Biogeochemistry **16**: 63–82, 1992

Sulfur speciation and distribution in soils and aboveground biomass of a boreal coniferous forest

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Received 22 March 1991; accepted 26 March 1992

Key words: balsam fir, biomass, forest soils, S constituents, S pool, S retention

Abstract. Major sulfur pools are quantified in soils and aboveground biomass of a coniferous boreal forest. Total ecosystem S averages 1395 kg·ha^{-1} of which 98% is found in the soil, with 89% being in the mineral horizons. Organic S dominates in soil, tree parts (trunks, branches + foliage, roots) and litterfall, ranging from 77 to 99% of total S concentration. Carbon-bonded S, ester sulfate and SO_4-S in soil profiles range respectively from 51–68%, 29–37% and 1–14% of total S concentrations and account respectively for 57, 33 and 10% of total S on an areal basis. Adsorbed SO_4 accounts for 82% of total SO_4, and can be predicted from Al bound to organic matter, amorphous Al and pH (r^2 = 0.81). There is a strong relationship between % carbon and carbon-bonded S in 4 of the 5 soil horizons studied which represent over 95% of the total soil organic matter, whereas ester sulfate is related to % carbon in 3 soil horizons representing only 37% of the soil organic matter. An analysis of atmospheric S loading and S data for 10 forested sites in Europe and North America suggests that the size of the organic S pool in forested systems is independent of atmospheric loading.

Introduction

Interest about S biogeochemistry has recently increased due to the high anthropogenic S loading reported in several parts of the world. Sulfate is the dominant anion in precipitations, surface waters and soil solutions of many temperate forested ecosystems. Seip (1980), Galloway et al. (1983) and Reuss & Johnson (1985) discussed the role of SO_4 as a 'carrier anion' for cations, and proposed that the transport of positively charged Al complexes, base cations and hydrogen ions, from the watershed to the surface water, is strongly influenced by the mobility of SO_4. Incorporation of SO_4 into an organic matrix (David et al. 1982; Swank et al. 1984) and its adsorption on iron and aluminium oxides (Galloway et al. 1983; Johnson & Todd 1983; Fuller et al. 1985) have been suggested as majors processes responsible for S retention in soils. Both processes would prevent leaching of SO_4 and would release alkalinity. Conversely, organic S mineralization and SO_4 desorption produce acidity and would be coupled to cation leaching. An understanding of the processes affecting SO_4 mobility in soils thus appears important to predict the effects of high S loading on ecosystems.

Generally, organic S, as carbon-bonded S and ester sulfate, predominates in most soil types, even in mineral horizons (Watwood et al. 1986; Mitchell et al. 1986; Schindler et al. 1986, Autry et al. 1990). Notable exceptions are soils showing a large adsorption potential, and which are receiving high SO_4 loads; in these soils, SO_4-S represents a relatively large percentage of total S (Johnson 1984). Although the organic S pool is clearly predominant in forested soils, abiotic reactions involving SO_4 have received much more attention. As a consequence, models describing acidification processes within watersheds take into consideration only SO_4 adsorption and desorption reactions (Mitchell & Fuller 1988).

Yet, studies conducted *in situ* (Strickland et al. 1985; Watwood & Fitzgerald 1988) and in the laboratory (Schindler et al. 1986; Fitzgerald et al. 1982; Watwood & Fitzgerald 1988; Swank et al. 1984) have shown that ^{35}S-SO_4 incorporation as ester sulfate and carbon-bonded S is important in forest soils. Furthermore, organic S can be mineralized to SO_4 (Fitzgerald et al. 1984; Strickland et al. 1986). Freney (1979), Strickland & Fitzgerald (1984) and Fitzgerald et al. (1983) demonstrated the direct implication of microorganisms in immobilization and mineralization processes. Extracellular enzymes have been suggested to play a role in organic S mineralization and SO_4 incorporation into organic matter (Strickland et al. 1984). Collectively, these results show that the organic S pool is actively involved in S cycling and suggest that the understanding of abiotic S transformations alone is insufficient to predict long term response of soils to increased S loading. A more complete knowledge of S dynamics in forested ecosystem appears necessary to answer such questions as (1) does S actually accumulate in soils subjected to high S loading? (2) if accumulation occurs, is the process reversible? and (3), on what time scale?

The boreal coniferous forest which covers a large part of Quebec and Ontario Provinces (Canada) has received high S loading through atmospheric input. Although a few studies on S biogeochemistry in forested systems have been published, the information available for coniferous forests is particularly limited. The present report quantifies the major S pools present in such a system with emphasis on soil-S speciation (carbon-bonded S, ester sulfate, adsorbed and soluble SO_4). Finally, the possibility that the organic S pool in soils may act as a sink for atmospheric S is examined by searching for relationships between S input and S sequestered in organic form for different forested sites.

