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Comparison of three different methods of determining soil sulphur mineralization in relation to plant sulphur availability in soils

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Abstract S mineralization in soils with different fertilizer histories [0, 188 and 376 kg superphosphate (SP) ha/year applied since 1952] and animal camping treatments (camp and non-camp soils) was determined simultaneously under the same glasshouse conditions using three different methods (i.e. open incubation, pots with and without plants). Results obtained showed that amounts and patterns of soil S mineralized differed from one system to the other. In the open incubation system, the pattern of S mineralization showed a rapid release of S in the first 4 weeks followed by no substantial release during the remaining 20 weeks of incubation. In both pot systems, S mineralization was slow initially and increased significantly with time. Total amounts of ^{32}S mineralized in the open incubation system ranged from 7.5 to 11.9 µg S/g soil, while corresponding values for pot systems were 2.3–3.7 and 2.3–5.9 µg S/g soil for pots with and without plants, respectively. Rates of soil ^{32}S mineralization with time as fitted by regression models were different in the three systems, showing the differential impact of leaching, crop removal and plant effects on soil S mineralization. Similar results were obtained using radioactive ^{35}S tracer. Overall, the results suggested that contrary to commonly postulated ideas, soil S mineralization determined by periodic leaching of soil in the open incubation system does not simulate crop removal of S or provide a means of predicting plant S availability.

Keywords Soil sulphur mineralization · Open incubation · Pots with plants · Pots without plants · Plant sulphur availability

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Introduction

In the past 25 years or more, several studies have been conducted to determine soil S mineralization using open and closed incubation methods (Tabatabai and Al-Khafaji 1980; Maynard et al. 1983; Pirela and Tabatabai 1988; Ghani et al. 1991; Tan et al. 1994). The open incubation method, which is often used as an index to predict soil S mineralization, involves periodic removals of SO_4-S through a leaching process to mimic the crop S removal process. However, the rate of SO_4-S release and the impact of leaching on soil S mineralization in the open incubation system has not been adequately evaluated or compared with that of crop removal in relation to plant S availability. The present study is aimed at comparing the determination of soil S mineralization by the open incubation system with those using pots with and without plants under the same glasshouse conditions. The comparison of the two pot systems with and without plants was made to examine the plant effect on S mineralization.

The study was conducted using soils from the same soil type under irrigated grazed pastures, fertilized long term with different rates of superphosphate (SP) over a period of 42 years (Nguyen and Goh 1990, 1992a). Soil samples were collected from camp and non-camp areas so as to obtain information on sheep camping effects on soil S mineralization in addition to fertilizer effects. For effective monitoring and tracing of S transformations in soils, radioactive tracer ^{35}S (carrier-free $^{35}SO_4$-S) was used.

Materials and methods

Soils

Soils used for the study were collected from the experimental plots of the long-term SP fertilizer trial at Winchmore Irrigation Research Station, mid-Canterbury, New Zealand (Nguyen et al. 1989; Nguyen and Goh 1990, 1992a). The soil type is a Lismore stony silt loam (Udic Ustochrept), derived from moderately

weathered greywacke loess over gravels (Fieldes 1968). The soil textural composition consisted of sand (45%), silt (30%) and clay (24%) (New Zealand Soil Bureau Bulletin 1968) and the soil pH is 6.0 (Nguyen and Goh 1992d). The field trial commenced in 1952 on a 2-year-old pasture which was sown in 1950 with perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.). Treatments consisted of three annual rates of fertilizer application (0, 188 and 376 kg SP ha/year) to provide an annual supply of 0, 21 and 42 kg S/ha respectively, applied in July of each year. Treatments were arranged in separately fenced border strips (each 64×11 m) in a randomized complete block design, with four replicates per treatment. Each treatment is grazed by a separate mob of sheep. The trial is irrigated using the border strip system (Taylor 1981).

The border strips were separated by mounds of soil (350 mm wide, 300 mm high) running the length of the strips which were termed "border levees" (Nguyen et al. 1989). The area within approximately 1,000 mm of the base of the levee is referred to as a "border crutch". Sheep camp on both the border crutch and border levee and hence the area is called the "camp area". Outside the camp area is termed the "non-camp area". The annual amount of irrigation applied is 600 mm and the average annual rainfall is 600–750 mm. Other details of the long-term trial are available from Nguyen et al.(1989) and Nguyen and Goh (1990, 1992a).

A total of 18 soil samples were collected from the trial. Each soil sample (0–75 mm depth, using a 150-mm corer) consisted of five cores taken randomly from each of the camp and non-camp areas in three replicates of the three long-term fertilizer treatments (0, 188 and 376 kg SP ha/year). Sampling was conducted at the end of June 1995 (nearly 1 month before the annual SP application). Collected soil samples were sieved to pass through a 2-mm sieve, mixed by hand using a spatula and stored in cool storage at 4°C until used.

Some general chemical properties of the soils were organic C (3.8–4.8%), SO_4^{2-} retention (2.0–6.0% of total S added), PO_4^{3-} retention (20–40% of total P added) and soil pH (4.9–5.4) (Nguyen and Goh 1992a). These results of anion retention capacity measurements (Saunders 1965, Saunders and Hogg 1971) show that the soils have low SO_4^{2-} and PO_4^{3-} retention capacities.

Experimental designs and treatments

Three systems (open incubation, pots with and without plants) were used to determine soil S mineralization simultaneously under the same glasshouse conditions.

