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Sulfur isotope values in a forested catchment over four years: Evidence for oxidation and reduction processes

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Abstract. A small catchment on the Swedish West Coast has been studied over four years to determine S dynamics by using S isotope ratios. A Norway spruce dominated forest covers the catchment, and small peat areas occur in the lower parts of the catchment. The runoff $\delta^{34}S_{SO_4}$ values varied both during the year, and from year to year. Over the period from February 1990 to December 1993, the $\delta^{34}S_{SO_4}$ values ranged from -1‰ to $+11$‰. Over the same period, the throughfall $\delta^{34}S_{SO_4}$ values ranged from $+1$‰ to $+15$‰. There was no correlation ($r^2 = 0.01$; $\Pr(F) = 0.57$) between $\delta^{34}S_{SO_4}$ values in throughfall and runoff. Since the only input of S to the catchment is atmospheric deposition, the long-term runoff S mass flux is controlled by the deposition. Therefore, processes in the catchment are responsible for the variation in the runoff $\delta^{34}S_{SO_4}$ values. During periods with $^{34}S_{SO_4}$ enriched runoff, bacterial dissimilatory SO_4^{2-} reduction occurs in the catchment. After very dry periods, oxidation of this reduced S, which is ^{32}S-enriched, can be traced in runoff. Previous studies of the catchment have not been able to distinguish between: 1) oxidation of reduced S and dry deposition, and 2) reduction and adsorption. From the current study, it can be concluded that adsorption and dry deposition cannot cause the observed variation in runoff $\delta^{34}S_{SO_4}$.

Introduction

Concerns about acidification related to anthropogenic S deposition have emphasized the importance of understanding S dynamics in forested catchments. Sulfur retention and release mechanisms have, therefore, been studied in several catchments in Scandinavian countries, e.g., Birkenes, Storgama in southern Norway and Lake Gårdsjön in southern Sweden (Christophersen & Wright 1981; Christophersen et al. 1982; Christophersen et al. 1983/84;

Grip et al. 1985). In these studies, it has been difficult to distinguish between processes such as oxidation of reduced S, desorption, dry deposition, bacterial dissimilatory SO_4^{2-} reduction (=BDSR) and adsorption, solely on the basis of SO_4^{2-} concentrations. One of the reasons may be that the net retention or release of S may be less than the error margin of the S mass balance. In the investigated catchment, the error in the runoff SO_4^{2-} mass flux was 24% of the total SO_4^{2-} mass flux during the period, 1980 to 1990 (Hultberg & Grennfelt 1992). Sulfur isotopes are one way of increasing the understanding of catchment S dynamics.

The S isotope composition of runoff SO_4^{2-} in any catchment is determined by the source of the SO_4^{2-} and by processes such as mixing, oxidation and reduction. In most studies of forested catchments, the runoff S isotope composition has varied considerably (Fuller et al. 1986; Hesslein et al. 1988; Andersson et al. 1992; Stam et al. 1992). This variation has been attributed to a combination of processes and sources, including deposition, oxidation of sulfides and BDSR. In the G1 catchment at Lake Gårdsjön, there were only small variations in runoff $\delta^{34}S_{SO_4}$ values and SO_4^{2-} concentrations and the $\delta^{34}S_{SO_4}$ values in runoff were almost identical to the $\delta^{34}S_{SO_4}$ values of the adsorbed soil SO_4^{2-} (Torssander & Mörth 1998). At G1, the only source for S was atmospheric deposition.

In cases where a S source other than atmospheric deposition dominates (which have different $^{34}S/^{32}S$ ratios compared to the deposition), e.g., acid mine drainage or SO_4^{2-} mineral deposits, the S isotope composition is indicative of the S source (Hitchon & Krouse 1972; Östlund et al. 1995; Cameron et al. 1995; Mörth & Torssander 1995). When the only source for S is atmospheric deposition, variations in the runoff $\delta^{34}S_{SO_4}$ value and SO_4^{2-} concentration must therefore be explained by variations in either the deposition or variations in processes that fractionate the S isotope composition in combination with the retention or release of S.

The importance of net S retention processes in peat bogs has been investigated (Gorham et al. 1984; Spratt Jr. et al. 1987; Urban et al. 1989; Wieder et al. 1990; Morgan 1992; Novak & Wieder 1992). These studies have suggested that BDSR may be an important process in this particular environment. Since peat bogs are present in the currently investigated catchment, BDSR may be an important net sink for S. During low discharge (dry periods), oxidation of organic S and sulfides in 'exposed' peat areas has been shown to be important, causing acid pulses (Gorham et al. 1984).

Studies of the small catchments in the Lake Gårdsjön area began in 1979 (Andersson & Olsson 1985) and have continued since (Andersson & Olsson 1985; Hultberg & Grennfelt 1986; Hultberg & Skeffington 1998). The catchment studied here (F1) is used as a control catchment for a nearby roof-

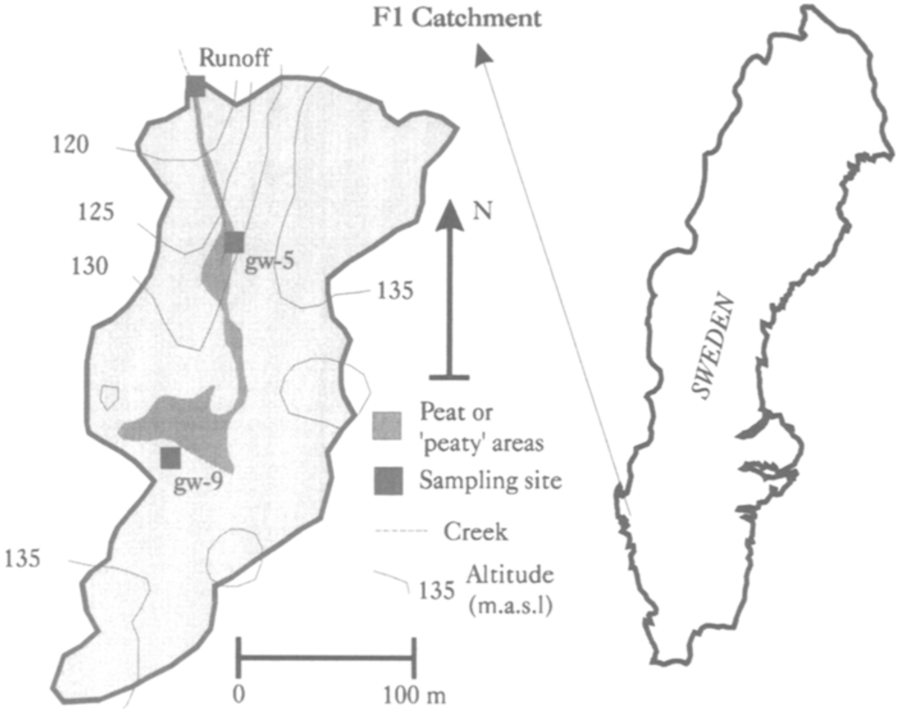

Figure 1. Map showing catchment F1 (gw-5 = groundwater well 5 and gw-9 = groundwater well 9).

covered catchment (G1), where 'clean' precipitation is added under the roof, in order to study acidification reversal processes (Hultberg & Skeffington 1998). The purpose of this study is to investigate the sources and sinks of S, and the processes that affect the S isotope abundance ratio.