Methods

Site description

The Lake Laflamme Watershed (LLW) is a small catchment (68.4 ha located 80 km north of Quebec city (47°17′ N, 71°14′ W, 777—844 m above sea level). Balsam fir (*Abies balsamea* 90%) and white birch (*Betula papyrifera* 10%) dominate in this catchment in association with *Oxalis montana*, and the mosses species *Pleurozium schreberi*, *Hylocomnium splendens*, and *Dicranum* sp. *Sphagnum* sp. is present in humid locations. According to records kept since 1981, this region receives a mean annual precipitation of 1300 mm (31.3% as snow), of mean pH 4.44 and of mean SO_4-S concentration 0.51 $mg \cdot l^{-1}$ and the annual S input in bulk precipitation averages 7.32 $kg \cdot ha^{-1}$ (Papineau 1989). The climate is characterized by long, cold and snowy winters and short, cool and wet summers. The soil is an orthic humo-ferric podzol of the Laurentide series developed on a glacial till deposited on the granitic bedrock of the Canadian Shield. Based on 29 pits, the average thicknesses for LFH, Ae, Bhf and Bf horizons are 8.77, 4.51, 7.55 and 28.7 cm respectively. The thickness of till deposit ranges from 0.1 m on top of the basin to 15 m at the bottom of the lake. The B horizon is a sandy loam with 71% sand, 19% loam and 10% clay. The trees of the basin were almost entirely harvested in 1943. The catchment has been undisturbed since.

Sample collection

Aboveground biomass and litterfall

Ten balsam firs of different DBH (diameter at breast height) classes (10.1 to 21.4 cm), were collected to determine the relation between biomass and DBH. White birch was ignored because of its negligible contribution to total biomass. Epiphytic lichens present on boles and branches were not removed and are included in the aboveground biomass. However, their contribution to total aboveground biomass is probably small. Trunks (including bark) and branches (including foliage) were chipped separately and subsampled. Herbaceous plants and roots were collected in 5 samplings on 19 evenly distributed plots (1 m^2). Herbaceous were collected from a 900 cm^2 surface. A larger surface was then carefully dug out to the C horizon ($\sim$60 cm) and the roots collected (approximative diameter

> 3.0 mm). Most were found in the forest floor and top 10 cm of the mineral soil. Because fine roots were not sampled, root biomass may be slightly underestimated. Twenty one litterfall collectors (0.871 m^2) were installed along two transects on the north and south parts of the watershed. Litter was collected every 1 or 2 months, except when snow was present on the ground.

Fallen boles

Fallen boles may represent a substantial fraction of total biomass in the balsam fir forest (Lambert et al. 1980; Lang et al. 1981). In order to estimate their contribution to total biomass and to total S ecosystem, the length (h) and end radius (R and r) of boles larger than 10 cm diameter at the largest end were measured on 20 evenly distributed plots (25 m^2). The equation for the right frustum of a cone ($V = \pi h/3\ (R^2 + r^2 + Rr)$) was then used to obtain volume (V) values. Three classes of fallen boles were established according to the state of decay: (1) slight decay (fresh wood, not or slightly decomposed, surface resistant to finger pressure), (2) moderate decay (partly decomposed, surface soft enough to be marked by fingers) and (3) advanced decay (the surface crumbles easily between the thumb and forefinger). Representative samples from every class (n = 4—5) were collected for density and total S measurements to allow conversion of volume values to mass and S amount.

Soils

The soil samples used for S pools speciation and quantification were obtained from 13 pits (1 m^2) evenly distributed. Samples from the forest floor (LFH horizons combined) and the Ae, Bhf, Bf and C (first 10 cm) horizons were collected and soil horizon thicknesses were recorded. Bulk densities of mineral soils were obtained by inserting a stainless steel tube of known volume in a given horizon. The number of replicates for bulk densities ranged from 4 (Ae) to 12 (Bf). Coarse fragment content ($>$2.00 mm) were determined from 3—4 pits at the same site and were used to correct bulk density measurements. To ascertain the importance of the C horizon as a S reservoir, 3 of the 13 pits were dug out to a depth of 100—150 cm, and the C horizon was sampled every 10 or 20 cm. The various soil samples were placed in plastic bags, transported to the laboratory within a few hours and stored at 4 °C until analysis.

Sample preparation and analysis

Plant material (tree parts, herbaceous, litterfall and fallen boles) and soil subsamples were dried at 65 °C to constant weight. Plant material was successively ground with Wiley and Cyclotec mills whereas soil samples were ground with a mortar and a pestle to obtain a fine powder. The total S concentration was determined with a LECO SC-132 analyzer (David et al. 1989). Plant material and soil samples were occasionally run in duplicates: the coefficient of variation (CV) was 4.25% and 4.63% respectively. Citrus leaves (NBS # 1572) were occasionally used to verify accuracy of the S measurements for plant material; the results were always within 5% of the certified value. Selected samples of litterfall and tree components (trunks, branches + foliage and roots) were also analyzed for extractable SO_4-S ($n = 5$). Samples were shaken for 1 hour with NH_4Cl (0.01M, 10:1 solution:sample ratio), centrifuged (20 min at 21 000 g), and the supernatant was filtered (Nuclepore membrane 0.4 μm) and analyzed for SO_4 by ion chromatography.

The determination of operational S fractions in soil samples (except total S) was performed on moist soils since drying may change the relative proportion of S forms in soils (David et al. 1982). Large roots were first removed by hand in the forest floor samples and mineral horizons were sieved on a 2.00 mm mesh. HI reducible S was measured in duplicates on every sample according to the Johnson and Nishita method (1952) as modified by Landers et al. (1983). The average CV for HI reducible S measurements was 7.9%. The HI reducible fraction should comprise mainly ester sulfate and SO_4 (Landers et al. 1983). Total and NH_4Cl extractable SO_4 (referred to as soluble SO_4) concentrations were obtained by shaking duplicate soil samples (10:1 solution:soil ratio) for 1 hour with NaH_2PO_4 (0.016 M) and NH_4Cl (0.01 M) respectively. The latter extractant was preferred to water because of a better consistancy with soil having important organic content (Maynard et al. 1987). Both extracts were centrifuged (20 m, 21 000 g), filtered (Nuclepore membrane 0.4 μm) and analyzed for SO_4 by ion chromatography. The average CV for SO_4 measurements was 7.65 and 10.33% for NaH_2PO_4 and NH_4Cl respectively. The amount of SO_4 extracted with the NH_4Cl solution was subtracted from the amount of SO_4 extracted with the NaH_2PO_4 solution to yield an estimation of adsorbed SO_4. Ester sulfate concentration was obtained by subtracting total SO_4 from the HI reducible portion. Carbon-bonded S was obtained by subtracting the HI reducible portion from total S. Total carbon was measured with a LECO CR12 analyzer. Duplicates were occasionally run and yielded an average CV of 4.63%. Soil pH was measured on moist samples with deionized water (5:1 solution:soil ratio).

