

# Sulphur mineralisation in some New Zealand soils

A. Ghani\*, R.G. McLaren, and R.S. Swift\*\*

Department of Soil Science, Lincoln University, Canterbury, New Zealand

Received April 30, 1990

Summary. An open incubation technique was used to measure S mineralisation in a range of New Zealand soils. For most of the soils studied, the release of S as sulphate was curvilinear with time, and during a 10-week incubation, the amounts of S mineralised ranged from less than  $3 \mu g S g^{-1}$  soil to more than  $26 \mu g S g^{-1}$  soil. The best predictor of mineralised S appeared to be the amount of C-bonded S in the soil (explaining 59% of the variation in mineralised S between soils). Examination of the soils after incubation also revealed that the bulk of the mineralised S was derived from the C-bonded S pool. Hydriodic acid-reducible forms of organic S appeared to make little contribution to mineralised S.

Attempts were made to predict total potentially mineralisable S  $(S_o)$  from incubation data using an exponential equation and a reciprocal-plot technique. However, the dependence of estimated values of  $S_o$  on the length and temperature of incubation cast doubts on the validity of this approach.

**Key words:** C-bonded S – Hydriodic acid-reducible S – Incubation – Potential S mineralisation – S mineralisation

Generally, more than 95% of the total S in soils is found in organic forms. Some of this may be mineralised to sulphate ( $SO_4^{2-}$ ) during the oxidation of C compounds by soil micro-organisms. Mineralisation or organic S may also be controlled in part by the microbial requirement for this element (McGill and Cole 1981). Organic S mineralised as sulphate in excess of microbial requirements becomes available for plant uptake, or for leaching, or adsorption by the soil. In situations where inputs of S from other sources, e.g. atmospheric or fertiliser, are low, then mineralisation of organic soil S can be an important source of S for agricultural crops and pastures. A good understanding of the factors controlling the mineralisation of S in soil is therefore highly desirable. In addition, estimates of the potential S mineralisation in soils could be useful in helping to assess S fertiliser requirements.

Mineralisation of soil S has often been studied in the laboratory using a "closed" incubation in which mineralised sulphate is allowed to accumulate (Williams 1967; Kowalenko and Lowe 1975a). More recently, an "open" incubation technique has been used by a number of workers (Tabatabai and Al-Khafaji 1980; Maynard et al. 1983; Pirela and Tabatabai 1988). With this incubation technique, mineralised sulphate is removed from the soil by elution at regular intervals. This more closely simulates field conditions where mineralised sulphate is either used by plants or lost by leaching.

Pirela and Tabatabai (1988) have used the amounts of S mineralised in an open incubation system to predict the potentially mineralisable S in soils  $(S_0)$  and determine S mineralisation rates. These workers used both an exponential equation and a reciprocal-plot technique to calculate  $S_0$  values from mineralisation data. However, the validity of this type of approach has not been examined in detail.

The aim of the present study was to compare the mineralisation of S from a range of New-Zealand soils using an open-incubation technique, similar to that described by Tabatabai and Al-Khafaji (1980). Attempts were made to relate the variation in S mineralisation between soils to differences in various soil chemical properties and to identify the source of the mineralised S. In addition, the applicability of Pirela and Tabatabai's (1988) approach to predicting mineralisable S and rates of mineralisation was examined.

Present addresses: \* Ruakura Agricultural Research Centre, MAF, Private Bag, Hamilton, New Zealand

<sup>\*\*</sup> Department of Soil Science, University of Reading, London Road, Reading, UK

#### Materials and methods

### Soils

The 0-10 cm layer of surface soil was sampled from a variety of sites in order to obtain samples with a wide range of soil properties that might affect the process of S mineralisation. A total of 18 soils were used in this study and the majority of the samples were from pasture sites. Field-moist samples were air-dried at room temperature, passed through a 2-nm sieve, and stored at room temperature. These <2 mm samples were used for the incubation procedure and for the determination of soil pH, water-soluble sulphate, and phosphate-extractable sulphate. Subsamples of the <2 mm air-dried soil were finely ground to pass a 100-mesh sieve and used for the analysis of organic C, total N, total S, and hydriodic acid-reducible S. The results of these analyses are shown in Tables 1 and 2.

