SULFUR AND OXYGEN ISOTOPE RATIOS IN SULFATE DURING AN ACIDIFICATION REVERSAL STUDY AT LAKE GÅRDSJÖN, WESTERN SWEDEN

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Abstract. The reversibility of acidification is being investigated in a full scale catchment manipulation experiment at Lake Gårdsjön on the Swedish west coast using isotopes as environmental tracers. A 6300 m^2 roof over the catchment enables researchers to control depositional variables. Stable S isotope values were determined in bulk deposition, throughfall, runoff, groundwater and soil-extracted water during one year prior to and two years of experimental control. Data collected prior to experimental control suggest that the inorganic SO_4^{2-} pool within the catchment has a homogeneous $\delta^{34}S$ value of about + 5.5‰. Sprinkling of water spiked with small amounts of sea-water derived SO_4^{2-} started in April 1991. The $\delta^{34}S$ value of this SO_4^{2-} is around + 19.5‰. Since April 1991, the SO_4^{2-} concentration in runoff has decreased by some 30%, however, the $\delta^{34}S$ value have increased by only 0.5‰. This suggests mixing of sprinkling water S with a large reservoir of S in the catchment. Oxygen isotopes in SO_4^{2-} suggest that less than one third of the SO_4^{2-} in runoff is secondary SO_4^{2-} formed within the soil profile. This is, however, no evidence for net mineralization of S. The SO_4^{2-} in runoff in the roofed catchment is a mixture of SO_4^{2-} previously adsorbed in the soil, mineralized organic S and SO_4^{2-} from the sprinkler water. Calculations based on isotope data indicate that the turnover time of S within the catchment is on the order of decades. Since SO_4^{2-} facilitates base cation flow, the acidification reversal will take a much longer time than concentration decreases of SO_4^{2-} would suggest.

1. Introduction

Atmospheric deposition of anthropogenic S and N is the cause for acidified surface waters and groundwaters in Scandinavia. The thin soil cover often found in Scandinavia cannot buffer and alter the incoming acid rain. Sulfur emissions in Europe have decreased over the last decade by 20–30% and a similar decrease has been observed in the deposition of SO_4^{2-} in Sweden during the same period (Hedin *et al.*, 1994). The reduction in S emissions has raised the question of reversibility in acidification and the time-scale for a full recovery. In acidified waters, SO_4^{2-} facilitates base cation flow from the soil and the mobility of SO_4^{2-} is consequently of great significance (Likens *et al.*, 1977; Christophersen and Wright, 1981). Wright *et al.* (1988) showed that a reduction in sulfate flux reduces the flux of base cations. Retention of SO_4^{2-} can reduce the acidification of streams (Mitchell *et al.*, 1992a). Conversely, during an acidification reversal SO_4^{2-} desorption may prolong the recovery. If SO_4^{2-} adsorption is a reversible process, SO_4^{2-} and base cations will desorb from the soil until a new steady state is reached (Reuss and Johnson, 1986). Output will exceed input and SO_4^{2-} and the base cations will be leached from the

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soil to a higher extent than the reduction in acid deposition predicts. The residence time for S in acidified soils is therefore of major importance when predicting the time scale for full recovery.

The Lake Gårdsjön area (Figure 1) has been studied since the late 1960's and monitoring of chemical parameters of deposition, ground waters and soils has been performed during this time interval (Andersson and Olsson, 1985; Hultberg and Grennfelt, 1992). Whole catchment manipulations have been carried out including experiments on S cycling, liming, and clear felling. Sulfur mass balance studies suggest that the residence time for S is short, in the order a few years (Hultberg and Grennfelt, 1992).

To test this hypothesis and to evaluate the reversibility of SO_4^{2-} retention and acidification processes in general, a roof was built over an entire catchment (Gl, Figure 1). The roof enables researchers to control depositional variables and evaluate the potential of using isotope tracers. Some 20 co-ordinated investigations are under way in Gl. Examples of these are: chemical budgets, hydrological studies, turnover of N and Hg, soil and soil water chemistry and effects on vegetation.

Sulfur isotope values have been used extensively in environmental studies to trace the source of S and to study geochemical processes (Caron *et al.*, 1986; Castleman *et al.*, 1973; Krouse and Grinenko, 1991; Krouse and Van Everdingen, 1984; Mitzutani and Rafter, 1969; Nriagu and Coker, 1983; Saltzman *et al.*, 1983; Trembaczowski, 1991; Winner *et al.*, 1978). Other studies have dealt with sulfur cycling in catchments and soils (Fuller *et al.*, 1986a; Krouse and Case, 1981; Krouse and Tabatabai, 1986; Mayer *et al.*, 1991a,b; Stam *et al.*, 1992; Van Stempvoort *et al.*, 1990, 1992). However, until now, very few whole catchment manipulations using stable S and O isotopes in SO_4^{2-} have been performed to study S dynamics in soils. This paper presents isotope monitoring data from one year before the experiment and from the first two years of experimental treatment.