Site description

Catchment, F1, located at Lake Gårdsjön (58°04′ N, 12°03′ E), has a drainage area of 3.6 ha (Figure 1). Altitude within the catchment ranges from 116 to 135 meter above sea level (Andersson & Olsson 1985). The area has a typical coastal climate, with high rainfall during autumn and winter. Annual average temperature is about 5 °C, annual average rainfall is 1198 mm and annual average runoff is 604 mm. During winter, the temperature is so mild that snow never covers the ground for long periods.

The bedrock in the Lake Gårdsjön area consists of granite and granodiorite which is practically devoid of S (Andersson & Olsson 1985). Soils are developed in glacial till that is mostly of local origin. The till is sandy silty, with a low gravel content. The soil depth is, on average, only about 40 cm thick. Most of the F1 catchment is covered by forest (mature Norway spruce, *Picea abies*). Small peat areas in the lower parts of the area cover approximately 10% of the catchment.

Methods

Sampling

Runoff water samples were taken on a regular basis (monthly or bimonthly) throughout the year, except in periods with very low or no discharge. Sampling was begun in February 1990 and has continued ever since. In this article, we report data from the period February 1990 to December 1993.

Groundwater was sampled on a monthly basis from two very shallow groundwater wells (about 1 m deep) except if they were dry: gw-5 and gw-9. Bulk deposition and throughfall were collected on a monthly or sometimes bimonthly basis. The setup used for this sampling is described by Grennfelt et al. (1985). The throughfall and bulk deposition data for the Cl^- and SO_4^{2-} concentration and $\delta^{34}S_{SO_4}$ values have been listed in Mörth (1995).

Runoff and groundwater samples were taken in 2L polyethylene bottles and were refrigerated (+4 °C) before processing. At the beginning of the study runoff water was sampled directly at a weir, but from mid 1993 samples were taken automatically under program control in proportion to flow rate by means of an ISCO$^{\grave{O}}$ sampler. Groundwater was sampled by pumping or sucking water from an installed groundwater tube (diameter about 5 cm).

Sample treatment and analysis

In the laboratory, samples were filtered through a 0.45μm membrane filter (Millipore$^{\grave{O}}$ HAWP). The Cl^- and SO_4^{2-} concentrations were analyzed using a Dionex (DX-300) ion chromatography system with electrical suppression, a 4mm AS4 anion double column system and a Na_2CO_3 (1.8mM)/$NaHCO_3$ (1.7 mM) eluent solution. Sulfate in water was ion-exchanged in columns filled with a strong basic anionic resin (DOWEX 1X8-type, mesh 20–50), in a setup described by Andersson et al. (1992).

After elution, the solution was acidified, boiled and SO_4^{2-} precipitated as $BaSO_4(s)$ with $BaCl_2$. The precipitate was left in a water bath at 90 °C for 2 hours. After filtering the solution through a polycarbonate filter (Millipore$^{\grave{O}}$ HTTP), 0.45 μm, the precipitate was washed with distilled water and dried in an oven at 60 °C overnight. The $BaSO_4(s)$ was weighed and collected in small glass tubes. $BaSO_4(s)$ was mixed with quartz and $V_2O_5(s)$ and burned at 950 °C in the presence of copper (Yanagisawa & Sakai 1983). The resulting $SO_2(g)$ was purified in a vacuum line, collected and sealed in small glass ampoules for later analysis.

Sulfur isotope measurements were carried out on a VG SIRA 10 mass spectrometer. The S isotope abundance ratio is reported relative to CDT (Cañyon Diablo Troilite) in the $\delta^{34}S$ notation:

$$\delta^{34}S(‰) = (\frac{R_{sample}}{R_{std}} - 1)^{*}1000 \tag{1}$$

where R is the abundance ratio:

$$R = \frac{^{34}S}{^{32}S} \tag{2}$$

The precision was always better than ±0.2‰, and typically ±0.1‰, based on standard measurements.

Calculations of S net retained

By rearranging the Rayleigh equation given by Chambers (1982), the amount net retained in a fraction between 0 and 1 can be written;

$$F = 1 - e\left(\frac{\alpha(\ln R_f - \ln R_0)}{1 - \alpha}\right) \tag{3}$$

where F = fraction removed, R_f = isotope abundance ratio of final solution, R_0 = isotope abundance ratio of initial solution, and α = fractionation factor.

Trend analysis

Trends from the scatterplots were determined using robust, locally weighted least-square regressions (Cleveland 1979). This algorithm requires the setting of two parameters: t, the number of iterations, and f, which specifies the neighborhood for each point. Iterations are carried out to deal with outliers (giving robust regressions), and t is usually set to 2 (Cleveland 1979). The f parameter is more arbitrary and is set to a value between 0 and 1, depending on trend resolution, i.e., how smooth the curve should be.

Table 1. Mean $\delta^{34}S_{SO_4}$ values, sulfate and chloride concentrations for throughfall, runoff and groundwaters (± refers to 95% confidence intervals), 1990–93. During the study period the average throughfall water volume was 627 mm year^{-1}. The runoff water volume was during the same period 437 mm year^{-1}.

Type of sample	$\delta^{34}S_{SO_4}$, ‰	[SO_4^{2-}], μM	[Cl^-], μM
Throughfall (weighted mean, n = 48)	+7.34	86.0	316
Groundwater well 5 (n = 30)	+8.02 ± 0.74	131 ± 18	646 ± 45
Groundwater well 9 (n = 28)	+6.94 ± 0.12	186 ± 11	741 ± 57
Runoff			
Arithmetic mean (n = 45)	+7.85 ± 0.56	125 ± 14	641 ± 53
Weighted mean (n = 45)	+7.51	128	597

Results

The accumulated water runoff from catchment F1 is presented in Figure 2a. Runoff was very small during summer. The accumulated runoff and throughfall SO_4^{2-} mass flux (Figure 2b) are more or less balanced. This was also observed during an earlier ten year study of the catchment (Hultberg & Grennfelt 1992). In Figure 2c we plotted the runoff and throughfall S mass flux as a function of sample dates (by integrating the mass flux between sample dates). Most of the runoff and throughfall sample dates coincide. The plot shows a clear correlation between the runoff and throughfall S mass flux, with some exceptions. During the summer of 1992, there is a high runoff S mass flux, but a low throughfall S mass flux. The opposite is observed from September to November 1991. The largest runoff and throughfall S mass flux correlation occurs during winter, when there is high water runoff and rainfall.

Mean values for the SO_4^{2-} and Cl^- concentration and the $\delta^{34}S_{SO_4}$ values at all sampling stations are presented in Table 1. The throughfall $\delta^{34}S_{SO_4}$ values ranged from +0.52‰ to 14.86‰ (Mörth 1995). Higher throughfall $\delta^{34}S_{SO_4}$ values were observed during winter, and lower $\delta^{34}S_{SO_4}$ values, during spring or late summer (Figure 3).

