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Role of SO_4 adsorption and desorption in the long-term S budget of a coniferous catchment on the Canadian Shield

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Abstract. The hypothesis that SO_4 desorption can explain apparent long term net SO_4-S losses (5 $kg{\cdot}ha^{-1}{\cdot}yr^{-1}$ on average) at the Lake Laflamme catchment from 1982 to 1991 is examined. Field observations show that SO_4 concentrations in the soil solution are strongly buffered during percolation through the Bf horizon. In the Bf horizon, SO_4 exchange reactions between the adsorbed and aqueous compartments are rapid (hours). Most (≈60%) of the adsorbed SO_4 may be readily desorbed with deionized water. These observations and the presence of an important adsorbed SO_4-S reservoir in the Bf horizon (113 $kg{\cdot}ha^{-1}$) as compared with annual wet SO_4-S deposition (7 $kg{\cdot}ha^{-1}$), suggest that on the short-term, adsorption and desorption reactions can control dissolved SO_4 concentration in the Bf horizon. To examine whether SO_4 adsorption/desorption could explain long-term SO_4-S losses by the catchment, an aggregated Langmuir isotherm for the Bf horizon was used to calculate the catchment's resilience to changing SO_4-S loads. The results indicate that the soil should adjust rapidly (within 4 years) to changing SO_4-S loads and that SO_4 desorption alone cannot explain long-term net SO_4-S losses. Other possibilities, such as an underestimation of dry deposition or the weathering of S-bearing minerals also appear unlikely. Our results suggest a net release of SO_4-S from the soil organic S reservoirs (1230 $kg{\cdot}ha^{-1}$) present in the catchment.

Introduction

Net sulfur losses have been reported for many forested catchments of northeastern America (Rochelle et al. 1987). Reasons invoked to explain real or apparent net S losses include inaccurate dry deposition measurements and internal catchment processes such as weathering of S-bearing minerals, net mineralisation of the organic S reservoir, and desorption of SO_4 from soils (Mitchell et al. 1986; Rochelle et al. 1987; Mitchell et al. 1992). Among these three potential internal sources, net SO_4 desorption from soils could explain excess SO_4 outputs in the context of the currently decreasing atmospheric S deposition in northeastern America (Hedin et al. 1987; Dillon & Lazerte 1992; Driscoll et al. 1989). If SO_4 adsorption is reversible and the adsorbed SO_4 reservoir is large compared to annual S deposition, the output of S from catchments could be delayed relative to current SO_4 deposition. This phenomenon may have important implications since SO_4 desorption is expected to be accompanied by the release of cations and hydrogen ions in soil solution (Galloway et al. 1983; Reuss & Johnson 1985) that could delay the recovery of surface water quality following reductions in S emissions to the atmosphere.

At our study site (lake Laflamme catchment), SO_4-S outputs (11.2 $kg \cdot ha^{-1} \cdot yr^{-1}$) have exceeded wet SO_4-S inputs by 5 $kg \cdot ha^{-1} \cdot yr^{-1}$, on average, between 1982 to 1991 (Couture 1994). The present report explores the role of SO_4 desorption as a possible mechanism to explain current net S losses by the catchment by combining laboratory measurements of SO_4 exchange kinetics and reversibility, SO_4 adsorption isotherms, and field measurements of SO_4 concentration in soil solutions.

Study site

The lake Laflamme catchment (68.4 ha) is located 80 km north of Quebec city (47°17′ N, 71°14′ W, 777–844 m above sea level). The catchment is dominated by Balsam fir (*Abies balsamea* 90%) and White birch (*Betula papyrifera* 10%). Canopy closure is estimated to 94% (D'Arcy & Carignan 1995). From 1981 to 1992, the catchment has received a mean annual precipitation of 1300 mm (33% as snow), with an average hydrogen ion of 36.3 $\mu mol \cdot l^{-1}$ (pH = 4.44) and an average SO_4 concentration (weighted for precipitation volume) of 16 $\mu mol \cdot l^{-1}$ corresponding to an annual SO_4-S wet deposition of 7 $kg \cdot ha^{-1}$ (Couture 1994). The soils are classified as orthic humo-ferric or ferro-humic podzols in the Canadian classification system which corresponds to a humic cryorthod in the American classification. The average thickness for LFH, Ae, Bhf and Bf horizons are 8.8, 4.5, 7.6 and 28.7 cm respectively (Houle & Carignan 1992). Root penetration is surficial; most are found in the first 20 cm of the soil profile, with over 95% found in the first 50 cm (Barry 1984). The thickness of the underlying till ranges from 0.1 m on top of the basin to 15 m under the lake. The bedrock consists of chanorckitic gneiss composed of granite, gabbro and mangerite. The catchment contains a large S reservoir (1395 $kg \cdot ha^{-1}$) mainly comprised within the first 50–60 cm of the soil profile. Most (90%) of this reservoir is organic (Houle & Carignan 1992).

Methods

Soil solutions and surface waters

Soil solutions were collected in four 25 m^2 plots equipped with zero-tension and tension lysimeters located at elevations ranging from 780 to 810 meters on the north, south and northeast sides of the catchment. Zero-tension lysimeters were made of 30 cm-long PVC tubes capped at both ends and cut in half to yield two half-cylinders. Lysimeter installation proceeded as follows: two lateral 1 m deep trenches (5 m long) oriented parallel to ground water flow lines were first dug. Horizontal holes (50 cm long, 5 or 10 cm diameter) were then bored under the LFH, Bhf and Bf horizons at average respective depths of 11, 26 and 60 cm. A 1–2 cm thick layer of quartz granules was placed in the bottom of the lysimeters which were then filled with the soil excavated from the horizontal holes. The lysimeters were then pushed inside the holes and fitted snugly against the ceiling of the horizontal galleries. Plastic tubing was used to connect the lysimeters to bottles located deeper in the soil and that could be emptied with a syringe from the surface via a second tube. The trenches were back filled after lysimeter installation.

Tension lysimeters made of hydrophilic porous teflon (Prenart, 5 cm long, 2.1 cm diameter 3 μm effective pore size) were inserted from the surface in the LFH, Bhf, upper Bf (Bf1) and lower Bf (Bf2) horizons in triplicate at each plot at average depths (for the 4 plots) of 8, 22, 33 and 48 cm respectively. Care was taken to minimize disturbance of the soil profile during installation. Samples were collected in 50 ml test tubes placed in 1 L bottles to which a 60 KPa vacuum was applied for 1 to 5 hours.

Plots 1 and 2 were sampled from August 1988 to November 1989 whereas plots 3 and 4 were sampled from April 1989 to November 1989. Soil solutions were collected every 2 days during the snowmelt and usually once or twice a week the rest of the year, except during winter when infiltration is normally negligible. Meltwater was collected from March 28 to May 18 1989 by 7 snow lysimeters (fiberglass tank, 1 $m^2 \times$ 50 cm height) located on the north side of the catchment within 50 m of plots 1 and 4. These lysimeters were connected to underground 50 L plastic vessels. Meltwater and soil solutions were analyzed for SO_4 by ion chromatography. Sulfate concentration in the stream output has been monitored weekly since 1981 by Environment Canada using the bromothymol blue method (Couture 1992). Precipitation, water content and infiltration in soil horizons of plots 1 and 2 (time domain reflectometry) were also monitored during the study (Roberge & Carignan unpublished).

