



doi: 10.1016/j.gca.2004.03.010

A S-isotope approach to determine the relative contribution of redox processes to net SO₄ export from upland, and wetland-dominated catchments

M. C. EIMERS,^{*,†} P. J. DILLON,² and S. L. SCHIFF³¹Department of Biology, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada²Environmental and Resource Studies Department, Trent University, Peterborough, Ontario, Canada³Department of Earth Sciences, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

(Received July 14, 2003; accepted in revised form March 8, 2004)

Abstract—Reoxidation of S stored in lowlands after summer droughts has been reported to be responsible for the excess SO₄ export observed in many catchments in south central Ontario. Stable S isotopes can be used to identify the source of SO₄ export in stream water, and are particularly well suited to evaluating zones of dissimilatory SO₄ reduction (DSR) and the contribution of oxidation of reduced S species to stream SO₄. The Plastic Lake-1 (PC1) stream drains an upland coniferous forest and then passes through a *Sphagnum*-dominated swamp before discharging to Plastic Lake. Measurements of SO₄ fluxes and isotope ratios were used to determine the source of net SO₄ export and the contribution of redox processes to S retention and export in the upland and wetland, respectively. Mass balance budgets for the years 1999/00 and 2000/01, which had comparatively wet summers, indicated that the upland part of the catchment consistently exported SO₄ in excess of bulk deposition inputs. In contrast, mass budget calculations for the swamp indicated a net retention of 3 and 2 g S-SO₄/m² of wetland area, in 1999/00 and 2000/01 respectively. Higher δ³⁴S ratios and lower SO₄ concentrations in the swamp outflow (average +8.6 ± 2.6‰; 1.5 ± 0.6 mg S-SO₄/L) compared to the inflow draining the upland (+5.4 ± 0.7‰; 2.4 ± 0.3 mg S-SO₄/L) indicated that DSR was at least partly responsible for net SO₄ retention in the swamp. Isotope values in upland stream water (+5.7 ± 0.7‰) were only slightly higher than values in bulk deposition (average +5.1 ± 0.6‰) and soil leachate (+4.4 ± 0.4‰) over the 2-year period of study. Similar δ³⁴S values in upland stream water compared to deposition and soil leachate, despite substantial variations in water table height in the streambed (92 cm), suggest that reoxidation of reduced sulphides is not an important contributor to SO₄ export from the upland. Rather, net SO₄ export from the upland subcatchment is likely due to net release from upland soil, and slight differences in δ³⁴S between bulk deposition and soil leachate are consistent with SO₄ release from organic S forms. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Sulphate (SO₄) input-output budget calculations have indicated that the majority of catchments in the Muskoka-Haliburton region of south-central Ontario currently export more SO₄ in stream water than is input in bulk deposition (Eimers and Dillon, 2002). The magnitude of net SO₄ export (average ~3.5 kg S/ha/yr: 1980–2000) from these catchments is similar to that measured at other sites in eastern North America, including the Lac Clair catchment, QC (~4.4 kg S/ha/yr; Houle et al., 1997), Huntington Forest, NY (~4.7 kg S/ha/yr; Mitchell et al., 1996) and Hubbard Brook, NH (~4.2 kg S/ha/yr; Hornbeck et al., 1997). Particularly large net SO₄ export (up to 60 kg S/ha/yr) occurs from catchments in central and eastern Europe, where S deposition inputs were historically the highest and where large reductions in deposition have occurred in recent decades (Novak et al., 1996; Novak et al., 2000; Alewell et al., 2001; Prechtel et al., 2001). Despite large variations in the magnitude of net export among regions, most studies agree that SO₄ is being released from internal pools, with net export most commonly attributed to a combination of

SO₄ desorption, net organic-S mineralization, and sulphide oxidation (Dillon and LaZerte, 1992; Houle and Carignan, 1995; Mitchell et al., 1996; Driscoll et al., 1998; Novak et al., 2000; Lofgren et al., 2001; Prechtel et al., 2001; Park et al., 2003). Although dry deposition and weathering likely contribute to S export at Muskoka-Haliburton catchments, they cannot explain entirely the net excess due to the region's remote location and low S content and weathering rates of local bedrock (Dillon et al., 1988; Jeffries and Snyder, 1983; Watmough and Dillon, 2001).

The magnitude of net SO₄ export from Muskoka-Haliburton catchments varies substantially from year to year, and is strongly related to interannual variations in summer precipitation and temperature (Dillon et al., 1997; Devito et al., 1999; Eimers and Dillon, 2002). Sulphate concentrations and SO₄ export in streams draining wetlands tend to be highest after summer drought, when wetland water tables decline and streams cease to flow, allowing exposure and aeration of S-enriched peat (LaZerte, 1993; Devito, 1995; Devito and Hill, 1999). Autumn rains subsequently flush newly oxidized sulphate into wetland outflows, and elevated SO₄ concentrations in streams can persist through the winter months, resulting in large increases in net SO₄ export (LaZerte, 1993; Dillon et al., 1997; Eimers and Dillon, 2002). In contrast, SO₄ input/output budgets at wetland-dominated catchments are approximately in balance or positive (net retention) during wet years when water

* Author to whom correspondence should be addressed (ceimers@trentu.ca).

† Present address: Department of Geography, Trent University, Environmental and Resource Department, 1600 West Bank Dr., Peterborough, ON, Canada K9J 7B8.

table levels remain near the peat surface and stream flow is virtually continuous year-round (LaZerte, 1993; Devito, 1995). Similar postdrought increases in SO_4 export have been reported at other wetland-draining catchments in Ontario, including at the Experimental Lakes Area (Bayley et al., 1986) and Turkey Lakes Watershed (Jeffries et al., 2002).

While SO_4 release from peat appears to explain interannual variations in SO_4 export in wetland-dominated catchments, an analysis of a range of catchments in the Muskoka-Haliburton region indicated that temporal patterns in SO_4 export are synchronous among both upland and wetland-draining catchments (Eimers and Dillon, 2002). Sulphate export from upland-dominated catchments increases similarly in drought years, but the magnitude of change between wet and dry years is substantially less than in wetland-draining streams (Dillon et al., 1997; Devito et al., 1999; Eimers and Dillon, 2002). Furthermore, whereas wetland-dominated catchments alternate between net SO_4 retention and net SO_4 export in wet and dry years, respectively, upland-dominated catchments exhibit net SO_4 export in every year of record (Eimers and Dillon, 2002).

Stable S isotope analysis has been used to identify sources and processes contributing to SO_4 export from catchments and is particularly appropriate for evaluating zones of SO_4 reduction (Mandernack et al., 2000; Alewell and Novak, 2001). Dissimilatory sulphate reduction (DSR) occurs under anaerobic, saturated conditions and results in marked isotopic fractionation between the ^{32}S -enriched product (lower $\delta^{34}\text{S}$) and ^{34}S -enriched reactant SO_4 (higher $\delta^{34}\text{S}$), because bacteria preferentially reduce the lighter ^{32}S when SO_4 is not limiting (Krouse and Tabatabai, 1986; Groscheova et al., 2000). Thus SO_4 in bog porewaters is generally more enriched in ^{34}S (i.e., more positive $\delta^{34}\text{SO}_4$ signature) compared to sulphides in peat, and fractionations of -11‰ to -27‰ between reactant SO_4 and product sulphide have been reported in field studies (Bottrell and Novak, 1997; Mandernack et al., 2000). Accordingly, substantial shifts in both $\delta^{34}\text{SO}_4$ and SO_4 concentrations can potentially occur in wetland outflows if dry periods result in water table draw down and oxidation of isotopically light sulphide compounds in peat (Mörth et al., 1999; Mandernack et al., 2000).

Mineralization of organic S compounds can also cause fractionation among S isotopes, although differences between reactants and products are generally smaller than for DSR (Fuller et al., 1986; Novak et al., 1995; Alewell and Gehre, 1999). At the Hubbard Brook, for example, consistently lower $\delta^{34}\text{SO}_4$ values in the upland-draining W6 stream ($+3.7\text{‰}$) compared to deposition ($+4.4\text{‰}$) were interpreted as evidence of mineralization (Zhang et al., 1998; Alewell et al., 1999), and Norman et al. (2001) documented a decrease in $\delta^{34}\text{SO}_4$ of $<1.5\text{‰}$ in SO_4 released from organic matter in a laboratory study. Similarly, plant assimilation of S has been associated with isotopic fractionation, with preferential accumulation of ^{32}S in plant tissues (Novak et al., 2001). Weathering may also contribute to spatial variations in $\delta^{34}\text{SO}_4$ values in catchments that have sizeable deposits of S-bearing minerals (Fitzhugh et al., 2001; Mitchell et al., 2001).