The runoff $\delta^{34}S_{SO_4}$ values and SO_4^{2-} concentrations are presented in Table 2 and plotted in Figure 4a. $\delta^{34}S_{SO_4}$ values were higher (up to +11‰) during the warm and wet parts of the year, and lower during the cold months of winter and spring. Figure 3 shows that runoff $\delta^{34}S_{SO_4}$ values decreased over the summer of 1990 to a minimum in winter 1991, and increased through the summer of 1991. The decrease during autumn and winter in 1991/92, was not as significant as in 1990/91. Accumulated runoff for these two winters (Figure 2a), illustrates that spring in 1992 was wetter than in 1991. After the

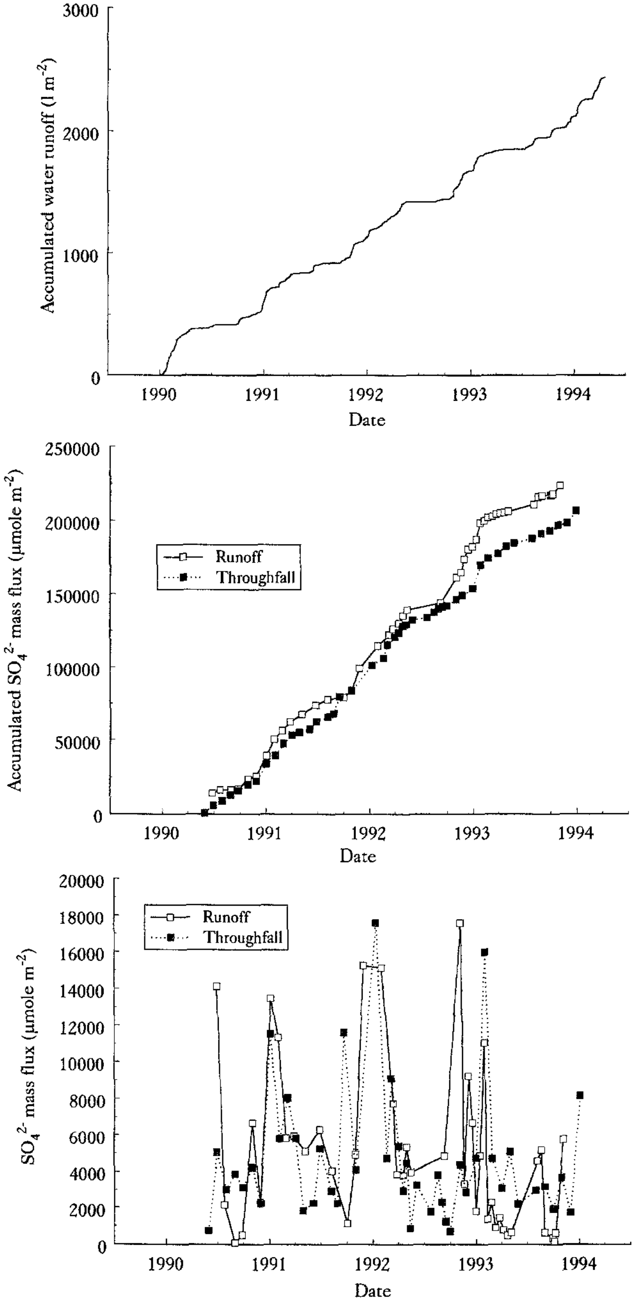

Figure 2. Fluxes of water and SO_4^{2-} from catchment F1 between 1990 and 1993. a) Accumulated water runoff versus date of sampling. b) Accumulated runoff and throughfall SO_4^{2-} mass flux versus date of sampling. c) Runoff and throughfall SO_4^{2-} mass flux between sample dates.

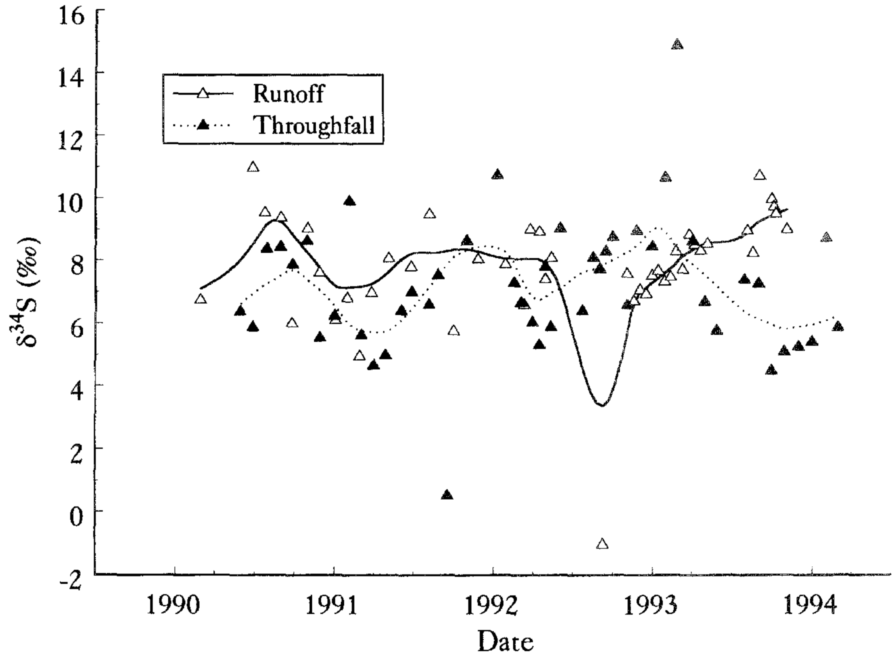

Figure 3. $\delta^{34}S_{SO_4}$ values in throughfall and runoff versus date of sampling. In the figure, the trends were plotted with t = 2 and f = 0.2 (see Methods section for a description of the smoothing method).

long summer drought in 1992, $\delta^{34}S_{SO_4}$ reached an extreme of −1.02‰ on September 9. In spring 1993, $\delta^{34}S_{SO_4}$ increased again to a value of approximately +8.5‰.

The runoff SO_4^{2-} concentration seems to be negatively correlated with the $\delta^{34}S_{SO_4}$ value. The highest SO_4^{2-} concentration peaks correlate well with the lowest $\delta^{34}S_{SO_4}$ values, and vice versa. The coefficient of determination, r^2, between the $\delta^{34}S_{SO_4}$ value and the SO_4^{2-} concentration was −0.66 (Pr(F) = 0.00), when including the extreme value {389 μM; −1.02‰} on September 3, 1992, and −0.28 (Pr(F) = 0.00) when excluding it. The highest SO_4^{2-} concentrations were generally observed in winter or spring. Low SO_4^{2-} concentrations were generally observed during summer, but the lowest (48 μM) were recorded in November 1993. There is no correlation between throughfall and runoff $\delta^{34}S_{SO_4}$ values, r^2 = 0.01 (Pr(F) = 0.57), Figure 3.

Also in the groundwater at gw-5, there seems to be a negative correlation between SO_4^{2-} concentration and the $\delta^{34}S_{SO_4}$ value (Table 3 and Figure 4b). The highest $\delta^{34}S_{SO_4}$ values each year occur in summer. Figure 4b shows a rather erratic pattern, where the $\delta^{34}S_{SO_4}$ value rapidly decreases and the SO_4^{2-} concentration increases at the end of dry periods (May/June 1991 and