SO_4 adsorption and desorption

These experiments were done in order to measure the SO_4 exchange rate between the solid and aqueous phases, to describe the equilibrium SO_4 partition between the solid and aqueous phases at different SO_4 concentrations in the soil solution (adsorption isotherms) and to determine the degree of SO_4 adsorption reversibility. Only the Bf horizon was considered because it contains 85% of the total SO_4-S pool in the catchment (Houle & Carignan 1992). All experiments were conducted at 10 °C.

Sulfate exchange rates between the solid and liquid phases were measured with $^{35}SO_4$, using moist samples of the Bf horizons from 3 sites sieved on a 2 mm mesh (5:1 solution:soil ratio). Deionized water was added to moist samples (corresponding to 60 g of dry soils) in a 500 ml plastic bottle and shaken on a rotary shaker (≈120 RPM) to obtain a uniform suspension. Sulfate and pH were measured every 1 or 2 h to verify that SO_4 concentrations were at steady state before tracer addition. Carrier-free $^{35}SO_4$ was added after equilibrium concentrations SO_4 were reached (1–2 h). Five-ml aliquots were then withdrawn at different times, decanted for 1–2 minutes, and the supernatant centrifuged. $^{35}SO_4$ concentration was measured by liquid scintillation in Atomlight (NEN). The supernatant was also analyzed for SO_4 at 45 m, 8 h and 18 h after tracer addition to confirm that equilibrium conditions were present during the experiment.

Sulfate adsorption isotherms were measured on 8 Bf moist samples collected at 8 sites (including the same three soils used above for the $^{35}SO_4$ exchange experiments). Duplicate samples were shaken for 24 h with solutions (5:1 solution:soil ratio) of different SO_4 concentrations (0, 42, 83, 167 and 323 $\mu mol \cdot l^{-1}$) added as Na_2SO_4. After 24 h, the samples were centrifuged, and the supernatant analyzed for SO_4. The solution with no added SO_4 (deionized water) was spiked with $^{35}SO_4$ in order to measure the native total SO_4 concentration (dissolved + adsorbed) by isotopic dilution and to assess the importance of organic S formation during the experiments.

Sulfate adsorption was described with the Langmuir isotherm:

$$\text{ADS } SO_4 = (A \times [SO_4])/(K + [SO_4]) \qquad (1)$$

where $[SO_4]$ = aqueous SO_4 concentration ($\mu mol \cdot l^{-1}$), ADS SO_4 = adsorbed SO_4-S concentration ($mg \cdot kg^{-1}$), A = maximum adsorption potential ($mg \cdot kg^{-1}$) and K = half saturation constant ($\mu mol \cdot l^{-1}$).

To measure the degree of SO_4 adsorption reversibility, the 8 moist soils samples from the Bf horizon used for isotherm definition and to which only $^{35}SO_4$ was added were sequentially extracted 5 times with deionized water (10:1 solution:soil ratio) after the 24 h incubation. At each step, the test tubes were shaken for 30 m, centrifuged and the $^{35}SO_4$ concentration in the supernatant determined. The supernatant was then discarded and the extraction procedure was repeated 4 times. A final extraction was performed with NaH_2PO_4 (0.016 M) to extract any remaining $^{35}SO_4$. In another experiment, a moist soil sample of the Bf horizon was submitted to 10 consecutive water extractions following a 24 h incubation with $^{35}SO_4$. $^{35}SO_4$ and SO_4 in the supernatants were measured at each extraction to ensure that $^{35}SO_4$ accurately traced the behavior of SO_4.

Results

SO_4 concentrations in soil solutions

Similar temporal and vertical variations in SO_4 concentrations are observed at the four plots in soil solutions collected with zero-tension lysimeters (Figs. 1 and 2). The SO_4 peaks observed in the LFH horizon during snowmelt and in the 1989 fall in the LFH horizon are synchronous at all plots. Similar trends are also observed with tension lysimeters (Figs. 1 and 2). At plot 4, however, tension lysimeters yield much higher SO_4 concentration than zero-tension lysimeters during snowmelt.

Generally, SO_4 concentrations in the forest floor (LFH) show a marked temporal variability: they decrease from the beginning to the end of snowmelt, reflecting concentration observed in the infiltrating meltwater (Fig. 2C) and show frequent variations the rest of the year. In the Bhf horizons, SO_4 concentrations also show a pronounced temporal variability. When the percolating water reaches the lower horizon (Bf1 and Bf2 for the tension lysimeters and Bf for the zero-tension), SO_4 concentration become less variable as reflected by decreasing coefficient of variation with depth (Table 1). Sulfate buffering differs between plots, however. Plot 4 shows a high variability at all depths with a CV of 71% for the Bf2 samplers ($n = 3$) compared to 18% for the Bf2 samplers at plot 1. The high CV's for plot 4 are influenced by extreme values encountered during snowmelt for the LFH, Bhf and Bf1 samplers and by one high value during the fall for the Bf2 samplers (Fig. 2).

Results for plot 2 are expressed separately in 1988 and 1989 in Table 1 because of their different trends in CVs with increasing depth. In 1988, CVs decrease with increasing depth as observed at the other plots but a higher temporal variability was observed in the low Bf horizon in 1989. The differences between the two years are probably attributable to the uprooting of all trees in this plot by strong winds in late fall of 1988 which may have perturbed the soil's structure and enhanced decomposition processes.

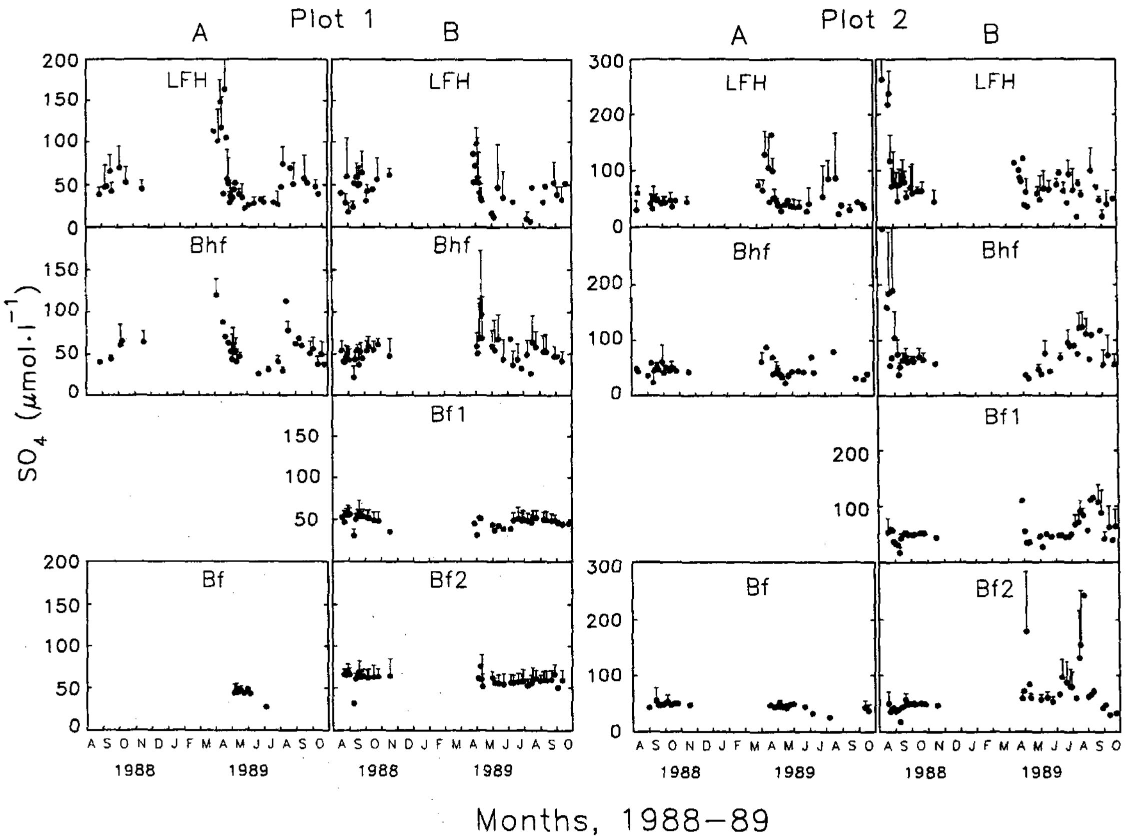

Fig. 1. Seasonal evolution of SO_4 concentrations ($\pm\sigma$ of 1 to 7 replicate samples when applicable) in soil solutions at plot 1 and 2 collected with zero-tension (A) and tension lysimeters (B).

