

Fertilizer Research 3: 337–351 (1982) 0167–1731/82/040337–15 \$00.20/0
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Field studies on the fate of radioactive sulphur fertilizer applied to pastures

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Key words: fate, fertilizer sulphur, field studies, pastures, transformations

Abstract. Nine field trials involving the application of ^{35}S -labelled gypsum fertilizer to various soil–pasture systems were conducted on five different soil types belonging to the New Zealand recent (Entisol) and yellow-brown earth (Inceptisol) soil groups. After application to the soil, the fertilizer sulphur (S) was converted rapidly into organic forms by microbial immobilization. Within 34 to 75 days from the time of S fertilizer application, 17 to 40% of the applied S was in organic forms in the topsoil (0–15 cm depth). A higher rate of incorporation occurred in improved pasture sites compared to unimproved sites. A lower rate of fertilizer S application enhanced the extent of organic incorporation while a difference in the time of fertilizer application reduced the fertilizer conversion. At most sites, leaching of fertilizer S beyond the topsoil was most important at two months after fertilizer application. The rate of plant uptake of fertilizer S decreased with time and was similar to the immobilization rate. The significance of these findings is discussed in relation to possible manipulations of the pasture–soil system to improve the efficiency of fertilizer S utilization.

The lack of information on the fate of fertilizer sulphur (S) applied to soils under pasture has recently been cited as one of the main factors responsible for predicted pasture S response patterns to be at variance with actual field trial results [15]. Whilst a large number of interrelated processes affect the fate of fertilizer S in the soil under field conditions, most studies have examined only a limited number of these processes together [e.g. 1, 3, 11, 12, 13]. This, in turn, has led to postulations of the possible mechanisms of S loss from pastoral systems and often fertilizer use is adjusted accordingly. Whilst postulations of S loss mechanisms are necessary, they are not a satisfactory substitute for measured data. To improve the efficient use of fertilizer S, the measurement of as many processes as possible is required at a field trial site.

This paper reports results of field studies investigating the fate of fertilizer S on a range of soil–pasture conditions in New Zealand. Some soil and plant processes affecting the fate of applied fertilizer S were examined simultaneously in order to assess their relative significance under field conditions.

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Table 1. Some properties of soils used

| Site | Soil ^a | Soil depth (cm) | Bulk density (gcm ⁻³) | Sand (%) | Silt (%) | Clay (%) | pH ^b | Total S (%) | Total N (%) | Total C (%) |
|------|-----------------------------|-----------------|-----------------------------------|----------|----------|----------|-----------------|-------------|-------------|-------------|
| I | Paparua sandy loam (i) | 0-15 | 1.30 | 60 | 25 | 17 | 6.0 | 0.025 | 0.18 | 2.87 |
| | | 15-30 | 1.45 | 55 | 20 | 15 | 5.4 | 0.013 | 0.11 | 1.53 |
| II | Kowai sandy loam (i) | 0-15 | 1.36 | 68 | 18 | 12 | 5.9 | 0.026 | 0.29 | 2.98 |
| | | 15-30 | 1.40 | 67 | 18 | 15 | 5.9 | 0.022 | 0.15 | 2.06 |
| III | Kowai sandy loam (u) | 0-15 | 1.11 | 68 | 21 | 11 | 5.2 | 0.025 | 0.28 | 5.00 |
| | | 15-30 | 1.29 | 66 | 22 | 12 | 5.4 | 0.022 | 0.15 | 2.72 |
| IV | Gorge silt loam (i) | 0-15 | 1.11 | 41 | 35 | 24 | 6.0 | 0.040 | 0.30 | 4.93 |
| | | 15-30 | 1.25 | 42 | 33 | 27 | 5.9 | 0.030 | 0.21 | 3.08 |
| V | Gorge silt loam (u) | 0-15 | 1.04 | 40 | 32 | 25 | 5.2 | 0.043 | 0.39 | 5.62 |
| | | 15-30 | 1.25 | 42 | 32 | 28 | 5.4 | 0.024 | 0.19 | 2.95 |
| VI | Hurunui stony silt loam (i) | 0-15 | 0.46 | 58 | 25 | 17 | 5.3 | 0.049 | 0.34 | 7.04 |
| | | 15-30 | 0.66 | 57 | 24 | 19 | 5.3 | 0.037 | 0.23 | 4.95 |
| VII | Craigieburn sandy loam (i) | 0-15 | 0.73 | 59 | 25 | 16 | 5.1 | 0.052 | 0.42 | 7.97 |
| | | 15-30 | 0.94 | 55 | 25 | 20 | 5.1 | 0.041 | 0.23 | 4.74 |

^ai = improved, u = unimproved pasture

^bpH H₂O, 1:2.5 soil/water ratio

Materials and methods

Sites and soils used

Nine field trial sites on five different soils belonging to the New Zealand recent (Entisols) and yellow brown earth (Inceptisols) soil groups were used [7]. Annual rainfall in the sites studied ranged from 466 to 1112 mm. Four sites occurred within a few km from each other and for two soils an improved (topdressed) and unimproved (never topdressed) pasture were contrasted on each soil. Detailed descriptions of all sites except one have been presented elsewhere [5, 8, 9]. Some properties of the soils used are presented in Table 1.