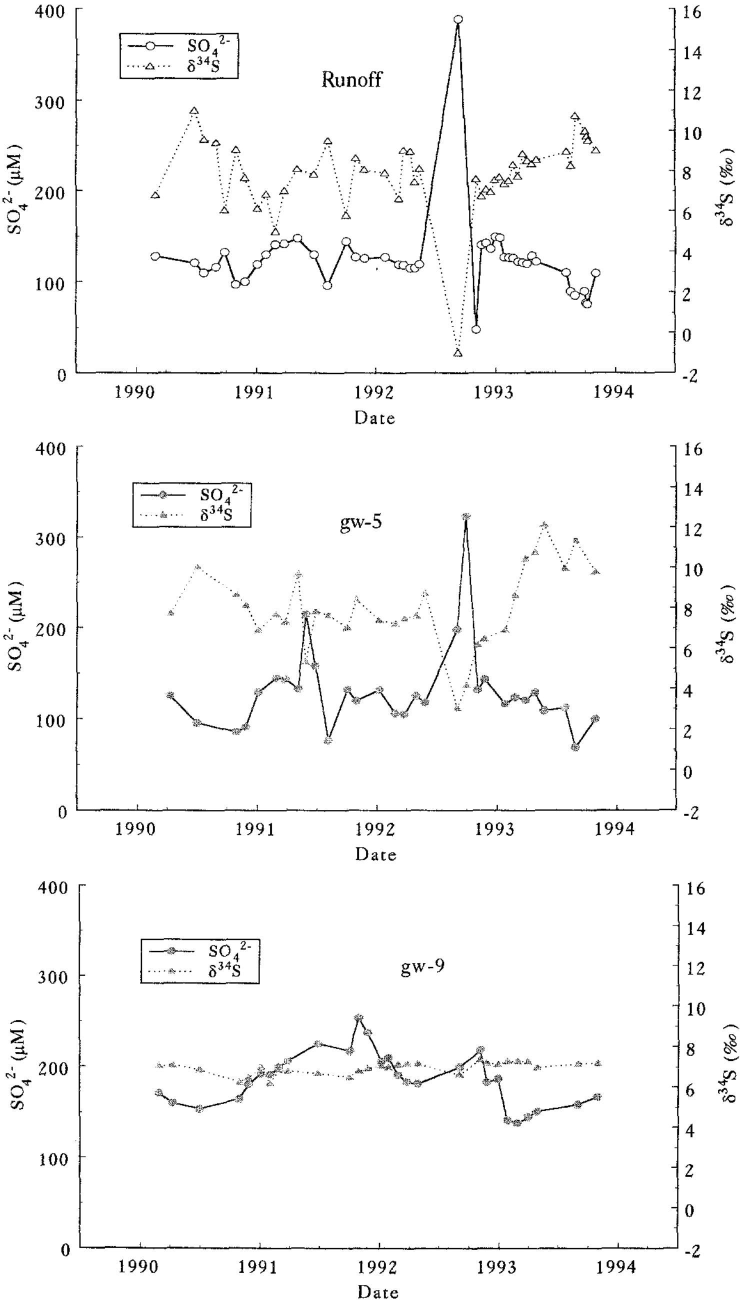

Figure 4. a) SO_4^{2-} concentration and $\delta^{34}SO_{SO_4}$ value in runoff versus date of sampling. b) SO_4^{2-} concentration and $\delta^{34}SO_{SO_4}$ value in groundwater well 5 versus date of sampling. c) SO_4^{2-} concentration and $\delta^{34}SO_{SO_4}$ value in groundwater well 9 versus date of sampling.

Table 2. Data from runoff water.

Sample date	$[Cl^-]$, μM	$[SO_4^{2-}]$, μM	$\delta^{34}S_{SO_4}$, ‰	Sample date	$[Cl^-]$, μM	$[SO_4^{2-}]$, μM	$\delta^{34}S_{SO_4}$ ‰
27-Feb-1990	440	128	+6.76	9-Sep-1992	605	389	−1.02
27-Jun-1990	574	121	+10.99	3-Nov-1992	297	48	+7.57
25-Jul-1990	694	110	+9.55	18-Nov-1992	1021	141	+6.71
31-Aug-1990	622	116	+9.38	2-Dec-1992	503	143	+7.06
26-Sep-1990	580	132	+6.01	16-Dec-1992	431	137	+6.93
31-Oct-1990	702	97	+9.03	30-Dec-1992	448	150	+7.52
28-Nov-1990	706	100	+7.62	13-Jan-1993	450	148	+7.67
4-Jan-1991	601	119	+6.11	27-Jan-1993	465	127	+7.33
30-Jan-1991	619	130	+6.81	10-Feb-1993	658	127	+7.48
27-Feb-1991	546	141	+4.96	23-Feb-1993	711	126	+8.29
27-Mar-1991	478	141	+6.97	10-Mar-1993	764	122	+7.71
6-May-1991	497	148	+8.07	24-Mar-1993	731	121	+8.83
26-Jun-1991	416	130	+7.80	7-Apr-1993	781	120	+8.49
7-Aug-1991	459	96	+9.49	21-Apr-1993	853	128	+8.31
2-Oct-1991	479	144	+5.76	5-May-1993	897	122	+8.53
31-Oct-1991	559	127	+8.61	4-Aug-1993	940	110	+8.96
27-Nov-1991	538	126	+8.04	18-Aug-1993	844	90	+8.24
29-Jan-1992	637	127	+7.88	1-Sep-1993	998	85	+10.72
11-Mar-1992	632	119	+6.59	30-Sep-1993	101	990	+9.97
25-Mar-1992	635	118	+9.01	5-Oct-1993	857	77	+9.72
15-Apr-1992	559	115	+8.93	9-Oct-1993	789	76	+9.50
29-Apr-1992	536	115	+7.41	3-Nov-1993	785	109	+8.99
13-May-1992	495	119	+8.08				

September 1992). After September 1992, the $\delta^{34}S_{SO_4}$ value increases, while the SO_4^{2-} concentration decreases. The coefficients of determination between runoff and gw-5 for $\delta^{34}S_{SO_4}$ values, SO_4^{2-} and Cl^- concentrations were 0.53, 0.75 and 0.57, respectively (Pr(F) = 0.00 in all cases).

The data for groundwater sampled at gw-9 is completely different from both runoff and gw-5 (Table 4 and Figure 4c). $\delta^{34}S_{SO_4}$ slowly increased with time from about +6.7‰ in the summer of 1990 to +7.3‰ in mid 1993, with little short-term variation. The mean value for the period was +6.94±0.12‰ (95% confidence interval, Table 1). The SO_4^{2-} concentration shows a larger temporal variation without a specific trend.

Table 3. Data from groundwater well 5, gw-5.

Sample date	$[\mathrm{Cl}^-]$, μM	$[\mathrm{SO}_4^{2-}]$, μM	$\delta^{34}\mathrm{S}_{\mathrm{SO}_4}$, ‰	Sample date	$[\mathrm{Cl}^-]$, μM	$[\mathrm{SO}_4^{2-}]$, μM	$\delta^{34}\mathrm{S}_{\mathrm{SO}_4}$ ‰
11-Apr-1990	489	125	+7.71	25-Mar-1992	775	105	+7.48
2-Jul-1990	532	96	+10.02	29-Apr-1992	604	125	+7.60
31-Oct-1990	657	86	+8.66	27-May-1992	519	118	+8.73
28-Nov-1990	689	91	+8.13	2-Sep-1992	631	198	+3.03
4-Jan-1991	772	130	+6.89	30-Sep-1992	646	324	+4.18
27-Feb-1991	596	145	+7.69	4-Nov-1992	591	132	+6.18
27-Mar-1991	450	144	+7.29	25-Nov-1992	574	144	+6.47
6-May-1991	478	133	+9.69	27-Jan-1993	608	116	+6.91
29-May-1991	610	215	+5.32	26-Feb-1993	775	124	+8.62
27-Jun-1991	516	159	+7.82	30-Mar-1993	754	121	+10.44
7-Aug-1991	578	77	+7.65	27-Apr-1993	772	129	+10.74
2-Oct-1991	544	132	+7.00	26-May-1993	792	109	+12.13
30-Oct-1991	586	120	+8.41	28-Jul-1993	931	112	+9.95
8-Jan-1992	578	132	+7.38	30-Aug-1993	840	69	+11.34
27-Feb-1992	768	106	+7.21	29-Oct-1993	724	100	+9.78

Table 4. Data from groundwater well 9, gw-9.