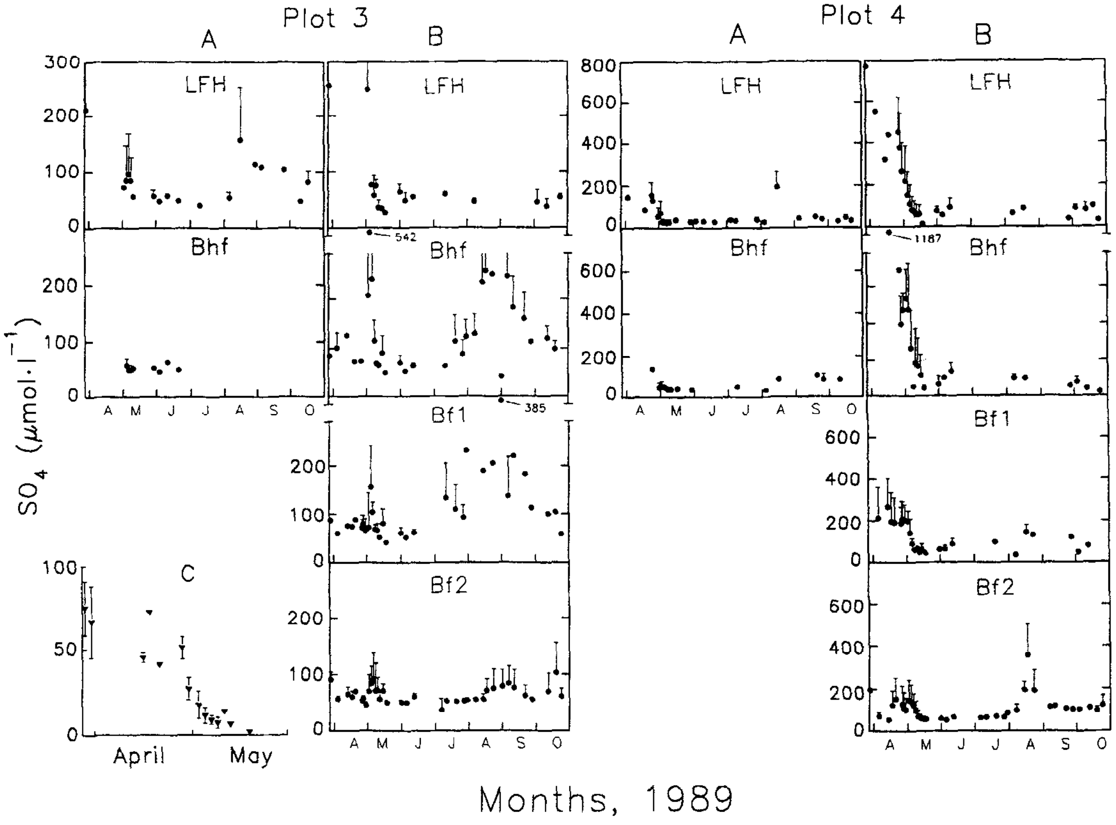

Fig. 2. Seasonal evolution of SO_4 concentration in the soil solution collected with zero-tension (A) and tension lysimeters (B) at plot 3 and 4, and in meltwater (C) collected near the plot 3 during the 1989 snowmelt.

Table 1. Average SO_4 concentration ($\mu mol \cdot l^{-1}$) and coefficient of variation in soil solutions collected in 1988–1989 with tension and zero-tension lysimeters in each plot. The number of replicates is given in parentheses.

Site	Location	Tension	Zero-tension
1	LFH	45 ± 55% (73)	56 ± 69% (128)
	Bhf	55 ± 46% (97)	58 ± 65% (80)
	Bf1	51 ± 18% (93)	
	Bf2	63 ± 18% (98)	47 ± 16% (30)
2 (1988)	LFH	101 ± 79% (53)	47 ± 32% (60)
	Bhf	89 ± 76% (34)	51 ± 27% (69)
	Bf1	49 ± 27% (29	
	Bf2	46 ± 23% (36)	51 ± 18% (87)
2 (1989)	LFH	66 ± 51% (51)	57 ± 67% (102)
	Bhf	81 ± 44% (36)	43 ± 30% (92)
	Bf1	69 ± 46% (56)	
	Bf2	86 ± 75% (38)	46 ± 15% (70)
3	LFH	75 ± 101% (29)	85 ± 73% (43)
	Bhf	143 ± 84% (62)	55 ± 16% (21)
	Bf1	99 ± 56% (60)	
	Bf2	87 ± 37% (91)	
4	LFH	160 ± 118% (47)	53 ± 96% (92)
	Bhf	238 ± 114% (45)	49 ± 69% (21)
	Bf1	130 ± 78% (61)	
	Bf2	110 ± 71% (91)	

Tension lysimeters generally gave higher SO_4 concentrations than zero-tension lysimeters (Table 1, Figs. 1 and 2). The differences were most pronounced during snowmelt in the Bhf horizon at plot 4 (Fig. 2). These observations are different from those reported by Haines et al. (1982) and Joslin et al. (1987). Haines et al. (1982) observed that zero tension lysimeters yielded higher SO_4 concentration than tension lysimeters made of porous ceramic at the litter-soil interface and at 30 cm at the Coweeta Hydrologic Laboratory, North Carolina. Joslin et al. (1987) observed that lateral flow collected with zero-tension lysimeter following storm events had higher SO_4 concentration than water collected with ceramic cup tension lysimeters in the Raven Fork watershed in western North Carolina. We attribute these differ-

Table 2. Langmuir isotherm parameters obtained for 8 Bf horizon soil samples and aggregated isotherm resulting from their aggregation. The r^2 values represent the fit between predicted and observed values of adsorbed SO_4. Native adsorbed SO_4/A is the amount initially found in the sample divided by the maximum adsorption potential.

	A ($mg \cdot kg^{-1}$, SO_4-S)	K ($\mu mol \cdot l^{-1}$)	r^2	Native adsorbed SO_4/A (%)
Bf1	30.0	51	0.96	43.8
Bf2	48.5	37	0.97	62.8
Bf3	37.9	279	0.95	22.9
Bf4	18.8	101	0.94	29.2
Bf5	16.5	52	0.95	32.0
Bf6	11.6	71	0.98	24.5
Bf7	24.2	63	0.95	41.7
Bf8	23.0	70	0.90	38.0
Aggregated isotherm:	22.9	51	–	–

ences to the fact that tension lysimeters can collect capillary water whereas zero-tension lysimeters only sample water moving freely into the soil during period of important infiltration.