2. Background

The roofed catchment Gl is a well-defined drainage area, situated at 110–170 m above sea level (Hultberg *et al.*, in press). The highest sea level after the last glaciation has been determined at 130 m above present-day sea level. The bedrock in the catchment is composed of granite and gneiss. Minerals in the soil are quartz, feldspar and micas (Olsson *et al.*, 1985). The soil is an orthic podzol and consists of till of local origin. Soil depth in Gl is on average 40 cm with a 5 cm average thickness of the A horizon. Peat deposits can be found in the lower segments of the Lake Gårdsjön area but are lacking in G1. In the roofed area mature Norway spruce is the dominant tree species.

Due to the closeness to the coast, a maritime climate prevails and there are only small variations in monthly mean temperatures. Snow cover is seldom stable. Maximum precipitation falls in late autumn and winter. The catchment annually

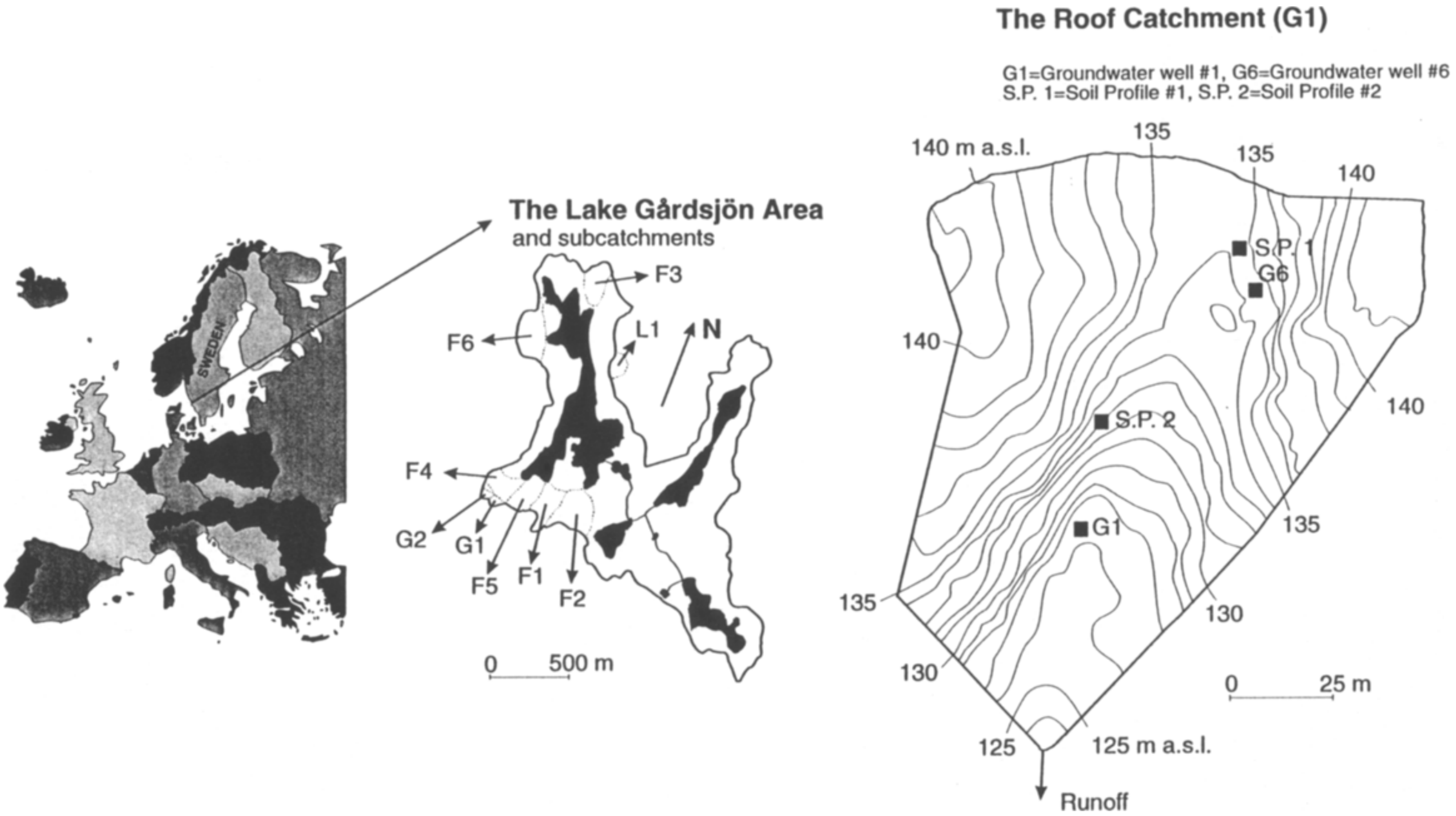

Fig. 1 Maps showing the location of Lake Gårdsjön, the Lake Gårdsjön area and the roofed catchment, G1.

receives 1198 mm of precipitation, 730 mm of throughfall, and loses 596 mm to evapotranspiration and 602 mm to runoff. These are mean values for the period 1979–1990. The turnover time for water in the G1 catchment has been estimated to be about three months (Nyberg *et al.*, 1993).

