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Soil organic sulfur dynamics in a coniferous forest

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Abstract. Sulfate microbial immobilization and the mineralization of organic S were measured *in vitro* in soil horizons (LFH, Ae, Bhf, Bf and C) of the Lake Laflamme watershed (47°17′ N, 71°14′ O) using $^{35}SO_4$. LFH samples immobilized from 23 to 77% of the added $^{35}SO_4$ within 2 to 11 days. The $^{35}SO_4$ microbial immobilization increased with temperature and reached an asymptote after a few days. The mineral soil generally immobilized less than 20% of the added $^{35}SO_4$, and an asymptote was reached after 2 days. An isotopic equilibrium was rapidly reached in mineral horizons. A two-compartment (SO_4 and organic S) model adequately described $^{35}SO_4$ microbial immobilization kinetics. The active organic reservoir in the whole soil profile represented less than 1% of the total organic S. The average concentrations of dissolved organic S (DOS) in the soil solutions leaving the LFH, Bhf and Bf horizons were respectively 334, 282 and 143 $\mu g \cdot L^{-1}$. Assuming that the DOS decrease with soil depth corresponded to the quantities adsorbed in the B horizons, we estimated that 12 800 $kg \cdot ha^{-1}$ of organic S could have been formed since the last glaciation, which is about 13 times the size of the actual B horizons reservoirs. Our results suggest that the organic S reservoirs present in mineral forest soils are mostly formed by the DOS adsorption resulting from incomplete litter decomposition in the humus layer. The capability of these horizons to immobilize SO_4 from the soil solution would be restricted to a 1% active fraction composed of microorganisms. Despite their refractory nature, these reservoirs can, however, be slowly decomposed by microorganisms and contribute to the S-SO_4 export from the watershed in the long term.

Introduction

Sulfate adsorption and desorption are known to be important reactions in the S dynamics of forest soils (Chao et al. 1962; Johnson & Todd 1983; Fuller et al. 1985; Vance & David 1992; Houle & Carignan 1995). However, biological S immobilization and mineralization reactions by microorganisms are less well known, and opinions vary widely in the literature regarding the reactivity of organic S reservoirs. Studies conducted *in situ* (Strickland et al. 1985; Watwood & Fitzgerald 1988) and in the laboratory (Schindler et al. 1986; Fitzgerald et al. 1983; Watwood & Fitzgerald 1988; Swank et al. 1984) have shown that significant amounts of $^{35}SO_4$ can be transformed into organic ^{35}S within a few days. However, part of the newly formed organic ^{35}S could rapidly (24–48 h) be remobilized into $^{35}SO_4$ (Strickland & Fitzgerald 1984; Strickland et al. 1984). Others (Foster 1989; MacDonald et al. 1995) have shown that organic S, present in the surface mineral horizons and in the humus layer, had high potentials for mineralization that increased with temperature.

Organic S reservoirs usually account for 75 to 90% of total S in forests (Autry et al. 1990; Houle & Carignan 1992; Mitchell et al. 1992a). Noticeable exceptions are soils with high sulfate adsorption capacity where adsorbed SO_4 may dominate (Johnson 1984). Given the size and the apparent reactivity of the organic S reservoirs, some authors (Strickland et al. 1986; Autry et al. 1990) have suggested that SO_4 microbial immobilization into organic matter could be more important than SO_4 adsorption onto Fe and Al oxides as a long-term S accumulation mechanism by forest ecosystems. These authors (Strickland & Fitzgerald 1984; Swank et al. 1985; Autry & Fitzgerald 1990) have also proposed that long-term SO_4 immobilization into organic fractions should be proportional to SO_4 concentration in soil solutions, suggesting that organic S reservoirs could accumulate S in response to increasing atmospheric deposition. These observations suggest that organic S reservoirs are dynamic. On the other hand, others maintain that organic S reservoirs (especially within mineral soils) are weakly reactive and that only a small proportion (<10%) is involved in short-term immobilization and mineralization reactions (McLaren et al. 1985; Schindler & Mitchell 1987; Mitchell et al. 1989). This view is supported by the absence of a relation between the size of the organic S reservoirs and the SO_4 deposition in 10 forested ecosystems (Houle & Carignan 1992), suggesting that the size of these reservoirs is independent of S deposition and that they do not accumulate atmospheric S. The present report tests these opposing views by characterizing the organic S dynamics of a humo-ferric podzol using $^{35}SO_4$ microbial immobilization kinetics and organic S measurements in soil solutions.

Methods

Sulfate microbial immobilization in organic reservoirs

The study was conducted at the Laflamme lake watershed (68.4 ha, 47°17′ N, 71°14′ O) located 80 km north of Quebec city, Quebec, Canada (Houle &

