

Modelling the oxidation of elemental sulfur in soils

J.H. Watkinson¹ & G.J. Blair²

¹NZ Pastoral Agriculture Research Institute Ltd, Ruakura Agricultural Centre, Private Bag 3123, Hamilton, New Zealand; ²Department of Agronomy and Soil Science, University of New England, Armidale, NSW 2351, Australia

Key words: Elemental sulfur, shape, size, size distribution, model, oxidation, rate, soils.

Abstract

Direct and recursive estimation models for the oxidation rate of elemental sulfur (S⁰) in soil have been proposed, both essentially based on a constant oxidation rate per unit area of exposed surface. Fertilizer S⁰ is taken to consist largely of blocky shaped particles, i.e. having similar dimensions along three axes, which can be treated as equivalent spheres. The most important implication in applying the rate assumption to these shaped particles is that the mass at any time is related to the cube of the time. This has been verified experimentally for oxidation by thiobacilli. Although the assumption is less likely for heterotrophs, experiments involving four soils conformed to the cubic relation.

Implications for the particle variables of size and size distribution have been given more limited testing. The data are generally consistent with theory, such as independence of the rate constant with particle size.

Assuming an activation energy for the oxidation process implies, in addition to the above, an exponential relation of rate constant with temperature. This is supported by experiment. Values for the activation energy are approximately 85 kJ mol⁻¹, and therefore consistent with the rate limiting step for the oxidation being a chemical or biochemical reaction, rather than a diffusion process.

Because absolute rate constants are generated by the models, they are useful for examining the effects of environmental variables not hitherto included. Empirical relationships, once established, can then be included in the model, such as the quadratic relation between rate constant and soil moisture, with the maximum at approximately field capacity.

The delay time (the time to reach maximum oxidation rate) was useful, together with the rate constant, for distinguishing species of oxidizing microorganisms. Typically, under optimum conditions at 25°C, thiobacilli have a delay time of several days and a rate constant of 50 μg cm⁻² day⁻¹ S, while heterotrophs have a negligible delay time but a rate constant of only 5 μg cm⁻² day⁻¹ S.

The cubic model with a single rate constant gave a surprisingly good fit to the oxidation rate over 12 months in New Zealand pastoral soils under field conditions of varying temperature and moisture. This was attributed to the balancing effect of moisture and temperature on the rate constant under the cool temperate climate. A knowledge of the annual average soil temperature is sufficient to provide advice on the optimum particle size for S⁰ fertilizer.

Introduction

In warm, moist soils elemental sulfur (S⁰) is almost the ideal sulfur (S) fertilizer for sustaining crop growth. This is particularly so for permanent pasture for grazing animals

under Mediterranean climates. Important features are:

1. S⁰ is the most concentrated form of S possible, minimizing transport and distribution costs.

2. S° is highly insoluble in water, minimizing leaching losses.
3. Oxidation to sulfate for growing plants requires the presence of S° -oxidizing microorganisms; and the overall system is partly self-regulating because conditions favourable to plant growth also often favour microbial oxidation.

The rate of S° oxidation is affected by soil moisture [12, 16, 21], soil temperature [12, 16], the nature of the S° -oxidizing biota and their nutrient supply [11, 15], and the surface area of S° exposed to microbial attack [9, 11, 25]. (See also Germida and Janzen in this issue). The latter can be controlled initially by choosing a particle size of S° suitable for maintaining maximum plant growth. Too small a size would result in an excess of sulfate and its potential leaching, while too coarse would produce insufficient sulfate for plant growth. Optimizing the particle size and amount of S° has been assisted by the development of oxidation rate models [4, 11, 12, 19, 24, 25]. These provide absolute values of rate constants [11], and take into account various S° and environmental properties. The present article examines these models, and research undertaken to verify them. The models have been developed using both direct estimation [11, 25] and recursive estimation [4, 19] methods. They are sufficiently different in their approach to warrant separate treatment, even though identical assumptions lead to identical results and conclusions.

Direct estimation model

Theoretical

Particle Variables

Following evidence from earlier work that initial S° oxidation rates were linearly related to initial surface area under standard conditions [9], Janzen and Bettany [11] proposed that, at any time, the oxidation rate per unit area was constant, i.e.

$$dm/dt = -ks \quad (1)$$

where m is mass of S° at time t , k is the rate constant, s is the surface area at time t . This assumption is consistent with surface attack by microbes after multiplication to reach complete coverage of the surface of the S° . Thereafter microbe numbers would always be in excess because of the diminishing area.

1. *Spherical particles of equal size.* Using Swartzendruber and Barber's [23] approach for the dissolution rate of limestone, Janzen and Bettany [11] showed that for spheres of the same size (initial diameter, d_o and mass, m_o) integration of (1) gave,

$$m/m_o = (1 - 2kt/\rho d_o)^3, \quad 1 \geq m/m_o \geq 0 \quad (2)$$

where ρ is the density of S° (2.07 g cm^{-3} [20])

2. *Blocky shaped particles of equal size.* This model for spheres of equal size was extended by Watkinson [25] to include particles of any blocky shape (i.e. of similar dimensions along the three axes). During oxidation of blocky shaped particles with a constant shape factor J ($J = A/V^{2/3}$, where A and V are the area and volume at any time), the rate equation is analogous to equation (2),

$$m/m_o = (1 - kJt/3\rho V_o^{1/3})^3 \quad (3)$$

and reduces to equation (2) on substituting $J/V_o^{1/3}$ for spheres.