Sample date	$[\mathrm{Cl}^-]$, μM	$[\mathrm{SO}_4^{2-}]$, μM	$\delta^{34}\mathrm{S}_{\mathrm{SO}_4}$, ‰	Sample date	$[\mathrm{Cl}^-]$, μM	$[\mathrm{SO}_4^{2-}]$, μM	$\delta^{34}\mathrm{S}_{\mathrm{SO}_4}$ ‰
27-Feb-1990	488	172	+7.07	29-Jan-1992	757	210	+6.96
11-Apr-1990	607	160	+7.08	27-Feb-1992	708	191	+7.12
2-Jul-1990	722	154	+6.86	25-Mar-1992	649	184	+7.17
31-Oct-1990	724	165	+6.24	28-Apr-1992	564	182	+7.15
28-Nov-1990	786	181	+6.44	2-Sep-1992	872	200	+6.61
4-Jan-1991	836	192	+6.98	4-Nov-1992	684	218	+7.37
1-Feb-1991	846	191	+6.17	25-Nov-1992	533	184	+7.18
27-Feb-1991	829	200	+6.83	29-Dec-1992	487	187	+7.13
27-Mar-1991	688	206	+6.80	27-Jan-1993	722	142	+7.28
27-Jun-1991	627	226	+6.67	26-Feb-1993	926	138	+7.28
2-Oct-1991	736	218	+6.49	30-Mar-1993	950	145	+7.29
30-Oct-1991	799	254	+6.79	28-Apr-1993	1008	151	+6.99
27-Nov-1991	647	237	+6.92	30-Aug-1993	1070	159	+7.15
8-Jan-1992	658	206	+7.07	29-Oct-1993	824	168	+7.20

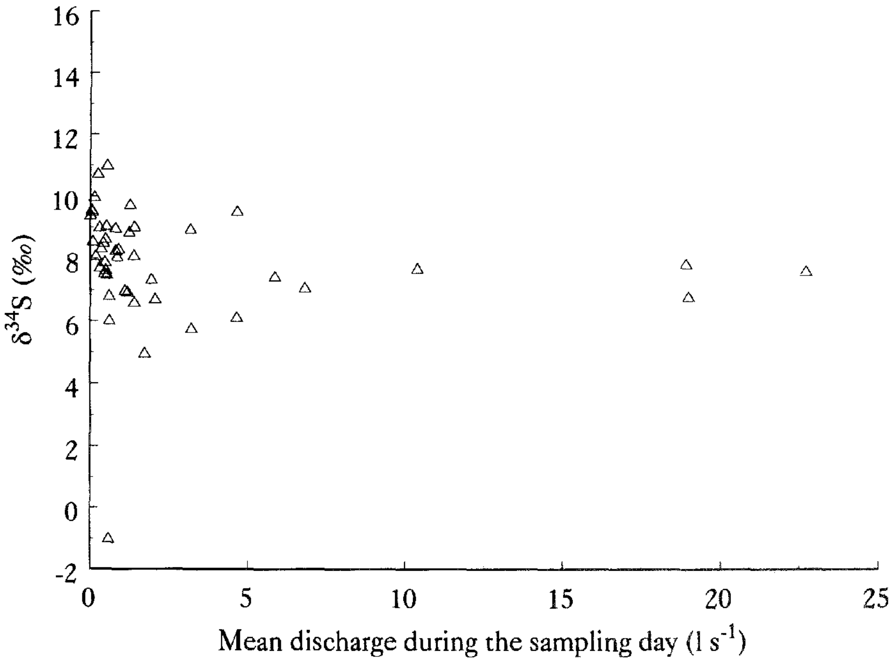

Figure 5. $\delta^{34}SO_{SO_4}$ in runoff plotted versus the mean discharge during the sample day.

Figure 5 shows that low daily discharge can be associated with both low and high $\delta^{34}S_{SO_4}$ values, but high discharge coincide with $\delta^{34}S_{SO_4}$ values in the range, +6.8 to +7.5‰. These $\delta^{34}S_{SO_4}$ values are close to the runoff weighted mean, +7.51‰ (Table 1), the gw-9 mean value, +6.94‰ and the weighted mean for throughfall, +7.34‰.

Discussion

Isotope fractionation of S at low temperatures (below 50 °C) occurs mainly in chemical reactions in which different isotopes have different reaction rates (Krouse & Grinenko 1991). Important reactions include: immobilization, BDSR, disproportionation of elemental S by bacteria (=SDB), oxidation of sulfides, mineralization and SO_4^{2-} sorption (Van Stempvoort et al. 1990; Krouse & Grinenko 1991; Canfield & Thamdrup 1994). Isotope fractionation during oxidation of reduced S and mineralization is small or negligible (Krouse & Grinenko 1991). The isotope fractionation for S immobilization is small, and no isotope fractionation has been measured for soil SO_4^{2-} sorption (Van Stempvoort et al. 1990; Krouse & Grinenko 1991).

At low temperatures, therefore, BDSR and SDB seem to be the only processes that significantly change the S isotope abundance ratio. Both processes enrich the lighter isotope in the reduced phase. The fractionation during BDSR can be as large as 50 to 60‰ in marine systems (Hartmann & Nielsen 1969; Chambers 1982), but is typically 20 to 30þ in freshwater systems (Krouse & Grinenko 1991). When the reduced S (formed from BDSR) is re-oxidized, no isotope fractionation, or only a small fractionation, is expected. This implies that the SO_4^{2-} formed (by oxidation) is isotopically light, compared to the SO_4^{2-} already present in solution.

Partial reoxidation of H_2S or sulfides after BDSR, to elemental S, followed by SDB, has been shown to increase the enrichment of ^{32}S in the reduced phase (Canfield & Thamdrup 1994). In these experiments, the fractionations during SDB, to SO_4^{2-} and H_2S, were of the order of +15‰ and −9‰, respectively.

Bacterial dissimilatory SO_4^{2-} reduction in boreal forests can occur in the peat areas. The rate of BDSR in peat areas has been reported to be equivalent to that in coastal marine sediments (Spratt Jr. et al. 1987; Wieder et al. 1990). Although the SO_4^{2-} concentration is much lower in peat water than in sea water, BDSR has been shown to occur in peat water with SO_4^{2-} concentrations as low as 7 to 30 μM (Morgan 1992). Bacterial dissimilatory SO_4^{2-} reduction is likely only important in the saturated zone (below the water table). Bacterial dissimilatory SO_4^{2-} reduction is indicated by a negative correlation between SO_4^{2-} concentrations and $\delta^{34}S_{SO_4}$ values (Hesslein et al. 1988). Hesslein et al. (1988) also used the $\delta^{34}S_{SO_4}$ variations over the year (low $\delta^{34}S_{SO_4}$ values during spring, increased $\delta^{34}S_{SO_4}$ over summer and decreased $\delta^{34}S_{SO_4}$ during autumn) to show that BDSR was an important process for S dynamics. If SDB is occurring, the effect on the runoff $\delta^{34}S_{SO_4}$ value will be dependent on the fractionation factor. The experiments on SDB by Canfield & Thamdrup (1994) were performed at high concentrations of elemental S. At lower elemental S concentrations the isotope fractionation is probably smaller. It is therefore likely that the SDB will result in lower runoff $\delta^{34}S_{SO_4}$ values, and higher SO_4^{2-} concentrations, than expected from BDSR only.