Variations in S isotopes in stream water may therefore be used to identify the sources of SO_4 as well as processes such as oxidation, reduction, and mineralization. The goal of this study was to contrast S concentrations and isotope values in upland

compared to wetland-draining streams by making intensive measurements at a representative catchment containing separately gauged upland, and wetland-dominated subcatchments. Our aim was to determine whether net S export from uplands was due to release from "mini wetlands" in the upland, namely S-rich streambed soil (often covered by *Sphagnum*), where similar precipitation-related variations in water table height presumably cause comparable changes in redox, or S-storage conditions; or conversely, whether net S export from uplands could be attributed to release from soil pools (e.g., via mineralization), as has been shown at European catchments using combined isotope/mass balance approaches (Novak et al., 2000). Identification of the source and processes controlling net SO_4 export from catchments is of critical importance, because SO_4 leaching drives the loss of base cations from soils and can lead to soil acidification. In this respect, the attribution of net S export to release from wetland pools (including "mini wetlands" in upland streambeds) would have less relevance for base cation losses from upland soils, but would still affect the SO_4 status of downstream lakes.

2. STUDY SITE

The study was conducted in the 23.3 ha Plastic Lake-1 (PC1) catchment, located in Haliburton County, Ontario, on a southern extension of the Precambrian Shield. Average annual precipitation depth in this region is 991 ± 132 mm (1980–2002); with average seasonal accumulations of 234 ± 76 , 305 ± 63 , 230 ± 50 , and 223 ± 50 mm in the summer, fall, winter, and spring, respectively. The annual average temperature is 5°C ; summer and winter averages are 18°C and -11°C , respectively.

The layout of the PC1 catchment (elevation range 380–420 m a.s.l.) is particularly relevant to this study, because it contains both upland and wetland areas, which are separately gauged for stream flow and chemistry (Fig. 1). More than 85% of the runoff from the PC1 catchment funnels through a 2.2-ha *Sphagnum*-dominated conifer swamp before discharging to the lake due to its location at the base of the catchment (Fig. 1). Runoff from the upland (PC1-08 subcatchment) enters the swamp as stream flow along its northeast border (Fig. 1). The upland stream is approximately 200 m in length, and occupies a narrow fault trough. The streambed is flanked by two steep convex side slopes and is underlain by relatively deep (up to 1.2 m) gleysols and histosols (Buttle and House, 1997). The streambed occupies an area of ~ 1100 m², and total S concentrations in streambed soil (top 40 cm) range from 900 to 1600 mg S/kg (~ 900 kg S/ha). In comparison, soils on the upland side slopes are generally thin (average 40 cm), coarse-textured (90% sand) humo-ferric and ferro-humic podzols underlain by granitic gneiss bedrock and thin (<1 m) sandy basal till deposits, and bedrock outcrops cover $\sim 10\%$ of the PC1 catchment (LaZerte and Scott, 1996; Canadian System of Soil Classification, 1998). Total S concentrations in upland soil are generally lower than in the streambed, and range from 300–600 mg S/kg in B-horizon mineral soil to 1000–2000 mg S/kg in the forest floor (LFH), respectively. The total S pool in upland soil (depth ~ 40 cm) was estimated to be around 900 kg S/ha, similar to the streambed pool (Neary et al., 1987; Eimers et al., 2004). The swamp, which is situated

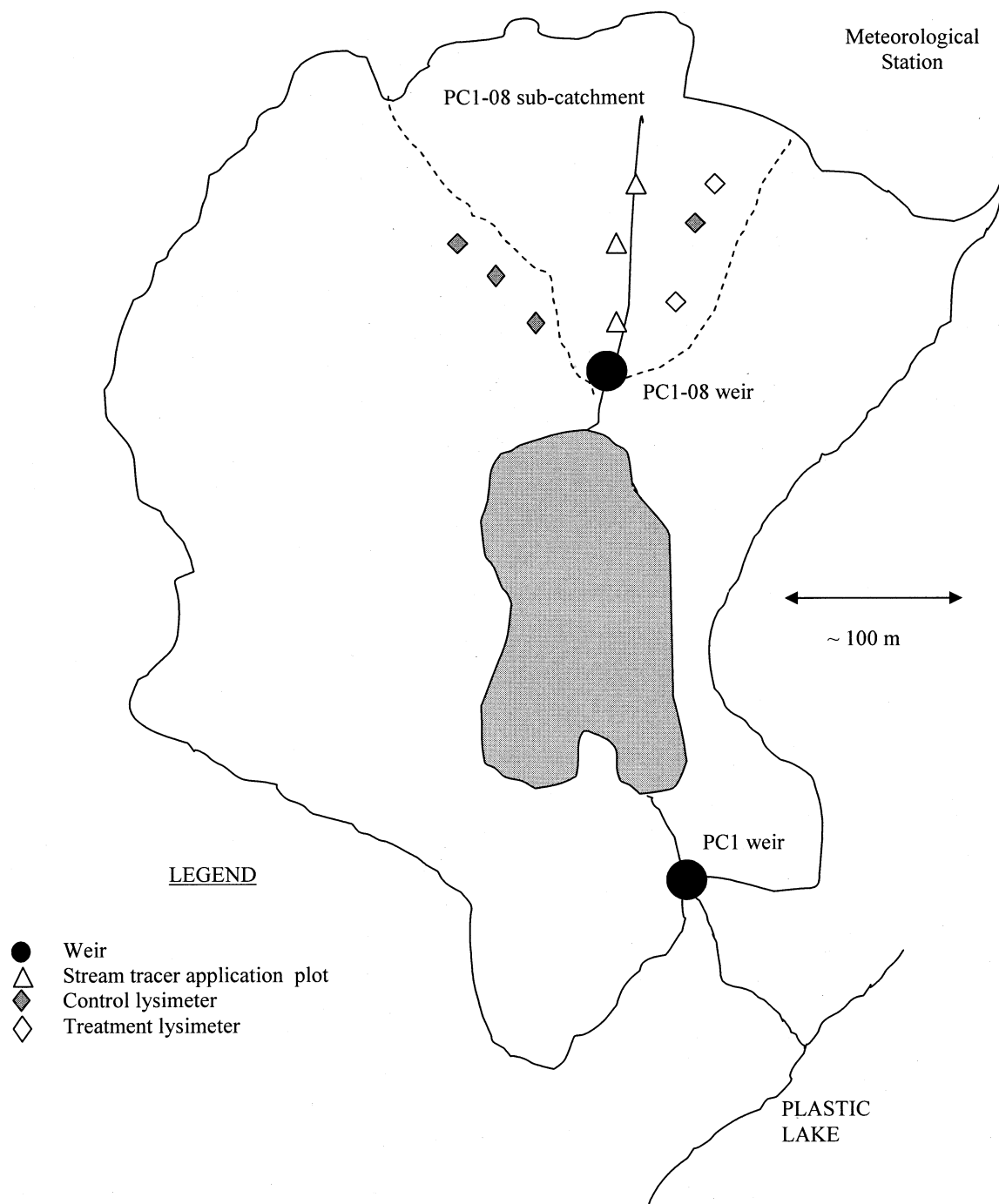


Fig. 1. Plastic Lake-1 (PC1) study catchment. Location of lysimeters and tracer application plots are indicated. Shaded area in centre of catchment indicates 2.2-ha conifer-*Sphagnum* swamp.

in a local bedrock depression, contains deep peat deposits (average 2–3 m in depth, maximum 7 m), which have high total S concentrations (2000–7000 mg S/kg). Devito and Hill (1999) estimated S storage in the top 40 cm of peat to be ~1600 kg S/ha. Vegetation in the upland is dominated by mature (average age 87 yr; baseline 2000) white pine (*Pinus strobus*) and eastern hemlock (*Tsuga canadensis*). Ground-cover in the swamp is primarily *Sphagnum* species, while

white cedar (*Thuja occidentalis*), black spruce (*Picea mariana*), and alder (*Alnus spp.*) are the dominant tree species (Watmough and Dillon, 2001).