The roof over the G1 catchment covers 6300 m^2, and is situated about 2–4 m above the ground. Holes were made in the roof to accommodate approximately 370 tree trunks. Small v-shaped dams have been placed around the holes so that runoff water from the roof is not included in stemflow. Small amounts of stemflow still reach the ground but mass balance measurements show that they are negligible for all elements (Moldan, pers. comm.). Therefore, we believe that the reduction in anthropogenic S deposition under the roof is almost complete. Throughfall water that reaches the roof is collected and analyzed. Needles that fall on the roof are collected, dried and spread over the forest floor by hand.

A small amount of sea water and KCI (for nutrient balancing) is added to deionized lake water from Lake Gårdsjön. Some 275 sprinklers with a capacity of 3 mm hr^{-1} are used to spread the artificial precipitation under the roof cover. The sprinkling is adjusted to natural precipitation, so that the amount of runoff from G1 is equal to a control catchment. It is only possible to estimate the proportion of sprinkler water to groundwater during high discharge events (Nyberg, pers. comm.). During these events, the proportion of sprinkler water is less than 25%. The sprinkler water contains no N compounds and is very different from natural throughfall in the area. It has much lower concentrations of S, 29 μM, compared to 125 μM in natural throughfall (IVL, 1991). The annual amount of S added is now about 110 moles for the first year compared to pre-treatment input that was about 700 mol yr^{-1}. Sea-water SO_4^{2-}, which is isotopically distinct from the natural input, is added to the catchment in water sprinkled under the roof. Sea-water SO_4^{2-} has very well defined $\delta^{34}S$ and $\delta^{18}O_{SO_4}$ values of + 20.7‰ (measured Kattegatte water) and + 9.5‰ (Claypool *et al.*, 1980) respectively. The $\delta^{34}S$ value of the sprinkler water is + 19.5‰ and the $\delta^{18}O_{SO_4}$ value is + 9.3‰.

3. Methods

3.1. SAMPLING

Sampling in the Lake Gårdsjön area started in February 1990, 14 months prior to the commencement of sprinkling under the roof in April 1991. Samples were taken from runoff, groundwater, soil, throughfall and bulk deposition (open field collectors). Sampling was performed very intensively, sometimes on a weekly basis, during a 3.5 year period. Runoff water was collected in two ways. Initially, a specific volume of water was taken at a certain time. Now, there is automatic sampling during a certain time period (two weeks) that is proportional to the runoff. All the waters were sampled and filtered through 0.45 μm membrane filters before processing. A few water samples were stored in 2 L polyethylene bottles and refrigerated when not immediately processed.

3.2. ANALYTICAL TECHNIQUES

3.2.1. *Chemical analyses*

Collected water samples were analyzed for Cl^- and SO_4^{2-} by anion chromatography.

3.2.2. *Extraction of SO_4^{2-} in water samples*

Dissolved SO_4^{2-} was converted to $BaSO_4$ for the isotopic analyses. An ion exchange system modified from Nehring *et al.* (1977) and Hesslein *et al.* (1988) was used to concentrate SO_4^{2-} and to ensure pure precipitates of $BaSO_4$, as described by Andersson *et al.* (1992).

3.2.3. *Extraction of SO_4^{2-} in soil samples*

Two different extractions were performed sequentially (0.01 M $CaCl_2$ and 0.04 M $NaHCO_3$). These two extraction solutions were described by Tabatabai (1982) and Van Stempvoort *et al.* (1990). The $NaHCO_3$ solution was used to limit interferences when precipitating $BaSO_4$. About 40 g of wet soil was weighed and 200 ml of extraction solution added. Extraction time was 30 min. Extracted SO_4^{2-} samples were prepared as described for water samples above.

3.2.4. *Isotope analyses*

Sulfur isotope analyses were performed by burning a mixture of 10 mg $BaSO_4$ with 200 mg V_2O_5 and SiO_2 at 950 °C in a vacuum line (Yanagisawa and Sakai, 1983). The $SO_2(g)$ produced was collected in small glass ampoules and analyzed for its S isotope composition.

Oxygen isotope analyses in SO_4^{2-} were performed in a similar manner by mixing 10 mg of $BaSO_4$ with 10 mg graphite and burning the mixture at 1200 °C under vacuum (Rafter, 1967). The $CO_2(g)$ produced was collected and analyzed for its O isotope composition.

