson, 1993) with New

Zealand data in Figure 3. Allowing for temperature, the Australian oxidation rate appears appreciably lower, suggesting, for example, that the soils are at a low moisture content for longer periods, or the microbes are less efficient oxidizers.

Effect of soil and site properties on the rate constant

Soil temperature has been found in this study to have the greatest effect on oxidation rate (38% of the variance), while other factors including soil moisture (rainfall), pH, and soil groups account for no more than 2% of the variance. Correcting for temperature, there is a maximum difference in rate among individual sites of $2\frac{1}{2}$ to 3 times. Watkinson (1989) also found approximately a 3-fold difference in rate constants for soils incubated at constant temperature and moisture, which was not attributable to soil group, texture or type of clay. He suggested the difference could arise from differences in S° -oxidizing efficiency of different species of thiobacilli (in agreement with Sinclair and Boswell, 1983), or possibly differences in soil

aeration caused by differences in soil structure. Phosphate rock (Chatupote *et al.*, 1988; Lee *et al.*, 1987; Watkinson, 1989) but not soluble phosphate fertilizer (Chatupote *et al.*, 1988) enhances the rate, possibly by improving soil structure and hence aeration, and/or by neutralizing the sulfuric acid produced, providing more favourable conditions for less efficient S⁰-oxidizers.

A small increase of 25 % in oxidation rate has been found for S⁰ sites under grazing (Ghani *et al.*, 1993) so the variables affected by grazing, e.g., mixing of S⁰ into soil by trampling, and nutrient supply, could also be minor factors. In Region 5, soil measurements showed that <5% of the applied S⁰ had moved into the 38 to 75 mm depth (Boswell, 1992). The rate constants based on the 0 to 38 mm depth results were therefore no more than 10% high. Boswell *et al.* (1992) found north and south facing slopes in the North Island differed in their mean annual soil temperatures by approximately 1°C, which gave corresponding oxidation rate differences. In the South Island hill country, differences of 5°C between slopes have been observed (Radcliffe and Lefever, 1981). Where required, good estimates of mean annual soil temperatures of the flat sites can be made from latitude and altitude values (Aldridge and Cook, 1983).

Overall, the most likely factor that would account for the balance of the 60% of the variance is the oxidizing efficiency of the associated soil microbes.

Comparison with agronomic results

On the basis of increased pasture production, soil sulfate or pasture S to different particle sizes of S⁰, Sinclair *et al.* (1985) divided New Zealand into two zones. They correspond to Region 1 of Table 1 (warm-temperate) and the remainder of New Zealand (cool-temperate), and required S⁰ particle sizes of <0.25 mm, and <0.15 mm, respectively, to give maximum responses. A third, high rainfall zone was later suggested to require larger particles (Boswell and Swanney, 1988), but lacked supporting evidence.

S⁰ particle sizes were also calculated for the five regions of Table 1 from the annual tempera-

tures, the regression of Figure 3 and Equation (1), based on 90% oxidation during the year. They are in agreement with those from the agronomic data, except that the more precise oxidation rate data indicate a third, smaller size of <0.075 mm for Region 5 (Table 1)

In summary Region 1, Regions 2, 3, 4 and Region 5 require S⁰ particles of <0.25 mm, <0.15 mm, and <0.075 mm, respectively. Although oxidation rate data do not take into account differences in losses among regions of sulfate to leaching and microbial absorption, they are likely to be much smaller than the differences in rate within a region of up to 2½ times.

For sites with atypical temperatures, recommendations could be made by adjusting the amount/size according to the site oxidation rate constant (Equation 3), (Watkinson, 1993), based on a mean annual temperature estimated simply from latitude and altitude values (Aldridge and Cook, 1983). Also, within each temperature region, i.e. where site temperatures are generally close to the regional mean, the greatest oxidation rate is only about twice the least, most likely from differences in microbial efficiency. Hence if the regional particle size is calculated on the geometric mean of the extreme oxidation rates, the maximum rate will be 40% greater ($\times \sqrt{2}$) than the mean, and the minimum 70% ($\times 1/\sqrt{2}$) of the mean. Faster oxidation rates simply mean that more sulfate is present than S⁰ towards the end of the year. Slower rates may mean that a full pastoral response to S may not be obtained until the second year, when the residue from year one would also contribute to oxidation. This delay must be balanced against the cost of measuring the rate experimentally and adjusting the amount or size of S⁰ (or form of S) applied, since increasing the number of size ranges of S⁰ available would itself lead to higher costs.

Acknowledgments

We thank B.S. Thorrold, R.G. Smith, J.D. Morton and C.C. Boswell for undertaking the field experiments throughout New Zealand, and M.P. Upsdell for statistical analyses.