# Analytical methods

Total C was determined as  $CO_2$  using a thermal conductivity detector mounted in an automated C and N analyser (Roboprep, Europa Scientific, Crewe, England). Total N was determined by integration of the m/e 28, 29, and 30 N<sub>2</sub> mass peaks in a continuous flow mass spectrometer (*Tracermass*, Europa Scientific) interfaced in series with the *Roboprep* unit. Soil pH was determined using a combined glass electrode in a 1:2.5 suspension of soil in distilled water.

Water-soluble sulphate was extracted from soils with distilled water on an end-over-end shaker for 2 h, and phosphate-extractable sulphate with  $KH_2PO_4$  solution (500 µg P ml<sup>-1</sup>) was shaken for 4 h. Both extractions were carried out at a soil: extractant ratio of 1:5 and after shaking, the suspensions were centrifuged (26000 g) for 10 min before filtering. Sulphate-S in the filtrates was determined by the Johnson and Nishita (1952) reduction method. Total S was determined by oxidation

#### Table 1. Characteristics of experimental soils

Soil	Classification (New Zealand)	pН	Organic C (%)	Total N (%)	Total S (µg g <sup>-1</sup> )	C:S	C:N	N:S
Horotiu	Yellow-brown loam	4.0	6.4	0.53	930	69	12,1	5.7
Lismore	Yellow-brown stony soil	5.5	4.3	0.37	280	153	11.4	13.4
Meyer	Yellow-grey earth	6.2	1.9	0.19	1 <b>96</b>	97	9.7	9.9
Mokotua	Yellow-brown earth	4.8	11.2	0.37	580	193	30.3	6.4
Rapaki	Brown granular loam	5.5	4.0	0.36	510	78	10.8	7.2
Selwyn	Recent soil	5.9	2.3	0.26	302	73	9.0	8.7
Summit	Yellow-brown earth	5.3	4.0	0.33	385	104	11.9	8.7
Takahe	Yellow-grey earth	4.9	2.4	0.21	255	102	11.5	8.8
Te Houka	Yellow-grey earth	4.3	6.0	0.42	470	72	14.3	9.0
Te Kowhai	Gley soil	4.9	2.7	0.21	615	45	13.0	3.4
Templeton (cropped)	Recent/yellow-grey earth	5.9	2.2	0.20	390	56	11.0	5.1
Templeton (pasture)	Recent/yellow-grey earth	5.7	3.3	0.23	364	91	14.4	6.3
Temuka	Gley soil	5.7	3.5	0.29	350	100	12.1	8.3
Teviot (limed)	Yellow-brown earth	5.0	7.4	0.38	421	176	19.5	9.0
Teviot (unlimed)	Yellow-brown earth	4.4	7.6	0.38	410	185	20.0	9.3
Waimakariri	Recent soil	6.1	1.4	0.16	185	79	9.1	8.6
Wairaki	Yellow-brown earth	4.5	4.0	0.36	370	108	11.1	9.9
Wakanui	Yellow-grey earth	5.0	2.6	0.25	250	104	10.4	10.0

Table 2. Forms of S in experimental soils

Soil	$CaCl_2$ -extractable $SO_4^{2-}$	Phosphate-extractable $SO_4^2$	Total organic S $(\mu g S g^{-1} soil)$	HI-reducible S	C-bonded S	
Horotiu	16.4	20.0	000	520	2/9	
Lismore	6.8	7.0	272	550	308	
Mever	1.2	1.5	105	125	148	
Mokotua	19.4	23.6	556	254	302	
Rapaki	4.6	11.4	499	255	244	
Selwyn	4.0	6.4	297	208	80	
Summit	4.9	8.5	377	180	197	
Takahe	4.9	6.1	244	105	139	
Te Houka	16.9	23.8	446	250	196	
Te Kowhai	12.7	17.5	598	360	238	
Templeton (cropped)	10.3	13.0	377	155	222	
Templeton (pasture)	8.9	11.0	353	134	219	
Temuka	9.2	9.2	341	138	203	
Teviot (limed)	11.4	14.6	406	170	236	
Teviot (unlimed)	9.2	17.6	392	162	230	
Waimakariri	1.7	1.8	183	100	83	
Wairaki	6.5	10.0	360	230	130	
Wakanui	4.6	4.8	245	150	95	