The $SO_2(g)$ and $CO_2(g)$ were analyzed with an upgraded Micromass 602 mass spectrometer at the Laboratory of Isotope Geology of the Naturhistoriska riksmuseet in Stockholm. The S isotope composition is defined as a deviation in ‰ of the ratio $^{34}S/^{32}S$ between a sample and a standard, expressed in the conventional $\delta^{34}S$ notation relative to Cañnon Diablo Troilite (CDT). The accuracy of the measurements based on standard measurements is better than $\pm$ 0.2‰ and generally around $\pm$ 0.1‰. The O isotope composition is defined as a deviation in ‰ of the value $^{18}O/^{16}O$ expressed in the conventional $\delta^{18}O$ notation relative to SMOW (Standard Mean Ocean Water). The accuracy of the measurements is better than $\pm$ 0.4‰.

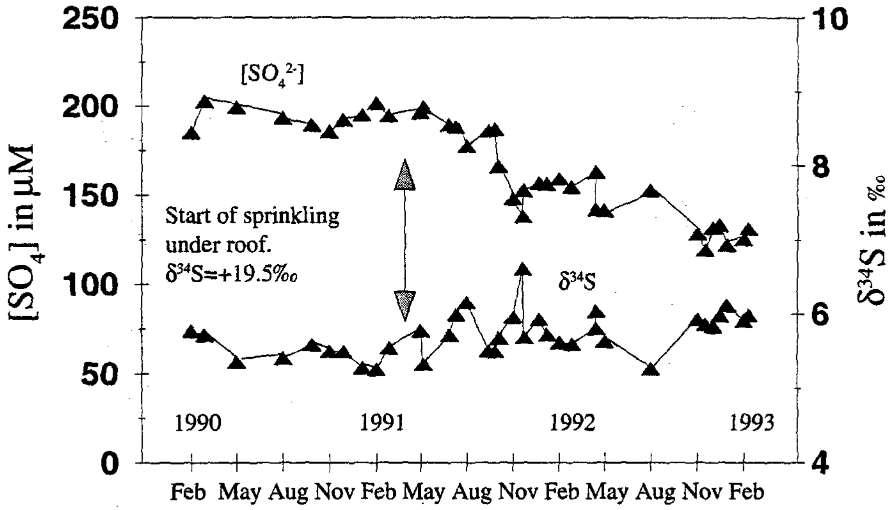

Fig. 2. Concentration of SO_4^{2-} and its S isotope composition in runoff through time.

4. Results

4.1. S ISOTOPES

The SO_4^{2-} concentration and $\delta^{34}S$ values in runoff are listed in Table I and shown in Figure 2. A trend of decreasing concentration of dissolved SO_4^{2-} and increasing $\delta^{34}S$ values with time can be seen from the start of sprinkling in runoff, but the change in the $\delta^{34}S$ values is minor (Figure 2). After two years of sprinkling, the SO_4^{2-} concentration in runoff had decreased by 30% while the shift in $\delta^{34}S$ was in the order of only +0.5‰. The mean $\delta^{34}S$ value in runoff for the pre-treatment year was +5.49‰ (±0.14‰ at 95% confidence interval) while the five-point moving averages after two years of sprinkling were close to +6.0‰. The change in $\delta^{34}S$ in groundwater well #1 and #6 is less and was not statistically significant (Tables II and III). The $\delta^{34}S$ values in groundwater do not show any trend with time, although the decrease in SO_4^{2-} concentration is around 15% (Figure 3). Groundwater well #6 had slightly higher $\delta^{34}S$ values than groundwater well #1 and the runoff.

Sulfate concentration in the soil and the $\delta^{34}S$ values of the adsorbed SO $_4^{2-}$ estimated using soil extracts. The results of extraction of soil samples with $CaCl_2$ and $NaHCO_3$ solutions are summarized in Table IV. There were large differences in the concentration of S recovered from the soil with respect to both the extraction method and depth, but the difference in the $\delta^{34}S$ values was small or none. It is interesting to note that the $\delta^{34}S$ values in the soil profiles were similar to those of the groundwater well in the vicinity of the soil profile. Different extraction methods were used as the basis for estimating the amount of soil S in the catchment prior to experimental treatment (Table V). Depending on the extraction method, different