At each trial site, radioactive gypsum fertilizer was applied to a square meter subplot located within the center of each main plot (3 m × 3 m). The rest of the area on each main plot received non-radioactive gypsum fertilizer applied at the subplot rate. This main plot constituted one of the four rates of non-radioactive gypsum fertilizer treatments used to construct the plant S response patterns. A randomized complete block layout with three replicates was used.

Field experiments were conducted over a period of two years. In the first year one rate of radioactive gypsum fertilizer (45 kg S ha⁻¹; 8.1 m Ci m⁻²) was used in seven sites (I to VII). The fertilizer was applied in September. In the second year, the experiment was repeated on two sites (IX and VIII) adjacent to sites II and IV. Two rates (22.5 and 45.0 kg S ha⁻¹) of radioactive (5.2 and 10.4 m Ci m⁻²) gypsum fertilizer were applied in November.

Sampling procedure and analytical methods

These are the same as described by Gregg and Goh [8].

Results

Transformations of labelled fertilizer sulphur

Initial changes in first year trials. Mean values for total labelled fertilizer S, labelled sulphate S (i.e. phosphate-extractable sulphate S) and labelled organic S (estimated as the difference between total labelled S and labelled sulphate S) at each sampling date (number of days from time of fertilizer application) in various soil depths for each site are shown in Figure 1. The results show that the incorporation of labelled fertilizer S into the organic fraction occurred mainly in the 0–15 cm soil sampling zone.

Mean values of labelled organic S in the 0–5 cm and 0–15 cm soil depths in relation to total labelled S over time, for each site are shown in Figure 2. By the time of the first soil sampling, varying amounts of labelled S had been incorporated into the organic fraction at all sites. At four sites (II, III, IV

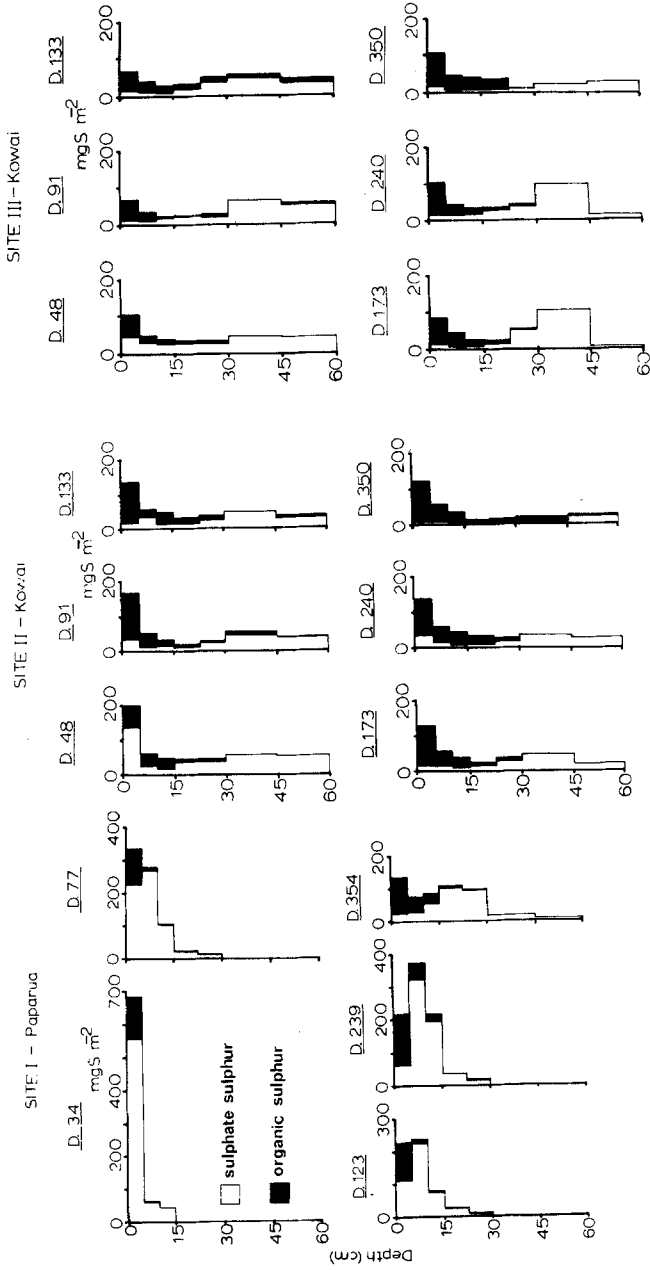


Figure 1A. Distribution of total labelled sulphur, sulphate sulphur and organic sulphur at different soil depths and sampling periods in sites I - III (D = days after fertilizer application)