SO_4 adsorption and desorption

Sulfate exchange kinetics are extremely rapid in the Bf horizon. The SO_4 concentration stabilized within 1–2 h in the three soil suspensions (Fig. 3). During the experiment, pH (not shown) ranged from 4.41 to 4.57, from 4.27 to 4.58 and from 4.43 to 4.58 in soils A, B and C respectively. Added $^{35}SO_4$ (at $t = 0$, Fig. 3) rapidly equilibrated between the adsorbed and aqueous phases. In soil A and B respectively, over 50% of the process was accomplished after only 2 minutes. In soil C, $^{35}SO_4$ adsorption proceeded more slowly at the beginning with only 4% of the adsorption taking place in the first 2 minutes. However, equilibrium conditions were reached in the three soils after 3 hours. In preliminary experiments, such a fast equilibration of $^{35}SO_4$ between the adsorbed and aqueous phases was also observed with dry and wet soils samples from the Bhf and Bf horizons (data not shown). Rapid SO_4 adsorption has also been reported by Chao et al. (1962) and Rajan (1978). Courchesne & Hendershot (1990) reported that treated (exposed to 2, 3, and 5 mmol SO_4 per kg of soil) and untreated sample (no SO_4 addition) from the B horizon of the Lake Laflamme catchment desorbed 50% of their adsorbed SO_4 within 5 minutes.

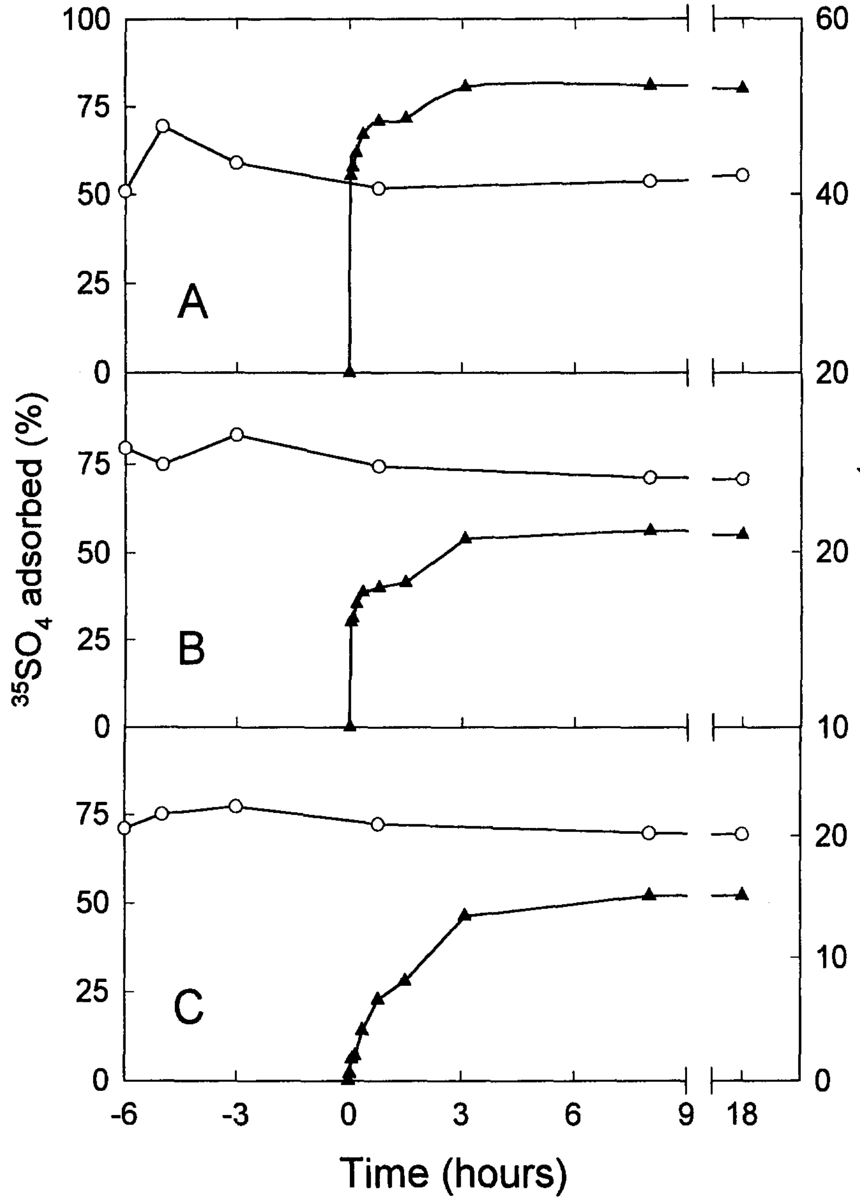

Fig. 3. Adsorption of $^{35}SO_4$ (triangles) added at $t = 0$ onto 3 soil samples from the Bf horizon. Sulfate concentrations (open circles) were measured before and after adding $^{35}SO_4$ to confirm the presence of steady state conditions.

The partition of SO_4 between solid and aqueous phases can be represented by a Langmuir isotherm, with an average r^2 of 0.95 ± 0.02 ($\pm\sigma$) for 8 samples of the Bf horizon (Table 2). The isotherm parameter A ranges from 11.6 to

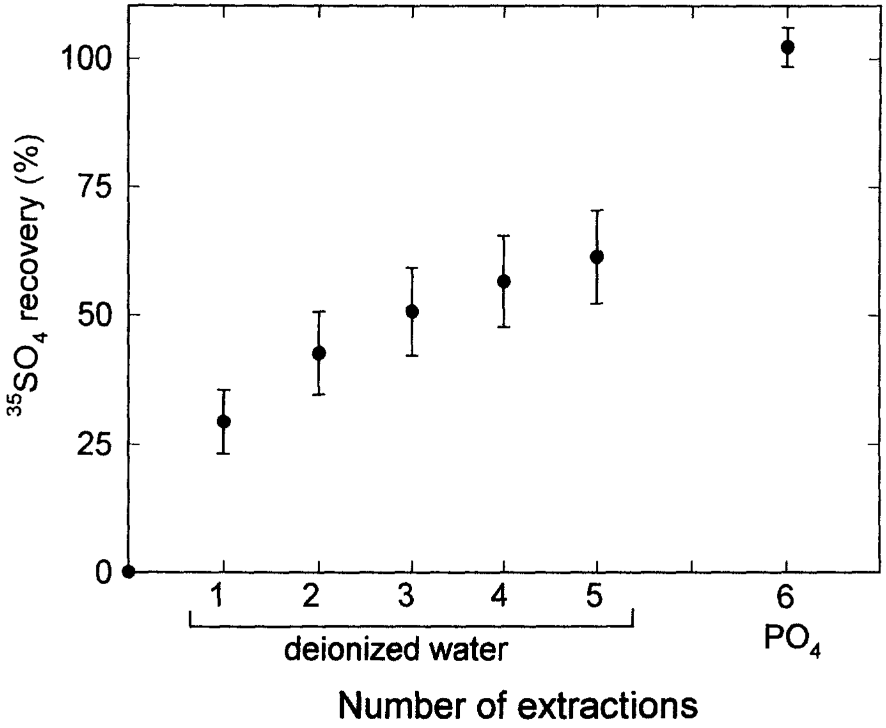

Fig. 4. Average cumulative recovery ($\pm\sigma$) of $^{35}SO_4$ from 8 Bf soil samples after a 5 consecutive water extractions followed by a final NaH_2PO_4 extraction. $^{35}SO_4$ was added to the samples 24 h prior to the extraction.