Open incubation

The open incubation system consisted of a set of 18 leaching tubes (40 mm diameter×200 mm length polypropylene columns) representing two camping treatments×three fertilizer treatments×three replicates arranged as a split-plot design in three randomized blocks with main plots (camp and non-camp) and sub-plots (fertilizer treatments). A duplicate set of 18 leaching tubes was also set up to improve the precision of the results.

Soils collected from the field and stored in cool storage were sub-sampled, air-dried and transferred to the leaching tubes (30 g air-dry soil per leaching tube). Carrier-free $^{35}SO_4$-S solution (0.9 ml) was applied to the soils at 1.48 MBq per leaching tube. The application procedure involved transferring the soil from each leaching tube into a plastic container and $^{35}SO_4$-S solution was added and thoroughly mixed with the soil using a spatula. After mixing, polythene beads (2.5–3.0 mm diameter, 10 g per leaching tube) were added and mixed with the soil. The soil was brought to 75% field capacity by adding an appropriate amount of distilled water and then transferred to the leaching tube, which was packed at the base with a plug of glass wool plus a thin layer of coarse-textured anti-bumping granules (Ghani et al. 1991). Soils in all leaching tubes were packed to the same height to create the same bulk density (1 g cm^3). The top of each soil column was covered with a thin layer of glass wool. The leaching tubes were then kept in an incubator for pre-conditioning the soils for 2 weeks at 20°C and 75% field capacity (Ghani et al. 1991; Tan et al. 1994). After the pre-conditioning, leaching tubes were transferred to the glasshouse which was maintained between 25°C and 28°C with automatic ridge and side ventilation control and hot air-blowers when the temperature dropped below 16°C. Light transmittance was approximately 25–35% of the outside light.

Soils in the leaching tubes were initially leached with 0.016 M KH_2PO_4 (100 ml per leaching tube) to keep the soil columns free of soil SO_4-S initially, and this was followed by leaching with distilled water (100 ml per leaching tube) to ensure the removal of excess KH_2PO_4 from the columns.

Leachate samples were collected at biweekly intervals by leaching the soil columns with 0.01 M $CaCl_2.2H_2O$ (100 ml per leaching tube). During leaching, the rate of out-flow was controlled at approximately 1 ml/min by a valve attached to the base of the leaching tube. At the end of each leaching period, excess moisture was removed from the columns by applying a suction of 670 mm Hg through the flow control valve to keep the moisture content of the soil column at about 75% field capacity. At the end of the last leaching period (i.e. tenth biweekly leaching), soils were finally leached with 0.016 M KH_2PO_4 to ensure the removal of any adsorbed SO_4-S in the soils (Ghani et al. 1991). Soils were then taken out from the leaching columns (after the removal of excess soil moisture by applying suction as before), separated from polythene beads by sieving through a 2-mm sieve and stored in a refrigerator (4°C) before being sub-sampled, air-dried and analysed for soil S fractions.

Each bi-weekly collected leachate was analysed for inorganic S as described later. The mineralization of soil S was calculated using inorganic S values as measured in the leachates bi-weekly, as follows:

net soil S mineralization at each leaching=inorganic S value obtained in each bi-weekly leachate period (1)

cumulative soil S mineralization=sum of net bi-weekly soil S mineralization (2)

In order to compare with results of the pot systems, two sets of consecutive bi-weekly data were combined to give values at 4-weekly intervals.

Pots with and without plants

The systems of pots with and without plants used consisted each of 90 pots (five harvests×two camping treatments×three fertilizer treatments×three replicates) arranged as a split-split plot design in randomized blocks. Each replicated block was divided into five main plots (five harvests), two sub-plots (camp and non-camp) and three sub-sub plots (fertilizer treatments).

Pots with plants

Black polythene planting bags (70 mm diameter×240 mm height) each filled with 300 g air-dried soil were used and referred to as "planting pots". Carrier-free $^{35}SO_4$-S solution (9.0 ml) was applied to the soils at 14.8 MBq per pot. The application procedure was similar to that described for the open incubation system. After thorough mixing, polythene beads (2.5–3.0 mm diameter, 100 g per pot) were added and mixed with the soil. Soils were brought to 75% field capacity and transferred to the pots. The soil in each pot was packed to the same bulk density (1 g cm^3) and the pots were kept in the incubator (where the leaching tubes were kept) and pre-conditioned for 2 weeks at 20°C and 75% field capacity.

After pre-conditioning, pots were transferred to the same glasshouse where the leaching tubes were kept under the same set of conditions. Perennial ryegrass (*Lolium perenne* L.), variety Yatsyn was sown, using ten seeds per pot and soils in all pots were brought to field capacity (0.1 bar). After the emergence of the seedlings, pots were thinned to six plants per pot. Plants removed

in the thinning were returned to the soil surface of the same pot to avoid the loss of radioactive material. Soil moisture was maintained gravimetrically at 75% field capacity by adding distilled water based on daily weight losses in the pots.

Soil and plant samples were collected at 4-weekly intervals up to 20 weeks. A total of five destructive harvests were carried out by removing a set of 18 pots at each harvest. Each plant sampling was conducted by cutting ryegrass tops to 20 mm above the soil surface with scissors. Soil from each pot after plant harvest was transferred to a 2-mm sieve to separate the roots, soil and polythene beads. Roots were carefully removed with minimum unrecovered roots and quickly washed with distilled water. The stems attached to the roots (about 20 mm) were separated from roots and mixed with the tops. Soils were stored in a refrigerator (4°C) until chemical analyses. Ryegrass tops and roots were dried in an oven at 65°C for 48 h (Pirela and Tabatabai 1988) and dry weights were recorded before they were ground and passed through a fine-mesh (500 µm) sieve and analysed for total S content, as described later. The S uptake in tops and roots were calculated by multiplying the dry weights of tops and roots with their respective S contents. Total S uptake was calculated as the sum of tops' and roots' S uptake.