3. MATERIAL AND METHODS

3.1. Sample Collection and SO₄ Analysis

Six zero-tension lysimeters (installed in 1987) are located at various sites in the upland portion of PC1 (Fig. 1), and were used to collect soil

percolate from beneath the LFH (0–10 cm), Ae (upper mineral soil horizon, zone of eluviation; 10–13 cm), and B (lower mineral soil horizon, zone of illuviation; 13–60 cm) horizons for chemical and isotopic analyses (LaZerte and Scott, 1996). Soil percolate was collected for chemical and isotopic analyses weekly, or more frequently after large storm events.

Stream water was collected for chemical concentration and isotopic analyses at weirs located at the outflows of the upland subcatchment (PC1-08) and at the base of the PC1 catchment downstream of the swamp (Fig. 1). Grab samples of stream water were collected on a weekly basis, or more frequently during periods of high flow. Stream stage is monitored continuously, and discharge was computed using established stage-discharge relationships.

Bulk deposition (defined as that caught in a continuously-open collector; surface area 0.25 m²) was collected less than 30 m away from the PC1 catchment boundary at a meteorological site maintained by the Ontario Ministry of Environment in Dorset. Continuous monitoring of precipitation depth and air temperature also occurs at this site. Bulk deposition was generally collected on a weekly basis, or more frequently after large storm events.

Water samples were analyzed for SO₄ by ion chromatography at the Ontario Ministry of Environment Dorset Research Centre. Sulphate fluxes (kg/ha) in bulk deposition and stream water were calculated as the product of SO₄ concentration and water volume and summed for each hydrologic year (June 1–May 31) of the 1999/2000–2000/2001 study period (Eimers and Dillon, 2002).

Depth to the water table in the PC1-08 streambed was monitored at 23 groundwater wells distributed along its length at least twice weekly over a 7-month period (May 2000–November 2000). A relationship between average depth to water table (WL; cm) and flow (Q; m³/d) at the PC1-08 weir (i.e., WL = 31*log(Q)–47; R² = 0.87, *p* < 0.001) was established, which allowed water table height in the stream to be extrapolated over the entire study period (June 1999–May 2001). Similarly, an equation relating water table height in the swamp with flow at the swamp outlet (PC1 weir) was established (i.e., WL = 1.9*ln(Q) – 25; R² = 0.91, *p* < 0.001), which enabled average daily water table height in the swamp to be estimated over the 1999–2001 monitoring period.

3.2. Isotopic Analysis

Sulphate in water samples was recovered on ion exchange (BioRad AG-1-X8) columns and precipitated as BaSO₄ using a method similar to that described in Hesslein et al. (1988). All isotopic and total S analyses were carried out at the University of Waterloo Environmental Isotope Laboratory, using a continuous flow Micromass IsoChrom isotope ratio mass spectrometer coupled to a Carlo Erba elemental analyzer (EA/IRMS). Analytical precision for S-isotope measurements was 0.2‰. Sulphur isotope ratios are expressed in the standard δ³⁴S notation as parts per thousand enrichment or depletion in the ratio of ³⁴S:³²S relative to the Canyon Diablo Troilite (CDT) standard:

$$\delta^{34}\text{S}_{\text{sample}}(\text{‰}) = \frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}} - (^{34}\text{S}/^{32}\text{S})_{\text{standard}}}{(^{34}\text{S}/^{32}\text{S})_{\text{standard}}} \times 1000$$

To examine potential changes in S content and isotopic signature with depth in peat, cores (60 cm) were extracted from three sites within the PC1 swamp in October 1999 using a Russian Peat Corer, and cores were sectioned into 10-cm depth intervals. Peat from different depth intervals was oven-dried and then ground in a Wiley Mill to obtain a fine powder before isotope and total S analysis by EA/IRMS.

3.3. ³⁴S-SO₄ Tracer Application

After 1 year of monitoring of natural variations in isotopic abundance in stream and soil water, a ³⁴S-enriched tracer (99.8% ³⁴S) was applied to two plots in the upland, and to three plots in the upland streambed on August 15, 2000 (Fig. 1). Sulphur enriched in ³⁴S was obtained from Trace Sciences Ltd. (Mississauga, Ontario) in elemental form, and was oxidized to SO₄ using a Schöniger combustion flask containing 25 mL of deionized H₂O and 2 mL 30% H₂O₂ to ensure complete oxidation to SO₄. The ³⁴S-SO₄ tracer was applied to plots in synthetic rainfall that had a similar chemistry to the current deposition

Table 1. Major element concentrations (mg/L) in synthetic rainfall used in tracer application, compared to bulk deposition chemistry at PC1 (average 1993–1998).

	S-SO ₄	Ca	Mg	NH ₄ -N	NO ₃ -N	pH
Synthetic rainfall	0.67	0.53	0.18	0.53	0.53	4.7
Bulk deposition	0.67	0.23	0.039	0.34	0.51	4.4

at PC1, and the pH was adjusted with HCl to ~4.7 (Table 1). Isotopic monitoring continued for another year after application of the tracer to evaluate its fate.

In total, 0.33 mg of ³⁴S was applied as SO₄ to each of two 2.4 m² plots on the hillslope, directly overlying lysimeter plates and to two 0.073 m² plots in the streambed (Fig. 1). At the time the tracer was applied to plots in the streambed, the water table in the stream was at least 19 cm below the soil surface. A higher dose (4.1 mg ³⁴S-SO₄) was applied to one additional plot in the streambed (Fig. 1). In total, 3 L of labeled synthetic rainfall was applied to each lysimeter plot (equivalent to a 1.25-mm rain event), and 0.5 L was applied to each stream plot (equivalent to a 6.8-mm rain event), containing either 0.33 mg ³⁴S-SO₄ or 4.1 mg ³⁴S-SO₄. Due to the very small mass of ³⁴S added relative to the size of the natural S pools in plots, the tracer was not expected to have a substantial or long-lasting effect on the δ³⁴SO₄ signature of soil percolate or stream water.

3.4. Statistical Evaluation

After confirming that data were normally distributed with equal variance, differences among mean isotope values in precipitation, soil percolate, and stream water were evaluated for significance (*p* < 0.05) using a two-tailed *t* test (SigmaStat 2.0, Jandel Scientific Co.).

4. RESULTS AND DISCUSSION

4.1. Bulk Deposition

Individual measurements of δ³⁴SO₄ in bulk deposition at PC1 ranged from +4.0 to +6.8‰ (*n* = 34) over the 1999/00–2000/01 monitoring period, with an overall arithmetic mean of +5.1 ± 0.6‰ (Fig. 2). By comparison, the mean δ³⁴S in deposition when weighted by the mass of SO₄ was also +5.1‰. Deposition δ³⁴SO₄ values measured in this study were similar to those reported by Van Stempvoort et al. (1991), who measured δ³⁴SO₄ values of +2.9 to +5.0‰ (seasonal averages) in bulk precipitation at PC1 between 1986 and 1988. The isotopic composition of bulk deposition at PC1 is comparable to values reported for the Experimental Lakes Area in north-western Ontario during the early 1980s (4-yr mean, 1982–1985: +5.0 ± 0.7‰) (Hesslein et al., 1988), the Hubbard Brook watershed in New Hampshire (28-yr mean, 1966–1994: +4.5 ± 0.5‰) (Alewell et al., 2000), and the Canadian Shield region of Quebec (range +3.1 to +6.7‰) (Caron et al., 1986). Passage of deposition through the forest canopy (throughfall) does not appear to affect the isotopic composition of SO₄ (Stam et al., 1992; Torssander and Mörth, 1998; Mörth et al., 1999), and previously reported δ³⁴SO₄ values in bulk deposition and throughfall at Plastic Lake are similar (Van Stempvoort et al., 1991). For example, pooled throughfall values of +4.3 ± 1.1 and +5.9 ± 1.3‰ were measured at PC1 in the summer and fall of 1986, respectively, compared with precipitation values over the same seasons of +3.5 ± 1.6 and +5.0 ± 0.4‰ (Van Stempvoort et al., 1991).