3. *Blocky shaped particles of different sizes.* Mechanical attrition of S° particles during fertilizer production and transport would tend to produce blocky shaped particles with a range of sizes. Treating these particles as equivalent spheres within diameter limits of c to b , the general solution to equation (2) for this system is a cubic of unequal roots [25, 27],

$$m/m_o = 1 - 3B_1kt + 3B_2k^2t^2 - B_3k^3t^3 \quad (4)$$

where B_1, B_2, B_3 are functions of b, c and the mass distribution with size of the S° particles. If the mass distribution with size is constant, the relation becomes readily calculable [25],

$$m/m_o = 1 - 3at(\ln(c/b))/(c-b) + 3a^2t^2/bc - a^3t^3(b+c)/2b^2c^2 \quad (5)$$

where a is the constant reduction in size per unit time [23], and $a = 2k/\rho$ [25].

However, equation (5) should be used in practice only for $0 \leq t \leq b/a$, i.e. up to the time when the smallest particles have only just dissolved. For longer times the function gives increasingly low results. Over the period $b/a \leq t \leq c/a$ i.e. the time between complete dissolution of the smallest and largest particles, the appropriate equation [26] is,

$$m/m_o = (1 + 3(at/c)(\ln(at/c) + 1/2) - 3(at/c)^2 + (at/c)^3/2)/(1 - b/c) \quad (6)$$

The above points are illustrated from equations (5) and (6) in Figure 1 [26].

However, it would be very rare for a practical mixture of a wide range of sizes to have a constant mass distribution. A useful formulation for practical mixtures can be obtained as follows [26]. First, it has been shown [23, 25] that, over the narrow size range $1 < c/b < 2$, equation (5) is very well approximated by

$$m/m_o = (1 - at/(bc)^{1/2})^3 \quad (7)$$

That is, the mixture acts as if it were equivalent to particles of one size equal to the geometric mean, \sqrt{bc} , of the extreme sizes. Further,

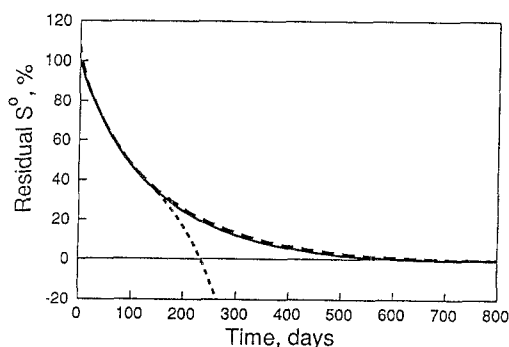


Fig. 1. Comparison of equations (5) (---) and (6) (- -) with equation (8) (—) comprising four terms. $k = 14.5 \mu\text{g cm}^{-2}\text{day}^{-1}$; $b_o = 10 \mu\text{m}$, $b_a = 150 \mu\text{m}$.

because of this narrow size range and the resultant cubic of equal roots, there are no time restrictions comparable to those for equations (5) and (6) [26] beyond the obvious requirement

$$0 \leq t \leq \sqrt{bc}/a, \text{ since } 1 \geq m/m_o \geq 0.$$

Second, mixtures of similar shape with a very wide size range and varying mass distribution can be regarded as the sum of particles with several narrow ranges, each with the above size restriction and having its own constant mass distribution [26, 27]. In particular, for n successive sieve fractions each of size b_{i-1} to b_i , with $1 < b_i/b_{i-1} < 2$, and weight fraction w_i

$$m/m_o = \sum_{i=1}^n w_i (1 - at/(b_{i-1}b_i)^{1/2})^3 \quad (8)$$

Figure 1 shows equation (8) is equivalent to equation (5) (short oxidation times) plus equation (6) (long times), to within 1.5% of m_o , for $n = 4$ and $w_1 = w_2 = w_3 = w_4$. The constants are taken from one treatment of a field experiment [14]. Note again that the range of sizes is better represented by the geometric than the arithmetic mean (equation (7)). Equation (7) is also very useful experimentally when a narrow size range is used [27].

4. *Surface colonization time.* Watkinson and Lee [27] showed that even at 30°C the time to reach maximum oxidation rate for given conditions, including time for microbial multiplication (often from thiobacilli numbers of less than 10 to 10^8 per g of soil [15]) and complete colonization of the particle surface, was not insignificant. At 30°C and moisture at Field Capacity (FC) this delay time was about 3 days for $100 \mu\text{m}$ particles, and the cutoff was quite sharp. Other work (Watkinson and Lee, unpublished) showed that the delay time, as would be expected, increased with both particle size (lower probability of S^0 -microbe contact) and decreasing temperature (lower microbe multiplication rate). Hence the time variable, t , in the foregoing equations should be replaced by $t - t_d$, where t_d is the delay time defined as the time to reach maximum oxidation rate [27]. Chapman [2] used

the sigmoid logistic equation to accommodate the time to reach maximum oxidation rate. The equation includes a rate constant with dimensions of reciprocal time.