Soils were analysed for inorganic S. The soil S mineralization was calculated by adding plant S uptake and soil inorganic S values. Since sampling in this system was destructive, soil S mineralization at each harvest was cumulative as follows:

cumulative soil S mineralization during period preceding an individual harvest=soil inorganic S at harvest+plant S uptake at a harvest-initial soil inorganic S (3)

net soil S mineralization during 4 weekly intervals between harvests=cumulative S mineralization at end of period-cumulative S mineralization before the period (4)

After the determination of soil S mineralization at each harvest, soils stored in the refrigerator were also sub-sampled, air-dried and analysed for soil S fractions.

Pots without plants

The same procedure as that used for pots with plants was followed except that pots (90) were left uncropped so as to provide the information on rhizosphere effects when the results were compared with those obtained from pots with plants. Pots were removed at 4-weekly intervals up to week 20 at the same time as pots with plants. Soils were analysed for inorganic S and other soil S fractions. Cumulative and net soil S mineralization were calculated using soil inorganic S values as follows:

cumulative soil S mineralization at a sampling =soil inorganic S at a sampling-initial soil inorganic S (5)

net soil S mineralization during 4 weekly intervals =soil S mineralization at a sampling-soil S mineralization preceding the sampling (6)

Chemical analysis

Inorganic ^{32}S in soils was determined by extracting the soils with 0.01 M $CaCl_2.2H_2O$ (1:5) for 16 h, centrifuging at 1,438 *g* for 5 min and filtering (Williams and Steinbergs 1959). Soil extracts (5 ml) were dried in an oven at 105°C and inorganic ^{32}S in the dried extracts was determined using the reduction-distillation procedure of Johnson and Nishita (1952). The evolved H_2S during the reduction-distillation procedure was entrapped in 20 ml of 1 M NaOH absorbing solution. This absorbing solution (after removing 1 ml for ^{35}S counting) was treated with 10 ml methylene blue reagent and 2 ml ferric ammonium sulphate (Nguyen and Goh 1992b). The intensity of the blue colour developed was measured colorimetrically at 670 nm. The above method is based on the results of a study by Nguyen and Goh (1992c), who evaluated methods for determining both ^{35}S and ^{32}S in the trapping solution used in the Johnson and Nishita (1952) distillation procedure.

Inorganic ^{32}S in the leachates was determined by taking 5 ml of leachate and drying in an oven at 105°C; the rest of the procedure was similar to that described for soil extracts. Total ^{32}S in the leachates was determined by the alkaline oxidation method (Tabatabai and Bremner 1970).

Total ^{32}S in plants and soils was determined by the Steinbergs et al. (1962) method (Nguyen and Goh 1992b). The determination of ^{35}S in the soil extracts, leachates, and plant samples was conducted by counting the radioactivity of the H_2S entrapped-NaOH absorbing solutions collected during the determination of ^{32}S in the reduction-distillation procedure (Patterson and Greene 1965; Nguyen and Goh 1992b) using toluene as the scintillant (Nguyen and Goh 1992c).

The recovery (%) of ^{35}S was calculated as the activity of ^{35}S present in the sample relative to the total activity of ^{35}S initially added to the soil and expressed as a percentage. Isotopic decay was taken into account by calculating the decay factor based on the rate of decay of standards which was counted at day zero and at the time of sample counting (Ghani et al. 1993). Soil organic ^{32}S and ^{35}S were calculated as the difference between total ^{32}S and inorganic ^{32}S, and between total ^{35}S and inorganic ^{35}S, respectively.

Statistical analysis

The ANOVA of repeated measures were conducted using the SYSTAT package to assess the significance of differences in the net and cumulative soil S mineralization between the three systems (open incubation, pots with and without plants), time (5 times at 4-weekly intervals) and soils (camp and non-camp soils of three fertilizer treatments). Where ANOVA indicated significant main effects or interactions, they were further analysed using Fisher's least significant difference test.

Regression analyses were conducted to relate the release patterns of cumulative soil S mineralization with time in the three systems, using linear, exponential, logarithmic and quadratic models.

Results and discussion

Comparisons of net soil ^{32}S mineralization in three systems

Results of comparisons of net soil ^{32}S mineralization at 4-weekly intervals in the three systems (Fig. 1) showed that differences between the systems were highly significant. These differences arose largely due to the rapid release of ^{32}S during first 4 weeks in the open incubation system. The lack of significant ^{32}S mineralization after the first 4 weeks in the open incubation system might be due to the removal of labile soil organic S by leaching plus decreases in the substrate availability for microbial activity with time. Similar S release patterns for open incubation systems have been reported by other workers (Ghani et al. 1991; Nguyen and Goh 1992b; Tan et al. 1994).