There was a slight tendency toward lower δ³⁴SO₄ values in bulk deposition in the summer compared with the winter months

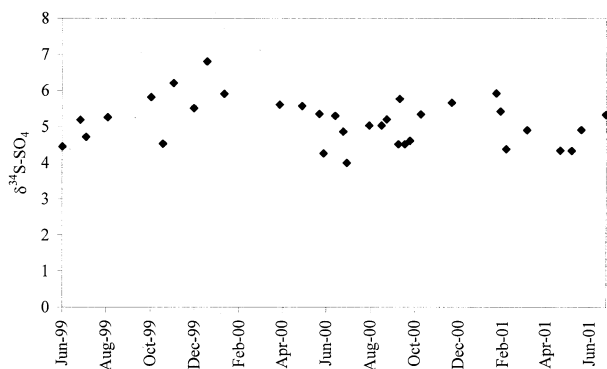


Fig. 2. Individual measurements of $\delta^{34}\text{S}\text{SO}_4$ (‰) in bulk deposition at PC1; June 1999–June 2001.

at PC1 (Fig. 2). The average $\delta^{34}\text{S}\text{SO}_4$ in bulk deposition during the “ice-free” season of April–November was $+4.9 \pm 0.5$ ‰ compared with $+5.6 \pm 0.7$ ‰ in December–March when deposition occurs mainly as snow. A similar seasonal pattern in deposition $\delta^{34}\text{S}\text{SO}_4$ has been reported at a number of sites in eastern North America, and has been attributed to either temperature-related shifts in equilibrium fractionation, or seasonal changes in the source of SO₄ in deposition, namely the relative contribution of bacteriogenic vs. marine, or anthropogenic S (Nriagu and Coker, 1987; Barrie, 1986; Van Stempvoort et al., 1991; Alewell et al., 2000).

4.2. Isotopic Composition of Upland and Wetland Drainage Streams Before ³⁴S-Tracer Application

4.2.1. Soil percolate

The isotopic composition of soil percolate was similar among all soil horizons over a 3-month period before application of a ³⁴S-enriched tracer, and was on average $+4.4 \pm 0.4$ ‰. Because accurate estimates of soil percolate volume are not available, isotope measurements in soil seepage could not

be mass weighted. However, Van Stempvoort et al. (1990) reported a similar isotopic composition of soil seepage water at PC1 ($+4.8 \pm 1.2$ ‰). There was a small but significant difference between average monthly $\delta^{34}\text{S}\text{SO}_4$ values in soil percolate before application of the tracer ($+3.8$ to $+4.7$ ‰) and the corresponding range in $\delta^{34}\text{S}\text{SO}_4$ in bulk deposition (Table 2). Similar significant patterns of $\delta^{34}\text{S}_{\text{leachate}} < \delta^{34}\text{S}_{\text{deposition}}$ were reported by Novak et al. (2000) and Zhang et al. (1998).

Similar to reports for other podzols (e.g., Houle and Carignan, 1995), SO₄ concentrations were higher in leachate draining the B-horizon compared to the LFH (Table 2; see also Eimers et al., 2004). LaZerte and Scott (1996) also measured higher SO₄ concentrations in deeper soil leachate at PC1 whereas CI showed little pattern with depth, suggesting that higher SO₄ concentrations in B-horizon leachate are due to net SO₄ release from mineral soil rather than evapo-concentration effects (Houle and Carignan, 1995).

4.2.2. Upland-draining stream (PC1-08)

Before application of a ³⁴S tracer to plots within the hillslope and streambed, $\delta^{34}\text{S}\text{SO}_4$ in upland-draining PC1-08 stream water was between $+4.7$ and $+7.4$ ‰, and was on average $+5.7 \pm 0.7$ ‰ (Fig. 3) compared to a mass-weighted average value of $+5.4$ ‰. Sulphate concentration in PC1-08 ranged from 1.5 to 2.9 mg S-SO₄/L, and was on average 2.3 ± 0.2 mg/L during the monitoring period (Fig. 4).

Between June 1999–August 2000 (i.e., pretracer application), the range in $\delta^{34}\text{S}\text{SO}_4$ values in upland stream water ($+4.0$ to $+7.4$ ‰, $n = 13$) was significantly ($p < 0.05$) higher than in soil percolate ($+3.8$ to $+5.1$ ‰, $n = 23$) but was similar to the range measured in bulk deposition ($+4.3$ to $+6.8$ ‰, $n = 18$). The relatively small number of samples over this time period makes it difficult to interpret slight differences in $\delta^{34}\text{S}\text{SO}_4$ values between soil percolate and upland stream water. However, negative $\delta^{34}\text{S}$ values (total S) have been measured in subsurface streambed soil (-0.03 ‰ at 20 cm depth, -4.4 ‰ at 40 cm depth; data not shown), which are consistent with the

Table 2. Mean (\pm SD^a) monthly $\delta^{34}\text{S}$ values and S-SO₄ concentration (mg/L) in bulk deposition, and in soil leachate from control and treatment lysimeters. Soil leachate averages for August-00 are for samples collected before application of the tracer on Aug. 15.

		LFH		Ae		B		
		Bulk dep.	Treat.	Control	Treat.	Control	Treat.	Control
Jun-99	$\delta^{34}\text{S}\text{SO}_4$	4.8 ± 0.5	4.4 ± 0.4	4.7	4.7 ± 0.2	3.8 ± 1.1	4.4 ± 0.21	-
	[S-SO ₄]	0.93	1.2 ± 0.7	1.7 ± 1.1	1.3 ± 0.5	1.7 ± 0.9	1.6 ± 0.4	3.1 ± 0.2
Jul-99	$\delta^{34}\text{S}\text{SO}_4$	4.7	4.3 ± 0.1	-	4.4	-	4.60	-
	[S-SO ₄]	0.83	1.5 ± 0.4	1.7 ± 1.2	1.3 ± 0.3	2.3 ± 1.0	2.0 ± 0.6	2.6 ± 1.0
Aug-00	$\delta^{34}\text{S}\text{SO}_4$	5.1 ± 0.1	5.0	4.6	4.4	4.4	4.7 ± 0.7	4.3
	[S-SO ₄]	0.53	1.1 ± 0.7	1.1 ± 0.4	0.7 ± 0.07	1.7 ± 0.9	1.4 ± 0.2	2.1 ± 1.0
Tracer application: August 15, 2000								
Sept-00	$\delta^{34}\text{S}\text{SO}_4$	4.8 ± 0.6	7.1 ± 0.9	5.8	7.9 ± 3.0	5.9	-	-
	[S-SO ₄]	0.8	1.8	2.1	-	2.1 ± 0.4	-	-
Oct-00	$\delta^{34}\text{S}\text{SO}_4$	5.3	-	-	-	3.0	-	-
	[S-SO ₄]	1.1	-	-	-	-	-	-
Nov-00	$\delta^{34}\text{S}\text{SO}_4$	5.7	4.9 ± 0.8	4.6	4.9 ± 0.4	4.6	4.3	-
	[S-SO ₄]	1.4	2.7 ± 0.7	3.3	-	-	-	-

^a Values presented without SD represent result of a single sample; - indicates insufficient volume for analysis.

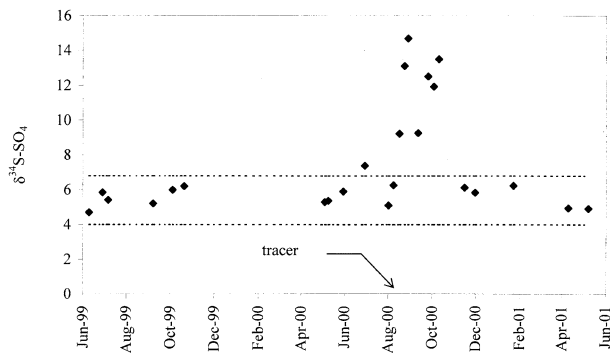


Fig. 3. $\delta^{34}\text{S}\text{-SO}_4$ values (‰) in upland stream water over a 2-yr period. Dashed lines indicate the range of $\delta^{34}\text{S}\text{-SO}_4$ in bulk deposition. A ^{34}S -enriched SO_4 tracer was applied to plots in the upland in August 2000.