48.5 mg·kg^{-1} (Table 2) which probably reflects variation in soil composition and pH (4.30 to 4.88). The native adsorbed SO_4 averages 36.7 ± 12.1% of the maximum adsorption potential, showing that the Bf horizon could adsorb more SO_4 if exposed to higher SO_4 concentrations.

The average $^{35}SO_4$ recovery after 5 consecutive water extractions is 61% ± 9% ($\pm\sigma$) for 8 Bf samples previously exposed to $^{35}SO_4$ for 24 h (Fig. 4). These results suggest that most of the adsorbed SO_4 pool present in the Bf horizon is readily exchangeable. The evolution of SO_4 and $^{35}SO_4$ concentrations in the supernatant during 10 consecutive water extractions of a Bf sample indicates that $^{35}SO_4$ recovery is representative of SO_4 recovery since the specific activity changes little during the consecutive extractions (Fig. 5). The final extraction with NaH_2PO_4, yielded an average $^{35}SO_4$ recovery of 102.2 ± 3.7% ($\pm\sigma$, $n = 8$) showing that adsorbed $^{35}SO_4$ is fully recovered and that organic ^{35}S formation may be neglected on the 24 h time-scale and using a 5:1 solution:soil ratio.

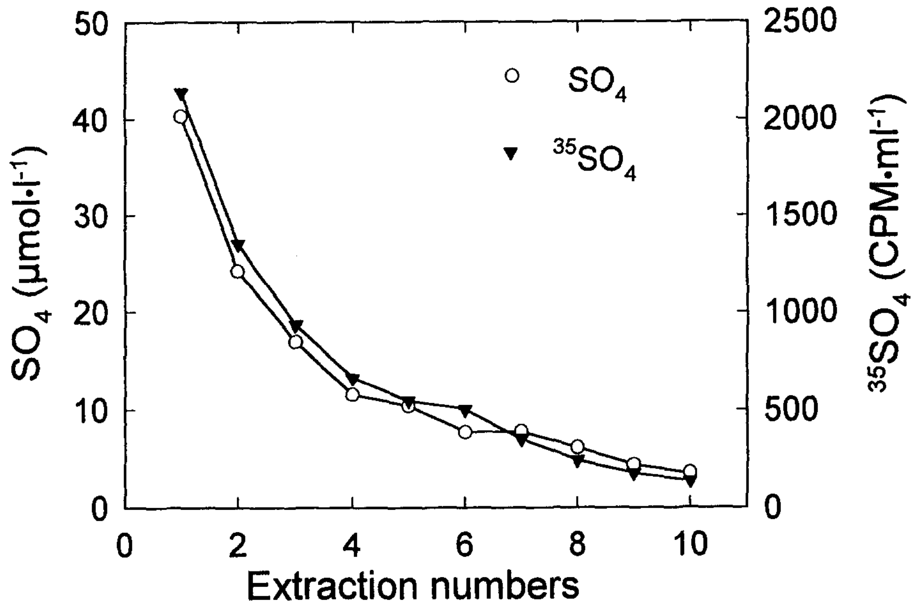

Fig. 5. Evolution of SO_4 and $^{35}SO_4$ concentrations in sequential water extracts from a Bf sample as a function of extraction number. The soil was incubated with $^{35}SO_4$ during 24 h prior to extraction.

Discussion

During snowmelt, SO_4 concentrations in the upper horizons (LFH and to a lesser extent Bhf) reflect that of the infiltrating water (Fig. 2C) which decreases markedly as the melt proceeds. The decrease in SO_4 concentration in meltwater is attributable to ion exclusion occurring during snow metamorphism (Davies et al. 1987). During the rest of the year, SO_4 shows frequent and sudden variations that may depend on changes in rain composition, microbial activity and root uptake. The increasing stability of SO_4 concentration with increasing depth (Table 1) reveals the presence of an important adsorbed SO_4-S reservoir in the Bf horizon that buffers SO_4 concentration in infiltrating water.

On the time scale of weeks to a few years, this buffering mechanism appears to control SO_4 concentrations at the outlet since they were fairly constant from 1981 to 1992 despite important temporal variations in the water and SO_4-S loading (Fig. 6). Because of this constancy, the amount of SO_4-S leaving the catchment on a weekly basis at the lake outflow is directly proportional to runoff: SO_4-S exported (kg) = 0.128 runoff (cm) + 0.012, $r^2 = 0.96$, $n = 590$ (Fig. 7). Since the lake water residence time is

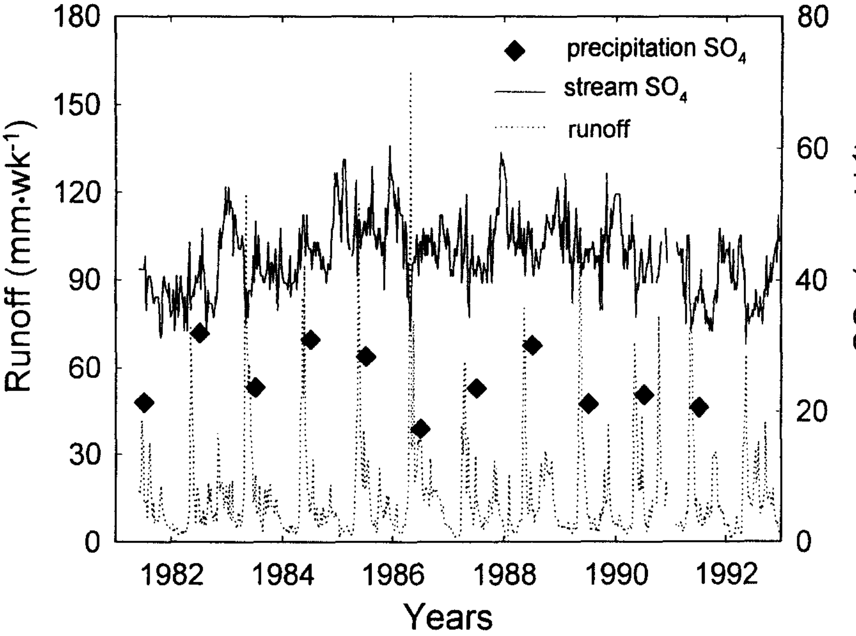

Fig. 6. Weekly runoff (dotted line) and SO_4 concentration (solid line) at the lake's outlet from 1982 to 1992. The diamonds show the average annual SO_4 concentration in precipitation weighted for volume and corrected for evapotranspiration (adapted from Couture 1994).

short (2 months), the stability of SO_4 concentration at the outlet cannot be attributed to a dampening effect by the lake. During the 1989 snowmelt, for instance, the average initial snowpack SO_4 concentration was 15 ± 2.5 $\mu mol \cdot l^{-1}$ (average $\pm\sigma$, 16 cores taken around the 4 plots, Houle & Carignan, unpublished results) and the lake water volume was renewed 1.6 times during the 4 weeks-long melt that followed; yet the lake SO_4 concentration remained fairly constant and averaged 44 $\mu mol \cdot l^{-1}$ during the same interval (Couture 1992, pers. comm.).