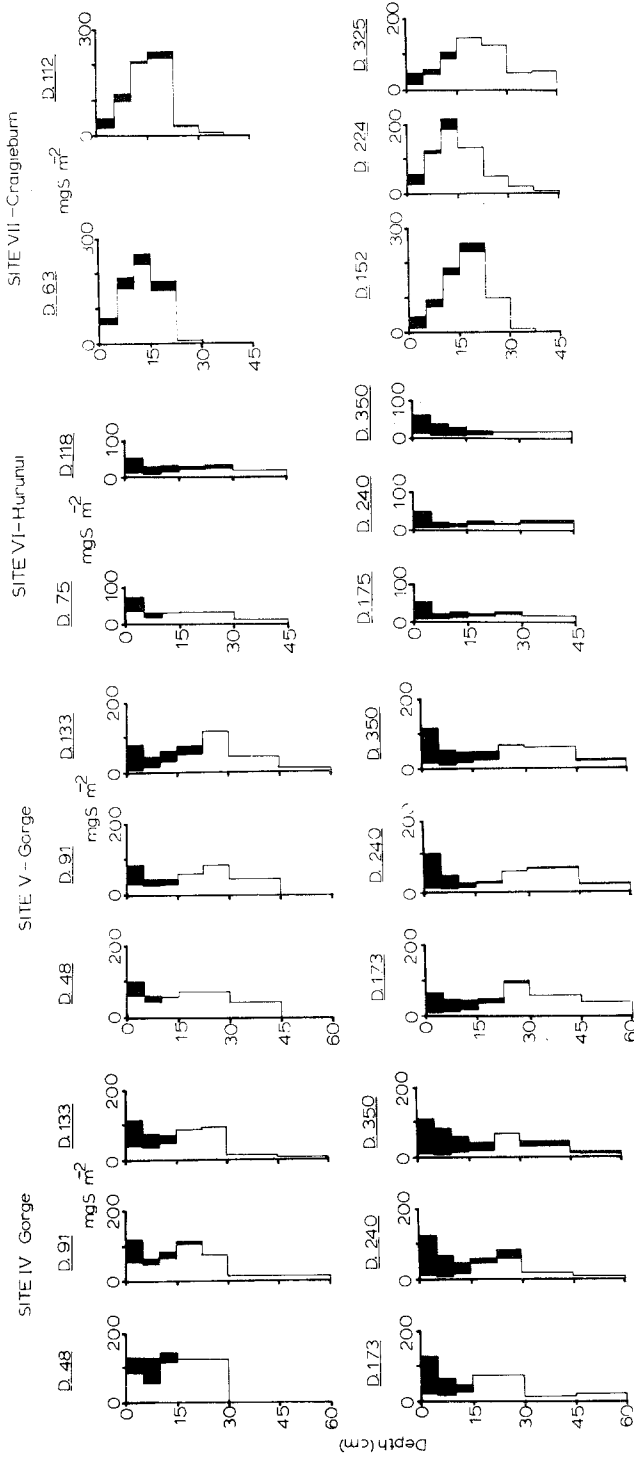


Figure 1B. As for Figure 1A, but in sites IV-VII

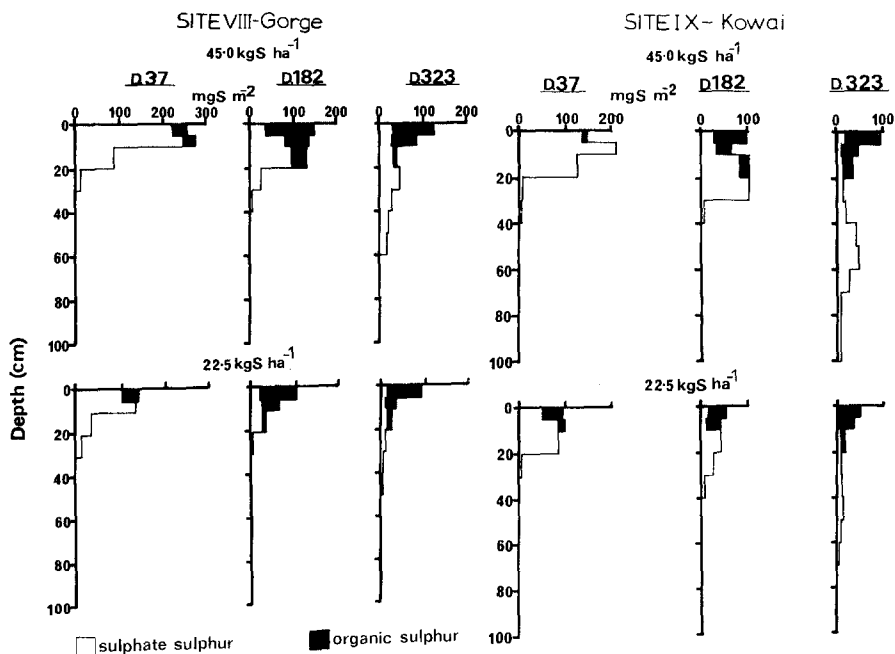


Figure 1C. As for Figure 1A, but in sites VIII–IX

and VI) labelled organic S comprised over 40% of the total labelled S in the 0–15 cm soil depth. At sites I, V and VII, however, only about 17% of the labelled S was in organic forms. At most sites, a greater proportion of this immobilization had occurred in the 0–5 cm soil depth

Rainfall decreased the amount of labelled S incorporation. The larger incorporation at the lower rainfall site I (rainfall = 446 mm) compared with that of site II (rainfall = 1112 mm) is associated with the presence of higher amounts of total labelled S.

The stage of pastoral improvement affected initially the extent of labelled S incorporation into organic matter. On both the Gorge and Kowai soils, the improved pasture sites (II and IV) contained higher amounts of labelled S in the organic fraction than their unimproved counterpart sites (III and V). Higher amounts of total labelled S were found on the improved sites (Figure 1). Additionally, consideration of soil C:S ratios presented by Goh and Gregg [5] and soil pH at the 0–15 cm soil depth (Table 1) show that on each soil, the improved site had a lower C:S ratio and higher pH than the unimproved site. It is assumed that microbiological activity, causing immobilization of labelled S is greater at improved sites.

The effect of soil type on the amount of organic labelled S incorporation was considered by contrasting the improved and unimproved sites on Gorge and Kowai soils. For both unimproved and improved sites, a larger proportion