occurrence of DSR in the streambed. If SO_4 concentrations are not limiting, microbial DSR favours the incorporation of ^{32}S in reduced products (sulphides) and leaves reactant SO_4 relatively enriched in ^{34}S , and therefore may have contributed to higher $\delta^{34}\text{S}\text{-SO}_4$ values in PC1-08 stream water compared to soil leachate. If DSR and reoxidation of sulphides are an important control on $\delta^{34}\text{S}\text{-SO}_4$ values in stream water, then changes in stream water table height should result in variations in $\delta^{34}\text{S}\text{-SO}_4$ and SO_4 concentrations. Previous studies have reported a significant negative relationship between stream $\delta^{34}\text{S}\text{-SO}_4$ values and both stream flow and SO_4 concentrations, and concluded that oxidation of reduced S (i.e., ^{34}S depleted) stored in the catchment was the only process which could account for increased concentrations of isotopically light SO_4 after dry periods (Hesslein et al., 1988; Mörth et al., 1999). Stream flow ceased in PC1-08 for 17 and 35 d in 1999/00 and 2000/01, respectively and the streambed water table declined by more than 40 cm during periods of zero flow (Fig. 4). There was no relationship between $\delta^{34}\text{S}\text{-SO}_4$ and SO_4 concentration in upland stream water during the pretracer monitoring period (Fig. 5), despite large variations in streambed water table level over the same time period (Fig. 4). Consideration of the pretracer period alone suggests that DSR and reoxidation of sulphide compounds are not important contributors to SO_4 export patterns at

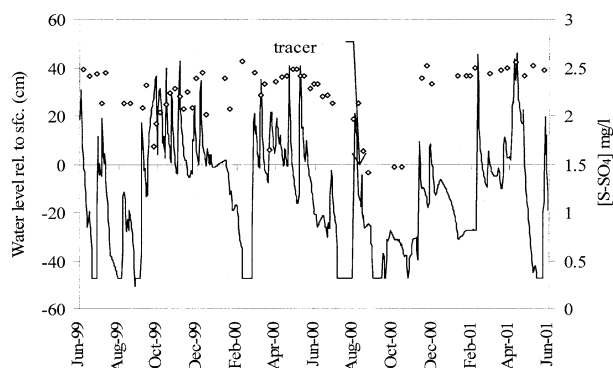


Fig. 4. Water table level (cm; solid line) relative to the streambed surface in PC1-08 and S- SO_4 concentration in upland stream water (mg/L; open diamonds).

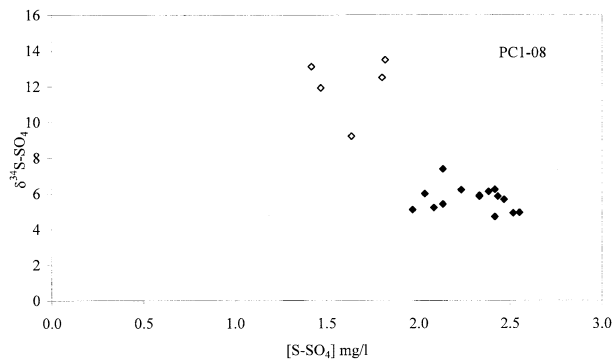


Fig. 5. $\delta^{34}\text{S}\text{-SO}_4$ (‰) vs. SO_4 concentration (mg/L) in upland-draining PC1-08 stream; closed diamonds indicate pretracer measurements, open diamonds are values measured after application of a ^{34}S -enriched SO_4 tracer to plots in the upland.

PC1-08. However, the ^{34}S -enriched tracer was applied during an extended dry period, when the water table remained more than 25 cm below the surface for more than 2 months (Fig. 4). While elevated $\delta^{34}\text{S}$ values in PC1-08 stream water measured during intermittent periods of flow after the tracer was applied may be due to release of ^{34}S from application plots, they could also indicate the occurrence of DSR in the streambed. As a result, SO_4 reduction in stagnant water below the streambed water table may have contributed to elevated $\delta^{34}\text{S}\text{-SO}_4$ values and low SO_4 concentrations measured in PC1-08 during the August–October 2000 period (Figs. 3 and 4). Nevertheless, while SO_4 concentrations rose after this dry period, $\delta^{34}\text{S}\text{-SO}_4$ values did not decline below the range measured in deposition or soil leachate, indicating that reoxidation of reduced sulphides was not an important contributor to SO_4 export in the upland stream.

4.2.3. Wetland-draining stream (PC1)

The isotopic composition of stream water draining the conifer *Sphagnum* swamp (PC1) was variable, but $\delta^{34}\text{S}\text{-SO}_4$ values in PC1 were significantly ($p < 0.05$) higher than values in the upland-draining inflow and bulk deposition, respectively (Fig. 6). Over the 2-yr monitoring period, $\delta^{34}\text{S}\text{-SO}_4$ in the swamp outflow ranged from +4.8 to +13.5‰, and was on average $+8.6 \pm 2.6\%$ compared to a mass-weighted average of +7.9‰. A comparatively low mass-weighted average suggests that the majority of SO_4 export from PC1 contains relatively little ^{34}S , whereas preferential bacterial reduction of ^{32}S during low flow periods results in decreased SO_4 concentrations (and export) and higher $\delta^{34}\text{S}$ values. The average SO_4 concentration in the swamp outflow (1.5 ± 0.6 mg S- SO_4 /L) was lower than in the upland-draining inflow and ranged from 0.15 to 2.9 mg S- SO_4 /L over the 1999–2001 monitoring period (Fig. 7). There was no relationship between $\delta^{34}\text{S}\text{-SO}_4$ in PC1 stream water and SO_4 concentrations over the relatively wet period of study (Fig. 8).

However, in contrast to the upland-draining PC1-08 stream, the water table in the swamp exhibited less variation over time, and was generally within 10 cm of the peat surface during the monitoring period (Fig. 7). Similarly, PC1 stream flow was continuous over the 2-yr study period except for 8 d in 1999/00. Wet conditions which maintained a continuously high water

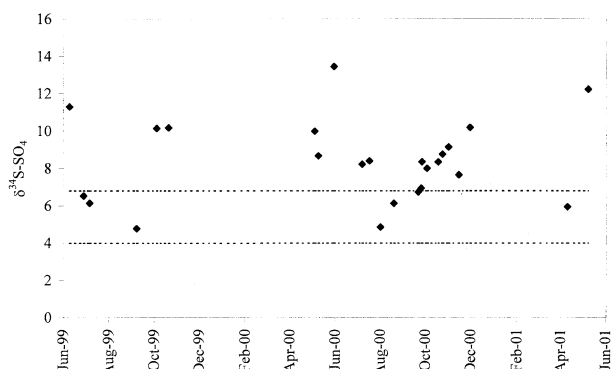


Fig. 6. $\delta^{34}\text{S-SO}_4$ values (‰) in wetland-draining PC1 stream water over a 2-yr period. Dashed lines indicate the range of $\delta^{34}\text{S-SO}_4$ in bulk deposition.

table would have favoured the development of reducing conditions in the swamp (Devito and Hill, 1999), and isotopic fractionations associated with DSR likely explain lower SO₄ concentrations and generally higher $\delta^{34}\text{S-SO}_4$ values in the swamp outflow relative to the upland-draining PC1-08 stream.

Evidence of preferential microbial reduction (DSR) of isotopically-light S in peat was indicated by the analysis of total S in three cores within the PC1 swamp. Total $\delta^{34}\text{S}$ values in the top 60 cm of peat were between -1.5 and $+3.2$ ‰ in the top 20 cm (data not shown). Additionally, total S concentrations in peat were high (2180–6560 mg S/kg) relative to total S concentrations in mineral soil (300–600 mg S/kg) or LFH (1000–2000 mg S/kg) at PC1, and the swamp represents a large pool of total S (i.e., 1600 kg S/ha in the upper 40 cm; Devito and Hill, 1999). High S concentrations (1000–10,000 mg S/kg) and relatively low isotope values in near-surface peat compared to deposition inputs have also been reported for peatlands in the United States and the Czech Republic (Novak et al., 1994).

The relatively few occasions when $\delta^{34}\text{S-SO}_4$ ratios in the swamp outflow fell within the range in bulk deposition (Fig. 6), tended to follow periods in which the water table in the swamp was depressed, and were accompanied by slight increases in SO₄ concentration (Fig. 7). Lighter $\delta^{34}\text{S-SO}_4$ values in PC1 after relatively dry periods may be due to export of ³²S-enriched SO₄

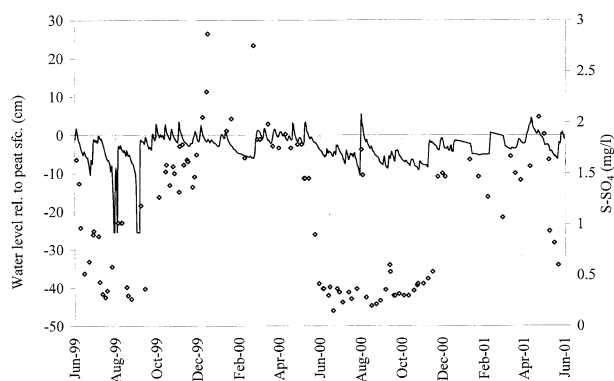


Fig. 7. Water table level (cm; solid line) relative to the peat surface (line) in the PC1 swamp and SO₄ concentration (mg S-SO₄/L; open diamonds) in the swamp outflow.