On a yearly basis, it was shown in the Storgama catchment (located in southern Norway) that the rate of BDSR exceeds that of oxidation of the reduced S pool (Christophersen et al. 1983/84). The warm and wet part of the year caused net SO_4^{2-} reduction. Only when the catchment was dry, the oxidation rate temporarily exceeded that of reduction. The reduction rate was also shown to be temperature dependent.

Runoff and gw-5

Data for runoff and gw-5 show similar patterns with large variations in both the $\delta^{34}S_{SO_4}$ values and the SO_4^{2-} concentrations. The following discussion will focus on the runoff data, but applies also to the gw-5 data. Two types of $\delta^{34}S_{SO_4}$ variations must be explained: increases over time and sudden drastic drops. The increased $\delta^{34}S_{SO_4}$ values, in combination with decreasing SO_4^{2-} concentrations, may be caused by: 1) variations in the deposition, 2) net adsorption, 3) immobilization and 4) BDSR. The observed low $\delta^{34}S_{SO_4}$ values, in combination with high SO_4^{2-} concentrations after dry periods, may be caused by: 1) dry deposition, 2) mineralization and 3) oxidation of reduced S.

Increased $\delta^{34}S_{SO_4}$ values coupled with decreased SO_4^{2-} concentrations

Not all of the water in runoff during a given rain storm event is derived from groundwater. If the $\delta^{34}S_{SO_4}$ in atmospheric deposition show a large variation with time, a mix of 'atmospheric' and groundwater SO_4^{2-} may shift the runoff $\delta^{34}S_{SO_4}$ value. In F1, throughfall $\delta^{34}S_{SO_4}$ values during storm events can be as high as +15‰ (Figure 3). By using oxygen isotopes in water, Rodhe (1987) showed in F1 that a mix of 80% groundwater and 20% direct surface runoff constituted the highest contribution from direct surface runoff in catchment runoff water. This was observed during snow melt in the spring. The mix between groundwater and direct runoff was also correlated with discharge. High discharge increased the direct runoff proportion. During high discharge in spring, the runoff $\delta^{34}S_{SO_4}$ value lies in the range, +6.8 to +7.5‰ (Figures 2a, 5). The highest runoff $\delta^{34}S_{SO_4}$ values are observed during summer, whereas the highest throughfall $\delta^{34}S_{SO_4}$ values are observed during winter storms (Figure 3). Figure 3, shows very clearly that after heavy winter storms with very high throughfall $\delta^{34}S_{SO_4}$ values, no response can be seen in runoff, illustrating that the runoff $\delta^{34}S_{SO_4}$ values are not controlled by the deposition. By contrast, Stam et al. (1992), concluded that the runoff $\delta^{34}S_{SO_4}$ variations were correlated with the atmospheric $\delta^{34}S_{SO_4}$ deposition. The absence of such a correlation in the Lake Gårdsjön G1 catchment was attributed the important contribution of adsorbed soil SO_4^{2-} to runoff $\delta^{34}S_{SO_4}$ values (Torssander & Mörth 1998), causing a small $\delta^{34}S_{SO_4}$ variation in runoff (lower than 0.5‰).

Since sorption does not fractionate the S isotope abundance ratio significantly (Van Stempvoort et al. 1990), net adsorption and desorption will not change the runoff $\delta^{34}S_{SO_4}$ value, although there will be a change in the SO_4^{2-} concentration. Assuming that the total inorganic SO_4^{2-} storage in the soil is the same as in the adjacent catchment, G1, then one-year of S deposition equals about 10% of the inorganic SO_4^{2-} storage (Mörth 1995). The deposition flux varies from year to year, but the soil SO_4^{2-} pool 'buffers' and evens out the runoff SO_4^{2-} flux. Thus, the runoff SO_4^{2-} flux and concentration changes due to net adsorption or desorption will be very minor.

The fractionation of S isotopes during immobilization is rather small, +1 to −3‰ (Krouse & Grinenko 1991), and probably even smaller during mineralization. The net retention of S by immobilization, required to explain the observed positive shifts in the runoff $\delta^{34}S_{SO_4}$ value, must then be large. At a fractionation factor of 1.002 (=α), equation (3) predicts that a 0.5‰ change in $\delta^{34}S_{SO_4}$ corresponds to a 22% change in the runoff SO_4^{2-} concentration. The slope for the regression line between the runoff SO_4^{2-} concentration and $\delta^{34}S_{SO_4}$ value was −19.9 μM/1‰. Calculating the SO_4^{2-} concentration decrease from the runoff weighted mean of 128 μM, a positive 0.5‰ shift corresponds to a SO_4^{2-} concentration change of about 8%. Organic S cycling, or immobilization followed by mineralization, can be ruled out since this process cannot cause changes in both the runoff $\delta^{34}S_{SO_4}$ value and the SO_4^{2-} concentration at the same time.

Hesslein et al. (1988) used the anti correlation between the SO_4^{2-} concentration and $\delta^{34}S_{SO_4}$ value to detect BDSR. The overall conclusion must therefore be that the observed anti-correlation between the SO_4^{2-} concentration and $\delta^{34}S_{SO_4}$ value also in this study was caused by BDSR.

Decreased $\delta^{34}S_{SO_4}$ values coupled with increased SO_4^{2-} concentrations

The dry deposition of S was about 26.1 mmol m^{-2} yr^{-1} in the early 1980s (Grennfelt et al. 1985), and is probably lower today. Assuming that a dry period is about three months long, and that the amount of S in the soil is the same as in the nearby catchment G1, dry deposition would provide about 1% of the total SO_4^{2-} storage in the soil. So dry deposition, which can be a substantial part of the total S deposition, cannot significantly affect $\delta^{34}S_{SO_4}$ in runoff.

Net mineralization of immobilized S would increase runoff SO_4^{2-} concentration, but cause only a very small negative shift in the runoff $\delta^{34}S_{SO_4}$ value.

Bacterial dissimilatory SO_4^{2-} reduction and oxidation of reduced S

By a process of elimination, the very low runoff $\delta^{34}S_{SO_4}$ values combined with high runoff SO_4^{2-} concentrations after dry periods, must therefore be attributed to the oxidation of reduced S stored in the catchment that is ^{34}S depleted. This ^{34}S depleted S-pool must be formed during BDSR. One indicator of BDSR is the negative correlation found between $\delta^{34}S_{SO_4}$ values and SO_4^{2-} concentrations in both gw-5 and runoff.

Groundwater well 9 (gw-9)

The $\delta^{34}S_{SO_4}$ values in gw-9 are very stable, although they slightly increase with time (Figure 4c). By plotting the long-term $\delta^{34}S_{SO_4}$ trend for gw-9 and throughfall, and using the smoothing method described in the Methods section, it can be seen that the long-term trend lines for gw-9 and throughfall are very close (Figure 6a). This clearly indicates that throughfall is the source for S in gw-9. As mentioned earlier, this conclusion was also reached for the groundwater wells in the adjacent catchment, G1 (Mörth 1995). Groundwater wells in G1 had $\delta^{34}S_{SO_4}$ values very near the B-horizon adsorbed $\delta^{34}S_{SO_4}$ values (Mörth & Torssander 1995). This suggests that gw-9 reflects the mean throughfall $\delta^{34}S_{SO_4}$ values through adsorbed soil SO_4^{2-} (for the turnover time of the soil SO_4^{2-}).