Comparing the pot systems, net soil ^{32}S mineralization was significantly greater in pots with than without plants during the first 4 weeks (Fig. 1), probably because of enhanced ^{32}S mineralization in the presence of plants and also the immobilization of ^{32}S observed in pots without plants (Tsuji and Goh 1979). However, at later harvests, no significant differences in net ^{32}S mineralization were observed between the two pot systems except be-

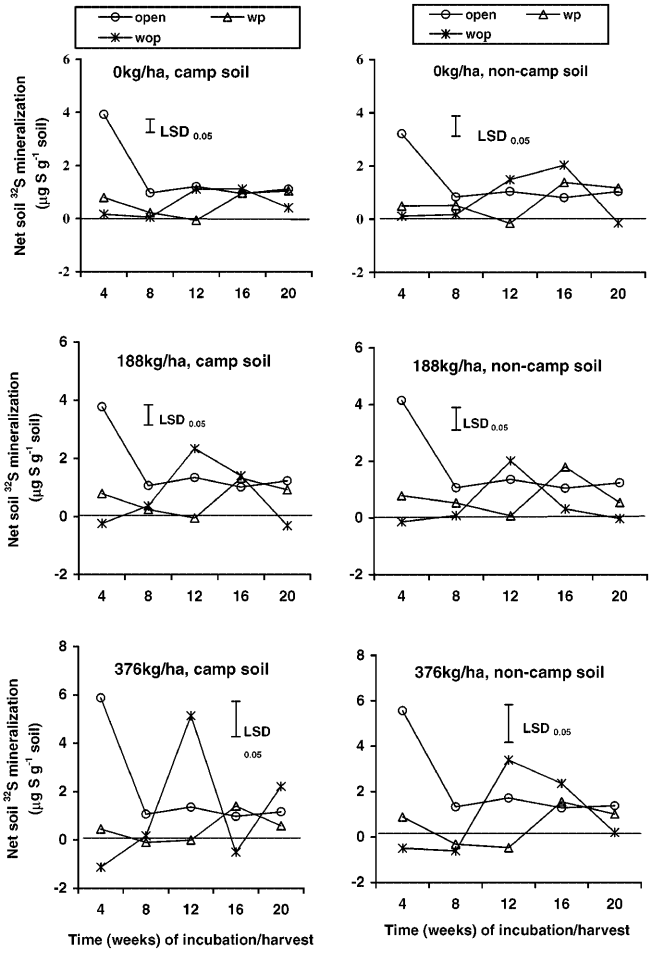

Fig. 1 Comparisons of net soil ^{32}S mineralization at 4-weekly intervals in soils in the three systems [kg/ha refers to superphosphate (SP) applied annually]. *Vertical bar* indicates significant interaction of systems×time in each soil according to Fisher's least significant difference ($LSD_{0.05}$). *Open* Open incubation, *wp* pots with plants, *wop* pots without plants

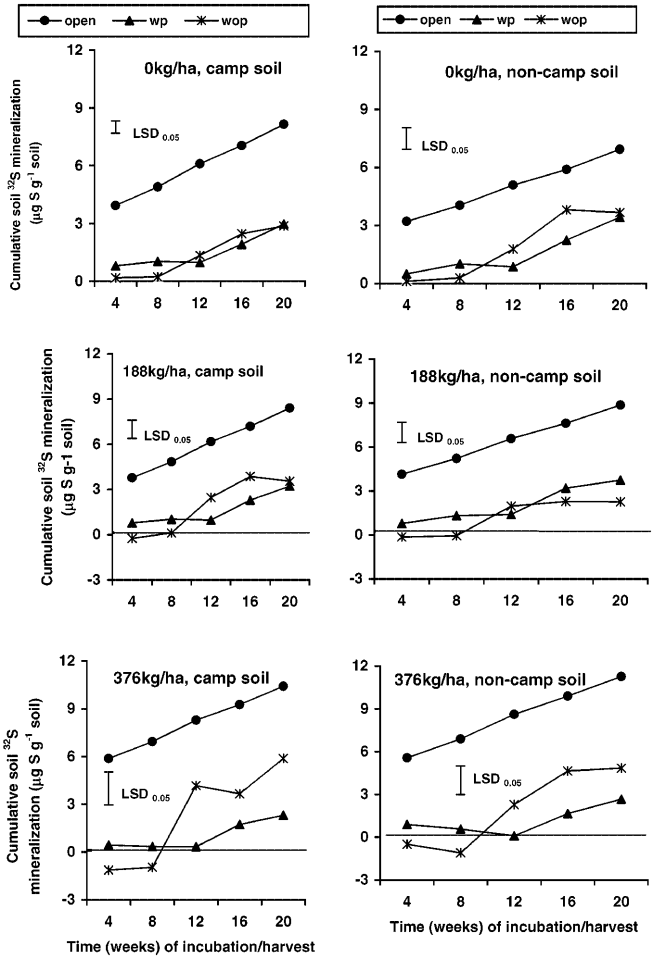

Fig. 2 Comparisons of cumulative soil ^{32}S mineralization at periodic harvests in soils in the three systems (kg/ha refers to SP applied annually). *Vertical bar* indicates significant interaction of systems×time in each soil according to $LSD_{0.05}$. For abbreviations, see Fig. 1

tween 8 and 12 weeks when soil S mineralization was significantly higher in pots without plants than those with plants. This could have been due to differences in the availability of substrates for microbial activity with time in the presence of actively growing plants. However, soil S mineralization was not suppressed in the presence of plants, as at the later harvests, and significant net ^{32}S mineralization occurred between 12 and 16 weeks in the presence of plants (Fig. 1). This might have been due to the production of sulphohydrolases by plant roots (Speir et al. 1980) and rhizosphere micro-organisms (Freney and Spencer 1960; Tsuji and Goh 1979). According to Maynard et al. (1985), in cropped soils, there is an increasing demand for available S by both plants and micro-organisms with time and a low SO_4-S concentration may encourage the production of sulphohydrolases in the rhizosphere by micro-organisms.