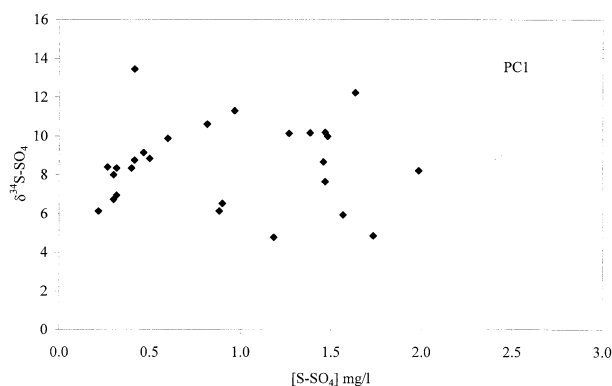


Fig. 8. $\delta^{34}\text{S-SO}_4$ (‰) vs. S-SO₄ concentration (mg/L) in the wetland outflow (PC1).

after periods of sulphide oxidation. However, further measurements over extended dry periods would be necessary to confirm this hypothesis, and to determine whether a relationship between $\delta^{34}\text{S-SO}_4$ and SO₄ concentration exists over a broader range of hydrologic conditions than occurred during the 1999–2001 period of measure (Fig. 8).

4.3. Effect of SO₄ Reduction and S Oxidation on Net SO₄ Export from the PC1 Catchment

In this region, summer rainfall is the primary determinant of changes in water table height and the duration of stream dryness, and the summers (June–August) of 1999/00 (274 mm) and 2000/01 (317 mm) were much wetter than previous years (1980–1998 average 236 mm) when substantial net SO₄ export was measured in PC1 (LaZerte, 1993; Devito, 1995; Devito and Hill, 1999; Devito et al., 1999; Eimers and Dillon, 2002). Net SO₄ export from PC1 was 3.3 and 1.0 kg S-SO₄/ha in 1999/00 and 2000/01 (Table 3), respectively compared to an average net export of 4.3 kg S-SO₄/ha/yr during the period 1980–1998 (Eimers and Dillon, 2002). Thus, small changes in $\delta^{34}\text{S-SO}_4$ and SO₄ concentrations as were measured in this study, are likely not indicative of patterns in previous dry years, particularly in the mid 1980s, when water table declines of up to -60 cm relative to the peat surface were measured (Devito and Hill, 1999).

In contrast, SO₄ export from the upland PC1-08 catchment exceeded input in bulk deposition by 7.3 and 3.3 kg S-SO₄/ha in 1999/00 and 2000/01, respectively (Table 3), compared to an average net export in previous years of monitoring (1983–1995) of 6.3 kg S-SO₄/ha/yr (Eimers et al., 2004). Despite relatively wet conditions during the two summers of study, PC1-08 ceased to flow for 17 and 35 d in 1999/00 and 2000/01, respectively, compared to an average of 57 d per year with zero-stream flow over the period 1983–1995 (Eimers and Dillon, 2002). Because SO₄ export and hydrologic conditions during the period of study were relatively similar to earlier years of record, it is likely that $\delta^{34}\text{S-SO}_4$ values measured in PC1-08 stream water during 1999–2001 were also typical of previous years. These results indicate that while DSR may contribute to elevated $\delta^{34}\text{S-SO}_4$ values and lower SO₄ concentrations during stagnant periods, such as August–October 2000, net SO₄ export from the upland catchment is not a result of

Table 3. Sulphate input-output budgets (kg/ha S-SO₄) for PC1-08 (upland) and PC1 (wetland-draining) catchments.

	Deposition	PC1-08 stream export	Deposition-PC1-08 export	PC1 stream export	Deposition-PC1 export
1999/00	7.0	14.3	-7.3	10.3	-3.3
2000/01	5.0	8.3	-3.3	6.0	-1.0

reoxidation of sulphide compounds in streambed soil, but is rather a result of loss from upland mineral soil. A combination of SO₄ desorption and mineralization of organic S compounds in mineral soil is likely responsible for net SO₄ losses from the PC1-08 upland, as has been suggested by other studies (e.g., Houle and Carignan, 1995; Novak et al., 2000). Sulphate desorption is suggested by the relative constancy of SO₄ concentrations in both B-horizon leachate and PC1-08 stream water (Eimers et al., 2004), whereas mineralization or weathering might explain slight differences in δ³⁴SO₄ values among bulk deposition, soil leachate, and upland stream water, respectively (Zhang et al., 1998; Alewell et al., 1999; Novak et al., 1995; Novak et al., 2000; Mitchell et al., 2001).

Comparison of SO₄ export from the upland and the wetland-draining portions of the PC1 catchment respectively, indicated that the swamp retained SO₄ (~25% of total input) in both years of study and that net export from PC1 was entirely from the upland part of the catchment (Table 4). Similarly, LaZerte (1993) calculated SO₄ input-output budgets for the PC1 swamp over the period 1983–1990 and found that SO₄ was retained during normal and wet years, but was exported in excess (-8 to -32% of total inputs) in years that had dry summers. Net SO₄ retention corresponded to 30 and 20 kg S/ha of swamp surface area in 1999/00 and 2000/01, respectively, compared to a total S pool of ~1600 kg S/ha in the upper 40 cm of peat (Devito and Hill, 1999).

4.4. Isotopic Composition of Upland and Wetland Drainage Waters After Tracer Application

4.4.1. Soil percolate

After application of a ³⁴S-enriched tracer to soil above two treatment lysimeters, the δ³⁴S signal increased to more than +7‰ in LFH and Ae percolate in September 2000 (Table 2). However, by November 2000 δ³⁴SO₄ values in soil percolate from control and treatment lysimeters were less than +5‰, and were similar to values measured before application (Table 2). These results indicate that either a) the tracer had been flushed from the upland plots by this time, or b) mixing of the small mass of tracer within the relatively large pool of ambient S in plots had diluted the tracer signal to below detection. Although all surface vegetation was removed from plots before tracer application, it is possible that roots of trees from outside the plots could have accumulated some

of the enriched ³⁴SO₄. The most direct way to assess within-plot retention of the tracer would have been to measure δ³⁴S signals in soil samples from the treatment plots. However, SO₄ extracts of soil did not produce sufficient mass of BaSO₄ to be analyzed by IRMS, and soil could not be analyzed directly due its low S and high inorganic content.

However, the mass of ³⁴S which must have been present in soil percolate to increase the δ³⁴SO₄ signature from background values to around +7.5‰, as was measured in treatment lysimeters in September 2000 (Table 2), could only account for ~15% of the total mass of ³⁴S applied to lysimeter plots. Therefore, although a small portion of ³⁴S-enriched SO₄ was immediately lost in soil percolate, the majority was at least temporarily retained in upland soil plots. By November 7, δ³⁴SO₄ values in control and treatment lysimeters were similar (Table 2), likely due to retention (and dilution) of the tracer in soil and vegetation.

4.4.2. Upland-draining stream (PC1-08)

Maximum δ³⁴SO₄ values in PC1-08 were measured immediately after the application of a ³⁴S-enriched tracer to sites within the upland hillslope and streambed (Fig. 2). Elevated δ³⁴S values were measured in PC1-08 stream water on seven dates between August 16 and October 10 inclusive, but by November 15, 2000, isotope signatures had returned to preapplication values (Fig. 2). Complete flushing of the tracer from the catchment and/or a gradual mixing and dilution of the isotope signal over time may explain the return of δ³⁴SO₄ in stream water to preapplication values. As with upland soil plots, it is possible to roughly calculate the mass of ³⁴S exported in stream water over the period during which δ³⁴S values were elevated, and to compare this estimate with the actual amount of ³⁴S added to treatment plots. Using daily flow measurements at the PC1-08 weir and weekly SO₄ chemistry data, it was estimated that approximately 215 g S-SO₄ was exported from the catchment between August 16 and October 10, 2000 inclusive (Fig. 9). Using a mass-weighted average δ³⁴SO₄ in stream water during this period of +9.0‰ (205.67 g ³²S and 9.34 g ³⁴S) and a preapplication δ³⁴SO₄ of +5.7‰ (205.69 g ³²S and 9.31 g ³⁴S), it was calculated by difference, that an additional ~30 mg ³⁴S would have had to be present in stream water to increase the δ³⁴SO₄ from +5.7 to +9‰. This

Table 4. Sulphate input-output budget for PC1 swamp.