References

- Aldridge R and Cook FJ (1983) Estimation of soil temperatures at 0.1 m, and 0.3m depths. *N Z Soil Bur Sci Rep* 62: 18 p
- Barrow NJ (1971) Slowly available fertilizers in south-western Australia. 1. Elemental sulfur. *Aust J Exp Agric Anim Husb* 11: 211–216
- Boswell CC (1992) Rate constants of oxidation of elemental sulphur in Otago and Southland. Invermay Technical Report No. 31: 66 p
- Boswell CC and Swanney B (1986) Alternative sulphur fertilisers in New Zealand. *Proc N Z Grassl Assoc* 47: 233–242
- Boswell CC and Swanney B (1988) The effects of particle size, rate and frequency of application of elemental sulphur on the release of sulphate to lucerne in the upper Waitaki basin. In: White RE and Currie LD (eds) Towards the more efficient use of soil and fertilizer sulphur, pp 159–168. Occasional Report No 2, Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand
- Boswell CC, Thorrold BS, Watkinson JH, Lee A and Power IL (1992) Effect of soil temperature on the rate of oxidation of elemental sulphur. *Proc N Z Grassl Assoc* 54: 49–53
- Chapman SJ (1989) Oxidation of micronized elemental sulphur in soil. *Plant Soil* 116: 69–76
- Chatupote W, Moodie H, Hedley MJ, Bolan NS and Macgregor AN (1988) Effect of phosphate fertilizer form on the oxidation of elemental sulphur in soils. In: White RE and Currie LD (eds) Towards the more efficient use of soil and fertilizer sulphur, pp 179–192. Occasional Report No 2, Massey Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand
- Germida JJ, Lawrence JR and Gupta VVSR (1984) Microbial oxidation of sulphur in Saskatchewan soils. *Proc Int Sulphur 1984 Conf*: 703–710
- Ghani A, Lee A, Watkinson JH, Boswell CC, Thorrold BS, Morton JD and Upsdell MP (1993) The quantification of oxidation of elemental sulphur in pastoral soils of New Zealand. *Proc XVII International Grassland Congress*: (In press)
- Janzen HH and Bettany JR (1987a) Measurement of sulfur oxidation in soils. *Soil Sci* 143: 444–452
- Janzen HH and Bettany JR (1987b) The effect of temperature and water potential on sulfur oxidation in soils. *Soil Sci* 144: 81–89
- Kittams HA and Attoe OJ (1965) Availability of phosphorus in rock phosphate-sulfur fusions. *Agron J* 57: 331–334
- Lee A, Boswell CC and Watkinson JH (1988a) Effect of particle size on the oxidation of elemental sulphur, thiobacilli numbers, soil sulphate, and its availability to pasture. *N Z J Agric Res* 31: 179–186
- Lee A, Watkinson JH, Orbell G, Bagyaraj J and Lauren DR (1987) Factors influencing dissolution of phosphate rock and oxidation of elemental sulphur in some New Zealand soils. *N Z J Agric Res* 30: 373–385
- Lee A, Watkinson JH and Lauren DR (1988b) Factors affecting oxidation rates of elemental sulphur in a soil under a ryegrass dominant sward. *Soil Biol Biochem* 20: 809–816
- McCaskill MR and Blair GJ (1989) A model for the release of sulfur from elemental S and superphosphate. *Fert Res* 19: 77–84
- Meyer B (1977) *Sulfur, Energy and the Environment*. Elsevier, Amsterdam
- Moser US and Olson RV (1953) Sulfur oxidation in four soils as influenced by soil moisture tension and sulfur bacteria. *Soil Sci* 76: 251–256
- New Zealand Meteorological Service (1984a) Climate map series. Part 3a: 10-cm soil temperatures. New Zealand Meteorological Service miscellaneous publication 175
- New Zealand Meteorological Service (1984b) Rainfall normals for New Zealand 1951–1980. New Zealand Meteorological Service miscellaneous publication 185
- Radcliffe JE and Lefever KR (1981) Aspect influences on pasture microclimate at Coopers Creek, North Canterbury. *N Z J Agric Res* 24: 55–66
- Sinclair AG and Boswell CC (1983) The agronomic properties of sulphur fertilisers. *Proc New Zealand Fert Manufacturers' Res Assoc Conf* 1: 377–389
- Sinclair AG, Boswell CC, Cornforth IS, Lee A, Morgan C, Nguyen L, Saunders WMH, Shannon P, Smith RG and Whelan G (1985) Agronomic requirements for sulphur in New Zealand pastures. *Proc New Zealand Fert Manufacturers' Res Assoc Conf* 2: 538–572
- Sinclair AG and Enright PD (1983) Effectiveness of elemental sulphur fertilisers. In: Gregg PEH and Syers JK (eds) *Sulphur in New Zealand Agriculture*, pp 164–174. Occasional Report No 4, Dept Soil Sci, Massey University, Palmerston North, New Zealand
- Solberg ED, Penney DC and Nyborg MN (1992) Factors affecting the effective use of elemental sulphur fertilizer in Western Canada. *Proc Int Symp on the Role of Sulphur, Magnesium and Micronutrients in Balanced Plant Nutrition 1991*: 222–233
- Wainwright M (1984) Sulfur oxidation in soils. *Adv Agron* 37: 349–396
- Watkinson JH (1989) Measurement of the oxidation rate of elemental sulfur in soil. *Aust J Soil Res* 27: 365–375
- Watkinson JH (1993) Oxidation rate of elemental sulfur particles with a wide range of sizes. *Aust J Soil Res* 31: 67–72
- Watkinson JH and Blair GJ (1993) Modelling the oxidation of elemental sulfur in soils. *Fert Res*: 35: 127–149
- Watkinson JH and Lee A (1992) A mechanistic model for the oxidation rate of elemental sulphur in soil tested on results by HPLC. *Proc Middle East Sulphur Symp Feb 1990*: 163–171
- Watkinson JH, Lee A and Lauren DR (1987) Measurement of elemental sulfur in soil and sediments: Field sampling, sample storage, pretreatment, extraction and analysis by high-performance liquid chromatography. *Aust J Soil Res* 25: 167–178