Environmental variables

Mechanistic models have not been developed to account for the effects of temperature and moisture. However, whatever the rate limiting step (biochemical/metabolic, chemical reaction or diffusion rate), an activation energy, E_a , would be involved [24], and hence the rate constant would be exponentially related to the Kelvin temperature by the Arrhenius equation,

$$k = k' \cdot \exp(-E_a/RT) \quad (9)$$

The effect of moisture would be more complex. Experimentally, the rate, for at least a few weeks, passes through a maximum at about FC [12, 13, 21]. At moisture values greater than field capacity (i.e. water filling up pore spaces) the rate decreases because oxygen transport is almost entirely in the gas phase [12, 21]. Below field capacity the oxidation rate would more likely be limited by aqueous nutrient transport [24] than water energetics [12, 21]. The detailed mechanism would be complex and depend on the limiting nutrient e.g. if phosphate then diffusion, but if nitrate then mass flow; and additional considerations would include the hydrophobicity and liquid film coverage of the S° particles.

Janzen and Bettany [12] assumed water potential, M , and temperature (celsius), $\theta^\circ\text{C}$, acted independently of each other and related them to k by,

$$k = AB^\theta \quad (10)$$

where $A = A_1 [\ln(-M)]^2 + A_2 \ln(-M) + C$, B is a constant for each soil.

Note that equation (10) is a good approximation for equation (9) at small values of θ/T_1 , i.e. where $1/(1 + \theta/T_1)$ can be approximated by the first two terms of the binomial expansion. In this case, approximately, $E_a = RT_1^2 \ln B$, where T_1 (273.15) on the Kelvin scale is at $\theta = 0$. The temperature limits of most S° -oxidizing organ-

isms would ensure that the approximation would apply.

Assumptions

The application of equation (1) involves several assumptions, mainly the constancy of k , and the lack of effect of oxidation products [25]. The rate constant would be primarily a function of microbial properties, including factors affecting metabolism and multiplication, as well as differences in these among strains and species. These in turn would be affected by soil properties. Constancy of rate would be reached only after complete colonization of the surface of the added S° . Thereafter it would be dependent on a constant microbial oxidation activity, governed by the temperature, and the diffusive transport of nutrients, oxygen and products, which would be affected by soil properties, particularly moisture and nutrient level [16, 24]. Product effects, particularly increase of sulfuric acid, would probably not affect k , but could require an opposing term to ks in equation (1). Oxidation by thiobacilli, little affected by acidity, would probably conform to equation (1), whereas in a system dominated by heterotrophs, which are affected by acid, a second term may well be required.

Shape of the S° particles is another consideration. The two main shapes other than the blocky shape already discussed are plates and prisms [25], but they would not be of importance in practical mixtures. A special case, however, is highly porous particles of S° , the oxidation kinetics of which can theoretically be described by the linear equation of the thin plate model [25],

$$m/m_o = 1 - kst/m_o \quad (11)$$

However, porous particles would, most probably, behave in practice like the solid particles previously considered. The microbes would colonize the outer geometrical surface and would invariably be too large to penetrate the pores [16, 25]. More importantly, even if any penetrated the internal pores, the slow diffusion of oxygen and nutrients from the surface to the organisms would rapidly reduce their oxidation rate to negligible proportions compared with that

on the surface. However, if the preceding argument is wrong, a test for highly porous particles would be conformity to the linear relation of equation (11).

Experimental data

Decrease in S° or increase in sulfate

The most accurate data for testing the various equations are those from measuring the residual S° rather than the increase in SO₄-S, the product of oxidation. During incubation, sulfate is immobilized by microbes while others mineralize it from organic-S, and the base level of sulfate is generally appreciable. In the field there are, in addition, gains from the atmosphere and losses by leaching. In contrast, the decrease in S° is only by oxidation, since the solubility in water is extremely low, and the base level of naturally occurring S° is very low in New Zealand soils at 0.1 to 1 ppm S [15]. Methods based on solvent extraction of S° are selective, with the HPLC method [28] being particularly sensitive and precise, and even capable of investigating the oxidation rate of S° occurring naturally in the S cycle.

Short term or long term

The measurement of oxidation rate from increase in sulfate was restricted to very short times, of the order of a week [11], for the reasons given above. This precludes rigorous testing of the equations which requires following oxidation to over 90% completion [25].

Model testing

Time, shape, size and size distribution

The published kinetic equations for the same blocky shape contain the effects of time and size [11, 25, 27], size distribution [25], and delay time [27] as variables whose influence can be directly tested experimentally as a function of the extent of oxidation.

Janzen and Bettany [11] formulated a cubic equation in time, to describe the oxidation rate of spherical particles of the same diameter, but did not test it, possibly because of limitations in their methodology. Extent of oxidation was measured as soil sulfate which could give unreli-

able measurement beyond six days' incubation at 23°C [11]. However, using the sulfate at six days and assuming the cubic, they calculated a mean rate constant for 40 soils of $4.8 \mu\text{g cm}^{-2} \text{ day}^{-1} \text{ S}$ (SD = 1.4), which can be compared with constants from other researchers.

Watkinson [25] tested equation (5) for blocky shaped particles of constant mass distribution and size range 30 to 125 μm using the data of Lee *et al.* [15], and assuming immediate colonization of the S° particles. Analysis of variance indicated the validity of the model and, including the effects of time, soil groups and a phosphate rock treatment, it accounted for 95% of variance. The test was reasonably rigorous as the data covered a 10-week period, during which up to 98% of the S° was oxidized in 15 soils.