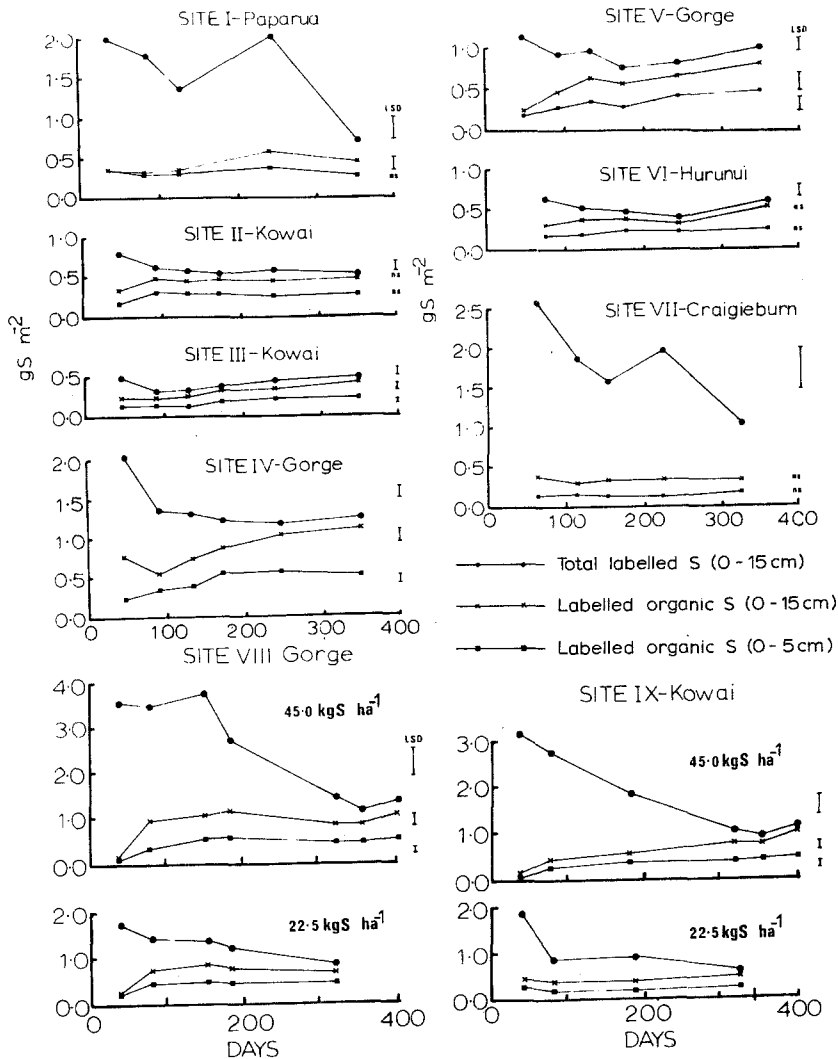


Figure 2. Distribution of total labelled sulphur, sulphate sulphur and organic sulphur in the 0-15 cm soil depth at different sampling periods in sites I-IX (LSD = least significant difference at $P \leq 0.05$)

of labelled S was incorporated in the Kowai soils (Figure 2). In contrast to the Gorge soils, lower levels of soil sulphate S (phosphate-extractable) and soil moisture exist in the upper 0-15 cm soil depth of the Kowai soils at the commencement of the fertilizer application [7]. Additionally, higher soil temperatures were recorded at site II compared with that at site IV [7]. This, together with less dilution of the added labelled S with the available

pool of soil S may have caused greater immobilization of labelled S in the Kowai soils.

At sites VI and VII, the later time of initial sampling prevented direct comparison with other sites (Figure 2).

Overall, it would appear that the major mechanism of labelled S reversion over the first sampling interval was by immobilization of labelled S by micro-organisms rather than the incorporation of labelled S into plant residues. The short duration of the first sampling interval and the conclusions reached above at sites II, III, IV and V, support this viewpoint. Additionally, the results at site VII show that some labelled S had been incorporated into the organic S fraction even in the absence of any observable plant growth [7].

Initial changes in second year trials. When the fertilizer was applied at a much later date (November) in the second year, the results obtained show only a small conversion of fertilizer S to organic S (compare results of sites VIII and IX with those of sites IV and II). This comparison is confounded by the time of the first sampling (37 days at sites VIII and IX and 48 days at sites II and IV). However, interpolated results of sites VIII and IX to day 48 still indicate that large differences exist when compared to sites II and IV. Rainfall associated with each of the two years were similar [8] for the same time period. Thus the time of fertilizer application has influenced the pattern of the initial incorporation of fertilizer S into the organic S fraction.

This initial difference between years did not persist at sites VIII and IX as by day 182 the amount of labelled S incorporated into the organic S fraction was somewhat similar to that at sites IV and II at the same time. Hence, the overall incorporation pattern of labelled S was similar in the two separate investigations.

When rates of fertilizer S used are compared within site VIII or IX, much higher initial amounts of labelled S were incorporated into the organic fraction at the 22.5 kg S ha⁻¹ treatment (Figure 2). This unexpected result may be due to the added fertilizer at the higher rate (45.0 kg S ha⁻¹) releasing greater amounts of non-labelled S by 'priming', which leads to a more diluted S pool for microbial immobilization. The presence of 'priming' was shown to occur at these sites [7].

Subsequent changes at all sites. The amount of labelled S incorporated into the organic S fraction at the 0–15 cm soil depth continued to increase at most sites up to day 350 (Figure 2). This increase was accompanied by a general decrease in labelled sulphate S levels (Figure 3). Two major exceptions were observed at sites VII and II. At site VII, the incorporation of labelled organic S after the first sampling showed no further increase probably due to insignificant plant growth. Clovers failed to establish at this site. [7] and the resultant low available nitrogen may have limited