Iron and aluminum concentrations in various fractions were determined on duplicate moist soil samples from 7 pits by using various extracting solutions: pyrophosphate (0.1 M $Na_4P_2O_7$, 18 h extraction) to estimate organically bound Fe (Fe_p) and Al (Al_p) (McKeague 1967);

oxalate (0.2 M $(NH_4)_2C_2O_4H_2$ adjusted to pH 2, 4-h extraction) to estimate organically bound plus amorphous Fe (Fe_o) and Al (Al_o) (McKeague et al. 1971); dithionite-citrate to estimate the sum of organically bound, amorphous and crystalline Fe oxides (Fe_d) (Mehra & Jackson 1960). Crystalline Fe (Fe_c) was estimated by the difference between Fe_d and Fe_o whereas amorphous Fe (Fe_a) and Al (Al_a) were estimated by the difference between Fe_o and Fe_p. The estimation of crystalline Al was not used in this study because the dithionite-citrate extraction is less specific for Al than for Fe (McKeague et al. 1971). Fe and Al in all extracts were measured by plasma emission spectroscopy. The CV for Al and Fe content in the various fractions was 4.58 and 6.56% respectively.

Regression analysis

Relationships between adsorbed SO_4-S and Fe and Al concentrations in the various operational fractions, carbon, and pH were examined by multiple regression analysis (stepwise forward). Data normality was first tested with the Kolmogorov Smirnoff test at the 0.05 level of significance. Many variables were not normally distributed and the data were transformed by log $(x + 1)$ when necessary. The regression included 35 observations from 7 soil profiles and 5 horizons. The relationships between % carbon and S constituents were also assessed by regression analysis. Data were normalized using log $(x + 1)$ or to $1/x$ transformations when necessary.

Results and discussion

Mass and sulfur concentration in aboveground biomass

DBH is a good predictor of dry weight (Fig. 1) of whole trees, trunks, and branches + foliage with r^2 values ranging from 0.92 to 0.98. Trunks account for the major part of tree biomass (71%), whereas branches + foliage (22%) and roots (7%) represent lower proportions. Because of their higher S concentration, branches + foliage account for 61% of total S in trees. Total tree biomass and S associated with trees was estimated for the whole watershed using population data from the Faculty of Forestry of Laval University (unpublished). The estimated average aboveground biomass (Table 1) for balsam fir (5.96 $kg{\cdot}m^{-2}$) in LLW is comparable to that reported by Lambert et al. (1980) for a balsam fir forest in the White Mountains, (New Hampshire) (4.4 $kg{\cdot}m^{-2}$). Total S associated with trees (including roots) is 18.9 $kg{\cdot}ha^{-1}$ in LLW. A similar value has been

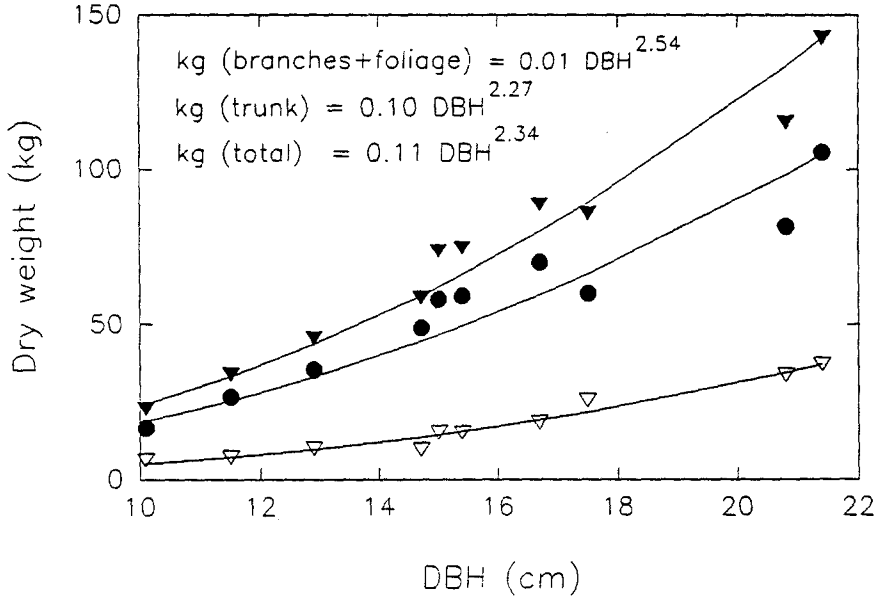

Fig. 1. Mass of branches+foliage (▽), trunks (●) and whole trees (▼) as a function of DBH for balsam firs collected at LLW.