Watkinson and Lee [27] tested the simplified equation (7) using narrow size ranges, the effects of initial particle size, and allowed for a delay time. Elemental S of two size ranges (75–125 μm , 125–150 μm) was incubated in an organic soil at the rate of $450 \text{ mg kg}^{-1} \text{ S}^\circ$, at 30°C. Samples were taken on up to 20 occasions over a period of up to 100 days, giving oxidation of 90–95%. Results showed an excellent fit (r^2 better than 99%). The discontinuity at the delay time was very sharp, probably because of the exponential growth of the oxidizing microbes until colonization of the surface was complete. The rate constants were 109 and 92 $\mu\text{g cm}^{-2} \text{ day}^{-1} \text{ S}$, respectively, for the smaller and greater sizes. Further work on other sizes of S° in the same soil and under the same conditions (Watkinson and Lee, unpublished) showed the same excellent fit of data to the simple cubic of equation (7), and sharp discontinuity at the delay time ie. the time intercept of the fitted line at zero oxidation (Figure 2). The delay time decreased with decreasing particle size (Figure 2) at a constant S° concentration probably because of the increased number of particles per unit volume of soil and the consequent greater probability of colonization within a given time. However, contrary to the theory, the rate constant decreased with increased particle size (Figure 3). This effect is possibly a consequence of the closed system incubation since field experiments (see later) showed no significant change in rate constant over a wider size range.

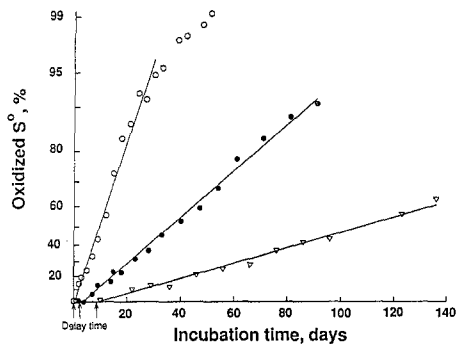


Fig. 2. Linearity test of equation (7) at three particle sizes: \circ 38–75 μm , \bullet 125–150 μm , ∇ 212–250 μm and illustration of delay time. Amount of S° oxidized (cubic scale) versus incubation time at 30°C (Watkinson and Lee, unpublished).

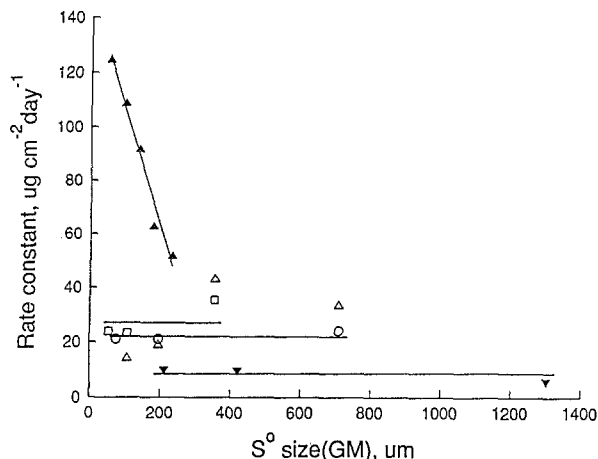


Fig. 3. Rate constant and particle size (GM-geometric mean). Incubation at 30°C: ∇ [17], \blacktriangle (Watkinson and Lee, unpublished). Field experiments: Δ [14], \circ [16], \square (Watkinson and Lee, unpublished).

Calculations (Watkinson, unpublished) on the data of Chapman [2] showed a good fit for each of three soils to equation (7) ($r^2 = 0.95, 0.96, 0.99$), and the corresponding delay times (t_d) increased, as predicted, with decreasing temperature.

Analysis (Watkinson, unpublished) of the incubation data of Li and Caldwell [17] at various sizes, application rates and temperatures also showed good conformity to equation (7) (Figure 3). Furthermore, in contrast to the previously described incubation [27], there was

no significant difference in rate constant over three sizes with geometric means of 210, 420 and 1300 μm , and extreme sizes of 177 to 2000 μm .

Numerous field experiments in New Zealand have confirmed the validity of equations (7) and (8), while four experiments covering a range of particle sizes, have confirmed the constancy of k with size. The closeness of fit of the cubic under conditions of changing temperature and moisture, which are known to affect the rate constant, is at first sight rather surprising. The field experiments acting apparently as systems at constant temperature and moisture is discussed further under environmental variables below.

Results from some 80 field experiments examining the oxidation rate of S° (75–150 μm) for one year, under grazing, and conducted throughout New Zealand under a wide range of climate (average soil temperatures 9° to 15°C, and annual rainfall 800 to 3000 mm) (Lee and Watkinson, unpublished) supported the simple cubic model of equation (7). It accounted for over 80% variance at some 70% of sites. Analysis of published results [14, 16] show they also are consistent with both equation (7) and, where the size range is wider at up to 10 to 150 μm , with equation (8).

Analysis of data from four field experiments at different sites [14, 16] (Lee and Watkinson, unpublished) give values for the rate constants which do not differ significantly among several sizes covering the range 75 to 1000 μm (Figure 3), but with one apparent exception at 354 μm . However this exception had an unusually large delay time, which gave rise to the larger constant. The constant from a 354 μm treatment in another experiment was not significantly larger than others. Increasing sampling error with size, gave greater variability for the corresponding rate constants but did not affect the overall conclusion.

In general, insufficient sampling times in these experiments do not permit reliable measurement of delay times, but estimates (Watkinson, unpublished) from the data of Lee *et al.* [14] ranged from 0 to 200 days, increasing with particle size.