At the Lake Laflamme catchment, the Bf horizon contains the most important SO_4-S pool (113 $kg \cdot ha^{-1}$) of which 84% is adsorbed (Houle & Carignan 1992). Because this pool represent about 16 years of the annual average wet SO_4-S deposition on the catchment (7 $kg \cdot ha^{-1}$) it could be sufficient to account for the observed SO_4 concentration buffering in the soil solution, provided that SO_4 exchange reactions are rapid compared to the residence time of water in this horizon, and provided that SO_4 adsorption is reversible. Our results show that the exchange reactions are rapid since they reached an equilibrium within 3 h (Fig. 3). Also, 60% of the previously adsorbed $^{35}SO_4$ can be recovered by 5 sequential water extractions (Fig. 4) suggesting that the

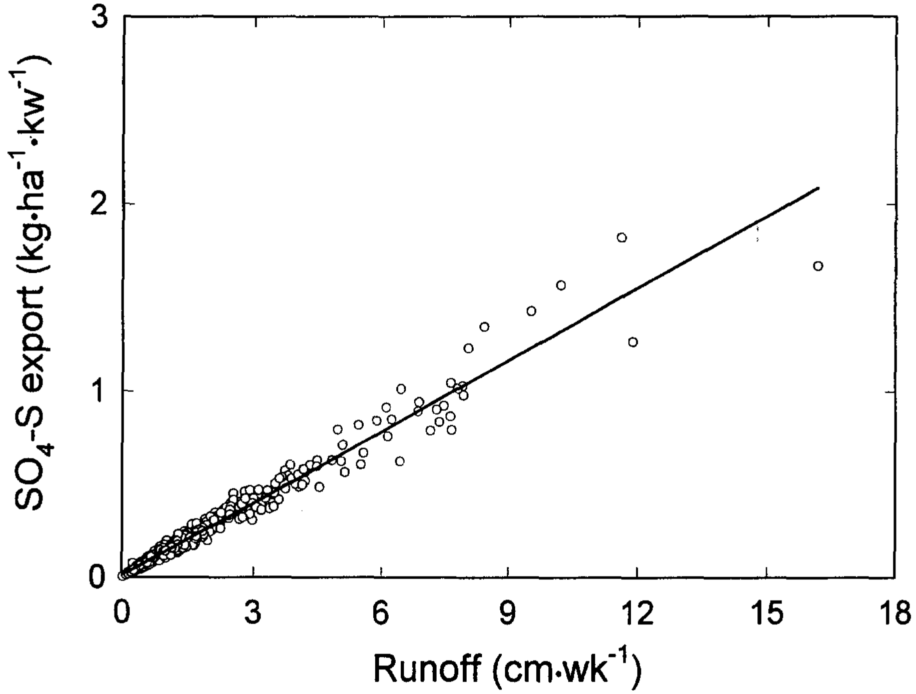

Fig. 7. Weekly SO_4-S export at the outlet of lake Laflamme as predicted with runoff for the 1982–1992 interval (adapted from Couture 1994).

adsorbed SO_4 can be readily desorbed. Different extents of SO_4 desorption have been observed in soil samples from different locations (Chao et al. 1962; Neary et al. 1987; Curtin & Syers 1990; Harrison et al. 1989; Courchesne & Hendershot 1990). Harrison et al. (1989) studied desorption in 36 soil samples from 20 forested sites in north America. These authors concluded that an average of 36% of adsorbed SO_4 was retained irreversibly. Others have reported that SO_4 adsorption on Fe oxides (Turner 1988) or freshly ground Fe and Al oxides (Aylmore et al. 1967) was almost irreversible.

Water residence times in the Bf horizon (Roberge & Carignan, unpublished) are far in excess of the time needed for SO_4 adsorption and desorption reactions to reach equilibrium. At plot 1 for instance, the minimum time observed for water to move from the top to the bottom of the Bf horizon was 10 days during snowmelt.

Although both field observations and laboratory experiments that adsorption-desorption reactions taking place in the Bf horizon can control SO_4 concentrations in the soil solution on a short term basis, it remains to be seen whether such reactions can explain net SO_4-S losses by the catchment as observed between 1981 to 1992 (Table 3). In order to test this hypoth-

Table 3. Annual SO_4-S budget for lake Laflamme catchment from 1982 to 1991 (Adapted from Couture (1994)).

Years	Wet atmospheric loading	Stream output	Net loss
	SO_4-S(kg·ha^{-1})		
1981	6.5	–	–
1982	7.0	8.9	1.9
1983	8.0	12.9	4.9
1984	7.7	11.4	3.7
1985	7.7	12.7	5.0
1986	6.1	14.5	8.4
1987	5.5	10.2	4.7
1988	8.2	12.4	4.2
1989	4.8	9.2	4.4
1990	5.6	10.1	4.5
1991	5.1	9.6	4.5

esis, we simulated the catchment's response to different scenarios of SO_4-S deposition. We used the aggregation method of Shaffer & Stevens (1991) to construct a 'master' isotherm from the 8 isotherms found above for the Bf horizon. We assumed that SO_4 adsorption and desorption in the Bf horizon was the only mechanism governing SO_4 concentrations in water leaving the Bf horizon. For the purpose of modeling SO_4 concentrations, the Langmuir isotherm was expressed as follows:

$$\text{total } SO_4 = ((A \times [SO_4])/(K + [SO_4])) + [SO_4] \qquad (2)$$

where total SO_4 is the sum of adsorbed and aqueous SO_4, and $[SO_4]$ is SO_4 concentration in the soil solution.

The evolution of SO_4 concentrations in water leaving the Bf horizon following a sudden increase or decrease in SO_4 deposition on the catchment was simulated iteratively. Calculations were performed for a 30-cm thick Bf horizon initially at equilibrium with a 25 μmol·l^{-1} SO_4 concentration. This concentration is equivalent to an annual SO_4-S deposition of 7 kg·ha^{-1}. For each iteration, a volume of water corresponding to the annual average amount of water stored in the Bf horizon (120 mm, Roberge & Carignan, unpublished) was allowed to equilibrate with the soil. The new SO_4 concentration in the soil water was solved by rearranging eq. 2 as a second degree polynomial:

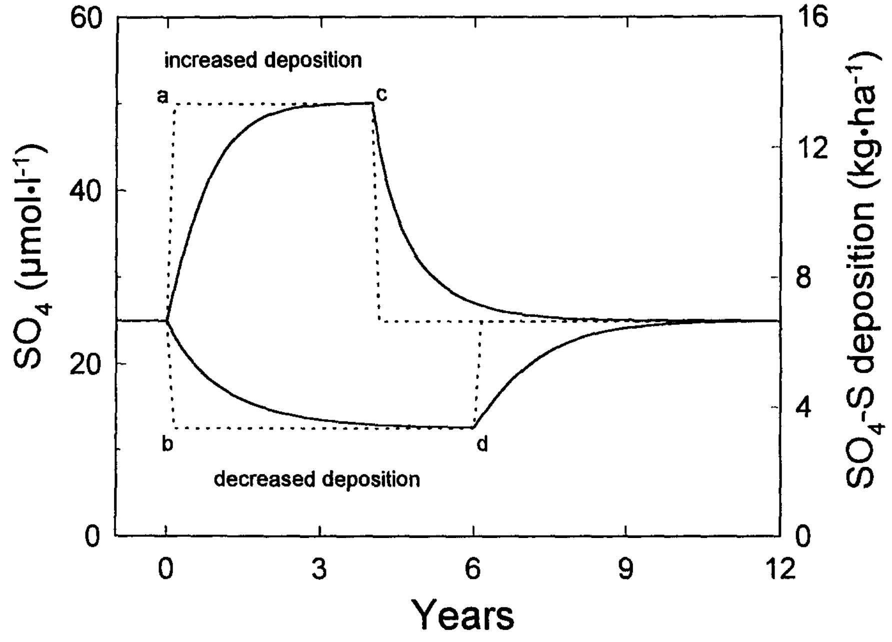

Fig. 8. Predicted stream output SO_4 concentrations (solid line) resulting from different scenarios of SO_4-S deposition on the catchment. The catchment is first assumed to be at steady state with respect an annual SO_4-S deposition of 6.67 $kg{\cdot}ha^{-1}$ before being submitted to SO_4-S depositions of 13.33 (a) and 3.33 $kg{\cdot}ha^{-1}{\cdot}yr^{-1}$ (b) (dotted lines). SO_4-S is then returned to 6.67 $kg{\cdot}ha^{-1}$ (c, d) upon establishment of new steady state conditions.