HI, hydriodic acid

of a sample of finely ground soil with a NaHCO<sub>3</sub>:  $Ag_2O$  mixture at 550 °C for 4 h (Steinbergs et al. 1962). The oxidised sample was extracted with KH<sub>2</sub>PO<sub>4</sub> solution and sulphate S determined as described above. Total organic S was calculated as the difference between total S and phosphate-extractable sulphate S. Hydriodic acid-reducible S was determined using the method of Freney et al. (1969), corrected for inorganic sulphate S (i.e. phosphate-extractable sulphate S). C-bonded S was calculated as the difference between total organic S and the hydriodic acid-reducible S (Freney et al. 1971).

#### The incubation procedure

Incubations were carried out in polypropylene columns which were packed at the bottom with a plug of glass wool covered by a layer of coarse-textured antibumping granules. Samples of soil (equivalent to 25 g air-dried soil), mixed with 15 g of inert glass beads (2.5-2.8 mm diameter), were placed in the columns on top of the layer of antibumping granules and the surface of the samples was protected with a thin layer of glass wool. The soil was mixed with glass beads in order to avoid compaction of the soils during leaching, maintain aeration, and enhance leaching. The rate of leaching was controlled by a valve attached to the base of the column.

An important feature is that the soils used in these experiments were preconditioned for 2 weeks at 75% field capacity and 20 °C. This was carried out in order to stabilise the soil microbial population and avoid the sudden flush of S mineralisation which can occur when dried soils are rewetted (Williams 1967). After the soils were placed in the columns, they were leached with 100 ml KH<sub>2</sub>PO<sub>4</sub> solution (500  $\mu$ g P ml<sup>-1</sup>) to remove inorganic sulphate, followed by 100 ml distilled water to remove any phosphate solution remaining in the columns. Before placing the columns in an incubator (at 10, 20, or 30°C), excess moisture was removed from the columns by applying a suction of 670 mmHg using a vacuum pump.

Mineralised sulphate was removed from the columns at 2-week intervals. The columns were leached with 100 ml 0.01 M CaCl<sub>2</sub> solution at a rate of approximately 1 ml min<sup>-1</sup>, and the leachates were analysed for sulphate S by the Johnson and Nishita (1952) method. After each leaching, excess moisture was removed from the columns by applying suction as described above. At the end of the incubation, the last leaching with CaCl<sub>2</sub> was followed by a leaching with 100 ml KH<sub>2</sub>PO<sub>4</sub> to remove any adsorbed sulphate that had accumulated during the incubation. The soils were then removed from the columns, and separated from the glass beads by sieving, prior to air-drying and analysis for total and hydriodic acid-reducible S. Four replicate columns were incubated for each soil and the results shown are the means of four values.

#### Estimation of potentially mineralisable $S(S_o)$

The two equations described by Pirela and Tabatabai (1988) were used to estimate  $S_0$ . The first of these is a modified Michaelis-Menton kinetic equation:

$$\frac{1}{S_{\rm m}} = \frac{1}{S_{\rm o}} + \frac{K_{\rm t}}{S_{\rm o}} \cdot \frac{1}{t}$$
(1)

where  $S_{\rm m}$  is the cumulative mineralised S at time *t*, and  $K_t$  is a constant  $(K_t = \text{the time required to mineralise 50\% of } S_{\rm o})$ . When experimental data is plotted as  $1/S_{\rm m}$  vs. 1/t the intercept on the *y* axis equals  $1/S_{\rm o}$  and the slope is equal to  $K_t/S_{\rm o}$  (reciprocal-plot technique).

The second equation is an exponential equation:

$$S_{\rm m} = S_{\rm o} \left( 1 - e^{-kt} \right) \tag{2}$$

where k is a 1st order rate constant, i.e., 1st order kinetics are assumed. The observed values of mineralised S  $(S_m)$  and incubation time (t) were fitted to this equation using an iterative procedure to determine the values of  $S_{\alpha}$  and k.