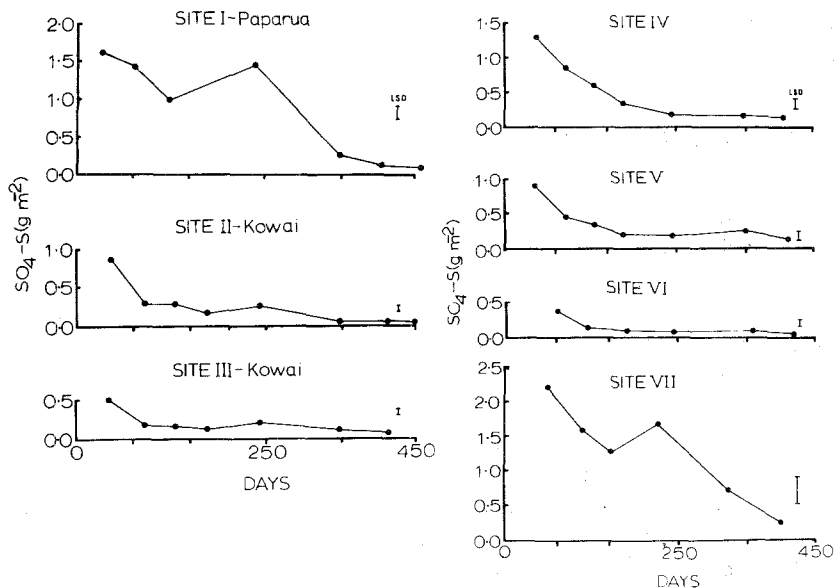


Figure 3. Distribution of labelled sulphate sulphur in the 0–15 cm soil depth at different sampling periods in sites I–VII (LSD = least significant difference at $P \leq 0.05$)

microbiological activity. At site II, by the second sampling, most of the labelled S present in the 0–15 cm depth was already in the organic fraction.

By the end of the year (day 350) differences between sites in amounts of labelled S incorporated into the organic fraction continued to exist (Figure 2). On the whole, the extent of these differences was similar to that at the first sampling. By day 350 almost all the total labelled S in the 0–15 cm depth at each site was in organic combination (Figures 1 and 2).

If changes in soil levels of labelled sulphate S are considered for the upper 0–15 cm at each site (Figure 3), significant increases were found at sites I (day 123–240), II (day 173–240), III (day 173–240) and VII (day 152–224). These increases might imply that mineralization of immobilized organic fertilizer S has occurred. However, at site I the increase is associated with an increase in total labelled S (Figure 1) which, is due probably to plant senescence. Hence, some of the increase in sulphate S may be due to microbial decomposition of freshly added plant residues. A similar explanation may account for the increase in labelled sulphate S at site VII, although this increase is more likely to be due to upward movement from the 25–30 cm depth as the increase is greater than that for total labelled S in the 0–15 cm depth. The upward movement of fertilizer S into the upper part of the soil profile had been reported previously [8].

Hence, the evidence from changes in soil levels of labelled sulphate S over time suggests that mineralization of fertilizer S previously incorporated

into organic S forms occurred at some trials during the first year. On both the Kowai soil sites (II and III) the magnitude of this effect was relatively small.

Relative significance of processes affecting the fate of fertilizer sulphur

If it is assumed that all the fertilizer S, applied initially, enters the pool of plant available S in the soil, then the rate and amount of decrease of fertilizer S in the plant available pool may be followed with respect to the major processes depleting this pool over the growing season. These major processes include plant uptake, leaching and immobilization into the soil organic S. In order to assess the relative significance of each of these processes, some assumptions have to be made.

Firstly, it is assumed that sulphate S (phosphate-extractable) measures the amount of plant available S in the soil. Secondly, the A horizon is considered to represent the major zone of plant uptake. Thirdly, leaching losses from the A horizon at the first soil sampling are considered to be the amount of labelled S within the soil sampling zone but excluding that in the A horizon. At site VI, because a large amount of fertilizer S was leached beyond the maximum sampling depth at first soil sampling [8], the amount leached is estimated as the amount of fertilizer S applied minus that measured in the soil A horizon and plant tops at the first soil sampling. An estimate was also made of the amount of labelled S in stubble and roots. Additionally, the amounts of labelled S leached from the A horizon of each site after the first soil sampling were calculated as the decrease in the total amount of labelled S within the A horizon over various sampling intervals. Due allowance was made for the decrease caused by plant uptake of labelled S over these periods. Previous published results have given considerable support to the validity of the first two assumptions [10, 14].

Plant uptake of labelled S at the first pasture sampling included both 'above ground' and 'below ground' or root levels of labelled S. Labelled S in the root systems at sites II and IV were measured at day 48 (Table 2). These levels were considered to remain unaltered over the first year. At sites I and VI labelled S in the root system at first sampling was estimated from the harvested pasture: root ratios at sites II and IV. Again these levels were assumed to remain similar over the first year. Labelled S in the root system of sites III and V at first pasture sampling was assumed to be the same as that measured on day 240. At first sampling the amount of labelled S in stubble was assumed to be 25% of that in harvested pasture.

Based on the above assumptions, generalized diagrams were constructed to portray the likely relative significance of the various processes at each site. These are shown in Figure 4.