Comparisons of cumulative soil ^{32}S mineralization in three systems

At all periods, significantly greater amounts of cumulative soil ^{32}S mineralization were observed in the open incubation than in the pot systems (Fig. 2). These differences were probably due to continuous leaching in the open incubation, higher release of soil organic S during the first 4 weeks (Fig. 1) and also cumulative summation of net ^{32}S mineralization results every 2 weeks in the open incubation method. These factors also account for significantly higher amounts of cumulative ^{32}S mineralization in fertilized than control soils (Fig. 2).

In the system of pots with plants, differences in cumulative soil ^{32}S mineralization between control and fertilized soils were not significant (Fig. 2), probably due to the significantly higher growth of plants in fertilized soils which could have created greater competition for SO_4-S by plants and micro-organisms in the limited amount of soil in the pots.

Table 1 Mean concentration of ^{32}S in ryegrass tops and roots at different harvests. *C* Camp, *NC* non-camp

Soils	Tops					Roots				
	4 weeks[b]	8 weeks	12 weeks	16 weeks	20 weeks	4 weeks[b]	8 weeks	12 weeks	16 weeks	20 weeks
	(% Dry matter)									
C (0 kg/ha)[a]	0.29	0.13	0.08	0.06	0.06	0.15	0.11	0.07	0.07	0.07
NC (0 kg/ha)	0.22	0.13	0.08	0.06	0.08	0.15	0.10	0.07	0.06	0.07
C (188 kg/h)	0.29	0.11	0.07	0.05	0.05	0.15	0.08	0.06	0.05	0.06
NC (188 kg/h)	0.33	0.17	0.09	0.07	0.06	0.15	0.09	0.07	0.06	0.07
C (376 kg/h)	0.27	0.12	0.07	0.06	0.05	0.14	0.08	0.07	0.05	0.06
NC (376 kg/h)	0.29	0.16	0.09	0.07	0.06	0.16	0.10	0.08	0.07	0.07

[a] Amount of superphosphate (SP) applied annually
[b] Values for these harvests are not mean values but values from bulked replicated plant samples

Table 2 Total (tops plus roots) dry matter yield of plants at different harvests. Values followed by the *same small and capital letters* in a row and column are not significantly different according to Fisher's least significant difference (LSD) ($P \leq 0.05$) for differences between times within each soil and between soils at each time, respectively. Abbreviations are explained in Table 1

Soils	Time of harvest(weeks)					Mean
	4	8	12	16	20	
	(g/pot)					
C (0 kg/ha)[a]	0.08 aA	0.34 bA	0.74 cA	1.32 dA	1.72 eA	0.84 A
NC (0 kg/ha)	0.07 aA	0.26 aA	0.57 bA	1.21 cA	1.51 cA	0.72 A
C (188 kg/ha)	0.14 aC	0.99 bC	1.81 cB	3.05 dB	3.53 eB	1.90 C
NC (188 kg/ha)	0.11 aB	0.76 bB	1.65 cB	2.90 dB	3.29 eB	1.74 B
C (376 kg/ha)	0.16 aC	1.08 bC	2.22 cD	3.45 dC	3.81 eC	2.14 D
NC (376 kg/ha)	0.15 aC	1.03 bC	1.96 cC	3.34 dB	4.03 eC	2.10 D
Mean	0.12 a	0.74 b	1.49 c	2.54 d	2.98 e	

*** Soils, *** time, *** soils×time, where ***$P \leq 0.001$
[a]Amount of SP applied annually

The ^{32}S concentration data (Table 1) were not analysed statistically because replicates were pooled and analysed in duplicate, separately for tops and roots. Concentrations of ^{32}S in ryegrass tops during the first 4 weeks of harvest (Table 1) ranged from 0.22 to 0.33% and were within the critical range of 0.25–0.30% (McNaught 1970). At subsequent harvests, the ^{32}S concentration decreased in both tops and roots (Table 1), and levels in the tops were below the critical levels although S deficiency symptoms did not appear. Similar decreases in the ^{32}S concentration to below critical levels have also been reported in other pot studies (Tsuji and Goh 1979; Eriksen et al. 1995) which showed S deficiency symptoms. In the present study, the healthy growth of plants was observed up to week 8, and after this plants started to show drying of tops. However, the growth of plants was not affected as total dry matter yield increased continuously with time (Table 2). The drying of tops could have been due to the restricted volume of soil in pots which occurred with increased root growth with time, especially in fertilized soils.

In the system of pots without plants, significantly higher ^{32}S was mineralized (Fig. 2) in the 376 kg SP ha/year treatment (camp and non-camp) than other treatments, probably because of higher microbial activity in the presence of a higher P level in the former (Nguyen and Goh 1990) compared with the other treatments. Net amounts of ^{32}S mineralized between 8 and 12 weeks in fertilized treatments in pots without plants (Fig. 1) were significantly higher than those of other SP treatments, indicating that there is a possibility of a higher rate of soil S mineralization in fertilized treatments if limitations in the pot systems, such as a limited amount of soil for actively growing plants, were overcome.

Differences in soil S mineralization between camp and non-camp soils were, in general, not significant (Fig. 2) in any of the three systems studied, contrary to the results reported by Nguyen and Goh (1992b) which showed significant effects of animal camping on soil S mineralization, with higher S mineralization in camp than non-camp soils. This could have been due to the initial S status of soils used by Nguyen and Goh (1992b), which was significantly higher in camp than non-camp soils, while in the present study these differences were not observed.