Table 1. Mean values of mass and total S concentrations (± SD) in vegetation biomass (*n*).

		Mass (kg·m^{-2})	S (μg·g^{-1})
Trees	Trunks	4.55	118 ± 10 (10)
	Branches	1.41	815 ± 57 (10)
	Roots	0.42 ± 0.21 (19)	461 ± 98 (19)
Herbaceous		0.26 ± 0.23 (19)	2047 ± 766 (19)
Fallen boles	Advanced	0.76 ± 0.99	363 ± 176 (5)
	Moderate	0.69 ± 0.81	182 ± 55 (4)
	Slight	0.34 ± 0.73	188 ± 24 (4)
	Total	1.79 ± 1.38	

reported for a mixed oak stand (18.0 kg·ha^{-1}) at Camp Branch Watershed (Tennessee) (Johnson et al. 1986). Other reported S values range from 33.8 to 108.4 kg·ha^{-1} for various stand types and locations in North America (Shriner & Henderson 1978; Johnson et al. 1986).

The average (± standard deviation of the population, SD) areal dry weight of fallen boles (1.79 ± 1.38 kg·m^{-2}) found in LLW (Table 1) is low compared to the value of 4.9 kg·m^{-2} found by Lambert et al. (1980) for a balsam fir forest in the White Mountains, New Hampshire. These authors reported that fallen and standing dead trees accounted for 53% of the total woody mass on the site compared to 22% at LLW. The lower contribution of dead wood at LLW may be attributable to the 1943 clear cutting which removed most of the trees which would not contribute to decaying biomass. Boles showing advanced, moderate and slight decay represent 42, 39 and 19% of total fallen boles mass respectively. The average (± SD) amount of S associated with fallen boles is 4.46 ± 3.7 kg·ha^{-1} (Table 3), the advanced, moderate and slight decay classes contributing for 58, 28 and 14% respectively. Average fallen boles densities (± SD) (0.19 ± 0.05 g·cm^{-3}, 0.30 ± 0.08 g·cm^{-3} and 0.32 ± 0.06 g·cm^{-3} in advanced, moderate, and slight decay classes respectively) is strongly related to total S concentration of fallen boles (Total S = $-1670 \times$ density $+ 660$, $r^2 = 0.80$, $n = 13$) suggesting that boles get enriched in S while losing mass during their decay. Average total S (± SD) associated with herbaceous is 4.17 ± 2.97 kg·ha^{-1} (Table 3). The great variability in herbaceous mass and S concentration is explained by their heterogenous distribution. For example, herbaceous biomass and S concentration average 0.552 kg·m^{-2} and 1320 μg·g^{-1} respectively in plots dominated by *Sphagnum* sp., and 0.092 kg·m^{-2} and 2740 μg·g^{-1} in plots dominated by *Oxalis montana.*

Sulfur partition in litterfall and tree components

The SO_4-S contribution to total S in tree parts is fairly constant (15.5 to 23.1%) despite the variations in SO_4-S concentration (Table 2). The contribution of SO_4-S to total S in litterfall (10.6 and 7%) is comparable to that found by David et al. (1987) for a hardwood site; it is, however, low compared to other sites where SO_4-S concentrations in litterfall represent 39, 74 and 70% of total S respectively (Turner & Lambert 1980; Tuner et al. 1980; Meiwes & Khanna 1981). Homann & Cole (1990) recently reported that Douglas-fir needle litter has an important initial soluble SO_4 concentration (36—50% of total S) whereas SO_4 represents around 10% of total S in red alder leaf litter. In both litter types, ester sulfate was in very low proportion. If we assume that ester sulfate is also in low proportion in LLW litter, litterfall may represent an important carbon-bonded S source for the forest floor.

Table 2. Sulfate-S concentrations (± SD) in litterfall and tree parts. Collection dates for litterfall samples were May 14 and July 30 1987 respectively for spring and mid-summer.

	Sulfate-S ($\mu g \cdot g^{-1}$)	% of total S
Litterfall		
Spring	89.0 ± 18	10.6%
Mid-summer	97.0 ± 16	7.0%
Tree parts		
Roots	105.0 ± 9	23.1%
Trunks	23.3 ± 13	19.9%
Branches + foliage	126.0 ± 39	15.5%

Total sulfur distribution in the ecosystem

The total S amount for the whole ecosystem averages 1395 $kg \cdot ha^{-1}$ (Table 3), of which 98% is found in the soil (1367 $kg \cdot ha^{-1}$) with 89% being in the mineral horizons. In the *Quercus-Carya* stand of Walker Branch Watershed (Tennessee), soils contained 98% of the total ecosystem S (Shriner & Henderson 1978). In a S cycling study for five different ecosystems Johnson et al. (1986) reported that soils accounted for 94 to 99% of the total ecosystem S. In Huntington Forest (New York), 88% of total S was found in the soil (David et al. 1987). Turner and Lambert (1980) found a lower value in New South Wales (Australia), where 37% of total S was found in the aboveground biomass. This exception may be attributable to a very low atmospheric input (1.9 $kg \cdot ha^{-1} \cdot yr^{-1}$ SO_4-S), a low S content in soil and S sequestration in tree tissues (Johnson 1984).

An important fraction of ecosystem S may be associated to the C horizon. If we assume an average thickness of about 1.0 meter for the C horizon, the estimate of total S (based on 3 pits) in soil increases to about 2100 $kg \cdot ha^{-1}$. The validity of this estimation is however limited by the difficulty to obtain reliable results concerning the thickness of till deposit.