Interpolation of the data for each process at day 48 shows that leaching is the most significant process depleting the sulphate S pool at five of the nine sites. Leaching was of little significance at sites I, IV, VIII and IX. At

Table 2. Mean amount (mg S m⁻²) of labelled sulphur in roots and stubble at sites II to V

| Site | Roots ^a | | Stubble | |
|------|--------------------|---------|------------|---------|
| | Day 48 | Day 240 | Day 48 | Day 240 |
| II | 182 | 191 ns | 90 | 82 ns |
| III | nd | 186 | nd | 192 |
| IV | 141 | 125 ns | 67 | 79 ns |
| V | nd | 181 | nd <td 195 | |

^a determined to 30 cm depth
 ns = no significant difference between sampling times
 nd = not determined

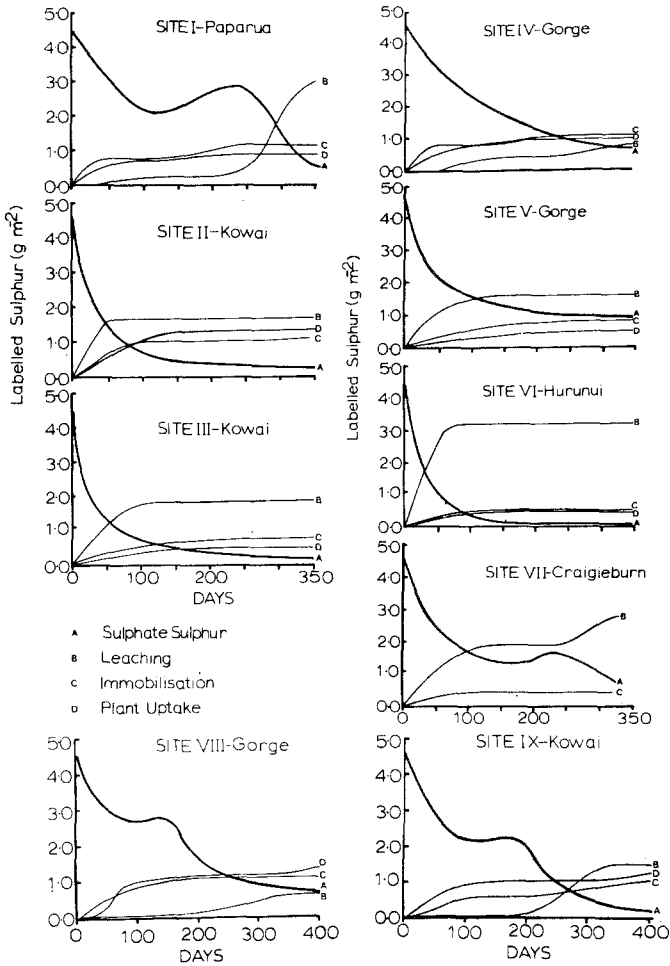


Figure 4. Generalized diagrams relating labelled sulphate sulphur pool depletion in the A horizon of soil to leaching, immobilization and plant uptake in sites I-IX

sites I and IV immobilization of labelled S into the organic fraction was more depleting than plant uptake while the reverse occurred in sites VIII and IX.

Between day 48 and late autumn day 240, the relative significance of processes affecting the fate of fertilizer S changed at most sites. Leaching was of major significance at sites II, III, V, VI and VII. Effects of immobilization into the organic S pool, except at site II, were not as pronounced and at most sites they were of similar magnitude to plant uptake. In fact, at sites II, VIII and IX, plant uptake was of more significance than immobilization.

Over the winter period, plant uptake of labelled S was assumed not to operate at any site and hence, the major processes likely to deplete the sulphate S pool were leaching and immobilization. Leaching was found to be of major significance at sites I, IV, VII, VIII and IX. Immobilization of labelled S was very low at most sites in the winter.

When the relative significance of leaching, plant uptake and immobilization was considered at sites II and IV for the same seasonal periods as at counterpart sites IX and VIII, dissimilar effects due to leaching were found. This suggests that the relative significance of processes examined is dependent on seasonal factors.

Discussion

Results obtained in the present study for the incorporation of fertilizer S into the organic fraction is consistent with the deductions made from the longer term field studies [2, 16]. However, not all of the labelled S to the maximum depth of soil sampling was in the soil organic fraction by day 350. A relatively large proportion of labelled S remained as sulphate S at lower depths (see Figure 1) on some sites (I, III, IV, V, VII).

There was substantial incorporation of labelled S into the soil organic S fraction in the upper 15 cm of some sites by first sampling. This early incorporation was probably mainly due to microbial incorporation because root decay between day 0 and the first soil sampling date is likely to be minimal at all sites. This field evidence for direct microbial incorporation supports the results from recent laboratory and glasshouse studies of other workers [4, 6] which showed that, in the absence of plants, a relatively high short-term incorporation of labelled S into the organic fraction occurred.