$$[SO_4]^2 + (K - \text{TOTAL } SO_4 + A) \times [SO_4] - (K \times \text{TOTAL } SO_4) = 0. \quad (3)$$

Adsorbed SO_4 concentration was then calculated from eq. 1. Since the average (1981–1991) amount of water exported annually from the catchment is 840 mm, 7 iterations per year were performed. The results (Fig. 8) indicate that the soil responds at different rates depending on whether the catchment is exposed to increased or decreased deposition. In every case however, the simulated SO_4 concentrations reach 95% of the final equilibrium SO_4 concentrations within 4 years. We examined the effect of discretizing the Bf horizon into many layers. The simulated SO_4 concentrations were essentially unchanged, except for the first few months of the simulation. The effect of raising the slope isotherm value (or A = maximum adsorption potential) on the simulated SO_4 concentration was also analysed; increasing A by as much as one order of magnitude did not produce a lag time long enough to explain the longterm (11 years, Table 3) SO_4-S loss by the catchment. We thus conclude that the long-term net SO_4-S loss by the catchment is not attributable to SO_4 desorption.

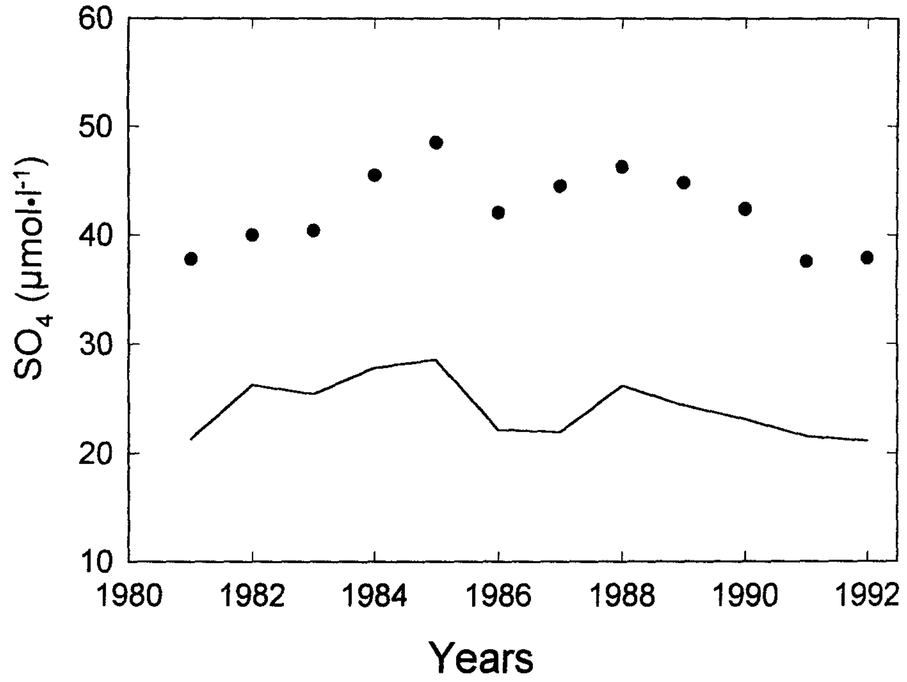

Fig. 9. Observed (circles) and predicted (solid line) average annual lake's outlet SO_4 concentration using the aggregated adsorption isotherm. Predicted values were obtained by submitting the catchment to the mean annual SO_4 concentration in precipitation (weighted for volume and corrected for evapotranspiration) observed on the catchment from 1981 to 1992.

The model was applied to the 12 years SO_4-S deposition history recorded at the catchment in order to compare the calculated mean annual lake water SO_4 concentration to the observed values. Average annual SO_4 concentrations in wet deposition (rain + snow weighted for precipitation volume and corrected for evapotranspiration) were used as input. Although calculated and observed values are significantly correlated ($r^2 = 0.48$, $n = 12$, $\alpha < 0.05$, Fig. 9), an important and unexplained difference between observed and predicted SO_4 concentrations is observed.

Since SO_4 desorption does not appear to be sufficient to explain the long-term net loss of SO_4 by the catchment, other mechanisms must be invoked. The remaining possibilities include 1– and analytical bias arising from the different methodologies used to measure SO_4 concentrations in the lake's outlet (colorimetry) and in precipitation (ion chromatography), 2– an underestimation of dry deposition, 3– the weathering of S-bearing mineral, 4– the presence of a large adsorbed SO_4-S pool below the Bf horizon, 5– a net mineralization of organic S reservoirs.

The imbalance in the SO_4-S budget may be an artifact attributable to an analytical bias between the two methods used to measure SO_4-S inputs and outputs. The colorimetric method may have overestimated SO_4 concentrations at the outlet because of interferences by humic substances (Cronan 1979). The colorimetric method used for measuring SO_4 concentration in the stream output was compared to ion chromatography by analysing SO_4 in 542 samples from 35 shield lakes (Bouchard & Haemmerli 1992). Although the SO_4 concentration measured with both methods are strongly correlated (SO_4 chro. = 1.08 SO_4 col. −8.02, $n = 542$, $r^2 = 0.93$), the colorimetric method gave significantly higher values (paired t-test, $\alpha < 0.05$, mean difference = 3.4 $\mu mol \cdot l^{-1}$, Bouchard 1993, pers. comm.). This relationship indicates that SO_4 concentrations at the outlet of Lake Laflamme, may have been overestimated an average of 4.5 $\mu mol \cdot l^{-1}$ between 1981 and 1992. When converted to a SO_4-S export figure, the overestimation is equivalent to only 1.3 $kg \cdot ha^{-1}$, suggesting that a possible analytical bias may only contribute for a part of the average net annual loss (5 $kg \cdot ha^{-1}$).

Dry S deposition on the catchment appears to be too low to account for the imbalance between SO_4-S inputs and outputs. A dry deposition value amounting to ≈40% of the total deposition would be necessary to explain the observed discrepancy. This value appears unrealistically high since Barrie & Sirois (1986) estimated the contribution of dry deposition to only 16 and 12% of the total inputs for the years 1981 and 1982 using airborne SO_2 and SO_4 concentrations at the site and deposition velocities. Robitaille & Boutin (1990) found an average 18% SO_4 enrichment in throughfall and stemflow relative to bulk deposition from 1981 to 1987 in samples collected from June to October. Because canopy closure is nearly complete (94%) at this site, the SO_4 enrichment observed in throughfall and stemflow is though to reflect dry S deposition (Lindberg & Garten 1989). The contribution of dry deposition to total S deposition at this site was the lowest recorded among 6 sites in eastern Canada and may be explained by its distance from industrial point sources (Sirois & Barrie 1988).

Weathering of S-bearing minerals is an unlikely source of internal SO_4-S in this catchment. The amount of SO_4 that can be weathered from the till can be estimated from the S content and the Si:S ratio (323:0.27) reported for granites (Krauskopf 1967). Assuming that both elements are weathered in this proportion and that Si is not precipitated after its dissolution, the Si concentration of the outlet (6 to 9 mg·l−1) indicates that 0.03 to 0.24 $\mu mol \cdot l^{-1}$ of SO_4 is attributable to weathering which corresponds to a SO_4-S exportation of only ≈0.05 $kg \cdot ha^{-1}$.