Soil sulfur constituents

Inorganic SO_4

Total SO_4-S concentrations range from 1.1 (Ae) to 36.6 $\mu g \cdot g^{-1}$ (Bf) of dry weight (Table 4), with adsorbed SO_4 accounting for 7, 0, 69, 84 and 69% of total SO_4 in LFH, Ae, Bhf, Bf and C horizons respectively. For the

Table 3. Global S distribution in Lake Laflamme Watershed.

		S ($kg{\cdot}ha^{-1}$)	% of ecosystem S
Trees	Trunks	5.35	0.38
	Branches + foliage	11.49	0.82
	Roots	2.04	0.15
Herbaceous		4.17	0.30
Fallen boles	Advanced	2.58	0.19
	Moderate	1.24	0.09
	Slight	0.64	0.05
Soil	LFH	119	8.54
	Ae	47	3.37
	Bhf	356	25.5
	Bf	720	51.6
	C	125	9.0

Table 4. General soil characteristics and S constituents (±SD). Soil mass estimates for mineral horizons do not include fragments > 2.00 mm. Values for S constituents, % carbon and pH are averages of 13 pits.

Horizon	Soil mass ($kg{\cdot}m^{-2}$)	pH	%C	Total	Ester	Ads.	Sol.	C-bonded
				S ($\mu g{\cdot}g^{-1}$)				
LFH	6.8	4.0	40.6 ±6.8	1748 ±379	616 ±134	0.5 ±0.6	7.2 ±2.7	1124 ±307
Ae	47.2	4.6	1.4 ±0.6	108[a] ± 45	40 ±21	ND*	1.1 ±0.4	67[a] ±22
Bhf	67.2	4.5	10.8 ±5.1	503 ±202	148 ±50	7.6 ±5.9	3.5 ±1.1	345 ±171
Bf	271.5	4.9	4.8 ±1.3	258 ± 69	92 ± 20	30.7 ±26.7	5.9 ±3.8	130 ±53
C (0–10 cm)	83.8	5.0	±1.7 ±0.8	114[b] ±39	41 ±13	6.4 ±2.8	3.0 ±1.1	65[b] ±21

*: not detected
a: $n = 9$
b: $n = 8$

whole soil profile, adsorbed SO_4 accounts for 82% of total SO_4 and amounts to about 15 times the annual S wet deposition; it may constitute a readily exchangeable source of SO_4 that could buffer SO_4 concentration in the soil solution. Since adsorbed SO_4 is often related to extractable Fe and Al fractions (Johnson & Todd 1983; Fuller et al. 1985; MacDonald & Hart 1990), their distribution and speciation in soils of LLW were examined. The concentrations of total extractable Fe and Al are low in the upper horizons (LFH and Ae) and reach maxima in the B horizons (Fig. 2). However, the highest extractable Fe concentration is found in the Bhf horizon while the highest Al concentration occurs in the Bf horizon. DeKimpe & Martel (1976) and Fuller et al. (1985) also found that Al usually accumulates deeper than Fe in spodosols. Most of the Fe and Al can be extracted with pyrophosphate in the B horizons suggesting that those elements are mainly bound to organic matter. Amorphous Fe and Al are present in all horizons ranging from 17 (Bhf) to 82% (Ae) and from 12 (Bhf) to 66% (Ae) of total extractable Fe and Al respectively. Crystalline Fe contribution is very low in all horizons. This could be explained by the high level of organic matter found in the LLW soil since organic matter inhibits crystalline oxide formation (Schwertmann 1966; Kodama & Schnitzer 1977).

The relationships between adsorbed SO_4-S ($\mu g{\cdot}g^{-1}$) and Fe and Al ($mg{\cdot}g^{-1}$) concentrations in various fractions, carbon, and H^+ (μM) were examined by multiple regression analysis (stepwise forward). The resulting relationship is:

$$\log(\text{adsorbed } SO_4\text{-S} + 1) = 0.617 \log(Al_a + 1) + 0.047\,(Al_p) - 0.366 \log(H^+ + 1) + 0.734 \quad (r^2 = 0.81)$$

Many researchers observed significant positive relationships between adsorbed SO_4 and various Al fractions (Harrison et al. 1990; MacDonald & Hart 1990; Fuller et al. 1985; Neary et al. 1987). These results differ from those of Johnson & Todd (1983) who reported that crystalline Fe was the major variable related to adsorbed SO_4 ($r^2 = 0.55$) in 9 soils from North America and Costa Rica. Although Fuller et al. (1985) also observed a significant relationship between adsorbed SO_4 and crystalline Fe in a soil from the Adirondack region, New York, only 4 of the 10 samples analyzed indicated the presence of any crystalline Fe, as pointed out by the authors.