TABLE I

Data from runoff. Concentrations are given in μM and δ values are given in ‰

Date	$[Cl^-]$	$[SO_4^{2-}]$	$\delta^{34}S$	$\delta^{18}O_{SO_4}$	Moving five-point average $\delta^{34}S$
90-Feb-27	551	185	5.77	4.78	
90-Apr-11	685	203	5.72		
90-Jun-27	807	199	5.36	5.57	
90-Sep-26	996	193	5.41		
90-Oct-31	943	190	5.59		5.57
90-Nov-28	923	186	5.50	5.09	5.52
91-Jan-30	692	195	5.28		5.43
91-Feb-27	671	202	5.26		5.41
91-Mar-27	655	195	5.55	5.70	5.44
91-May-06	661	196	5.78		5.47
91-Jun-27	770	199	5.33	5.30	5.44
91-Jul-10	799	189	5.72		5.53
91-Jul-24	774	188	5.99		5.67
91-Sep-13	1175	178	6.16	5.88	5.8
91-Sep-25	1006	186	5.51		5.74
91-Oct-02	1032	187	5.50		5.78
91-Oct-31	1084	166	5.68		5.77
91-Nov-20	1049	148	5.96		5.76
91-Nov-22	995	138	6.61	5.35	5.85
91-dec-23	914	153	5.69		5.89
92-Jan-08	954	157	5.93		5.97
92-Jan-29	861	156	5.73		5.98
92-Feb-26	854	159	5.62		5.92
92-Apr-15	790	155	5.60		5.71
92-Apr-15	825	163	5.81		5.74
92-Apr-29	761	142	6.04	6.09	5.76
92-May-13	735	142	5.64		5.74
92-Sep-09	1084	153	5.27		5.67
92-Nov-18	906	128	5.93		5.74
92-Dec-02	702	119	5.86		5.75
92-Dec-16	660	132	5.83	5.59	5.71
92-Dec-30	670	133	5.98		5.77
93-Jan-27	596	122	6.12		5.94
93-Feb-10	570	125	5.91		5.94
93-Mar-01	593	132	5.99	5.07	5.97
93-Mar-10	605	136	5.90		5.98

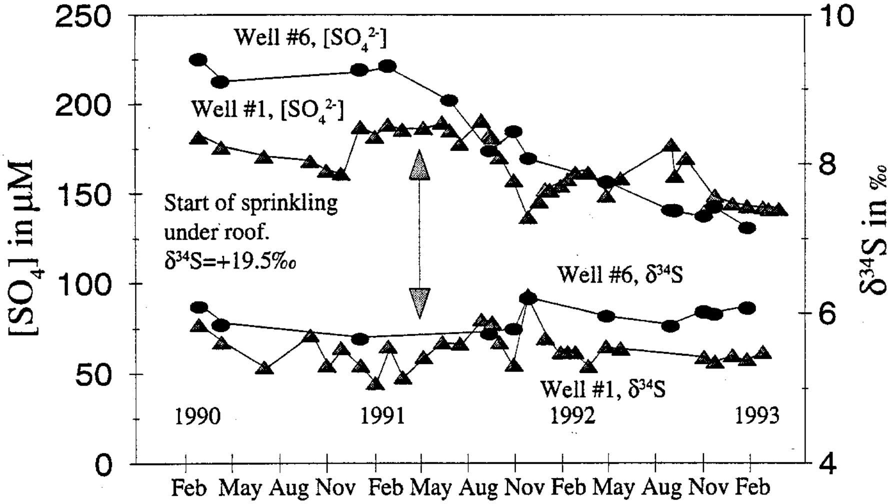

Fig. 3. Concentration of SO_4^{2-} and its S isotope composition in groundwater well #1 and #6 through time.

amounts of S were estimated. Calcium chloride solutions extract the soluble fraction of S in soils. Sulfur species extracted by $NaHCO_3$ are not well characterized (Tabatabai, 1982). Van Stempvoort *et al.* (1990) concluded that $NaHCO_3$ extracts the same S species as CaH_2PO_4, but that $NaHCO_3$ should be preferred because of interferences by PO_4^{3-} during the preparation of $BaSO_4$. Distilled water and 0.01 M $CaCl_2$ extracted approximately equal amounts of S. Similarly, 1 M KCI and 0.04 M $NaHCO_3$ extracted equal amounts of S, but approximately five times more than was extracted using water or $CaCl_2$. The $K_4P_2O_7$ solution extracted large amounts of S, mostly organic.

4.2. O ISOTOPES

Oxygen isotope values of SO_4^{2-} in throughfall, sprinkler water, runoff and groundwater are presented in Tables I, III and VI. The change in $\delta^{18}O_{SO_4}$ values in the sprinkler water compared to the pre-treatment throughfall was small, therefore the $\delta^{18}O_{SO_4}$ value was not expected to change very much in runoff and groundwater during the treatment. However, there was an isotopic shift of around 4‰ between input (throughfall and sprinkler water) and output (runoff).