Although Pirela and Tabatabai (1988) did not attempt to calculate  $K_t$  values from Eq. (2), this can be achieved using the following relationship:

$$K_{\rm t} = \frac{0.693}{k} \tag{3}$$

#### **Results and discussion**

#### S mineralisation rates and patterns

In an initial study, eight of the experimental soils were incubated for 28 weeks at 30°C using the open incubation system. Figure 1 shows the cumulative amounts of sulphate S leached from five of these soils with CaCl<sub>2</sub> during the incubation. For most of the soils the release of S was curvilinear with time, and was described well by lines fitted to the data using quadratic equations (Fig. 1). The shape of the curves indicates a slower rate of organic S mineralisation in the later stages of the incubation. In some soils the amounts of sulphate released in the  $CaCl_2$ leachates after 26-28 weeks of incubation were below the limits of analytical detection (equivalent to  $0.2 \,\mu g \, S \, g^{-1}$ soil). The reduction in the rate of mineralisation with time varied from soil to soil. With the Teviot soil, the rate of S mineralisation declined significantly after the 4th week of incubation; however, with most of the soils the decline became most apparent only after 10-16 weeks of incubation (Fig. 1). In general, more than 70% of the total sulphate S released by the soils was mineralised during the first 14 weeks of incubation.

These results are significantly different from those reported by Tabatabai and Al-Khafaji (1980) who observed that the release of sulphate in an open incubation system was linear with time even when the incubation was continued for a period of 26 weeks. However, some of the results reported by Maynard et al. (1983), Ellert and Bettany (1988), and Pirela and Tabatabai (1988) also show a curvilinear relationship between mineralised S and incubation time. Since S mineralisation is dependent on microbial activity it is not surprising that mineralisation rates generally decrease with incubation time. Once easily metabolisable sources of C in the soil have been used up,



Incubation period (weeks)



microbial activity and hence S mineralisation is likely to decline. It is possible that soils showing a constant rate of S release over long periods of time are the exception rather than the rule.

On the basis of the initial study it was decided to compare S mineralisation between soils using an incubation period of only 10 weeks. It was hoped that this procedure would overcome difficulties resulting from the depletion of easily metabolisable organic C substrates. In the field there is likely to be a fairly constant renewal of such material from plant litter, roots, and root exudates, etc. It has been shown (McLaren et al. 1988) that S mineralisation over a 10-week period in the open incubation system is unlikely to be affected by depletion of other nutrients which might be removed from the soil by the frequent leachings.

Figure 2 shows the cumulative amounts of sulphate mineralised from soils during incubation at 30°C for 10 weeks. The data in Fig. 2 include any mineralised S retained by the soils as adsorbed sulphate and eventually released by the final leaching with potassium phosphate. For the purpose of constructing the curves in Fig. 2, this adsorbed sulphate was distributed throughout the entire incubation period in proportion to the amounts of sulphate removed from the soils with CaCl<sub>2</sub> at each leaching. The amounts of adsorbed sulphate were most significant for the Rapaki, Te Houka, Summit, and Horotiu soils (Table 3). There was a considerable variation between soils in the total amounts of sulphate S released, ranging from  $2.9 \,\mu g \, S \, g^{-1}$  soil for the Waimakariri soil to 26.8  $\mu$ g S g<sup>-1</sup> soil for the limed Teviot soil. Although several of the soils (e.g., Temuka, Wakanui) showed an approximately constant rate of sulphate release throughout



Incubation period (weeks)

Fig. 2. Cumulative mineralisation of S in some New Zealand soils incubated at  $30^{\circ}$ C for 10 weeks

Table 3. Cumulative amount of S mineralised from experimental soils during a 10-week incubation at  $30 \,^{\circ}\text{C}$ 

Soil	Mineralised S ( $\mu$ g S g <sup>-1</sup> soil)						
	In CaCl <sub>2</sub> leachates	Adsorbed <sup>a</sup> SO <sub>4</sub> <sup>2-</sup>	Total				
Horotiu	15.6	9.4	25.0				
Lismore	5.1	1.2	6.3				
Meyer	8.7	0.2	8.9				
Mokotua	13.6	3.0	16.6				
Rapaki	6.5	3.7	10.2				
Selwyn	6.8	1.6	8.4				
Summit	12.8	4.1	16.9				
Takahe	9.2	1.5	10.7				
Te Houka	6.5	5.1	11.6				
Te Kowhai	11.7	4.2	15.9				
Templeton (cropped)	11.5	3.1	14.6				
Templeton (pasture)	14.9	2.4	17.3				
Temuka	15.6	0.8	16.4				
Teviot (limed)	24.3	1.6	25.9				
Teviot (unlimed)	11.3	2.2	13.5				
Waimakariri	2.4	0.5	2.9				
Wairaki	13.2	2	15.2				
Wakanui	6.6	1.4	8.0				