Carignan 1992, 1995). The soil is an orthic humo-ferric podzol according to the Canadian soil classification system (Agriculture Canada Expert Committee on Soil Survey 1987). The forest is composed of 90% balsam fir (*Abies balsamea*) and 10% white birch (*Betula papyrifera*). This region receives a mean annual precipitation of 1300 mm (33% as snow). The mean annual temperature is –0.6 °C. Fresh soil samples were collected near the study plot on the north side of the watershed (LFH, Ae, Bhf, Bf, C). LFH samples were gently sieved (2.5 cm mesh) to eliminate large fragments (roots, leaves, etc.) whereas mineral soils were passed through a 2 mm mesh sieve. The samples (4–10 g) were incubated for 2 to 12 days in test tubes with 50 $\mu l \cdot g^{-1}$ of carrier free $^{35}SO_4$ at three temperatures (1, 10 and 20 °C). Triplicate samples were taken at different times and $^{35}SO_4$ was extracted for 30 minutes with 30 ml of a 0.25 M Na_2SO_4 (LFH) or 0.16 M NaH_2PO_4 (mineral horizons) on a mechanical shaker. Recovery tests using the two extraction methods showed a 100% recovery of $^{35}SO_4$ introduced in the sample and extracted immediately after addition. For the LFH samples, Na_2SO_4 was preferred to NaH_2PO_4 because of the rapid immobilization (immobilization refers to microbial immobilization throughout the manuscript) observed in preliminary experiments. It was preferable, in this case, to end the immobilization reaction immediately by isotope flooding to prevent $^{35}SO_4$ immobilization during the extraction. After extractions, test tubes were centrifuged and $^{35}SO_4$ concentrations were measured by liquid scintillation using the external standard method to correct for a weak (0–3%) quenching of emitted photons. The extractants used quantitatively recover the $^{35}SO_4$ (soluble and adsorbed) which was not immobilized into organic matter. Immobilized $^{35}SO_4$ was then calculated by the difference between added and recovered amounts.

Additional experiments were carried out with large soil quantities in order to obtain sufficient water volume to measure SO_4 concentrations and $^{35}SO_4$ to obtain specific activity values. Fifty ml of carrier-free $^{35}SO_4$ were added to fresh samples (1 kg) placed in polyethylene containers. This solution was added as 100 uniformly distributed amounts of 0.5 ml. Ten g samples were collected at different times in triplicate and extracted as mentioned above. Samples (50 g) were also collected in duplicate at different times and centrifuged in double bottom bottles to extract the soil solution for SO_4 and $^{35}SO_4$ measurements. Between samplings, the containers were hermetically closed to prevent water loss by evaporation.

Immobilization (in organic matter) and mineralization constants were estimated for the LFH layer using a two-compartment model where adsorption and desorption reactions are assumed negligible:

$$SO_4 \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Organic S} \tag{1}$$

where

$$-d[SO_4]/dt = k_1 \times [SO_4] - k_2 \times [\text{organic S}] \tag{2}$$

which has the time-dependent solution:

$$[^{35}SO_4]_t = [^{35}SO_4]_o \times [k_1 \times e^{-(k1+k2)t} + k_2]/(k_1 + k_2) \tag{3}$$

where $[^{35}SO_4]_o$ is the initial activity in solution.

The quantity of organic ^{35}S formed with time can be described by:

$$\text{Organic}^{35}S = 1 - [[^{35}SO_4]_o \times [k_1 \times e^{-(k1+k2)t} + k_2]/(k_1 + k_2)] \tag{4}$$

When steady state conditions are preserved during the incubations (constant SO_4 concentration), this model can be used to estimate k_1 and k_2 constants. Then, microbial immobilization (S inc) and mineralization (S min) rates can be calculated by:

$$\text{S inc} = k_1 \times [SO_4] \quad \text{and} \quad \text{S min} = k_2 \times [\text{organic S}] \tag{5, 6}$$

where $[SO_4]$ is the SO_4 concentration in solution.

Assuming steady states conditions:

$$\text{S inc} = \text{S min}, \tag{7}$$

$$k_1 \times [SO_4] = k_2 \times [\text{organic S}] \tag{8}$$

$$k_1/k_2 = [\text{organic S}]/[SO_4]. \tag{9}$$

Renewal time (RT) and the organic reservoir size can be calculated respectively by:

$$RT = [\text{organic S}]/(k_1 \times [SO_4]) \tag{10}$$

and

$$[\text{organic S}] = (k_1 \times [SO_4])/k_2 \tag{11}$$

For mineral horizons (Bhf, Bf and C) with substantial adsorbed quantities of SO_4 (Houle & Carignan 1992), the first order immobilization-mineralization model is not entirely correct because $^{35}SO_4$ immobilization and adsorption are taking place simultaneously. Immobilization and adsorption kinetics should ideally be described by a four-compartment model. However, an equilibrium between adsorbed and soluble $^{35}SO_4$ is reached within 2–3 hours in these soils with 50% of the added $^{35}SO_4$ being adsorbed within 2 minutes (Houle & Carignan 1995). A two-compartment model can therefore be used to describe organic S kinetics because immobilization and mineralization take place on a much longer time scale.

Dissolved organic S in throughfall and soil solutions

Throughfall was sampled between May and October 1989 with 20 collectors spaced 1 m from each other on the perimeter of a 25 m^2 plot located on the north side of the watershed. Stemflow was collected on 6 balsam firs present near the plot. Soil-water was collected with zero-tension lysimeters under the LFH and the Bhf horizons (Houle & Carignan 1995). Sulfate and total S concentrations were respectively measured by ion chromatography and plasma emission spectrometry (Mitchell et al. 1986). A SO_4 standard ($4\,mg \cdot L^{-1}$) was regularly analyzed with both methods to ensure that there was no systematic bias. Dissolved organic S (DOS) concentrations were obtained by difference between total S concentrations and SO_4 concentrations.