In the open incubation system, total amounts of ^{32}S mineralized over 20 weeks in camp and non-camp soils in the three fertilizer treatments ranged from 7.5 to 11.9 µg S/g soil. Corresponding values for pots with and without plants were, 2.32–3.74 and 2.27–5.88 µg S/g soil respectively. These represented 2–3% of soil organic S in the open incubation and <1% soil organic S in the pot systems.

The relationship of cumulative soil ^{32}S mineralization with time in each system in six soils was fitted by regres-

Table 3 Relationship of cumulative soil ^{32}S mineralization with time in different soils in each of the three systems as fitted by linear and quadratic models Abbreviations are explained in Table 1

	Linear model				Quadratic model				
	$y=a+bx$				$y=A+bx+cx^2$				
	Intercept	Slope	R^2	P value	Intercept	bx	cx^2	R^2	P value
Open incubation									
C (0 kg/ha)[a]	2.85	0.26	0.97	***	5.85	0.26	0.000	0.97	***
NC (0 kg/ha)	2.24	0.23	0.91	***	5.33	0.21	0.001	0.91	***
C (188 kg/ha)	2.59	0.29	0.96	***	5.59	0.29	0.000	0.96	***
NC (188 kg/ha)	2.94	0.30	0.87	***	5.95	0.29	0.000	0.88	***
C (376 kg/ha)	4.73	0.28	0.89	***	7.64	0.31	–0.001	0.90	***
NC (376 kg/ha)	4.13	0.36	0.88	***	6.95	0.40	–0.002	0.89	***
Pots with plants									
C (0 kg/ha)	–0.04	0.13	0.77	***	4.29	–0.15	0.012	0.93	***
NC (0 kg/ha)	–0.51	0.18	0.74	***	3.91	–0.13	0.013	0.82	***
C (188 kg/ha)	–0.17	0.15	0.63	***	4.19	–0.14	0.012	0.75	***
NC (188 kg/ha)	–0.25	0.19	0.64	***	3.63	0.01	0.008	0.68	***
C (376 kg/ha)	–0.50	0.13	0.28	*	3.89	–0.17	0.012	0.40	***
NC (376 kg/ha)	–0.21	0.12	0.39	**	5.13	–0.39	0.021	0.74	***
Pots without plants									
C (0 kg/ha)	–0.88	0.19	0.79	***	2.49	0.11	0.003	0.81	***
NC (0 kg/ha)	–1.25	0.27	0.71	***	1.70	0.27	0.000	0.73	***
C (188 kg/ha)	–1.44	0.28	0.68	***	0.40	0.53	–0.010	0.73	***
NC (188 kg/ha)	–0.88	0.18	0.55	***	1.17	0.38	–0.009	0.61	***
C (376 kg/ha)	–3.26	0.47	0.67	***	–1.04	0.63	–0.007	0.69	***
NC (376 kg/ha)	–2.89	0.41	0.61	***	0.41	0.35	0.003	0.64	***

*$P\leq0.05$, **$P\leq0.01$, ***$P\leq0.001$, R^2 coefficient of determination
[a] Amount of SP applied annually

Table 4 Relationship of cumulative soil ^{32}S mineralization with time in different soils in each of the three systems as fitted by logarithmic and exponential models. *NS* Not significant; other abbreviations are explained in Table 1

Soils	Logarithmic model				Exponential model			
	$y=a+b\ [\log_e(x)]$				$y=e^{(a+bx)}$			
	a	b	R^2	P value	K_0	K_1	R^2	R^2
Open incubation								
C (0 kg/ha)[a]	0.02	2.56	0.91	***	1.24	0.04	0.96	***
NC (0 kg/ha)	–0.22	2.24	0.85	***	1.03	0.05	0.91	***
C (188 kg/ha)	–0.51	2.81	0.90	***	1.20	0.05	0.95	***
NC (188 kg/ha)	–0.22	2.86	0.82	***	1.29	0.04	0.87	***
C (376 kg/ha)	1.66	2.77	0.84	***	1.66	0.03	0.89	***
NC (376 kg/ha)	0.25	3.50	0.83	***	1.60	0.04	0.87	***
Pots with plants								
C (0 kg/ha)	–1.16	1.15	0.58	***	–0.94	0.10	0.90	***
NC (0 kg/ha)	–2.12	1.59	0.57	***	–1.27	0.12	0.82	***
C (188 kg/ha)	–1.52	1.36	0.49	***	–0.93	0.10	0.74	***
NC (188 kg/ha)	–2.13	1.80	0.54	***	–0.56	0.10	0.68	***
C (376 kg/ha)	–1.54	1.10	0.19	NS	–2.02	0.14	0.39	***
NC (376 kg/ha)	–0.94	0.90	0.21	NS	–2.04	0.15	0.61	***
Pots without plants								
C (0 kg/ha)	–2.78	1.79	0.69***	***	–1.34	0.12	0.76	***
NC (0 kg/ha)	–4.00	2.53	0.65***	***	–0.92	0.12	0.65	***
C (188 kg/ha)	–4.60	2.80	0.67***	***	–0.81	0.11	0.57	***
NC (188 kg/ha)	–2.91	1.78	0.55***	***	–1.18	0.11	0.46	***
C (376 kg/ha)	–8.30	4.53	0.63***	***	–1.22	0.15	0.56	***
NC (376 kg/ha)	–7.01	3.86	0.54***	***	–1.35	0.15	0.53	***