Summarising, the simple cubic model described by equations (7) and (8) including a delay time, is consistent with data from field oxidation of S° covering the range of particle

sizes and climatic conditions encountered in New Zealand pastoral farming.

Environmental variables

The moisture/temperature data of Janzen and Bettany [12] (which they fitted to equation (10)) also conform to the theoretical equation (9) [24] because of the validity of the approximation previously discussed. The calculated values for E_a of 77 to 103 (89 ± 9) kJ mol^{-1} [24] were independent of moisture potential [12] and were suggested consistent with the rate limiting step being a chemical or biochemical reaction rather than diffusion [24]. The latter would have required values in a soil system of less than 40 kJ mol^{-1} . The data of Li and Caldwell [17] (omitting data at 40°C which is above the biological optimum [17]), Chapman [2] (k values recalculated using equation (7)), Deng and Dick [7] (k values calculated using equation (7)), and of Watkinson and Lee (unpublished) also conform to equation (9). They yielded values for r^2 of 0.94 ($n = 4$), 0.94 ($n = 4$), 0.98 ($n = 4$) and 0.99 ($n = 6$), respectively, with corresponding values for E_a of 85, 69 ± 5 , 103 ± 12 , and 87 kJ mol^{-1} . The average value of 103 kJ mol^{-1} for the Oregon [7] soils, and also the values for the Saskatchewan soils [24], are overestimates because the experimental data did not permit an allowance for the delay time [2], which increases with decrease in temperature. It is noteworthy that the E_a values from soils of New Zealand, Scotland and U.S.A. are similar to those found [24] in the Saskatchewan (Canada) soils. It is likely also that quite different organisms were

involved (thiobacilli in New Zealand [15] and heterotrophs in N. America [10] and Scotland [3]), which oxidize at rates differing by an order of magnitude [25]. In spite of many differences the activation energy values are similar, suggesting the rate limiting step is a reaction common to all S° -oxidizing microorganisms in any environment.

Rate constants from six soils incubated at constant temperature, and at constant moisture have shown consistency with equation (10) [12]. The equation has not been tested under field conditions, although extrapolation from incubation data was made for oxidation at several latitudes [12].

In free-draining soils of New Zealand both temperature and moisture vary with season. Generally conditions are warm and dry in summer, cool and moist in winter. The soils typically show seasonal changes of 10°C in the average daily temperature and moisture changes of perhaps 3-fold [14, 16]. Under these conditions, the effects of changing temperature and moisture on the rate constant tend to balance each other out. The data of Lee *et al.* [16] for soil temperature and moisture, and their effect on the rate constant permit estimation of the amount of S° oxidized during each of the four simulated seasons as shown in Table 1. (Estimates are based on the inoculated samples [16], since delay times are evidently larger at low temperatures than the two weeks of the incubation.) The amount varies little among the seasons, the relative standard deviation being only about 10%. This is probably the main reason for the

Table 1. Calculated amount of S° oxidized over the three months of each of the four seasons according to average soil temperature and moisture.

	Simulated Season				Average SD	
	Summer	Autumn	Winter	Spring		
Soil temperature ^a , °C	18	15	10	13	–	
Soil moisture ^a , % w/w	35	53	57	55	–	
Soil moisture, % FC ^b	56	85	92	89	–	
S° oxidized ^c , % initial S°	55	60	53	58	55.5	4.2

^aField values from Fig. 5 in Lee *et al.* [16]

^bField capacity moisture approximately 62% (w/w) (Watkinson unpublished)

^cEstimate of S° oxidized during incubation at the tabulated soil temperature and moisture combination for each season (Fig. 3, Lee *et al.* [16]).

unexpectedly good fit of the cubic model, when the value of k is assumed constant over the seasons [14, 16] (Watkinson and Lee, unpublished). A contributing factor would be the relatively few samples taken at different times over the course of a year and the resultant averaging effect. This result is of practical importance in giving fertilizer advice for annual application since only the yearly average rate constant for a specific site needs to be considered. This will determine the optimum particle size range to give complete oxidation within say two years. The severity of deficiency, as determined from standard soil tests (New Zealand Pastoral Agriculture Research Institute Ltd, Soil Fertility Service) for mineralizable organic-S and sulfate-S [29], will determine the amount of S° to be applied.

Recursive estimation model

Shedley [22] reviewed the literature on the effects of temperature, soil moisture and particle size of S° on oxidation rates, and established regression relationships between each variable, with a maximum potential oxidation rate for a given level of each factor. Hence a 0 to 1 scalar was derived for each. The highest S° oxidation rate reported in the literature was 8.6% day⁻¹ for S° particles < 66 μm in soil at FC by Kittams and Attoe [13], and this was used as the maximum. The oxidation scalars were produced by multiplying the individual scalars for temperature, soil moisture and S° particle size.

Shedley [22] pointed out that this multiplicative model may have resulted in an inordinately large reduction in predicted oxidation rates when more than one factor departed significantly from the optimum. For example, at very low temperatures when metabolic rates of soil micro-organisms are low, the effect of variations in soil moisture could be expected to be less than at near optimal temperatures. Another limitation of this study was that the data were drawn from incubation studies, the deficiencies of which have been outlined earlier.