	S-SO ₄ input (kg) from upland (18.64 ha)	Direct S-SO ₄ (kg) deposition to swamp (2.2 ha)	Total input (kg S-SO ₄) (20.84 ha)	Swamp + upland export (kg S-SO ₄) (20.84 ha)	Input - Export kg S-SO ₄
1999/00	267	15	282	215	67
2000/01	155	11	166	125	41

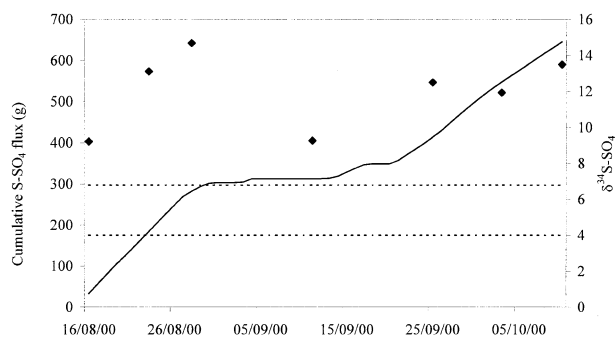


Fig. 9. Cumulative SO₄ flux (line) and δ³⁴S-SO₄ (diamonds) in PC1-08 Aug. 16, 2000. Dashed lines indicate range in δ³⁴S-SO₄ in bulk deposition.

estimate is sixfold higher than the actual mass of ³⁴S that was applied to stream plots (4.76 mg ³⁴S). A difference of 29 mg ³⁴S is relatively small compared to the mass of S flux over the same time period (215 g S), and may be due to inaccuracies in the SO₄ flux calculation, but as discussed earlier, could also indicate the occurrence of SO₄ reduction in the streambed.

5. CONCLUSIONS

Sulphate mass balance budgets for the PC1 catchment indicated that net SO₄ losses were entirely from the upland (PC1-08) part of the catchment. Despite large variations in water table height and negative total δ³⁴S values in upland streambed soil, δ³⁴S-SO₄ values in PC1-08 stream water were relatively constant during the pre-tracer period. While higher δ³⁴S values and lower SO₄ concentrations in PC1-08 during the posttracer period may in part be due to DSR, the opposite pattern was not evident, and reoxidation of sulphide compounds in streambed soil is not an important contributor to SO₄ export from the upland. Instead, net SO₄ export from the upland is likely due to desorption and/or net mineralization in mineral soil. A conifer *Sphagnum* swamp retained SO₄ over the relatively wet 2-yr study period, and high δ³⁴S-SO₄ values and low SO₄ concentrations in the swamp outlet are consistent with SO₄ retention in the swamp through DSR. Presumably, in the absence of the wetland, SO₄ export from PC1 would be similar to that measured in the upland-draining catchment PC1-08. Although the 1999–2001 study period was relatively wet, summer droughts are common in this region (Dillon et al., 1997), and future droughts which result in major declines in wetland water table height may result in lower δ³⁴S-SO₄ values in the wetland outflow. Results of this study confirm those presented by LaZerte (1993) and Devito (1995), who reported that the swamp at PC1 was a net sink for SO₄ in wet years, but was an important source of SO₄ after droughts. While SO₄ export from wetlands is responsible for large peaks in SO₄ concentration and greater net export after droughts, upland soil at PC1 is consistently a net source of SO₄ in both wet and dry years. Sulphate leaching from upland forest soils drives base cation losses, and net SO₄ export may have negative consequences for soils that have low base cation reserves. Further, the net release of SO₄ from terrestrial catchments will maintain relatively high SO₄ inputs to downstream lakes and delay their response to decreases in SO₄ deposition.

Acknowledgments—This work was carried out as part of a NSERC/Ontario Power Generation Inc. Industrial Chair held by P.J.D. at Trent

University. An NSERC PGSB to M.C.E. is gratefully acknowledged. Special thanks to Ron Ingram, Sheila Davids, and Heather Broadbent for assistance with sulphate extractions, Carolyn Paterson, Lem Scott, and Geoff Eerkes for field support, and Richard Elgood for S-isotope analyses. Particular thanks to Shaun Watmough for useful discussions on the project. Comments by the associate editor Dr. Martin Novak, Dr. Dale Van Stempvoort, and two anonymous reviewers improved the final version of the manuscript.

Associate editor: M. Novak

REFERENCES

- Alewell C., Armbruster M., Bittersohl J., Evans C. D., Meesenburg H., Moritz K., and Prechtel A. (2001) Are there signs of acidification reversal in freshwaters of the low mountain ranges in Germany? *Hydrol. Earth Syst. Sci.* **5**, 367–378.
- Alewell C. and Novak M. (2001) Spotting zones of dissimilatory sulfate reduction in a forested catchment: The ³⁴S-³⁵S approach. *Environ. Pollut.* **112**, 369–377.
- Alewell C., Mitchell M. J., Likens G. E., and Krouse R. (2000) Assessing the origin of sulfate deposition at the Hubbard Brook Experimental Forest. *J. Environ. Qual.* **29**, 759–767.
- Alewell C. and Gehre M. (1999) Patterns of stable S isotopes in a forested catchment as indicators for biological S turnover. *Biogeochem.* **47**, 317–331.
- Alewell C., Mitchell M. J., Likens G. E., and Krouse H. R. (1999) Sources of stream sulfate at the Hubbard Brook Experimental Forest: Long-term analyses using stable isotopes. *Biogeochem.* **44**, 281–299.
- Barrie L. A. (1986) Background pollution in the Arctic air mass and its relevance to North American acid rain studies. *Wat. Air Soil Pollut.* **30**, 765–777.
- Bayley S. E., Behr R. S., and Kelly C. A. (1986) Retention and release of S from a freshwater wetland. *Wat. Air Soil Pollut.* **31**, 101–114.
- Bottrell S. H. and Novak M. (1997) Sulphur isotopic study of two pristine *Sphagnum* bogs in the western Br. Isles. *J. Ecol.* **82**, 125–132.
- Buttle J. M. and House D. A. (1997) Spatial variability of saturated hydraulic conductivity in shallow macroporous soils in a forested basin. *J. Hydrol.* **203**, 127–142.
- The Canadian System of Soil Classification*, 3rd ed. (1998) Agriculture and Agri-Food Canada Publication. **1646**, 187 pp.
- Caron F., Tessier A., Kramer J. R., Schwarcz H. P., and Rees C. E. (1986) Sulfur and oxygen isotopes in precipitation and lakewater, Quebec, Canada. *Appl. Geochem.* **1**, 601–606.
- Devito K. D., Hill A. R., and Dillon P. J. (1999) Episodic sulphate export from wetlands in acidified headwater catchments: Prediction at the landscape scale. *Biogeochem.* **44**, 187–203.
- Devito K. D. and Hill A. R. (1999) Sulphate mobilization and pore water chemistry in relation to groundwater hydrology and summer drought in two conifer swamps on the Canadian Shield. *Wat. Air Soil Pollut.* **113**, 97–114.
- Devito K. J. (1995) Sulphate mass balances of Precambrian Shield wetlands: The influence of catchment hydrology. *Can. J. Fish. Aquat. Sci.* **52**, 1750–1760.
- Dillon P. J., Molot L. A., and Futter M. J. (1997) Effect of El Niño-related drought on the recovery of acidified lakes. *Environ. Monit. Assess.* **46**, 105–112.
- Dillon P. J. and LaZerte B. D. (1992) Response of the Plastic Lake Catchment, Ontario, to reduced sulphur deposition. *Environ. Pollut.* **77**, 211–217.
- Dillon P. J., Lulis M., Reid R. A., and Yap D. (1988) Ten-year trends in sulphate, nitrate and hydrogen deposition in central Ontario. *Atmos. Environ.* **22**, 901–905.
- Driscoll C. T., Likens G. E., and Church M. R. (1998) Recovery of surface waters in the northeastern U.S. from decreases in atmospheric deposition of sulfur. *Wat. Air Soil Pollut.* **105**, 409–415.
- Eimers M. C., Dillon P. J., and Schiff S. L. (2004) Sulphate flux from an upland forested catchment in south-central Ontario Canada. *Wat. Air Soil Pollut.* **152**, 3–22.