***$P\leq0.001$
[a] Amount of SP applied annually

sion models (Tables 3, 4), and the parameters in these models were used to compare soil S mineralization between the systems in different soils. In all three systems, amounts of cumulative ^{32}S mineralized were, in general, significantly accounted for by linear, quadratic, logarithmic and exponential models. However, the intercepts, slopes and R^2 values were considerably different from one system to the other, indicating that the rate of ^{32}S mineralization was different from one system to the other. The slopes in the linear model in the open incubation

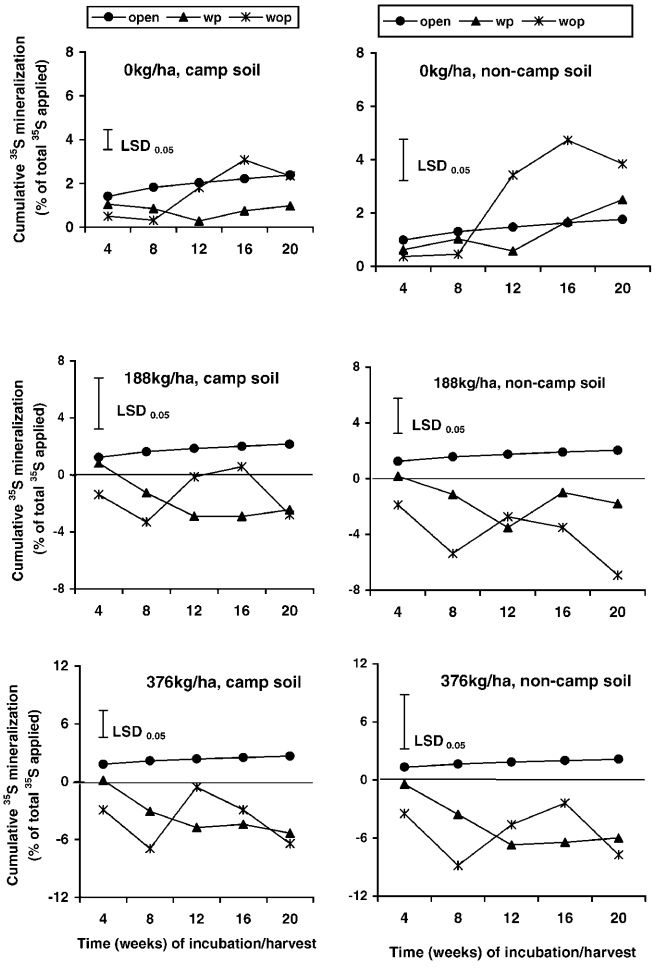

Fig. 3 Comparisons of cumulative soil ^{35}S mineralization at periodic harvests in soils in the three systems (kg/ha refers to SP applied annually). *Vertical bar* indicates significant interaction of systems×time in each soil according to $LSD_{0.05}$. For abbreviations, see Fig. 1

system (Table 3) were in the range of 0.23–0.36, which agreed with those (0.25–1.27) reported by Pirela and Tabatabai (1988) in an open incubation study using soils from Iowa and Chile with varied physical and chemical properties.

Cumulative soil ^{35}S mineralization in three systems

Significant differences in cumulative soil S mineralization between the three systems and between soils shown by ^{32}S (Fig. 2) data were also shown by ^{35}S data (Fig. 3). The trends were similar although the magnitude of differences differed. As soils were pre-conditioned for 2 weeks before the commencement of the mineralization experiments using the three different systems, the ^{35}S applied was found to be rapidly immobilized during the pre-conditioning period as shown by significantly reduced soil inorganic ^{35}S in all soils and consequent increases in organic ^{35}S fractions (Table 5). Thus, any ^{35}S measured after pre-conditioning had been mineralized to ^{35}S. Initial S status in the soils used before pre-conditioning ranged from 2.5 to 6.3 and 376 to 447 µg S/g soil for inorganic and organic S, respectively (Table 6). In the open incubation system, the proportions of ^{35}S mineralized (% of total ^{35}S applied) were small throughout the incubation period (Fig. 3). This could have been due to the loss of labile soil organic ^{35}S by initial leaching with 0.01 M KH_2PO_4, especially in fertilized soils, as inorganic and total ^{35}S recoveries were high in initial leachates (Table 7).

In the pot systems with and without plants, mineralization of ^{35}S was observed in control soils similar to that for the open incubation, but in fertilized soils immobilization was the dominant process at all harvest times

Table 5 Effect of pre-conditioning on recovery of soil ^{35}S fractions. Values followed by the *same small letters in a column* are not significantly different at LSD ($P \leq 0.05$) for differences between soils before and after pre-conditioning. Abbreviations are explained in Table 1

Soils	Inorganic ^{35}S		Organic ^{35}S		Total ^{35}S	
	Before[a]	After[a]	Before	After	Before	After
	(% Total ^{35}S applied)					
C (O kg/ha)[b]	16.9 a	3.7 a	71.7 b	80.7 b	88.6	84.4
NC (O kg/ha)	15.9 a	2.2 a	72.6 b	77.9 b	88.5	80.1
NC						
C (188 kg/ha)	31.3 b	13.5 b	61.3 a	70.2 a	92.6	83.7
NC (188 kg/ha)	41.0 b	18.0 b	48.4 a	63.9 a	89.5	81.9
C (376 kg/ha)	35.1 b	19.9 c	55.0 a	56.7 a	90.1	76.5
NC (376 kg/ha)	40.9 b	26.7 d	50.3 a	54.0 a	91.2	80.7