McCaskill and Blair [19] developed a similar set of scalars based on a wider data set. Particle size effects were accommodated by means of an

exfoliation principle, ie the radius decreases by a constant amount per unit time. The recursive estimation of the constant decrease in radius per unit time using a computer was run on a daily timestep with a constant depth Δr (mm day⁻¹) released from each particle each day. The ratio of the residual mass at time t to the original mass, designated E_t (equals m/m_0 in the previous section), is related to the ratio of the corresponding radii of spherical particles r_t, r_0 , by

$$E_t = (r_t/r_0)^3$$

Since the rate of decrease in radius is constant at Δr , or $(r_0 - r)/t$, therefore

$$\Delta r = r_0 (1 - \sqrt[3]{E_t})/t \quad (12)$$

Release rates, Δr , for elemental S calculated from the literature [1, 5, 18, 22], by this method ranged from 0.1×10^{-3} to 0.4×10^{-3} mm day⁻¹ depending on the environmental conditions prevailing. The highest value of 0.4×10^{-3} mm day⁻¹, designated Δr_{max} , was then reduced by scalars for temperature and soil moisture effects.

The temperature scalar (f_T) was derived from published literature as a linear function,

$$f_T = \max(0, -0.013 + 0.0315T_s) \quad f_T \leq 1.0$$

where T_s is the soil temperature in $^{\circ}\text{C}$ up to 35 $^{\circ}\text{C}$.

Moser and Olsen [21], Kittams and Attoe [13] and Fawzi Abed [8] found that a soil moisture content of 90% of maximum fractional FC was optimal for S° oxidation. Using this data McCaskill [18] established the following relationship:

$$f_{\theta} = -0.386 + 2.37F_{\theta} - 0.945(F_{\theta})^2$$

$$\text{and } 0 \leq f_{\theta} \leq 1$$

for $0 \leq F_{\theta} \leq 0.9$

where F_{θ} = (volumetric soil moisture)/(volumetric soil moisture at FC)

and $f_{\theta} = 10 - 10F_{\theta}$
for $0.9 \leq F_{\theta} \leq 1.0$

The attrition rate of particles (Δr) was then calculated on a daily timestep as:

$$\Delta r = \Delta r_{\max} \cdot f_T \cdot f_\theta$$

Recently Chatupote [4] compared two methods of recursive estimation, namely the constant attrition rate of McCaskill and Blair and a second in which the oxidation rate constant, k , as defined in equation (1), is used. The approximation used by Chatupote [4], where r_n is the radius on the n th day, is as follows:

$$r_{n+1} = (r_n^2(r_n - 3k/\rho))^{1/3}$$

Chatupote [4] found that both methods produced a narrow range of k values for different S° particle sizes in undisturbed soil cores from two New Zealand locations, but with the second method giving 1.5 times the variability, and much greater values for large particles. This is consistent with the fact that the approximation of Chatupote is less exact than that of McCaskill and Blair.

Chatupote [4] compared variants of the attrition model that included the moisture and temperature scalars of McCaskill and Blair [19], for

- (a) surface area alone,
- (b) surface area \times soil moisture and
- (c) surface area \times soil moisture \times temperature

for five New Zealand soils. He found that where the experimental soil moisture scalar of 0.72 was used in his pot experiment, the R^2 value between the observed and predicted oxidation rates increased slightly. In contrast, Chatupote found that the inclusion of soil moisture or temperature effects decreased the predictability of S° oxidation rates below the use of the k value alone ($18 \mu\text{g S cm}^{-2} \text{day}^{-1}$) at two locations in NZ which have wet winters and dry summers.

Dana [6] used the McCaskill and Blair [19]

model to predict the annual oxidation of S° at four diverse locations in Australia. In this calculation a maximum attrition of $0.3 \mu\text{m day}^{-1}$ was used, because of earlier over prediction of S° oxidation rates in a glasshouse experiment. The results (Table 2) predict sizeable differences. At Dalwallinu, which has a Mediterranean climate, oxidation was lower than at Armidale, which has wetter summers, and Darwin and Cairns which have contrasting rainfalls but high temperatures throughout the year. This illustrates the value of modelling in matching S° oxidation to plant requirements, including possible effects of temperature and moisture. Field trials in major climate regions of Australia and elsewhere are needed to test the modelling predictions, particularly the effects of soil moisture and temperature, and their interaction.

Discussion

Relationship between direct and recursive estimation models

Particle size

Swartzendruber and Barber [23] showed that the assumption of a constant dissolution rate of limestone per unit area was equivalent to a linear decrease in particle radius with time. For spheres, substituting $m = (4/3) \pi \rho r^3$ and $s = 4 \pi r^2$ in equation (1) gives

$$dr/dt = -k/\rho \quad (13)$$

This is analogous to equation (11) of McCaskill and Blair [4, 19], noting that Δr in their equation (11) is really equivalent to dr/dt . (This can be confusing because earlier they defined Δr in their equation (5) as simply the decrement in radius [4, 19].) Hence the two models are equivalent, providing a sufficiently short time step is used, and rate constants from both would be the same.

Table 2. Predicted annual oxidation (%) of S° particles at four Australian locations. [6]

Particle size (μm)	Cairns	Darwin	Armidale	Dalwallinu
200	88.4	83.6	71.2	56.7
100	100.0	99.9	96.5	86.3
50% mixture	94.5	91.6	82.4	69.2

The use of Δr is much simpler than that of Δm which would, from equation (2), involve $dm = -(6m_0 k/\rho d_0)(1 - 2kt/\rho d_0)^2 dt$.