Results

SO_4 immobilization into organic matter

A first experiment (20 °C, 48 h) showed that 60% of the added $^{35}SO_4$ was immobilized in the LFH horizon and that $^{35}SO_4$ immobilization was still taking place after 48 h (Figure 1). However, in the Ae, Bhf and Bf horizons, immobilization rapidly reached (< 8 h) an asymptote with small immobilized amounts (<10% of added $^{35}SO_4$). In a second experiment, incubations were carried out at different temperatures (LFH: 1, 10 and 20 °C, Bhf: 1 and 10 °C) and the incubation time was doubled (96 h). LFH samples immobilized significant quantities of $^{35}SO_4$ with 23, 48 and 71% of added $^{35}SO_4$ at temperatures of 1, 10 and 20 °C respectively (Figure 2). As observed in the first experiment, immobilization by the LFH horizon had apparently not reached a maximum after 96 h for the three temperatures. In the Bhf horizon, $^{35}SO_4$ immobilization was low (<10%) and reached a plateau after 4 h. Although temperature

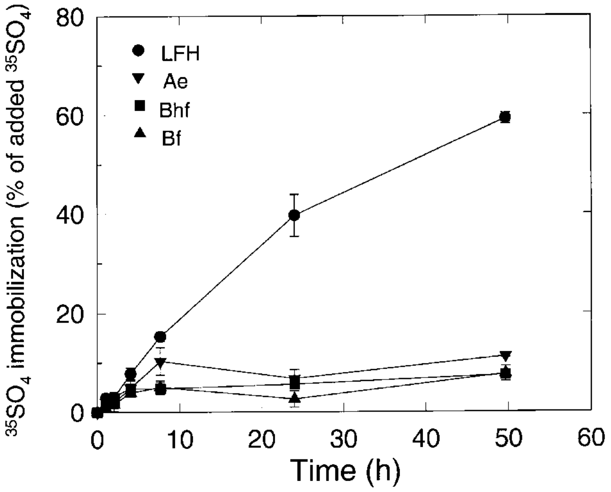

Figure 1. Immobilization kinetics (means ± standard deviations, $n = 3$) of $^{35}SO_4$ at 20 °C in 4 soil horizons from the Laflamme lake watershed.

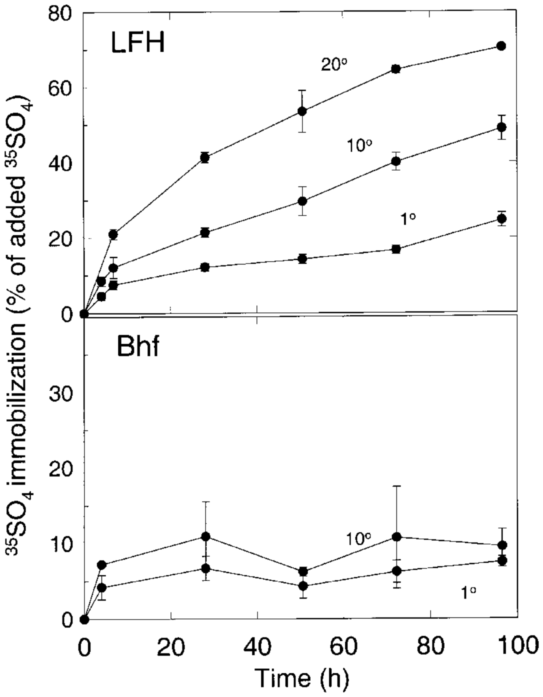

Figure 2. $^{35}SO_4$ immobilization kinetics as a function of temperature (°C) in 2 soil horizons from the Laflamme lake watershed.

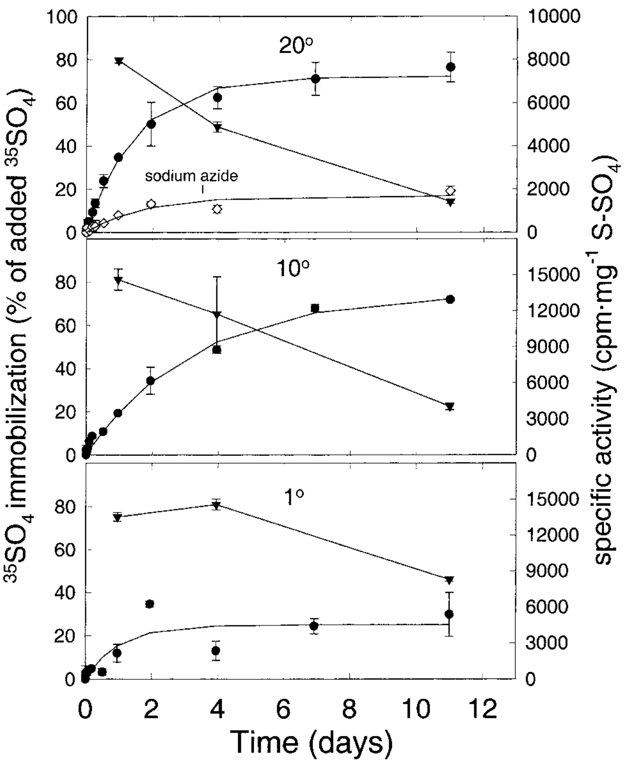

Figure 3. $^{35}SO_4$ immobilization kinetics (circle) as a function of temperature in the LFH horizon. The curves adjusted to immobilization values come from a two-compartment model. Immobilization in the samples treated with sodium azide (open lozenge) and the SO_4 specific activity in solution (triangle) are also indicated.

clearly stimulated immobilization in the LFH horizon, this effect was less pronounced in the Bhf horizon.