Organic sulfur

Organic S dominates in the various soil horizons of LLW, ranging from 87 (Bf) to 99% (LFH) of total S concentrations (Table 4). The dominance of

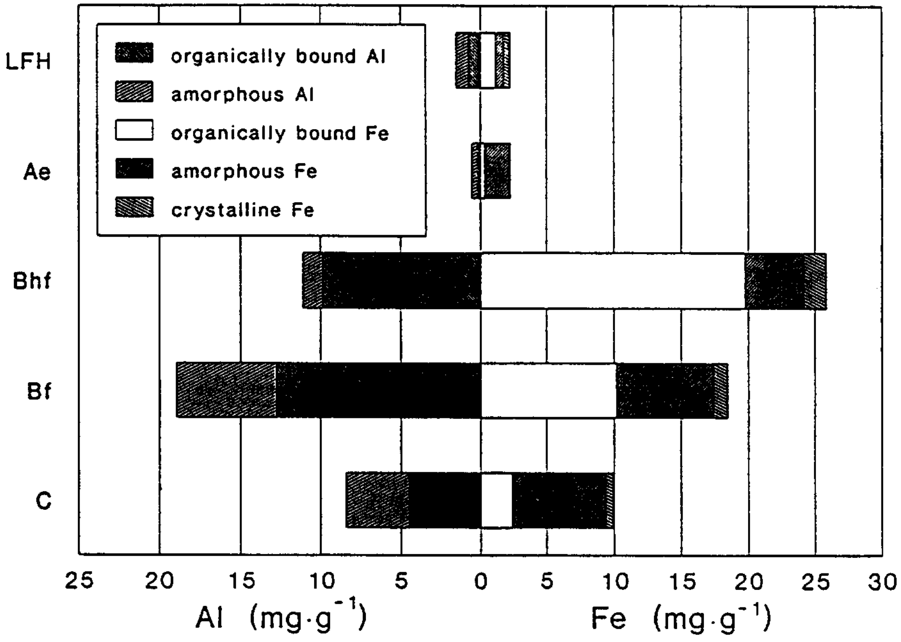

Fig. 2. Concentration of Fe and Al in various fractions of the various soil horizons of LLW ($n = 7$).

organic S has also been reported for other types of forested ecosystems from different locations (Johnson et al. 1982, 1986; Mitchell et al. 1986; Schindler et al. 1986; Watwood et al. 1986; Autry et al. 1990). Organic S present in forest soils originates from *in situ* production (Strickland et al. 1985; Watwood & Fitzgerald 1988) and external sources such as litterfall, root turnover, animal feces and plant exudates (Freney 1967). In the mineral horizons, a significant part of the organic S may originate from the deposition of dissolved organic S leached from the forest floor (David et al. 1987; Mitchell et al. 1989). In the various soil horizons of LLW, carbon-bonded S concentrations range from 51 to 68% of total S concentrations, followed by ester sulfate (29—37%) and SO_4-S (1—14%). Carbon-bonded S, ester sulfate and SO_4-S represent 775, 458 and 133 $kg \cdot ha^{-1}$ respectively.

The correlation coefficients between % carbon and S constituents are shown in Table 5. When all observations for different horizons are included in the analysis, % carbon, carbon-bonded S and ester sulfate are positively correlated together ($\alpha < 0.01$) whereas SO_4 is negatively correlated with the other variables ($\alpha < 0.01$). Although grouping soil

Table 5. Correlation coefficients between % carbon and S constituents.

	% Carbon	Ester sulfate	Sulfate
All horizons ($n = 63$)			
Ester sulfate	0.948**	1	
Sulfate	−0.517**	−0.521**	1
C-bonded S[a]	0.964**	0.890**	−0.546**
LFH ($n = 13$)			
Ester sulfate	−0.095	1	
Sulfate	0.030	−0.414	1
C-bonded S	0.571*	0.375	−0.214
Ae ($n = 13$)			
Ester sulfate	0.923**	1	
Sulfate	−0.448	−0.496	1
C-bonded S[b]	0.465	0.233	−0.145
Bhf ($n = 13$)			
Ester sulfate	0.661*	1	
Sulfate	−0.217	−0.362	1
C-bonded S	0.967**	0.502	−0.093
Bf ($n = 13$)			
Ester sulfate	−0.181	1	
Sulfate	−0.067	0.071	1
C-bonded S	0.853**	−0.006	−0.358
C ($n = 11$)			
Ester sulfate	0.839**	1	
Sulfate	−0.584	−0.443	1
C-bonded S[c]	0.916**	0.718*	−0.291

*, **: Significant at the 0.05 and 0.01 levels respectively.
a: $n = 56$
b: $n = 9$
c: $n = 8$

horizons for regression purposes is a common practice, it may be inadequate to look at relationships between soil characteristics because distinct soil horizons are statistically distinct populations. In the present study, the relatively high number of observations for each horizon permits a finer analysis of relationships existing between S constituents and % carbon inside each horizon.

Sulfate is not related to any other variable in the five soil horizons, which suggests a clear differentiation between SO_4, % carbon and organic

S species. Ester sulfate and carbon-bonded S are related only in the C horizon, suggesting that these fractions are independent from each other. Their relationships with % carbon also differs: carbon-bonded S is correlated with % carbon in 4 horizons (LFH, Bhf, Bf and C) that represent over 95% of the soil organic matter whereas ester sulfate is correlated to % carbon in 3 horizons (Ae, Bhf and C) representing only 37% of the soil organic matter.

The differentiation between ester sulfate and carbon-bonded S and their different degree of association with % carbon is in agreement with the conceptual model of McGill & Cole (1981) on the cycling of C, N, P and S in soils. According to this model, carbon-bonded S and ester sulfate have different mode of stabilization; ester sulfate mineralization (which may be accomplished by extra-cellular sulfohydrolases) increases with the biological requirement for S, whereas carbon-bonded S mineralization is primarily associated with the mineralization of carbon for energy needs. Their model predicts that the size of the ester sulfate pool will increase with increasing SO_4 availability. However, the absence of a relationship between SO_4 and ester sulfate in the 5 horizons studied (Table 5) suggests that the McGill & Cole model (1981) is not totally useful in interpreting S speciation in forest soils.