The SO_4^{2-} concentration in gw-9 varies with time (Figure 4c). Since the S isotope data does not change, the S source is the same (throughfall). From Figure 6b it can be concluded that the excess SO_4^{2-} is deposited at a more steady rate than the Cl^- mass flux rate, which increased episodically during winter storms. The Cl^-/SO_4^{2-} ratio in gw-9 varies in relation to changes in the mass fluxes of excess SO_4^{2-} and Cl^-(Figure 6b). Periods with low and high Cl/SO_4 ratios follow the deposition rate of excess SO_4^{2-} and Cl^-. This rules out the possibility that temporal changes in the SO_4^{2-} concentration are due to evapotranspiration. If the soil is near SO_4^{2-} saturation (or is saturated), however, an increase in S deposition will cause an increased groundwater SO_4^{2-} concentration, but no change in the $\delta^{34}S_{SO_4}$ value.

Together, the data suggest that soil exchange processes (adsorption – desorption) control the gw-9 $\delta^{34}S_{SO_4}$ values and SO_4^{2-} concentrations, and that the variation in the throughfall $\delta^{34}S_{SO_4}$ signal will be evened out by mixing with soil SO_4^{2-}.

Calculations of the amount S net retained

Assuming that the system is open and that part of the incoming SO_4^{2-} to the saturated zone is removed at a constant rate by BDSR, the isotope shift between runoff and the source for S can be used to calculate the net amount of S net retained. If net retention of S is below 20–25% of the total S flux, the amount retained can be approximated by a Rayleigh distillation equation (see Methods section, equation 3).

The question arises as to whether or not the F1 catchment can be considered to be at steady state. The close correspondence between input and output fluxes indicate that the catchment is close to steady-state with respect to S (Figure 2b). The small difference between accumulated throughfall and

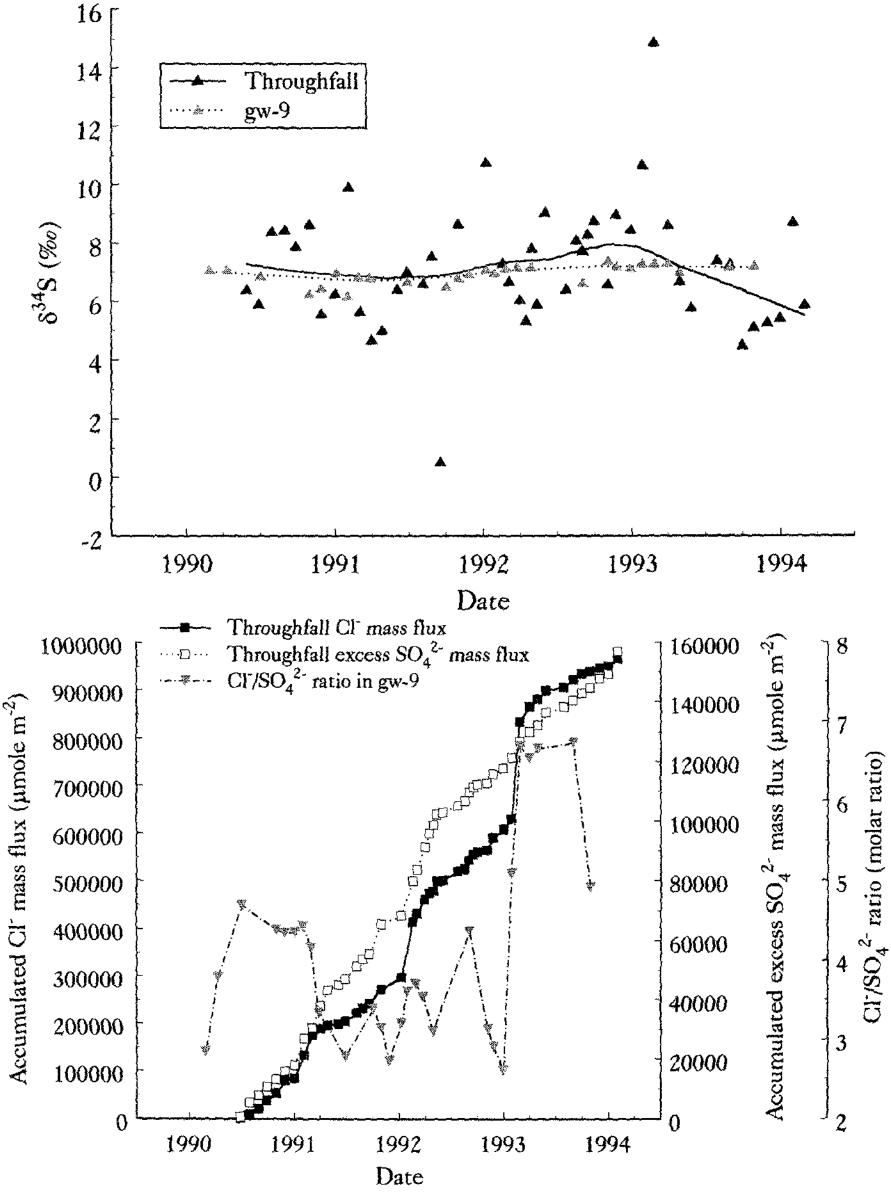

Figure 6. a) Long-term variation in $\delta^{34}S_{SO_4}$ in throughfall and gw-9. The trends were plotted with t = 2 and f = 0.5. b) Accumulated Cl^- and excess SO_4^{2-} mass flux in throughfall and the Cl^-/SO_4^{2-} ratio in groundwater well 9 plotted versus sampling dates.

Table 5. Calculated amount of sulfur net retained in relation to the total sulfur mass flux. Figures are given in % of the total sulfur mass flux.

Fractionation factor	Isotope shift between gw-9 and the weighted runoff mean value (+6.94 to +7.51‰). Percent net retained	Isotope shift between gw-9 and the mean runoff value (+6.94 to +7.85‰). Percent net retained
$\alpha = 1.010$	5.7	9.1
$\alpha = 1.020$	2.8	4.6
$\alpha = 1.030$	1.9	3.1
$\alpha = 1.040$	1.5	2.3

runoff may be attributed to the decrease in S deposition (Hedin et al. 1994) and subsequent leaching of SO_4^{2-} from the soil.

Since Figure 6a suggests that the variation of $\delta^{34}S_{SO_4}$ in gw-9 is related to the throughfall $\delta^{34}S_{SO_4}$ value, it can be assumed that the mean gw-9 $\delta^{34}S_{SO_4}$ value reflects the mean long-term $\delta^{34}S_{SO_4}$ value in the input. Equation (3) indicates that the net retention of S is about 3 to 8% of the total S mass flux, depending on the used fractionation factor (see Table 5). Most of this must be accumulated as reduced S in peat areas.

Conclusions

Atmospheric deposition is the dominant source of S in the investigated catchment. The runoff S isotope composition does not reflect the S isotope composition in throughfall on a short-term basis, because the runoff $\delta^{34}S_{SO_4}$ values and the runoff SO_4^{2-} concentrations are regulated by processes in the soil.

High runoff SO_4^{2-} concentrations after droughts are coupled with low $\delta^{34}S_{SO_4}$ values, indicating oxidation of previously reduced inorganic S that was formed by bacterial dissimilatory SO_4^{2-} reduction. High $\delta^{34}S_{SO_4}$ values are coupled with low SO_4^{2-} concentrations. These variations cannot be caused by adsorption, since sorption processes do not fractionate the S isotope abundance ratio. We therefore suggest that SO_4^{2-} undergoes dissimilatory reduction by bacteria. Apart from adsorption/desorption, redox processes control the runoff SO_4^{2-} concentration and the runoff $\delta^{34}S_{SO_4}$ value.