<sup>a</sup> Removed by final KH<sub>2</sub>PO<sub>4</sub> leaching

the relatively short incubation period, this was by no means true of all soils. Some, such as the Teviot and Rapaki soils, showed higher rates of release during the first 2 or 4 weeks of incubation, followed by a slower but constant rate of release during the rest of the incubation period. Other soils (e.g., Horotui) started to show a decline in the rate of S mineralisation after the 6th week of incubation.

#### Effect of soil chemical properties on S mineralisation

With the open incubation system as described above, differences between soils in physical factors, such as soil moisture, temperature, and aeration, should have been minimal. Thus variations in the amounts of S mineralised from soils should have been mainly due to differences in soil chemical or biological properties. Possible relationships between S mineralisation and individual soil properties were examined by means of statistical correlations (Table 4). Although several significant correlations were obtained, most accounted for a relatively small proportion of the total variation in mineralised S between soils.

Of the various soil S fractions determined, the best predictor of mineralised S appeared to be C-bonded S, accounting for 59% of the variation in mineralised S between soils. The other S fractions accounted for at best between 29 and 47% of the variation in mineralised S between soils. Hydriodic acid-reducible S, water-soluble sulphate S and phosphate-extractable sulphate S were particularly poor predictors of S mineralisation. Glasshouse and field studies have shown that the mineralisation of Cbonded S in greater than the mineralisation of S present in hydriodic acid-reducible forms. For example, Freney et al. (1975) observed that S taken up by plants from recently formed organic S was derived predominantly (60%)

**Table 4.** Linear correlation coefficients (r) between mineralised S and individual soil properties

Soil property	Correlation with mineralised S $(r)$			
$CaCl_2$ -extractable $SO_4^2$	0.62**			
Phosphate-extractable $SO_4^2$	0.66**			
Total S	0.69**			
Total organic S	0.68**			
HI-reducible S	0.54*			
C-bonded S	0.77***			
Total N	0.52*			
Organic C	0.52*			
N:S ratio	-0.45			
C:N ratio	0.43			
C:S ratio	0.17			
Soil pH	-0.49*			

\*P<0.05; \*\*P<0.01; \*\*\*P<0.001; HI, hydriodic acid

from C-bonded forms of S. Similarly, the loss of C-bonded forms of S from continuously cultivated soils accounted for 75% of the total organic S loss (McLaren and Swift 1977). These observations suggest that it may be possible to use C-bonded S for predicting S mineralisation from soils.

There are considerable disagreements as to whether S mineralisation is strongly influenced by the relative amounts of C, N, and S in the soil. In the light of evidence presented by previous workers, it is difficult to associate the level of S mineralisation with the mineralisation of these other nutrients (Swift 1977; Maynard et al. 1983). Therefore it is not surprising that S mineralisation showed only low or non-significant correlations with soil properties such as total C, total N, and N:S, C:S, and C: N ratios. In some studies, the rate of release of S from soil organic fractions has been slower than the release of N (Haque and Walmsley 1972; Kowalenko and Lowe 1975b; Swift 1977), while other studies have reported faster release of S in comparison to N (Nelson 1964; Tabatabai and Al-Khafaji 1980). Saggar et al. (1981) found that S was immobilised concurrently with N mineralisation. These observations suggest that N and S are not necessarily associated with the same organic components in soils (Maynard et al. 1983). The results from this present study cast doubt on the usefulness of the relative proportions of C, N, and S as predictors of S mineralisation.

In addition to the relationships discussed above, Table 4 also shows a significant negative correlation between mineralised S and soil pH. This has similarities with the results reported by Tabatabai and Al-Khafaji (1980) and Pirela and Tabatabai (1988), who found that S mineralisation in soils from Iowa and Chile was negatively related to soil pH. In this present study, the apparent decrease in mineralisation with increasing pH was almost certainly related to the observation that, for the group of soils used in the study, there was an inverse relationship between soil pH and organic C ( $r = 0.61^*$ ) and, probably more importantly, between soil pH and C-bonded S ( $r = 0.51^*$ ). A partial correlation between mineralised sul-

phate and soil pH, with the effect of organic C remaining constant, was not significant. This tends to confirm that the negative correlation between mineralised S and soil pH is an artifact, due to the interrelationship between soil pH and organic C. In general, it has been observed that liming a soil increases S mineralisation (Williams and Steinbergs 1962; Williams 1967). Certainly this was evident for the Teviot soil in this present study, where liming produced a substantial increase in S mineralisation (Fig. 2).