In a third experiment conducted for 12 days at three temperatures, LFH samples immobilized 30–80% of the added $^{35}SO_4$ and the specific activity of SO_4 in solution decreased rapidly (Figure 3). This decrease was caused by a net ‘cold’ SO_4 mineralization from the organic S reservoir which diluted the $^{35}SO_4$ present in solution (Table 1). The results obtained at 1 °C were inconsistent at the beginning of the incubation and were possibly attributable to small temperature fluctuations below the freezing point which allowed ice formation in the samples as was observed 24 h after the start of the incubation. It is known that frost and thaw can affect the rates of the organic reservoirs mineralization (Walworth 1992). The utilization of sodium azide, a respiration inhibitor, considerably (but not totally) reduced $^{35}SO_4$ immobilization in

Table 1. SO_4 concentrations (± standard deviation, n = 2) in soil solutions extracted by centrifugation.

Horizons	°C	Days				
		0.5	1	4	11	12
				mg·L^{-1}		
LFH	1		12.7 ± 1.4	12.5 ± 1.9	17.9 ± 0.9	
	10		9.7 ± 0.4	9.9 ± 1.0	16.3 ± 1.1	
	20		10.4 ± 0.1	12.9 ± 0.2	18.8 ± 0.30	
Ae	1	11.5 ± 0.4		12.5 ± 1.3		—
	10	9.9 ± 0.2		9.5 ± 0.1		—
Bhf	1	4.1 ± 0.3		3.6 ± 0.0		4.8 ± 0.3
	10	4.1 ± 0.3		6.0 ± 0.2		3.5 ± 0.1
Bf	1	4.3 ± 0.1		4.9 ± 0.0		4.9 ± 0.1
	10	4.8 ± 0.5		5.0 ± 0.0		4.4 ± 0.0
C	1	4.2 ± 0.0		4.5 ± 0.0		5.2 ± 0.1
	10	5.7 ± 0.0		4.7 ± 0.0		4.3 ± 0.0

the LFH horizon at 20 °C (Figure 3). In the mineral horizons, SO_4 concentrations remained fairly stable during incubations, suggesting that equilibrium conditions were preserved. Although SO_4 concentrations increased in LFH samples, especially between 4 and 11 days, we assumed that equilibrium conditions were preserved. In fact, if the two-compartment model is applied to the results obtained between 0 and 4 days of incubation (when equilibrium conditions were preserved), the results were almost similar. The curves obtained with the two-compartment model were generally well adjusted to experimental values (Figures 3 and 4). The k_1 and k_2 constants and their standards errors, the renewal time of organic S compartments (assuming that the totality of the S reservoirs is exchangeable), and the estimation of the active fraction of the organic S compartment (calculated with equation (11)) are given in Table 2. In some occasions (Ae horizon at 10 °C and C horizon at 1 °C), standard errors of the k_1 and k_2 constants were very high, and were not used to estimate S fluxes. However, the k_1/k_2 ratio only depends on the ^{35}S distribution in the two compartments at equilibrium, and can be used to estimate the active fraction of the S reservoir despite high standard errors.

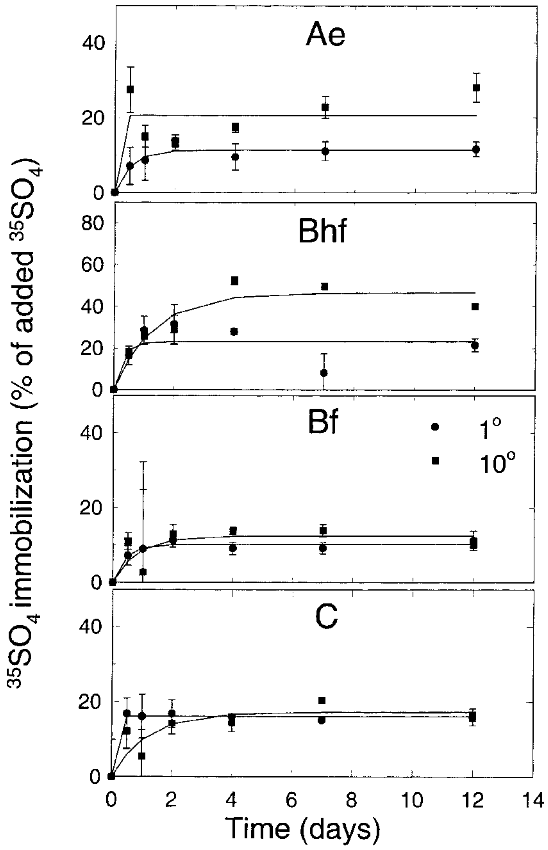

Figure 4. $^{35}SO_4$ immobilization kinetics as a function of the temperature in the mineral horizons.