- Eimers M. C. and Dillon P. J. (2002) Climate effects on sulphate flux from forested catchments in south-central Ontario. *Biogeochem.* **61**, 337–355.
- Fitzhugh R. D., Furman T., and Korsak A. K. (2001) Sources of stream sulphate in headwater catchments in the Otter Creek Wilderness, West Virginia, USA. *Hydrol. Process.* **15**, 541–556.
- Fuller R. D., Mitchell M. J., Krouse H. R., Wykowski B. J., and Driscoll C. T. (1986) Stable sulfur isotope ratios as a tool for interpreting ecosystem sulfur dynamics. *Wat. Air Soil Pollut.* **28**, 163–171.
- Groscheova H., Novak M., and Alewell C. (2000) Changes in the delta ^{34}S ratio of pore-water sulfate in incubated *Sphagnum* peat. *Wetlands* **20**, 62–69.
- Hesslein R. H., Capel M. J., and Fox D. E. (1988) Stable isotopes in sulfate in the inputs and outputs of a Canadian Shield watershed. *Biogeochem.* **5**, 263–273.
- Hornbeck J. W., Bailey S. W., Buso D. C., and Shanley J. B. (1997) Streamwater chemistry and nutrient budgets for forested watersheds in New England: Variability and management implications. *For. Ecol. Manage.* **93**, 73–89.
- Houle D., Paquin R., Camire C., Ouimet R., and Duchesne L. (1997) Response of the Lake Clair Watershed (Duchesnay, Quebec) to changes in precipitation chemistry (1988–1994). *Can. J. For. Res.* **27**, 1819–1821.
- Houle D. and Carignan R. (1995) Role of SO_4 adsorption and desorption in the long-term S budget of a coniferous catchment on the Canadian Shield. *Biogeochem.* **28**, 162–182.
- Jeffries D. S., Semkin R. G., Beall F. D., and Franklyn, J. (2002) Temporal trends in water chemistry in the Turkey Lakes Watershed, Ontario, Canada, 1982–1999. *Wat. Air Soil Pollut. Focus* **2**, 5–22.
- Jeffries D. S. and Snyder W. R. (1983) *Geology and geochemistry of the Muskoka-Haliburton study area*. Ontario Ministry of the Environment. DR 83/2.
- Krouse H. R. and Tabatabai M. A. (1986) Stable sulfur isotopes. In *Sulfur in Agriculture*, Soil Science Society of America, Wisconsin.
- LaZerte B. D. and Scott L. (1996) Soil water leachate from two forested catchments on the Precambrian Shield, Ontario. *Can. J. For. Res.* **26**, 1353–1365.
- LaZerte B. D. (1993) The impact of drought and acidification on the chemical exports from a minerotrophic conifer swamp. *Biogeochem.* **18**, 153–175.
- Löfgren S., Bringmark L., Aastrup M., Hultberg H., Kindbom K., and Kvarnas H. (2001) Sulphur balances and dynamics in three forested catchments in Sweden. *Wat. Air Soil Pollut.* **130**, 631–636.
- Mandernack K. W., Lynch L., Krouse H. R., and Morgan M. D. (2000) Sulfur cycling in wetland peat of the New Jersey Pinelands and its effect on stream water chemistry. *Geochim. Cosmochim. Acta* **64**, 3949–3964.
- Mitchell M. J., Mayer B., Bailey S. W., Hornbeck J. W., Alewell C., Driscoll C. T., and Likens G. E. (2001). Use of stable isotope ratios for evaluating sulfur sources and losses at the Hubbard Brook Experimental Forest. *Wat. Air Soil Pollut.* **130**, 75–86.
- Mitchell M. J., Driscoll C. T., and Raynal D. J. (1996) Biogeochemistry of a forested watershed in the central Adirondack Mountains: Temporal changes and mass balances. *Wat. Air Soil Pollut.* **88**, 355–369.
- Mörth C. M., Torssander P., Kusakabe M., and Hultberg H. (1999) Sulfur isotope values in a forested catchment over four years: Evidence for oxidation and reduction processes. *Biogeochem.* **44**, 51–71.
- Neary A. J., Mistry E., and Vanderstar L. (1987) Sulphate relationships in some central Ontario forest soils. *Can. J. Soil Sci.* **67**, 341–352.
- Norman A. L., Giesemann A., Krouse H. R., and Jager H. J. (2001) Sulphur isotope fractionation during sulphur mineralization: Results of an incubation-extraction experiment with a Black Forest soil. *Soil Biol. Biochem.* **34**, 1425–1438.
- Novak M., Bottrell S. H., and Prechova E. (2001) Sulfur isotope inventories of atmospheric deposition, spruce forest floor and living *Sphagnum* along a NW-SE transect across Europe. *Biogeochem.* **53**, 23–50.
- Novak M., Kirchner J. W., Groscheova H., Havel M., Cerny J., Krejc R., and Buzek F. (2000) Sulfur isotope dynamics in two central European watersheds affected by high atmospheric deposition of SO_x . *Geochim. Cosmochim. Acta* **64**, 367–383.
- Novak M., Bottrell S. H., Fottova D., Buzek F., Groscheova H., and Zak K. (1996) Sulfur isotope signals in forest soils of central Europe along an air pollution gradient. *Env. Sci. Technol.* **30**, 3473–3476.
- Novak M., Bottrell S. H., Groscheova H., Buzek F., and Cerny J. (1995) Sulphur isotope characteristics of two North Bohemian forest catchments. *Wat. Air Soil Pollut.* **85**, 1641–1646.
- Novak M., Wieder R. K., and Schell W. R. (1994) Sulfur during early diagenesis in *Sphagnum* peat: Insights from $\delta^{34}\text{S}$ ratios in ^{210}Pb -dated cores. *Limnol. Oceanogr.* **39**, 1172–1185.
- Nriagu J. O. and Coker R. D. (1987) Biogenic sulfur and the acidity of rainfall in remote areas of Canada. *Science* **237**, 1189–1192.
- Park J. H., Mitchell M. J., McHale P. J., Christopher S. F., and Meyers T. P. (2003) Impacts of changing climate and deposition inputs on S and N drainage losses from forested watershed in Adirondack Park, New York State. *Global Change Biol.* **9**, 1602–1619.
- Prechtel A., Alewell C., Armbruster M., et al. (2001) Response of sulphur dynamics in European catchments to decreasing sulphate deposition. *Hydrol. Earth Syst. Sci.* **5**, 311–325.
- Stam A. C., Mitchell M. J., Krouse H. R., and Kahl J. S. (1992) Stable sulfur isotopes of sulfate in precipitation and stream solutions in a northern hardwood watershed. *Wat. Res. Res.* **28**, 231–236.
- Torssander P. and Mörth C. M. (1998) Sulfur dynamics in the roof experiment at Lake Gardsjon deduced from sulfur and oxygen isotope ratios in sulfate. In *Experimental Reversal of Acid Rain Effects*. John Wiley and Sons Ltd., New York.
- Van Stempvoort D. R., Wills J. J., and Fritz P. (1991) Aboveground vegetation effects on the deposition and cycling of atmospheric sulfur: Chemical and stable isotope evidence. *Wat. Air Soil Pollut.* **60**, 55–82.
- Van Stempvoort D. R., Reardon E. J., and Fritz P. (1990) Fractionation of sulfur and oxygen isotopes by soil sorption. *Geochim. Cosmochim. Acta* **54**, 2817–2826.
- Watmough S. A. and Dillon P. J. (2001). Base cation losses from a coniferous catchment in central Ontario, Canada. *Wat. Air Soil Pollut. Focus* **1**, 507–524.
- Zhang Y., Mitchell M. J., Christ M., Likens G. E., and Krouse H. R. (1998) Stable sulfur isotopic biogeochemistry of the Hubbard Brook Experimental Forest, New Hampshire. *Biogeochem.* **41**, 259–275.