### Source of mineralised S

One of the advantages of the open incubation system is that because substantial amounts of S can be mineralised from the soil, it is possible to determine the source of the mineralised S. Figure 3 shows the changes in various soil S pools that occurred during a 28-week incubation at  $30^{\circ}$ C. The results are the means of four replicates and the standard errors are shown. In spite of the errors associated with the determination of S in the three pools, in most cases, gains and losses of S were reasonably well balanced.

It is evident from the data in Fig. 3 that C-bonded forms of S appear to represent the major source of mineralisable organic S. This appears to support the earlier finding that C-bonded S was the best single variate for predicting S mineralisation in soils. It is interesting that hydriodic acid-reducible forms of S appeared to make little net contribution to mineralised S; indeed, in some soils an increase the hydriodic acid-reducible forms of S was apparent after incubation.

McGill and Cole (1981) have suggested that the mineralisation of S occurs by two different pathways, biological and biochemical. According to their hypothesis, biological mineralisation occurs when microorganisms use compounds containing C-bonded S as C sources and sulphate is released as a byproduct of that process. Biochemical mineralisation takes place when inorganic sulphate levels are too low to meet microbial S requirements. The low sulphate levels either activate enzymes or stimulate soil micro-organisms to produce enzymes which hydrolyse sulphate from ester sulphate compounds (hydriodic acid-reducible forms of S). In this present study, the removal of inorganic sulphate from soils at frequent intervals might have been expected to stimulate biochemical mineralisation, and thus result in a decrease in hydriodic acid-reducible S. However, in all soils, only C-bonded forms of S decreased significantly during the incubation, suggesting that biological mineralisation was the dominant process taking place. This raises the question of whether the overall net changes in S pools observed during 28 weeks of incubation give a complete picture of the processes involved during this period. The samples of Teviot soil (Fig. 3) showed an increase in hydriodic acid-reducible S during the incubation, indicating a transformation from C-bonded to hydriodic acid-reducible forms of S. Whether these transformations occurred directly or via inorganic sulphate was impossible to determine from this study. However, the occurrence of any short-term biochemical mineralisation of hydriodic



**Table 5.** Values for  $S_0$  and  $K_t$  calculated using the reciprocal-plot exponential-equation techniques (10-week incubation data)

Soil	Reciprocal plo	t	Exponential equation		
	$\frac{S_{o}}{(\mu g S g^{-1} soil)}$	K <sub>t</sub> (weeks)	S <sub>o</sub> (μg S g <sup>-1</sup> soil)	K <sub>t</sub> (weeks)	
Horotiu	444.4	146.2	56.4	11.7	
Lismore	61.7	80.2	12.6	9.9	
Meyer	48.3	47	67.2	49.0	
Mokotua	64.1	27.1	28.6	7.9	
Rapaki	11.8	3.7	11. <b>9</b>	4.3	
Selwyn	24.6	17.6	11.1	5.0	
Summit	24.0	5.9	22.6	5.4	
Takahe	19.9	11.3	30.8	16.5	
Te Houka	30.9	17.2	20.4	8.4	
Te Kowhai	138.5	69.8	29.9	9.0	
Templeton (cropped)	22.5	7.4	19.4	5.3	
Templeton (pasture)	21.7	5.4	34.4	10.3	
Temuka	62.5	28.6	37.7	12.4	
Teviot (limed)	38.5	6.2	33.7	5.0	
Teviot (unlimed)	1 <b>7.9</b>	3.8	13.5	2.6	
Waimakariri	5.0	9.3	5.5	9.4	
Wairaki	31,4	10.1	18.5	4.1	
Wakanui	20.0	16.5	17.3	11.3	

acid-reducible S could be obscured by the biological mineralisation of C-bonded forms of S to sulphate and subsequent transformation to hydriodic acid-reducible forms.