The $^{35}SO_4$ (Figure 5) and SO_4 (Table 1) concentrations, and the SO_4 specific activity (Figure 5) in solution in the mineral soils (Ae, Bhf, Bf, C) remained fairly stable after 4 days of incubation at the exception of small SO_4 concentration variations for the Bhf horizon incubated at 10 °C. These observations are consistent with the $^{35}SO_4$ immobilization asymptote reached early during incubation (Figure 4) and suggest a rapid establishment of isotopic equilibrium.

Dissolved organic S

Substantial dissolved organic sulfur (DOS) concentrations (Table 3) were measured in throughfall (309 $\mu g \cdot L^{-1}$) and in stemflow (1021 $\mu g \cdot L^{-1}$), DOS representing respectively 20 and 28% of total S. The DOS was not meas-

Table 2. Kinetics rate (± standard error, SE) of SO_4 immobilization (k_1) and mineralization (k_2) for organic S reservoirs, renewal times (RT) of the reservoirs (supposing that all the reservoir is exchangeable), and S reservoir sizes actively involved in S exchanges.

Horizon	T	k_1	SE (%)	k_2	SE (%)	RT[1]	Active S	Organic S[2]
	°C	Day^{-1}				Year	mg·kg^{-1}	%
LFH	AZ (20)	0.10	21.9	0.49	29.8	—	—	—
	1	0.25	46.0	0.74	56.3	4.37	2.73	0.16
	10	0.23	7.1	0.08	20.8	5.64	20.20	1.15
	20	0.48	5.9	0.18	11.7	2.26	21.30	1.22
Ae	1	0.22	30.5	1.67	34.0	2.04	0.15	0.13
	10	19.58	2263	75.24	2263	—[3]	0.24	0.22
Bhf	1	0.79	112.7	2.63	122.4	4.41	0.22	0.05
	10	0.35	24.9	0.40	34.4	9.11	0.71	0.14
Bf	1	0.25	24.3	2.16	26.7	6.58	0.08	0.04
	10	0.15	62.6	1.05	72.3	10.65	0.10	0.05
C	1	4.33	156500	22.46	156600	—[3]	0.07	0.07
	10	0.45	41.9	0.70	50.4	12.27	0.08	0.08

[1] Based on a 200-day annual activity, supposing that S reservoirs (Houle & Carignan 1992) are totally reactive.
[2] Organic S concentrations used for these calculus come from Houle and Carignan (1992).
[3] SE too high to estimate RT.

ured in incident precipitation, but incident precipitation is not expected to contain significant DOS quantities (Homann et al. 1990). The canopy seemed to represent an important source of DOS. Average DOS concentrations in the water coming out from the LFH, Bhf and Bf horizons were respectively 334, 282 and 143 $\mu g \cdot L^{-1}$ (Table 3). DOS accounted for a decreasing proportion of total S (DOS+SO_4) in water percolating from the LFH (20%) to the Bf (9%) horizon.

Discussion

$^{35}SO_4$ immobilization

In the tracer addition experiments, $^{35}SO_4$ immobilization rates decreased with time for all the soil horizons: immobilization reached an asymptote after about 7 days in the LFH horizon (Figure 3), and after 2–4 days in

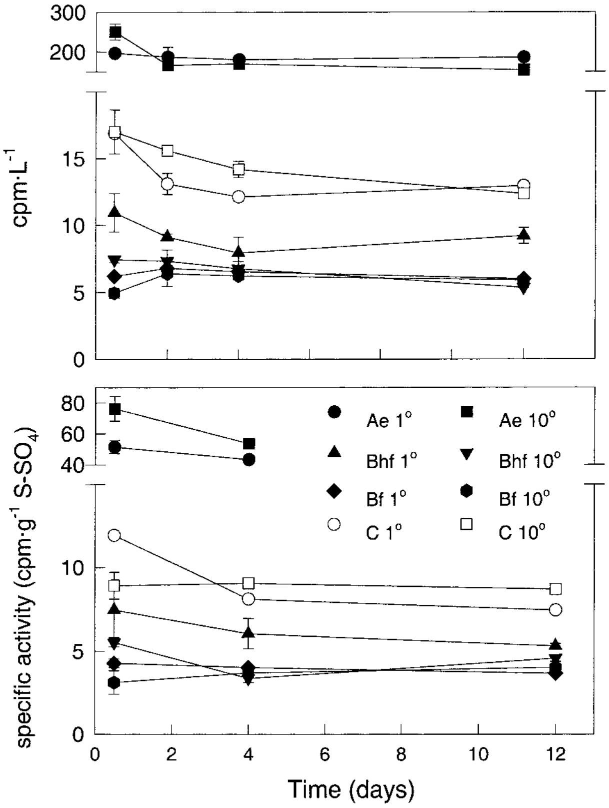

Figure 5. $^{35}SO_4$ concentration (cpm·L^{-1}) and SO_4 specific activity in the soil solutions collected by centrifugation in mineral horizons (Ae, Bhf, Bf and C) at 1 and 10 °C.

Table 3. Average concentrations (± standard deviation) and contribution of dissolved organic S (DOS) to total S in throughfall, stemflow and in soil solutions collected with zero-tension lysimeters.