Temperature and moisture

Janzen and Bettany [12] proposed the general relationship of equation (10) between k , and moisture and temperature. The model of McCaskill and Blair [19] is similar in two respects: the effects of the two variables are assumed independent of each other; and the effect of moisture is a quadratic. The moisture data of Moser and Olsen [21] permitted normalization to a maximum of unity when the variable is taken as a fraction of the moisture at Field Capacity [4, 19]. However, the effects of moisture at values greater than FC are not as simple as the quadratic model suggests. For example, at longer times [13] or higher temperatures [7], the rate is independent of moisture; while the rate continues to increase, with no maximum, in a New Zealand soil [16].

The assumption of a linear instead of an exponential relation between rate and temperature [4, 19] is likely to be valid over only a narrow temperature range, but would probably be adequate over the average range of temperature in the field. However, the assumption that all soils show the same relation with temperature, including a maximum at the same temperature [4, 19] is probably an oversimplification, particularly with the variety of microbes and soils involved in S° oxidation.

Rate constants

The two constants used, k from equation (1) [4, 25] and k/ρ from equations (12) and (13) [4, 19], are equally useful: The former in contexts where the amounts of sulfate produced are of importance; and the latter where there is interest in the diminution of the particle size.

Particle shape

Watkinson [25] calculated rate constants for blocky shaped particles as equivalent spheres. The fact that their shape gives them the minimum area per unit volume makes spheres a reasonable standard. Results for spheroidal particles fitted the cubic model, but with a corre-

sponding higher value for the rate constant as an equivalent sphere [19]. The same effect would be true for all other shapes because of their greater area per unit volume than spheres.

Particle size

Provided there is complete coverage of the S° surface by microbes (after the delay time), and adequate transport of nutrients and reactants (oxygen) to the surface, and products away from it (only minor surface obstruction by soil), there seems no reason why solid particles should exhibit a dependence on rate with size. Possibly when particles are oxidized to a small size similar to the organisms, the rate may decrease e.g. at more than 95% oxidation of the 38–75 μm particles in Figure 2, when the geometric mean diameter is about 15 μm .

The linear decrease in rate with size for the soil at 30°C in Figure 3 could be associated with the very high oxidation rates (50–120 $\mu\text{g cm}^{-2} \text{day}^{-1} \text{S}$) under the closed system of incubation stressing the transport systems, since rates are independent of size in the data of Li and Caldwell [17] with a rate constant of only 9 $\mu\text{g cm}^{-2} \text{day}^{-1} \text{S}$.

Organisms

Thiobacilli

It seems very likely that thiobacilli dominate S° oxidation in New Zealand soils [15], and generate large rate constants, at 25°C of the order of 50 $\mu\text{g cm}^{-2} \text{day}^{-1} \text{S}$ [25]. Consistent with their low initial numbers in soil (about 10 gm^{-1}) [15] is the relatively long delay time to reach maximum oxidation rate, eg. 3 to 4 days even at 30°C [27]. This delay time precludes accurate measurement of rate constants from data taken over similar periods. Further, the oxidation rate of thiobacilli was unaffected, up to at least 95% oxidation [27], by the dramatic increase in the sulfuric acid produced [15]. The activation energy associated with S° oxidation in one of these soils was 87 kJ mol^{-1} (Watkinson and Lee, unpublished). Rate constants calculated (Watkinson, unpublished) from the data of Deng and Dick [7] using equation (7) for four soils are $51 \pm 26 \mu\text{g cm}^{-2} \text{day}^{-1}$, suggesting they may be from thiobacilli, in the absence of other information.

Heterotrophs

In contrast, it is likely that heterotrophs dominate S° oxidation in N.E. Scotland [3] and the North American soils of Saskatchewan [10] and Minnesota. Rate constants for 40 Saskatchewan soils averaged only $5 \mu\text{g cm}^{-2}\text{day}^{-1} S$ at 23°C [11], while calculations from the data of Li and Caldwell [17] for a Minnesotan soil also give the low value, at 23°C , of $3 \mu\text{g cm}^{-2}\text{day}^{-1}$ (Watkinson, unpublished). (Even after 60 days there was negligible evidence of interconversion of sulfate and organic-S, or of inhibition of the more sensitive heterotrophs by acid products.) Heterotroph numbers were large and changed little after incubation at 23°C [15], so that a very short delay time would be expected. Even at 4°C the delay time calculated from the data of Li and Caldwell [17] was only about a week, whereas for thiobacilli it was about 7 weeks (Watkinson and Lee, unpublished). S° -oxidation in N.E. Scotland is dominated by heterotrophs and thiosulfate-oxidizing bacilli [3]. These microbes are associated with low rate constants for three soils (calculated from the data of Chapman [2] using equation (7)) of $12 \pm 3 \mu\text{g cm}^{-2}\text{day}^{-1}$ (25°C).

The involvement of heterotrophs and therefore a negligible delay time at 23°C would support the validity of the small rate constants calculated from a single time measurement from the short 6-day incubations of Janzen and Betany [11]. However, activation energies for all these soils averaged 81 kJ mol^{-1} , the same order as for the New Zealand thiobacilli (87 kJ mol^{-1}).