5. Discussion

5.1. S ISOTOPES

Many studies support the use of throughfall data as an estimate of total S deposition in forested catchments (Lindberg and Garten, 1988; Hultberg and Grennfelt, 1992;

TABLE II

Data from ground water well #1. Concentrations are given in μM and δ values are given in ‰

Date	$[Cl^-]$	$[SO_4^2-]$	$\delta^{34}S$	Moving five-point average $\delta^{34}S$
90-Feb-27	506	182	5.85	
90-Apr-11	529	176	5.62	
90-Jul-02	599	171	5.29	
90-Sep-29	689	168	5.71	
90-Oct-31	779	163	5.31	5.56
90-Nov-28	757	161	5.54	5.49
91-Jan-04	699	187	5.31	5.43
91-Feb-01	642	182	5.07	5.39
91-Feb-27	632	188	5.56	5.36
91-Mar-27	615	186	5.15	5.33
91-May-06	632	187	5.42	5.3
91-Jun-12	653	190	5.62	5.36
91-Jul-17	662	178	5.60	5.47
91-Aug-28	710	191	5.92	5.54
91-Sep-18	1135	181	5.88	5.69
91-Oct-02	1037	170	5.62	5.73
91-Oct-30	1061	157	5.32	5.67
91-Nov-27	1055	137	6.24	5.8
91-Dec-31	955	152	5.67	5.75
92-Jan-29	844	154	5.48	5.67
92-Feb-12	838	158	5.49	5.64
92-Feb-27	846	162	5.48	5.67
92-Mar-25	826	161	5.30	5.48
92-Apr-29	783	149	5.56	5.46
92-May-27	764	158	5.53	5.47
92-Nov-04	999	140	5.42	5.46
92-Nov-25	794	149	5.36	5.43
92-Dec-29	688	144	5.44	5.46
93-Jan-27	626	143	5.39	5.43
93-Feb-26	608	142	5.49	5.42
93-Mar-10	622	141	5.70	5.48
93-Mar-30	631	142	5.49	5.5

Mitchell *et al.*, 1992b). Hultberg and Grennfelt (1992) showed that data from a 10-year time span are needed to balance the amount of SO_4^{2-} deposited and the amount of SO_4^{2-} in runoff at Lake Gårdsjön. The annual variation was large, showing both a negative and positive S mass balance.

TABLE III

Data from ground water well #6. Concentrations are given in μM and δ values are given in ‰

Date	[Cl^-]	[SO_4^{2-}]	$\delta^{34}S$	$\delta^{18}O_{SO_4}$	Moving five-point average $\delta^{34}S$
90-Feb-27	647	224	6.08	5.01	
90-Apr-11	632	212	5.84		
91-Jan-04	877	219	5.65		5.86
91-Sep-13	1191	173	5.72		5.74
91-Oct-30	1321	184	5.78		5.72
91-Nov-27	1081	169	6.19	5.38	5.9
92-Apr-29	730	156	5.95		5.97
92-Sep-02	1162	140	5.82		5.99
92-Nov-04	1122	137	6.01		5.93
92-Nov-25	885	142	5.98		5.94
93-Jan-27	580	131	6.06	4.61	6.02

TABLE IV

Sulfate extractions of pretreatment soil. Soil samples were extracted with 0.01M $CaCl_2$ and 0.04M $NaHCO_3$ sequentially. Wet soil was used for the extraction with the soil:solution value 1:5 for 30 min. C = Concentration of SO^{4}_{-2} in μmol $(100\ g)^{-1}$ dry soil; δ values are given in ‰

Sample	Depth	$\delta^{34}S$, $CaCl_2$	$\delta^{34}S$, $NaHCO_3$	$\delta^{34}S$, Tot	C_{CaCl_2}	C_{NaHCO_3}	C_{Tot}
S.P.#1	0–10				21	16	37
S.P.#1	20–25	6.39	6.34	6.35	49	257	306
S.P.#1	38–48	6.33	6.13	6.18	25	70	95
S.P.#1	67–77	6.49	5.51	5.69	20	92	112
S.P.#2	0–6				89	66	155
S.P.#2	12–20	5.59	5.46	5.48	75	444	519
S.P.#2	30–40	5.46	5.02	5.09	76	419	495
S.P.#2	62–75	5.4	5.56	5.52	48	145	193

The 14-month pre-treatment sampling period showed that S deposited to the catchment (bulk deposition and throughfall) had a significantly higher $\delta^{34}S$ value than the runoff (Mörth and Torssander, in press). The calculated weighted mean $\delta^{34}S$ values for bulk deposition and throughfall were +7.4‰ and +8.0‰, respectively. Sulfur deposition to the Lake Gårdsjön area can be described as a mixture between sea salt and anthropogenic sources. Calculation of the anthropogenic $\delta^{34}S$ value by calculating excess SO_4^{2-} or using the Na^+ to SO_4^{2-} value suggests an anthropogenic source with a $\delta^{34}S$ value of around +4.5‰ (Mörth and Torssander,

TABLE V

Calculations of the inorganic S pool in the roofed catchment before the treatment. The calculations are based on the assumptions that the catchment area is 6300 m^2, the soil depth is 40 cm and the bulk density is 1 g cm^{-3} (Hultberg, pers. comm.)

Extraction Method	Reservoir size in moles (kg)
Water[a]	1615 (52)
$CaCl_2$, 0.01 M	1815 (58)
KCl, 1 M*	8145 (261)
$NaHCO_{31}$, 0.04 M	8565 (275)
$K_4P_2O_7$*)	42000 (1347)

[a] Data calculated from Schweda, P. (unpublished data).