# Prediction of potentially mineralisable $S(S_0)$

Estimates of potentially mineralisable S for the experimental soils were calculated from the 10-week (30°C) incubation data using the two methods described by Pirela and Tabatabai (1988). The values obtained for  $S_0$  and  $K_t$ (the time in weeks required to mineralise 50% of  $S_0$ ) are shown in Table 5. The  $S_0$  values calculated using either

Fig. 3. Changes in soil S pools during 28-week incubation at 30°C. *HI*, hydriodic acid

the reciprocal-plot techniques or the exponential equation show a wide variation between soils. For some soils the two methods gave similar estimates of  $S_o$ , but for others, particularly the Meyer, Lismore, Te Kowhai, and Horotiu soils, the differences were substantial. In general, the exponential equation gave lower values for  $S_o$  than the reciprocal-plot technique,  $K_t$  values also varied widely between soils and between the methods of estimation. With the reciprocal-plot technique,  $K_t$  values ranged from 4.7 weeks to 144.4 weeks, whereas the highest  $K_t$ value obtained using the exponential equation was 13.2 weeks.

Table 6 shows a comparison of  $S_{\circ}$  values calculated by the reciprocal plot and exponential equations using both 10-week and 28-week incubation data. Clearly, with both methods for estimation, the length of incubation period used to obtain the data has a considerable influ-

**Table 6.** Comparison of values for  $S_0$  and  $K_1$  calculated from 10- and 28-week (30 °C) incubation data using the reciprocal-plot and exponential-equation techniques

Soil	Reciprocal plot				Exponential equation			
	10-week data		28-week data		10-week data		28-week data	
	S <sub>o</sub> a	K <sub>t</sub> <sup>b</sup>	S <sub>o</sub> <sup>a</sup>	K <sub>t</sub> <sup>b</sup>	$S_0^a$	K <sub>t</sub> <sup>b</sup>	$S_0^a$	$K_{\rm t}^{\rm b}$
Meyer	48.3	47.0	48.8	47.4	67.2	49.0	21.0	12.3
Summit	24.0	5.9	38.8	11.3	22.6	5.4	45.2	14.8
Takahe	19.9	11.3	38.5	24.6	30.8	16.5	52.2	30.6
Templeton (pasture)	21.7	5.4	41.7	13.1	34.4	10.3	46.0	14.5
Temuka	62.5	28.6	68.5	31.6	37.7	12.4	43.5	14.6
Teviot (limed)	38.5	6.2	50.8	9.1	33.7	5.0	44.8	8.0
Teviot (unlimed)	17.9	3.8	<b>2</b> 1.4	5.4	13.5	2.6	19.9	6.1

 $a \ \mu g \ S \ g^{-1}$  soil

<sup>b</sup> weeks

**Table 7.** Comparison of values for  $S_{\rm c}$  and  $K_{\rm t}$  calculated using the reciprocal-plot and exponential-equation techniques from data obtained for 10-week incubations at different temperatures

Soil	Incubation temperature								
	10°C	<b>.</b>	20°C		30°C				
	So <sup>a</sup>	K <sub>t</sub> <sup>b</sup>	S <sub>o</sub> <sup>a</sup>	K <sub>t</sub> <sup>b</sup>	$\overline{S_0^a}$	$K_{t}^{b}$			
Reciprocal plot									
Lismore	12.6	17.6	115.7	147.0	61.7	80.2			
Rapaki	9.7	11.8	22.2	19.9	11.8	3.7			
Temuka	- 54.3	-109.8	24.7	9.3	62.5	28.6			
Teviot (limed)	36.9	18.7	-27.0	-21.6	38.5	6.2			
Exponential equ	ation								
Lismore	15.7	18.5	28.6	24.2	12.6	9.9			
Rapaki	4.5	3.1	10.7	6.4	11.9	4.3			
Temuka	4.9	3.9	18.2	5.4	37.7	12.4			
Teviot (limed)	13.5	3.8	34.2	11.1	33.7	5.0			