Rate limiting step

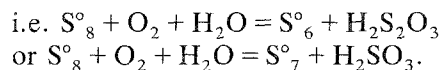
From existing experimental data, any rate limiting step in the microbial oxidation of S° must be consistent with the following:

1. Have a constant oxidation rate, k , per unit area of S° surface under conditions of constant temperature and moisture.
2. At varying temperature and constant moisture (over a range of moisture values) have a rate constant that:
 - a) Is related to the exponential of the nega-

tive reciprocal of the Kelvin temperature (Arrhenius equation).

- b) Generates activation energy values of the order of 85 kJ mol^{-1} .
 - c) Has activation energy values that are independent of moisture.
3. At varying moisture and constant temperature have a rate constant that:
 - a) Is approximately parabolically related to the volumetric moisture for at least a week or two after incubating with S° .
 - b) Has a maximum at approximately the FC of soils.

The activation energy of approximately 85 kJ mol^{-1} at all moisture values suggests the rate is controlled by a chemical reaction rather than diffusion of reactants to (or products from) the reaction site, and the oxidation of S° to $\text{H}_2\text{S}_2\text{O}_3$ or H_2SO_3 has been suggested [24],



The effect of moisture on k could then be explained in terms of decreasing oxygen concentration of surface reaction sites at moisture values above FC; and decreasing moisture coverage of S° (ie. decreasing active sites) at moisture values below FC. The latter would require a decreasing area of S° covered with moisture (through the hydrophobicity of S°), rather than a decreasing thickness of a moisture film over the whole of the S° surface. Increasing moisture above FC would increasingly lower the cross-sectional area of the gaseous pathway for oxygen, but at the same diffusion rate per unit area, giving lowered surface concentrations.

Conclusion

The simple cubic model is generally consistent with experimental data. (A dependence of rate constant with size was found in one closed system.)

Field systems in New Zealand, because of the balancing effect of changes in temperature and moisture on the rate constant, can be treated as

systems at constant temperature and moisture for the purpose of giving S^o fertilizer advice on particle size.

Acknowledgements

We thank M.J. Kear and J.E. Waller for technical and statistical assistance.

References

- Barrow NJ (1971) Slowly available fertilizers in south-western Australia. 1. Elemental sulfur. *Aust J Exp Agric Anim Husb* 11: 211–6
- Chapman SJ (1989) Oxidation of micronized elemental sulphur in soil. *Plant and Soil* 116: 69–76
- Chapman SJ (1990) Thiobacillus populations in some agricultural soils. *Soil Biol Biochem* 22: 479–482
- Chatupote W (1990) An investigation of some factors influencing the rate of oxidation of elemental sulphur fertilizers. PhD Thesis. Palmerston North, New Zealand: Massey University
- Chopra SL and Kanwar JS (1968) Effect of some factors on the transformation of elemental sulfur in soils. *J Indian Soc Soil Sci* 16: 83–8
- Dana M (1992) Sulfur sources for flooded and non-flooded rice and pastures. PhD Thesis. Armidale, Australia: University of New England
- Deng S and Dick RP (1990) Sulfur oxidation and rhodanese activity in soils. *Soil Sci* 150: 552–560
- Fawzi Abed MAH (1976) Rate of elemental sulfur oxidation in some soils of Egypt as affected by the salinity level, moisture content, temperature and inoculation. *Beitr Trop Landwirtschaft Veterinaermed* 14: 179–85
- Fox RL, Atesalp HM, Kampbell DH and Rhoades HF (1964) Factors influencing the availability of sulfur fertilizers to alfalfa and corn. *Proc Soil Sci Soc Am* 28: 406–408
- Germida JJ, Lawrence JR and Gupta VVSR (1984) Microbial oxidation of sulphur in Saskatchewan soils. *Proc Int Sulphur 1984 Conf*: 703–710
- Janzen HH and Bettany JR (1987) Measurement of sulfur oxidation in soils. *Soil Sci* 143: 444–452
- Janzen HH and Bettany JR (1987) 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: 331–4
- Lee A, Boswell C and Watkinson JH (1988) Effect of particle size on the oxidation of elemental sulphur, thiobacilli numbers, soil sulphate, and its availability to pasture. *New Zealand 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. *New Zealand J Agric Res* 30: 373–385
- Lee A, Watkinson JH and Lauren DR (1988) Factors affecting oxidation rates of elemental sulphur in a soil under a ryegrass dominant sward. *Soil Biol Biochem* 20: 809–816
- Li P and Caldwell AC (1966) The oxidation of elemental sulfur in soil. *Proc Soil Sci Am* 30: 370–372
- McCaskill, MR (1984) The residual effects of elemental sulfur as a pasture fertilizer. MRurSc Thesis. Armidale, Australia: University of New England
- 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. Amsterdam: Elsevier
- 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
- Shedley CD (1982) An evaluation of elemental sulfur as a pasture fertilizer. PhD Thesis. Armidale, Australia: University of New England
- Swartzendruber D and Barber SA (1965) Dissolution of limestone particles in soil. *Soil Sci* 100: 287–291
- Watkinson JH (1988) Rate equations for the oxidation of elemental sulphur in soil. Massey Fertilizer and Lime Research Centre Occasional Report No. 2: 26–31
- 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 Lee A (1992) A mechanistic model for the oxidation rate of elemental sulphur in soil tested on results by HPLC. *Proc Middle East Sulphur Sym 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
- Watkinson JH and Perrott KW (1990) A new soil test for sulphate and mineralised organic sulphur. *Proc New Zealand Fert Manufacturers' Res Assoc Conf*: 188–198