TABLE VI

Oxygen isotopes in sulfates

Sample	Average or range, $\delta^{18}O_{SO_4}$ in ‰
Bulk deposition, pretreatment (4 values)	range: +9.50 to +12.30
Throughfall, pretreatment (6 values)	+9.7 ±2.4, 95% confidence interval
Runoff, pretreatment and treatment, (10 values)	+5.4 ±0.3, 95% confidence interval
Groundwater well #6, pretreatment and treatment (3 values)	range: +4.6 to +5.4
Sprinkler water	+9.3 (sea water +9.5)

in press). Seasonal variation in the $\delta^{34}S$ values in bulk deposition has been reported from other investigations (Andersson *et al.*, 1992; Caron *et al.*, 1986; Nriagu and Coker, 1978) but cannot be seen at Lake Gårdsjön (Mörth and Torssander, in press) or at the Northern Hardwood catchment (Stam *et al.*, 1992). Sulfate deposition has decreased 25 % during the last decade due to reduced emissions of SO_2 (Hedin *et al.*, 1994). This decrease in depositional SO_4^{2-} can explain the higher $\delta^{34}S$ values in throughfall relative to runoff, because the anthropogenic $\delta^{34}S$ value is lower than the deposition $\delta^{34}S$ value.

The cause for the small shift in $\delta^{34}S$ in runoff can be uptake/fixation, mineralization or mixing of S within the catchment. Pyrite and organic S formed from bacteriogenic H_2S can be a sink for S in forested catchments. Bacterial sulfate reduction has been shown to be important at Mjösjön in central Sweden (Andersson *et al.*, 1992) and in the ELA area in Ontario, Canada (Hesslein *et al.*, 1988). An indication of bacterial sulfate reduction, especially during low discharge periods is a decrease in SO_4^{2-} concentration with a corresponding rise in the $\delta^{34}S$ values of dissolved SO_4^{2-}, resulting from isotopic fractionation during bacterial sulfate reduction. Changes in SO_4^{2-} concentrations and $\delta^{34}S$ values as described above were not observed in the roofed catchment except during high discharge when the sprinklers were run to simulate rainstorms. Single sprinkling events have shown that 25% of the runoff consisted of sprinkler water (Nyberg *et al.*, 1993).

Isotope fractionation of S during its incorporation into biomass as organic S compounds was investigated by Kusakabe *et al.* (1976). They showed that there is little or no difference in $\delta^{34}S$ values of biomass, organic S in soil and adsorbed/soluble SO_4^{2-}. These results are supported by investigations of Van Stempvoort *et al.* (1992) and Krouse and Tabatabai (1986). Recently, Mayer (1993) showed that S isotope fractionation during immobilization and mineralization could amount to several ‰, but the change in the $\delta^{34}S$ value of SO_4^{2-} in solution was smaller. In two investigated catchments, the difference between throughfall and dissolved SO_4^{2-} in the soil water was never larger than 1.2‰ (enrichment of ^{32}S in soil water SO_4^{2-}).

The small difference in $\delta^{34}S$ values between the two soil SO_4^{2-} extraction methods suggests that there is an exchange between the soluble SO_4^{2-} fraction and the specifically adsorbed SO_4^{2-}. The SO_4^{2-} pool in the soil available for exchange with SO_4^{2-} in solution must include the $NaHCO_3$-extractable S pool. The similarity of $\delta^{34}S$ values of SO_4^{2-} in the groundwater and that of adsorbed SO_4^{2-} suggests that fractionation during adsorption/desorption is negligible, as shown also by Fuller *et al.* (1986a) and Van Stempvoort *et al.* (1990).

Thus, the statistically significant change in $\delta^{34}S$ values in runoff is probably caused by mixing of sprinkler (throughfall) SO_4^{2-} with a large reservoir of S in the soil. Because the pool of adsorbed SO_4^{2-} is very large relative to the amount of SO_4^{2-} from the sprinkler system, a small change in the $\delta^{34}S$ values in runoff is predicted. The soil SO_4^{2-} is more or less adsorbed to solid phases (Fe, Al oxides and hydroxides), therefore, a mixing of the sprinkler water SO_4^{2-} and the soil SO_4^{2-} must include exchange between dissolved and adsorbed SO_4^{2-}. Singh (1984) has shown that when a B-horizon podzolized soil sample is equilibrated with a small amount of $^{35}SO_4^{2-}$ in distilled water, $^{35}SO_4^{2-}$ is detected in solution and in the adsorbed SO_4^{2-} pool. The exchange process is rapid: almost complete exchange is reached within 30 min (Rajan, 1979; Singh, 1984). A rapid process is needed considering that the turnover time for water in the G1 catchment is only about three months (Nyberg *et al.*, 1993).