Collector type	DOS (μg·L^{-1})	DOS/Total S (%)
Throughfall (*n* = 13)	309 ± 317	19.5 ± 13.8
Stemflow (*n* = 21)	1021 ± 839	27.9 ± 11.0
LFH (*n* = 47)	334 ± 261	20.1 ± 10.1
Bhf (*n* = 30)	281 ± 265	14.1 ± 8.3
Bf (*n* = 5)	143 ± 72	8.6 ± 4.3

the mineral horizons (Figure 4). Immobilization increased with temperature, but was strongly reduced by sodium azide, a respiration inhibitor (Figure 3). These observations suggest that microorganisms play an important role in SO_4 immobilization. The incomplete inhibition of $^{35}SO_4$ immobilization by sodium azide may be due to the presence of extracellular enzymes capable of immobilizing SO_4 (Strickland et al. 1984). Similar temperature and NaN_3 inhibition effects have been observed by others in the 5 to 30 °C range (Watwood et al. 1986; Fitzgerald et al. 1983, 1985). Our results show that immobilization and mineralization can still be appreciable near the freezing point, and that these reactions may remain important, most of the year, even in wintertime, when the upper soil horizons are slightly above freezing due to the insulating effect of the snow cover.

The increase in SO_4 concentrations in solution during incubation of the LFH samples (Table 1) corresponded to net S mineralization rates of 7.3, 9.3 and 11.8 $kg{\cdot}ha^{-1}\ y^{-1}$ respectively, at temperatures of 1, 10 and 20 °C. Because these measurements were carried in the laboratory on perturbed soils, the observed mineralization rates may not accurately reflect *in situ* conditions, however. There was no attempt to measure alteration of soil chemistry during the incubation procedure at the exception of SO_4 and $^{35}SO_4$ concentration. Previous experiments on short time incubation (Houle & Carignan 1995), have shown that the pH of the Bf horizon did not change significantly over a 24 hours period. Since most of the immobilization process is made on this time scale in mineral horizons, it suggests that alteration of soil chemistry had little effects on the experimental data. The SO_4 concentration within the soil solution also remain fairly stable in all the mineral soil horizons between 2 and 12 days (Table 1) which suggests no important changes in pH since SO_4 adsorption is strongly pH dependent especially in the B horizons.

Nevertheless, mineralization within the forest floor is potentially important in the global S cycle of this system since the estimated values are comparable to the annual atmospheric S-SO_4 deposition on the watershed (7 $kg{\cdot}ha^{-1}$, Houle & Carignan 1995). In the mineral soil, SO_4 concentrations and the specific activity remained fairly constant during the 12 day-long incubations (Table 1, Figure 5) suggesting low net SO_4 mineralization rates.

The soil incubation results suggest that, although organic reservoirs do not form important net quantities of organic S directly from SO_4, they recycle large amounts of SO_4 through immobilization and mineralization reactions. These observations support the conclusions of Gélineau et al. (1989), based on the $^{18}O/^{16}O$ ratio of the SO_4 molecule according to which 32 to 61% of the SO_4 entering the Lake Laflamme watershed had been reduced and oxidized before leaving the watershed.

The two-compartment model was adequate to fit the experimental $^{35}SO_4$ immobilization data (Figures 3 and 4). The renewal time of the organic S compartments (assuming that the totality of the S reservoirs is exchangeable (equation (10)), varied from 2 (LFH and Ae) to 12 years (C). These renewal times are rapid considering the refractory nature of forest soil organic matter, of which over 90% is considered weakly reactive (McLaren et al. 1985; Schindler & Mitchell 1987). In fact, the size of the active reservoirs (calculated from equation 8), represent only 1% of the total organic S in horizon LFH and <1% in all the other horizons (Table 2). These values are apparently small but are in good agreement with microbial biomasses (<1% of the dry mass) measured in different forest soils (Anderson & Domsh 1978; Jenkinson & Powlson 1976; David et al. 1982). These results are also comparable to those of McLaren et al. (1985) who found that 3 to 6% of the organic S present in agricultural soil samples was reactive. The higher percentages observed by these authors are probably attributable to the higher reactivity of organic matter in agricultural soils as compared to forest soils. Overall, it seems that the organic S reservoir in the soils of the Lake Laflamme watershed would be constituted by more than 99% of refractory S, and that the remaining 1% would be strictly composed of microorganisms actively recycling SO_4-S.

Comparison with other studies

Our results are in good agreement with those of Fuller et al. (1986) who developed a simulation model of sulfur transformations in forested spodosols based on reversible first-order reactions. These authors also found that formation of organic S (C-bonded S and ester-sulfate) was not linear with time and that only a small portion of the organic S pool may be rapidly cycled through labile forms. Our $^{35}SO_4$ immobilization results and those of Fuller et al. (1986), however, contrast with several studies (Watwood et al. 1986, 1988; Watwood & Fitzgerald 1988; Autry & Fitzgerald 1990, 1991a, 1991b, 1991c). These authors concluded that $^{35}SO_4$ immobilization was linear with time for several sites and soil types, whereas we found that immobilization reached an asymptote after 2–7 days (Figures 1, 2 and 3). Assuming a linear $^{35}SO_4$ immobilization, rate measurements can be done by using only one incubation time (48 h) and by calculating the slope between 0 and 48 h (Autry & Fitzgerald 1990, 1991a, 1991b, 1991c). These different interpretations of the kinetics of S immobilization lead to totally opposite views regarding the role of the organic S reservoirs in forest ecosystems. Linear immobilization rates lead to the conclusion that there is a net organic S accumulation in forested soils. On the other hand, a two-compartments model indicates that although organic reservoirs recycle SO_4 actively, they do not accumulate S on a net basis.