To further test the possibility that SO_4 availability may influence organic S speciation, we searched for empirical relationships between S speciation in the forest floor and atmospheric SO_4 deposition at various locations (Fig. 3). Carbon-bonded S contribution to total S is not related to S input (r^2 = 0.001) whereas ester sulfate contribution seems to diminish with increasing input (r^2 = 0.36). This apparent decrease is caused, however, by the very low contribution of ester sulfate at only two sites receiving high S input in northeastern Bavaria (Zucker et al. 1986). These results suggest that the S speciation of forest floor is independent of SO_4 input.

Relationships between soil and sulfur status and SO_4 loading

Because organic S forms are dominant in most soils, they have been hypothesized to act as sinks for atmospheric S (Strickland et al. 1986; Mitchell et al. 1986; Autry et al. 1990). In support of this assumption, laboratory and *in situ* experiments have shown a rapid transformation of $^{35}SO_4$ into organic forms. Furthermore, the observation that $^{35}SO_4$ incorporation was a function of exogenous SO_4 concentration (Strickland & Fitzgerald 1987; Swank et al. 1985; Autry & Fitzgerald 1990) suggests that soil microorganisms may take up more S in response to increased S loading. However, an analysis of the data available for 10 ecosystems

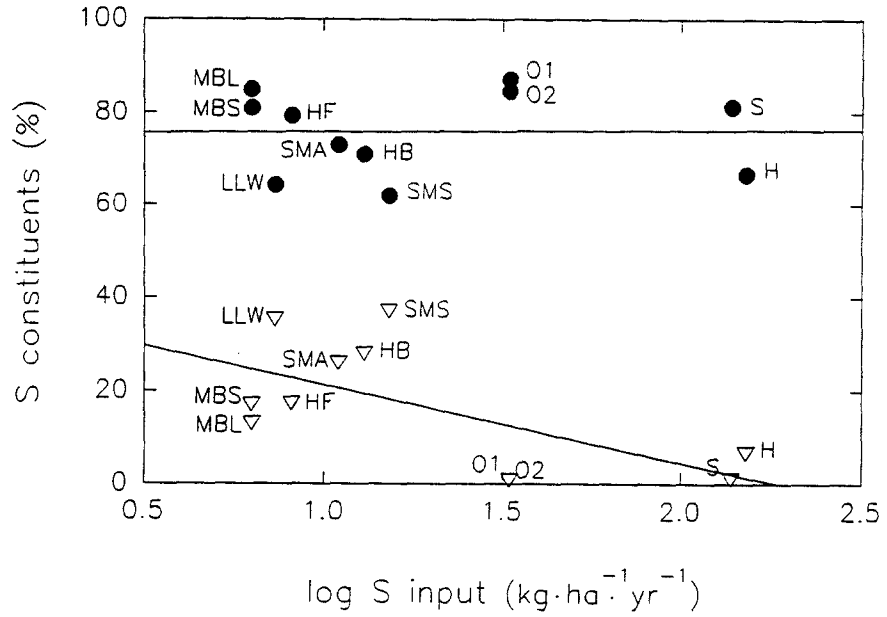

Fig. 3. Relations between S input and the contribution of carbon-bonded S (●) and ester sulfate (▽) to total S in the forest floor of Spruce (MBS) and Lodgepole (MBL) sites at Marmot Bassin, Alberta, Canada (Mitchell et al. 1986); Lake Laflamme Watershed (LLW), Quebec, Canada (this study); Huntington Forest (HF), New York, USA (David et al. 1987); Aspen (SMA) and Spruce (SMS) stands at Sangre de Cristo mountains, New Mexico, USA ((Watwood et al. 1986); Hubbard Brook Forest (HB), New Hampshire, USA (Likens et al. 1977; Schindler et al. 1986); Oberwaiz I (OI), Oberwaiz II (OII), Silberstain (S) and Hollental (H) sites in Northeast Bavaria, Germany (Zucker et al. 1986).

indicates a weak and nonsignificant negative relationship between areal organic S and S input ($r^2 = 0.18$) whereas sulfate-S is significantly related to S input (Fig. 4, $r^2 = 0.59$, $P < 0.05$). This observation supports the hypothesis of Johnson et al. (1982) that forest S cycling may shift from a biogeochemical to a predominantly geochemical cycling in response to increasing S deposition. There is no relationship between total S concentration in forest floor and S input (Fig. 5). This is different from the results of David et al. (1988) who concluded that total S concentrations adjusted for total N in forest floors reflects sulfate deposition patterns, despite the fact that the average total S concentrations and S depositions of the five zones studied by David et al. (1988) have been included in our compilation. The use of N adjusted S values and a narrow S deposition range (2.5 to 6.1 kg·ha^{-1}·yr^{-1}) (David et al. 1988) as opposed to non adjusted S values and the large deposition range (2.0 to 152 kg·ha^{-1}·yr^{-1}) of our compilation may explain the different conclusions.