Bacterial dissimilatory SO_4^{2-} reduction and subsequent oxidation can be traced with stable S isotope measurements in runoff and groundwater. The indicators are variations in the $\delta^{34}S_{SO_4}$ value and corresponding changes in the SO_4^{2-} concentration. The amount of S reduced is difficult to calculate, mainly due to uncertainties about the fractionation factor and large errors in the mass balance calculation. At a fractionation factor of 1.020, retention of reduced S in catchment is of the order of 3–4%.

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References

Andersson F & Olsson B (1985) Lake Gårdsjön: An Acid Forest Lake and Its Catchment. Ecological Bulletin 37, Publishing House of the Swedish Research Councils, Stockholm

Andersson P, Torssander P & Ingri J (1992) Sulphur isotope ratios in sulphate and oxygen isotopes in water from a small watershed in Central Sweden. Hydrobiol. 235/236: 205–217

Cameron EM, Hall GEM, Veizer J & Krouse HR (1995) Isotopic and elemental hydrogeochemistry of a major river system: Fraser river, British Columbia, Canada. Chem. Geol. 122: 149–169

Canfield DE & Thamdrup B (1994) The production of ^{34}S-depleted sulfide during bacterial disproportionation of elemental sulfur. Science 266: 1973–1975

Chambers LA (1982) Sulfur isotope study of a modern intertidal environment and the interpretation of ancient sulfides. Geochim. Cosmochim. Acta 46: 721–728

Christophersen N & Wright RF (1981) Sulfate budget and a model for sulfate concentrations in stream water at Birkenes, a small forested catchment in Southernmost Norway. Water Resour. Res. 17: 377–389

Christophersen N, Seip HM & Wright RF (1982) A model for streamwater chemistry at Birkenes, Norway. Water Resour. Res. 18: 977–996

Christophersen N, Dymbe LH, Johannssen M & Seip HM (1983/84) A model for sulphate in streamwater at Storgama, Southern Norway. Ecol. Model. 21: 35–61

Cleveland WS (1979) Robust locally weighted regression and smoothing scatterplots. J. Am. Stat. Assoc. 74: 829–836

Fuller RD, Mitchell MJ, Krouse HR, Wyskowski BJ & Driscoll CT (1986) Stable sulfur isotope ratios as a tool for interpreting ecosystem sulfur dynamics. Water Air Soil Pollut. 28: 163–171

Gorham E, Bayley SE & Schindler DW (1984) Effects of acid deposition upon peatlands. Can. J. Fish. Aquat. Sci. 41: 1256–1268

Grennfelt P, Larsson S, Leyton P & Olsson B (1985) Atmospheric deposition in the Lake Gårdsjön area, SW Sweden. In: Andersson F & Olsson B (Eds) Lake Gårdsjön; An Acid Forest Lake and Its Catchment. Ecological Bulletins 37 (pp 101–108). Publishing House of the Swedish Research Councils, Stockholm

Grip H, Jansson P-E, Johnsson H & Nilsson SI (1985) Application of the "Birkenes" model to two forested catchments on the Swedish west coast. In: Andersson F & Olsson B (Eds) Lake Gårdsjön; An Acid Forest Lake and Its Catchment. Ecological Bulletins 37 (pp 176–192). Publishing House of the Swedish Research Council, Stockholm

Hartmann M & Nielsen H (1969) $\delta^{34}S$ werte in rezenten meeresedimenten und ihre deutung am biespiel einiger sedimentprofile aus der westlichen Ostsee. Geol. Rundsch. 58: 621–655

Hedin LO, Granat L, Likens GE, Buishand TA, Galloway JN, Butler TJ & Rodhe H (1994) Steep declines in atmospheric base cations of Europe and North America. Nature 367: 351–354

Hesslein RH, Capel MJ & Fox DE (1988) Sulfur isotopes in sulfate in the inputs and outputs of a Canadien shield watershed. Biogeochem. 5: 263–273

Hitchon B & Krouse HR (1972) Hydrogeochemistry of the surface waters of the Mackenzie river drainage basin, Canada – III. Stable isotopes of oxygen, carbon and sulphur. Geochim. Cosmochim. Acta 36: 1337–1357

Hultberg H & Grennfelt P (1986) Gårdsjön project: Lake acidification, chemistry in catchment runoff, lake liming and microcatchment manipulations. Water Air Soil Pollut. 30: 31–46

Hultberg H & Grennfelt P (1992) Sulphur and seasalt deposition as reflected by throughfall and runoff chemistry in forested catchments. Environ. Pollut. 75: 215–222

Hultberg H & Skeffington R (1998) Experimental Reversal of Acid Rain Effects: The Gårdsjön Roof Project. John Wiley & Sons, New York

Krouse HR & Grinenko VA. (1991) Stable Isotopes. Natural and Anthropogenic Sulphur in the Environment. SCOPE 43. John Wiley & Sons, New York

Morgan MD (1992) Sulfur pool sizes and stable isotope ratios in HUMEX peat before and immediately after the onset of acidification. Environ. Int. 18: 545–553

Mörth C-M (1995) Sulfur Isotopes Used as a Tracer of Acidifcation Reversal, Dispersion of Aciud Mine Drainage and Sulfur Dynamics in Small and Large Catchments. Meddelanden från Stockholms Universitets institution för Geologi och Geokemi, No 290, Stockholm University, Dept. of Geology and Geochemistry, Stockholm

Mörth C-M & Torssander P (1995) Sulfur and oxygen isotope ratios in sulfate during an acidification reversal study at Lake Gårdsjön, Western Sweden. Water Air Soil Pollut. 79: 261–278

Novak M & Wieder RK (1992) Inorganic and organic sulfur profiles in nine Sphagnum peat bogs in the United States and Czechoslovakia. Water Air Soil Pollut. 65: 353–369

Rodhe A (1987) The Origin of Streamwater Traced by Oxygen-18. Report Series A, No 4. Uppsala University, Uppsala

Spratt Jr HG, Morgan MD & Good RE (1987) Sulfate reduction in peat from a New Jersey pinelands Cedar Swamp. Appl. Environ. Microbiol. 53: 1406–1411

Stam AC, Mitchell MJ, Krouse HR & Kahl JS (1992) Stable sulfur isotopes of sulfate in precipitation and stream solutions in a northern hardwood watershed. Water Resour. Res. 28: 231–236

Torssander P & Mörth C-M (1998) Sulfur dynamics in the roof experiment at Lake Gårdsjön deduced from sulfur and oxygen isotope ratios in sulfate. In: Hultberg H & Skeffington R (Eds) Experimental Reversal of Acid Rain Effects: The Gårdsjön Roof Project (pp 185–206). John Wiley & Sons, New York

Urban NR, Eisenreich SJ & Grigal DF (1989) Sulfur cycling in a forested sphagnum bog in northern Minnesota. Biogeochem. 7: 81–109

Van Stempvoort DR, Reardon EJ & Fritz P (1990) Fractionation of sulfur and oxygen isotopes in sulfate by soil sorption. Geochim. Cosmochim. Acta 54: 2817–2826

Wieder RK, Yavitt JB & Lang GE (1990) Methane production and sulfate reduction in two Appalachian peatlands. Biogeochem. 10: 81–104

Yanagisawa F & Sakai H (1983) Thermal decomposition of barium sulphate vanadium pentaoxide-silica glass mixtures for preparation of sulphur dioxide in sulphur isotope ratio measurements. Anal. Chem. 55: 985–987

Östlund P, Torssander P, Mörth C-M & Claesson S (1995) Lead and sulphur isotope dilution during dispersion from the Falu mining area. J. Geochem. Expl. 52: 91–95