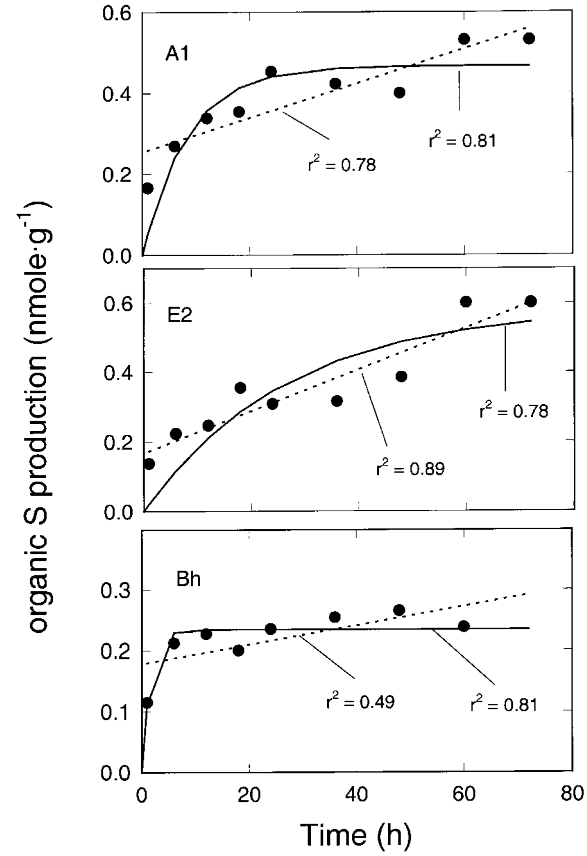

Figure 6. Comparison of a linear (dotted line) and a two-compartment model (solid line) on data reproduced from Watwood et al. (1988). The linear model represent the regression of observed data against time as used by Watwood et al. (1988).

In order to compare both models on the same data, the results of Watwood et al. (1988) which were interpreted as a linear organic ^{35}S formation for three soil horizons, were reanalyzed. Indeed their results (Watwood et al. 1988) can be equally well fitted to a two-compartment model (Figure 6). The r^2 values obtained are better than the linear model for two of the three soil horizons. The linear model also has a major shortcoming as compared to a two-compartment model: the intercept is significantly different from zero, which means that organic ^{35}S would be formed before tracer addition, which is impossible. On the other hand, the two-compartment model offers a conceptual frame, based on well known equations describing the immobilization of radioactive tracers. Other results (Watwood et al. 1986; Fitzgerald et al. 1983) have been reanalyzed with the same success (data not shown). These results strongly suggest that the linear model and its implications must be considered with caution.

In particular, these authors (Strickland & Fitzgerald 1984; Swank et al. 1985; Autry & Fitzgerald 1990) have proposed that long-term SO_4 immobilization into organic fractions is proportional to SO_4 concentration in soil solutions, suggesting that organic S reservoirs could accumulate S in response to increasing atmospheric deposition. Autry and Fitzgerald (1991) and Fitzgerald and Autry (1992) also maintained that the capacity of soil samples coming from different sites to form organic S (as estimated from linear immobilization of $^{35}SO_4$ at saturating SO_4 concentration) should correlate with the quantity of organic S present in these sites.

To evaluate these possibilities, the organic S reservoir sizes at various forested sites were compared to SO_4 deposition and to the organic S accumulation potential at SO_4 saturation (Figure 7) as calculated by Fitzgerald and Autry (1992). The analysis clearly demonstrates that there is no relation between the size of organic S and these two variables. In fact, considering the non-limiting nature of S in forest soil solution as compared to N or P, it would have been surprising to observe S accumulation in the organic reservoirs.

These observations are also in good agreement with field and laboratory experiments where SO_4 addition has failed to trigger S accumulation into the organic S reservoir (Rustad et al. 1996; David et al. 1995; Mitchell et al. 1998). The current study and those cited above also question the McGill and Cole (1981) model which predicts that excess inorganic S should be accumulated in ester sulfate forms. This model may not be totally adequate to describe S dynamics in forest soils.

Dissolved organic S

As discussed above, except for the microbial biomass most of the organic S present in mineral horizons is practically unreactive and does not participate to form organic S from SO_4 on a net basis. According to some authors (David et al. 1987; Mitchell et al. 1989), the major fraction of the organic S in mineral horizons would be formed from adsorption of the DOS produced in the humus layer and percolating through the soil profile. To estimate the potential for organic S formation by DOS adsorption, we calculated the difference of DOS concentration between the solution flowing from the LFH horizon and the Bf horizon respectively (Table 3). This difference was then multiplied by the annual water fluxes (800–900 mm) under the Bf horizon. The resulting accumulation rate of organic S amounts to 1.6 $kg \cdot ha^{-1} \cdot year^{-1}$. This value is about five times higher than reported by Mitchell et al. (1989) for the Huntington forest site. However, an estimation for several sites for which DOS concentrations have been published (Homann et al. 1990), suggest formation