<sup>a</sup> μg S g <sup>-1</sup> soil

<sup>b</sup> weeks

ence on the subsequent estimated values for  $S_0$ . Similarly, a change in the temperature of incubation also produced significant differences in the estimated values for  $S_{0}$  (Table 7). Use of the reciprocal-plot technique on incubation data obtained at 10°C produced some negative values of  $S_0$ , which clearly calls into question the validity of this particular approach. If  $S_0$  values calculated from an equation fitted to incubation data give a true measure of potentially mineralisable S in soils, then they should be independent of the incubation conditions such as temperature and length of incubation. This is clearly not the case of either of the procedures described by Pirela and Tabatabai (1988). Ellert and Bettany (1988) have compared a wider range of kinetic models for describing S mineralisation in soils and concluded that some of the commonly used kinetic models were incapable of describing mineralisation patterns in all soils. A range of models was required to fit the different mineralisation patterns observed by these workers. They suggested (Ellert and Bettany 1988) that the complex mineralisation processes, composed of several substrates, biochemical pathways and microbial communities, may preclude identification of a kinetically homogeneous "potentially mineralisable S pool" (i.e.  $S_0$ ).

#### References

- Ellert BH, Bettany JR (1988) Comparison of kinetic models for describing net sulfur and nitrogen mineralisation. Soil Sci Soc Am J 52:1692-1702
- Freney JR, Melville GE, Williams CH (1969) Extraction, chemical nature and properties of soil organic sulphur. J Sci Food Agric 20:440-445
- Freney JR, Melville GE, Williams CH (1971) Organic sulphur fractions labelled by addition of <sup>35</sup>S-sulphur. Soil Biol Biochem 3:133-141
- Freney JR, Melville GE, Williams CH (1975) Soil organic matter fractions as a source of plant-available sulphur. Soil Biol Biochem 7:217-221
- Haque I, Walmsley D (1972) Incubation studies on mineralisation of organic sulphur and organic nitrogen. Plant and Soil 37:255-264
- Johnson CM, Nishita H (1952) Micro-estimation of sulphur in plant materials, soils and irrigation waters. Anal Chem 24:736-742
- Kowalenko CG, Lowe LE (1975a) Evaluation of several extraction methods and of a closed incubation method for sulphur mineralisation. Can J Soil Sci 55:1-8
- Kowalenko CG, Lowe LE (1975b) Mineralisation of sulphur from soils and its relationship to soil carbon, nitrogen and phosphorus. Can J Soil Sci 55:9-14
- McGill WB, Cole CV (1981) Comparative aspects of cycling of organic C, N, S and P through soil organic matter. Geoderma 26:267-286
- McLaren RG, Swift RS (1977) Changes in soil organic sulphur fractions due to the long term cultivation of soil. J Soil Sci 28:267-286
- McLaren RG, Ghani A, Swift RS (1988) Studies on sulphur mineralisation from soils using an open incubation system. In: White RE, Currie LD (eds) Towards the more efficient use of soil and fertiliser sulphur. Massey University, Palmerston North, New Zealand, pp 65-75
- Maynard DG, Stewart JWB, Bettany JR (1983) Sulphur and nitrogen mineralisation in soils compared using two incubation techniques. Soil Biol Biochem 15:251-256
- Nelson LE (1964) Status and transformation of sulfur in Mississipi soils. Soil Sci Soc Am Proc 97:300-306
- Pirela HJ, Tabatabai MA (1988) Sulphur mineralisation rates and potentials of soils. Biol Fertil Soils 6:26-32
- Saggar S, Bettany JR, Stewart JWB (1981) Sulphur transformations in relation to carbon and nitrogen in incubated soils. Soil Biol Biochem 13:499-511
- Steinbergs A, Iismaa O, Freney JR, Barrow NJ (1962) Determination of total sulphur in soil and plant materials. Anal Chim Acta 27:158-164
- Swift RS (1977) Mineralisation of nitrogen and sulphur from soil organic matter. In: Soil organic matter studies. International Atomic Energy Agency, Vienna, vol 1, pp 275-281
- Tabatabai MA, Al-Khafaji AA (1980) Comparison of nitrogen and sulphur mineralisation in soils. Soil Sci Soc Am J 44:1000-1006
- Williams CH (1967) Soma factors affecting the mineralisation of organic sulphur in soils. Plant and Soil 26:205-223
- Williams CH, Steinbergs A (1962) An evaluation of plant-available sulphur in soils. 1. The chemical nature of sulphate in some Australian soils. Plant and Soil 17:279-294