Clearly the amount of fertilizer S immobilized by micro-organisms must be considered as a retention mechanism operating within soils. The magnitude of this microbiological retention will therefore have a direct influence on the extent of downward fertilizer S movement. This form of retention must be considered additional to the chemical S retention. It would appear worthwhile to further investigate this aspect, as when the extent of initial incorporation of fertilizer S into organic S is low, the potential for leaching

of fertilizer S will be higher than in situations where this initial incorporation is substantial.

After the first sampling, it was difficult to resolve whether the incorporation of labelled S was due to either microbial incorporation or plant root decay or both. However, at sites I and VII which show no general increase in labelled organic S levels after the first sampling, both immobilization and mineralization of fertilizer S must be preceeding at the same rate.

It would be unwise to assume that, in situations where pasture has been developed for a longer period of time than the sites studied, similar immobilization patterns would exist. In field situations where the accumulation of organic S has ceased, incorporation of fertilizer S into the organic fraction may still occur. Similarly, the extent of incorporation at other times of fertilizer S application (i.e. autumn) is unknown.

The inclusion of a lower rate of labelled fertilizer S application gives results on the fate of fertilizer S more closely akin to those likely to happen under normal farming conditions on these soils, as this rate was similar to that used by farmers. At either site VIII or IX the results obtained showed that the magnitude of the processes measured were in proportion to the rates used. Plant uptake on the lower fertilizer rate applied ($22.5 \text{ kg S ha}^{-1}$) was only just over half that on the higher rate (45 kg S ha^{-1}). A similar pattern of S movement resulted in the soil, with slightly less penetration occurring after winter rainfall. However, the magnitude of organic immobilization of labelled S was higher than expected. A major difference between the two rates of application was in the time required for the added fertilizer S to reach equilibrium in the pasture. At the lower fertilizer rate applied, the equilibrium was reached almost 100 days earlier. When the higher rate of fertilizer was used 'priming' release of native soil organic S may have led to the dilution of the soil S pool for microbial incorporation.

In the present study labelled S in the soil organic S fraction was measured as the difference between total labelled S in the soil and labelled sulphate S (phosphate extractable). It is possible that labelled S in the organic fraction has been over-estimated as it may have included some labelled S from living plant roots. The magnitude of this possible effect was calculated at site IV for the 0–15 cm soil depth at day 240 using root labelled S data [7]. It was found that if all the labelled S present in roots of the 0–15 cm soil depth were added to the labelled S in the soil fraction, root labelled S comprises approximately 11%. However, it was also determined that only about 10% of the roots in the 0–15 cm soil depth were likely to be included in the soil sample in which labelled S is determined. Hence the labelled S contribution from roots in the < 2 mm soil fraction is likely to be 1% at the maximum, and is thus of little significance.

Results from the present study suggest that major advantages may be gained by altering the time of fertilizer S application. On improved pastures,

spring topdressing normally coincides or precedes active spring growth. Leaching or water percolation through the soil profile is high at this time. In view of the fact that the rate of plant uptake for fertilizer S is far less than the rate of S leaching at this time, increased efficiency of fertilizer S uptake may result if topdressing is withheld until mid-October. Similarly, autumn applications in March and April may have little significant effect on S uptake by plants. As plant uptake and microbial immobilization appear to be inactive over the winter months, the potential for downward movement of fertilizer S is high. The use of elemental S and granulated superphosphate may reduce this potential. Furthermore, deep rooting pasture plants (e.g. cocksfoot) when included in the pastures may extend the utilization of fertilizer S to lower soil profile depths.

Conclusions

Varying amounts of fertilizer S were incorporated into the organic fraction. By the time of the first sampling mean values ranged from 17 to 40% of the amount applied. Higher incorporation occurred in improved sites compared to unimproved pastures and also at improved sites receiving higher amount of annual rainfall. A lower rate of fertilizer used enhanced the conversion of fertilizer S only at the initial stages. However, when the fertilizer was applied at a later date in the second year, only a relatively small amount of fertilizer S was converted to the organic fraction.

At most trials leaching of fertilizer S beyond the topsoil was particularly significant in the period two months after fertilizer application. It is concluded that when conducting and interpreting the results of field trials using gypsum as a S source or when applying superphosphate, under farming conditions, particular note should be taken of the amount of rainfall after fertilizer application. Preventive measures to reduce the initial leaching include the use of well-granulated superphosphate, a change in application time and the addition of elemental S to superphosphate mixtures. The introduction of deeper rooting plant species would also have considerable benefits on some soils.

Acknowledgement

The authors wish to thank the Research Division of the New Zealand Ministry of Agriculture and Fisheries, the Sulphur Institute, Washington, USA and the Lincoln College Research Committee for providing funds and other assistance for the study.

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