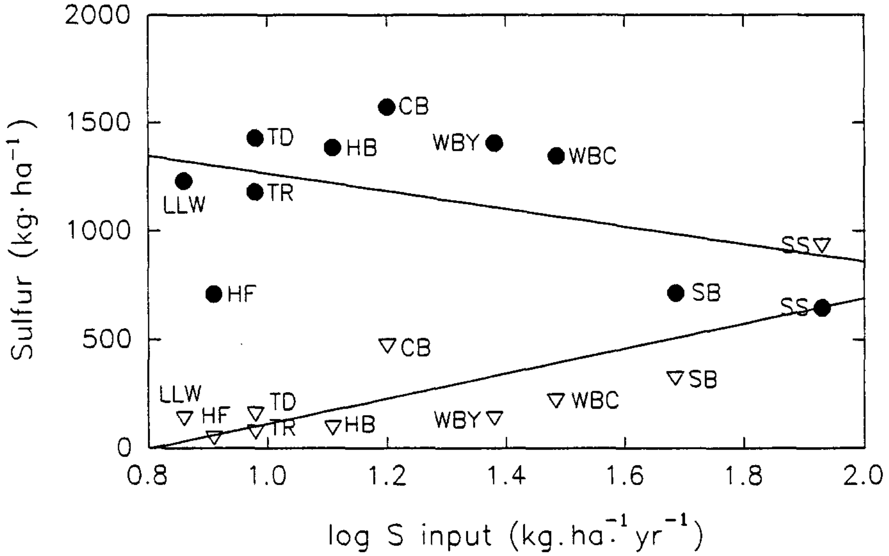

Fig. 4. Relations between organic S (●) and SO_4-S (▽) on an areal basis and S input at Lake Laflamme Watershed (LLW), Quebec, Canada (this study); Huntington Forest (HF), New York, USA (David et al. 1987); Red Alder (TR) and Douglas Fir (TD) stands at Thompson site, Washington, USA (Johnson et al. 1986); Hubbard Brook Forest (HB), New Hampshire, USA (Likens et al. 1977; Mitchell et al. 1989); Camp Branch Watershed (CB), Tennessee, USA (Johnson et al. 1986); Yellow Poplar (WBY) and Chestnut Oak (WBC) stands at Walker Branch Watershed, Tennessee, USA (Johnson et al. 1986); Beech (SB) and Spruce (SS) stands at Solling, West Germany (Meiwes and Khanna 1981).

Microbial S immobilization in soils of forested catchments does not seem to depend on S input. Also, there is no clear relation between the tree species present on a catchment and the S status of soils for the sites included in this compilation. Concentration and speciation of organic S in soils must therefore be controlled by other ecosystem characteristics and, since organic S dominates most catchments, it seems likely that S transformations simply follow organic matter transformations. Two mechanisms may explain organic S accumulation in forest soils. The first one is that the S concentration in organic matter increases and the second is that the soil accumulates organic matter. Total S concentration of forest floor does not increase with increasing input as shown in Fig. 5. If we assume that the forest floors of the sites included in our compilation are composed mainly of organic matter, the data strongly suggest that the C:S ratio remains constant despite a strong gradient in S input. To fully address this statement, a complete description of the S status would be needed for

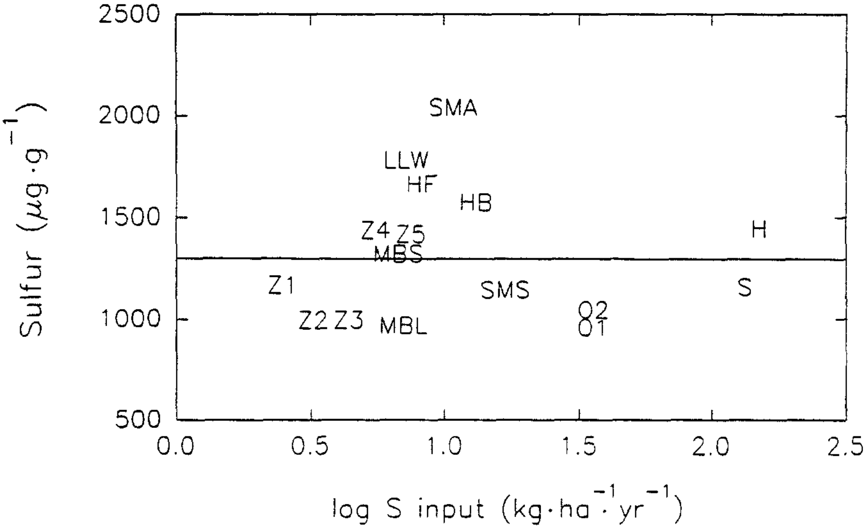

Fig. 5. Relation between total S concentration of the forest floor and S input in zones 1 to 5 (Z1 to Z5), Minnesota, Wisconsin, Michigan, USA (David et al. 1988); Spruce (MBS) and Lodgepole (MBL) sites at Marmot Bassin, Alberta, Canada (Mitchell et al. 1986); Lake Laflamme Watershed (LLW), Quebec, Canada (this paper); Huntington Forest (HF), New York, USA (David et al. 1987); Aspen (SMA) and Spruce (SMS) stands at Sangre de cristo mountains, New Mexico, USA (Watwood et al. 1986); Hubbard Brook Forest (HB), New Hampshire, USA (Likens et al. 1977; Schindler et al. 1986); Oberwaiz I (OI), Oberwaiz II (OII), Silberstain (S) and Hollental (H) sites in Northeast Bavaria, German (Zucker et al. 1986).

many forested sites including mineral horizons. However, the present data suggest that systems in steady state with respect to organic matter do not accumulate organic S in response to increased atmospheric S loading even though organic S is clearly dominant in most soils.

Acknowledgements

This project was supported by the Quebec Fonds pour la Formation de Chercheurs et l'Aide à la Recherche and the Natural Sciences and Engineering Research Council of Canada. The critical comments of A. Tessier are gratefully acknowledged.

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