Adsorbed SO_4 concentrations for the whole soil profile including samples from different depths in the C horizon are available for 3 pits dug in 1987

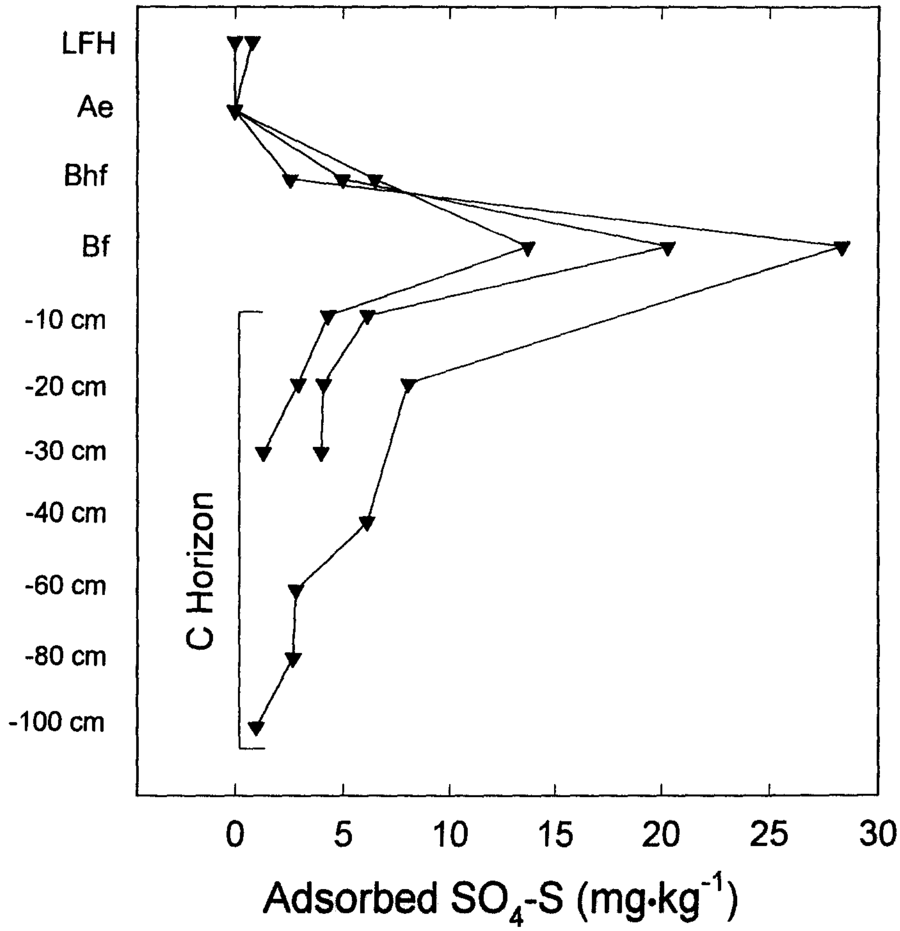

Fig. 10. Adsorbed SO_4-S concentrations in 3 soils profiles from the lake Laflamme catchment.

(Fig. 10). The adsorbed SO_4 concentrations exhibit an increasing pattern from the surface to the Bf horizon and a decreasing pattern from the Bf horizon to the bottom of the C horizon. We estimated this additional adsorbed SO_4-S reservoir to ≈33 kg·ha^{-1} which appears insufficient to account for the long-term SO_4-S loss by the catchment.

Sulfate budgets for the 2 plots for which we have at least one year of observations (14 months) also indicate that the source of unaccounted SO_4-S is located above the C horizon. In order to quantify the SO_4-S budgets, the SO_4-S fluxes in the incident precipitation (Couture 1994) corrected for dry S deposition (Barrie & Sirois 1986) were used as the input while SO_4 concentrations at the bottom of the Bf horizon and water fluxes out of the Bf horizon (720 mm annually, Roberge & Carignan, unpublished) were combined to

Table 4. Ecosystem S content (from Houle & Carignan 1992) and SO_4-S budgets for plots 1 and 2 and for the whole catchment calculated from September 1988 to October 1989 (14 months). Input value SO_4-S in bulk precipitations (from Couture 1994) are corrected for an estimated dry S deposition representing 14% of the total deposition (Barrie & Sirois 1986).

SO_4-S Fluxes ($kg{\cdot}ha^{-1}{\cdot}14\,months^{-1}$)	Input	Output	Net loss
Plot 1			
Zero-tension	8.9	12.6	3.7
Tension	8.9	16.8	7.9
Plot 2			
Zero-tension	8.9	13.0	4.1
Tension	8.9	17.8	8.9
Catchment	8.9	12.8	3.9
Ecosystem S content ($kg{\cdot}ha^{-1}$)			
Balsam fir (with roots)	18.9		
Herbaceous	4.2		
Fallen boles	4.5		
Soil			
Organic S	1230		
SO_4-S	137		

yield the SO_4-S output for plots 1 and 2. The results show a SO_4-S loss at both pots and for the whole catchment (Table 4). Since over 95% of the roots are located in the first 50 cm soil profile (Barry 1984), SO_4 can not be taken up by roots below this depth and the SO_4-S fluxes out of the Bf horizon (50–60 cm) may be considered as a net loss.

These considerations point out to the long-term net mineralisation of soil organic S as a possible net SO_4-S source in the catchment. The potential importance of this mechanism is supported by the size of the organic S reservoir (1230 $kg{\cdot}ha^{-1}$, Table 4) which amounts to about 175 times the annual wet SO_4-S deposition (Houle & Carignan 1992). A small annual loss of 0.4% of the soil organic S reservoir would be sufficient to explain long term SO_4-S losses by this catchment. Furthermore, an oxygen isotope study of the dissolved SO_4 in the Lake Laflamme catchment demonstrated that 32–61% of the SO_4-S leaving the catchment originated from organic S present in the soil (Gélineau et al. 1989).

Such SO_4-S losses have been previously reported for other soils and catchment in northeastern America but have been attributed to other causes. For instance, the apparent net SO_4-S loss at Hubbard Brook (HB) was attributed to unaccounted dry deposition (Likens et al. 1990). In Huntington Forest (HF), the increase in SO_4 concentration of the soil solution after its passage through the mineral soil was attributed to SO_4 desorption (Mitchell et al. 1992). Although Mitchell et al. (1992) attributed their observations to SO_4 desorption, they did not provide supporting data on the size of the adsorbed SO_4-S pool, on SO_4 adsorption reversibility and on resilience of the soil SO_4-S pool to changing S inputs.

At all three sites (Lake Laflamme, HB, HF), 90% of the total S content is found in the organic matter of the mineral soil (Houle & Carignan 1992; Mitchell et al. 1989; Mitchell et al. 1992) and these organic S pools represent 100 to 200 times the annual S deposition. Organic S mineralisation could also have been responsible, at least in part, for the observed S losses at HB and HF but this possibility has been overlooked in both studies.

Long term trends in temperature, hydrology, atmospheric NO_3 loading and commercial exploitation of forest may have affected the mineralisation rates of soil organic S pools. In a context of global change, more attention should be devoted to the possibility that organic S reservoirs may be currently decreasing in soils since such a phenomenon could overcome the beneficial effects expected from the reduction of atmospheric S emissions recently observed in northeastern America (Hedin et al. 1987; Dillon & Lazerte 1992; Driscoll et al. 1989).

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