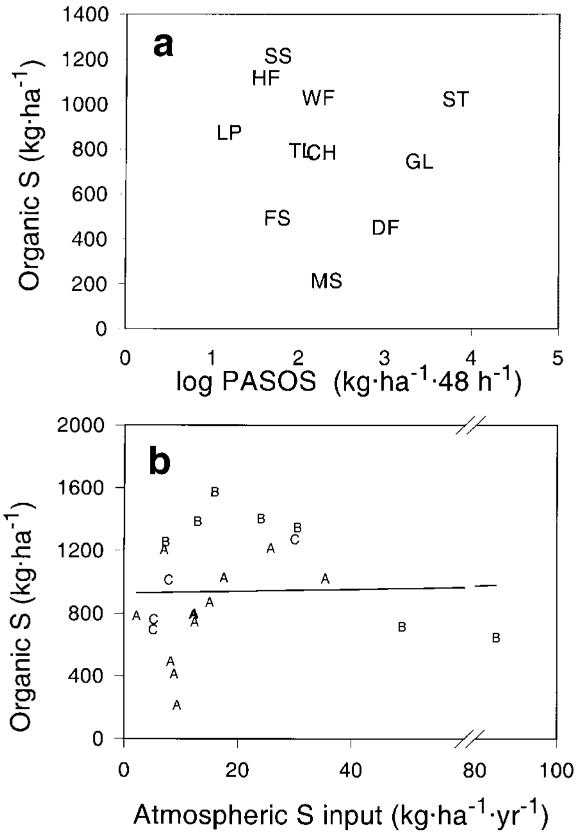

Figure 7. Relation (a) between the accumulation potential of organic S at saturation (PASOS) as measured by Fitzgerald and Autry (1990) and the quantities of organic S present at 11 forest sites in North America (compilation made from Mitchell et al. 1992b) and relation between atmospheric S inputs and the size of organic S reservoirs at 24 forested sites (b). The data is from a compilation of Mitchell et al. (1992) (**A**) and from a compilation of Houle and Carignan (1992) (**B**). When different values for a same site were present in the two compilations, the average of both values was used (**C**).

potentials close to our estimate for the lake Laflamme watershed. Informations are missing regarding the stability of the newly formed organic S from DOS adsorption. Qualls and Haines (1992) reported that over 95% of the DOC concentration diminution in percolating water of forested spodosols was due to adsorption in B horizons and not to decomposition in the short term, which suggests that adsorbed DOS must be relatively stable. However, a significant but unknown part of DOS must be decomposed in the long term after adsorption, otherwise the size of the S reservoir would be much higher: if we suppose that a forest was established just after deglaciation, some 8000 years ago at our site, this process (at the actual rate) should have formed 12 800 kg·ha^{-1} of organic S in the B horizons, which is about 13 times the quantity actually measured within the Bhf and Bf horizons (967 kg·ha^{-1}, Houle & Carignan 1992).

The role of forest floor appears crucial as a site of DOS (and DOC) formation and exportation to the B horizons. The size of organic S reservoir found in the forest floor amounts to 119 kg·ha^{-1} (Houle & Carignan, 1992). The forest floor itself accumulates organic S principally from litterfall and ultimately, in the mechanism describe above, the vast majority of the organic S found within the whole soil profile would be derived from litterfall. It may be speculated that, in the long term, the factors that would affect organic matter turnover within the forest floor, may also affect the rate of organic S (and carbon) formation within the B horizon. In fact, long-term S dynamic (over hundreds of year) is probably controlled by long term carbon dynamics since soil microorganisms are not currently accumulating S and since they are not responding to increased S loading (Figure 7).

Whole tree harvesting and recurrent forest fires may potentially affect the size and the turnover rate of soil organic S. It was observed that forest fires significantly raised the S-SO_4 exportation from coniferous forests on the Canadian shield while whole tree harvesting had no impacts (Lamontagne et al. 2000): estimated S-SO_4 exportations (10–12 kg·ha^{-1}·y^{-1}) from burnt catchments were 2 to 3 times higher that for harvested or reference catchments from the same area. However, giving the size of the soils organic S reservoir for a boreal coniferous forest on the Canadian shield (1200 kg·ha^{-1} for the Lake Laflamme catchment, Houle & Carignan 1992) the S exportation would not cause a significant decrease in the total S pool.

Conclusion

Significant $^{35}SO_4$ microbial immobilization into the organic fraction was observed in all the soil horizons collected at the lake Laflamme Watershed. A first order two-compartment (SO_4 and organic S) model adequately described $^{35}SO_4$ immobilization kinetics. The $^{35}SO_4$ immobilization increased with temperature and reached an asymptote after a few days in all the soil horizons indicating that an isotopic equilibrium was rapidly reached. The ^{35}S repartition at equilibrium revealed that the size of the active S reservoirs amounted to only 1% of the total organic S found in the forest floor and to less than 1% in all the other horizons. These results suggest that organic S reservoirs are very unlikely to directly immobilize SO_4 at the exception of a small fraction (<1%) that would be composed of microorganisms. Although microorganisms are actively recycling S through immobilization and mineralization reactions, they do not accumulate S on a net basis. We suggest that the organic S reservoir in the forest floor is mainly formed by incomplete litter decomposition while the organic S present in the B horizons would be formed by DOS adsorption produced within the forest floor and transported through the soil profile via the percolating soil solution.

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