[a] Before and after pre-condition
[b] Amount of SP applied annually

Table 6 Soil ^{32}S fractions in initial soils before pre-conditioning. Values followed by the *same capital letters within a column* are not significantly different at LSD (≤0.05); data *in parentheses* give percentages of total ^{32}S. Abbreviations are explained in Table 1

Soils	Inorganic ^{32}S	Organic ^{32}S	Total ^{32}S
	(µg S/g soil)		
C (0 kg/ha)[a]	2.5 A (0.6)	398.5 A (99.4)	401.0 A
NC (0 kg/ha)	2.2 A (0.6)	375.8 A (99.4)	378.0 A
C (188 kg/ha)	4.0 B (0.9)	452.0 C (99.1)	456.0 C
NC (188 kg/ha)	4.8 B (1.2)	412.9 B (98.8)	417.7 B
C (376 kg/ha)	4.5 B (1.0)	444.8 C (99.0)	449.3 C
NC (376 kg/ha)	6.3 C (1.4)	447.4 C (98.6)	453.7 C

[a] Amount of SP applied annually

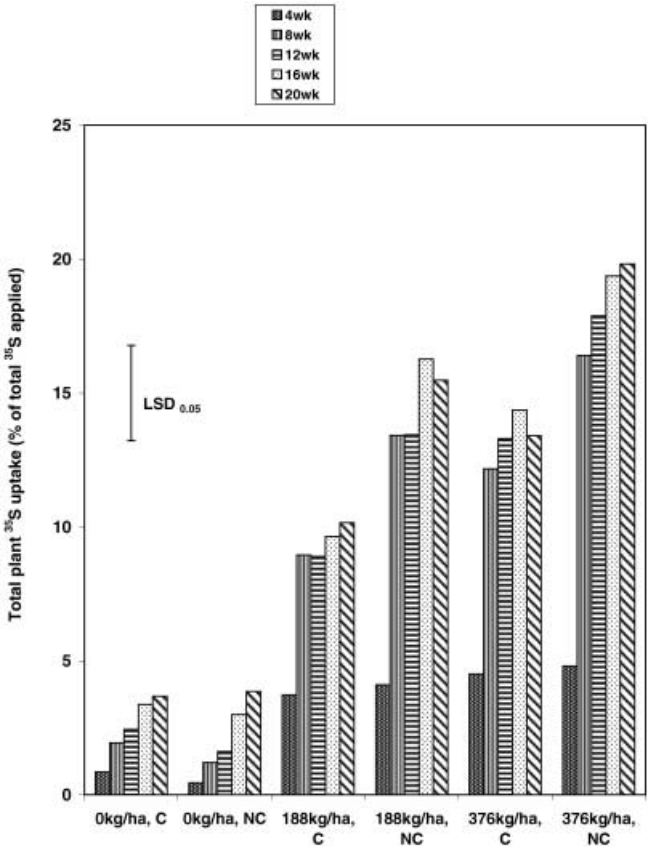

Fig. 4 Total plant (tops plus roots) ^{35}S uptake in different soils at different harvests (kg/ha refers to SP applied annually). *Vertical bar* indicates significant interaction of soils×time according to $LSD_{0.05}$. *C* Camp, *NC* non-camp; for other abbreviations, see Fig. 1

Table 7 Recoveries of inorganic and total ^{35}S in initial leachates (with 0.01 M KH_2PO_4). Abbreviations are explained in Table 1

Soils	Inorganic ^{35}S	Total ^{35}S
	(% of total ^{35}S applied)	
C (0 kg/ha)[a]	6.39	6.93
NC (0 kg/ha)	2.08	2.41
(188 kg/ha)C	21.88	23.13
NC (188 kg/ha)	31.92	33.74
C (376 kg/ha)	29.52	31.18
NC (376 kg/ha)	34.82	36.75

[a]Amount of SP applied annually

except during the first 4 weeks (Fig. 3). The intensity of immobilization in fertilized soils in pot systems was reduced at certain times (e.g. at 12 and 16 weeks in pots without plants), indicating a net release of ^{35}S, thus suggesting that concurrent mineralization and immobilization of S occurred. As expected, total plant ^{35}S uptake was several times higher in fertilized than in control soils (Fig. 4).

Tsuji and Goh (1979) reported net S mineralization of native soil S, but net immobilization of added ^{35}S, in pot trials using perennial ryegrass. The immobilization of added S was observed even though the soils were incubated for 70 days to reach the apparent steady-state condition before plants were grown in the pots (Tsuji and Goh 1979).

Total amounts of ^{35}S mineralization or immobilization over 20 weeks in control (camp and non-camp) soils were similar in all the three systems studied (1–4% of total ^{35}S applied). However, in fertilized soils, a mineralization of 2–3% of total ^{35}S applied was observed in the open incubation system, while an immobilization of 5–6% and 6–8% of total ^{35}S applied was observed in the pot systems with plants and without plants, respectively. This showed that in fertilized soils, the type of system affected the release and retention of ^{35}S with time.

In conclusion, results obtained in this study showed that the determination of soil S mineralization varied according to the methods used. Results obtained in an open incubation system by periodic leaching do not simulate crop S removal as commonly postulated; hence this method could not be used to predict soil S mineralization. The presence of plants is important in determining soil S mineralization. Comparisons of methods for determining soil S mineralization need to be conducted simultaneously under the same experimental conditions.

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