The S isotope composition within the roofed catchment reflects the isotopic composition of deposited S. Short-term variations in throughfall and sprinkler water are no longer detectable in runoff because of mixing with a large reservoir of adsorbed S. Variation and response time in runoff to changes in the deposited $\delta^{34}S$ values must, therefore, reflect transfers and mixing among different S pools in the catchment. The slightly higher $\delta^{34}S$ values found at groundwater well #6 and soil profile 2 reflect a more rapid response time to and less smoothing of the throughfall signature because the site is mostly a recharge area.

Mass balance calculations after one year of sprinkling suggest that 25% of the runoff had its origin in the sprinkler water, but δ^{34}S values do not support this hypothesis (Mörth and Torssander, in press). If the SO_4^{2-} in runoff is a mixture of sprinkler water SO_4^{2-} and that already fixed within the catchment, almost all SO_4^{2-} in runoff is derived from fixed S. At Risdalsheia in Norway, a similar ongoing experiment with a roof cover over a catchment shows the change in the δ^{34}S value of the runoff after seven years of sprinkling to be less than 2‰ (Mörth and Torssander, unpublished data), which is in agreement with results from Lake Gårdsjön reported here. The reversibility of acidification as observed in SO_4^{2-} concentration in runoff at Risdalsheia is fairly rapid. After a few years of treatment, the SO_4^{2-} concentration by 50% (Wright *et al.*, 1988), whereas the S isotope data suggest a turnover time of several decades.

5.2. O ISOTOPES

Possible causes for the O isotope difference between SO_4^{2-} in sprinkler water and that in runoff are: isotopic exchange between water and SO_4^{2-}, fractionation during adsorption/desorption, and microbially mediated assimilatory reduction followed by oxidation of organic S in the upper soil horizons. The isotopic exchange between water and SO_4^{2-} at low temperatures is slow even at low pH ratios (Lloyd, 1967; Chiba and Sakai, 1985). Little or no fractionation of the O isotopes is observed during the absorption/desorption of SO_4^{2-} (Van Stempvoort *et al.*, 1990). Oxygen isotopes of SO_4^{2-} in soils can be modeled as a mix between deposited SO_4^{2-} and a SO_4^{2-} reservoir that has undergone transformations in the soil, i.e., secondary SO_4^{2-} (Van Stempvoort *et al.*, 1992).

In many investigations (Taylor *et al.*, 1984; Van Everdingen and Krouse, 1985; Caron *et al.* 1986; Gélineau *et al.*, 1989 and Van Stempvoort *et al.*, 1992), $\delta^{18}O_{SO_4}$ values have been used to trace geochemical reactions using the following formula:

$$\delta^{18}O_{SO_4} = X\,(\delta_w + \varepsilon_w) + (1 - X)\,(\delta_a + \varepsilon_a) \tag{1}$$

where the parameters are: X = fraction of O provided from water, δ_w = O isotope composition of water, ε_w = fractionation of water O, δ_a = O isotope composition of dissolved O_2 in water and ε_a = fractionation of dissolved O_2.

Toran and Harris (1989) showed that the mixing fractions used in this formula are difficult to specify since the exact reaction pathway must be known. Kelly (1982) suggested that all the O may be taken from water because of the aerobic respiration mechanism in microorganisms. Another difficulty in calculating oxygen isotope composition of secondary SO_4^{2-} lies in the possibility of fractionation in assimilatory reduction. The fractionation of O isotopes ought to be a preferential uptake of ^{16}O in SO_4^{2-} as for dissimilatory reduction. The contribution of secondary SO_4^{2-} in a mixing model based on the O isotope composition will therefore normally be overestimated.

Calculations of the $\delta^{18}O_{SO_4}$ value for the secondary SO_4^{2-} can be made with the assumption that the microbially mediated reduction processes involve little fractionation, and that O involved in the oxidation is taken from the water in the soil. The Lake Gårdsjön water has $\delta^{18}OH_2O$ values of around –9‰ (Nyberg *et al.*, 1993). Application of a mixing model with two sources for the SO_4^{2-} in runoff can be used to calculate the fraction of secondary SO_4^{2-}. The sources would in this case be SO_4^{2-} from throughfall and sprinkler water and secondary SO_4^{2-}. The mixing model indicates that the fraction of secondary SO_4^{2-} is around 17 to 26 %, depending on the fractionation during the reaction. The reported abiotic fractionation term, ε_w, has a range of –6 to 2.6‰ (Lloyd, 1967; Taylor *et al.*, 1984; van Everdingen and Krouse, 1985; Toran and Harris, 1989). The amount of secondary SO_4^{2-} reported by other investigators (Caron *et al.*, 1986; Gélineau *et al.*, 1989; Van Stempvoort *et al.*, 1992) is in the same order.

It has been shown that SO_4^{2-} in soils can be microbially reduced (assimilatory reaction pathway), and incorporated into organic S fractions and later mineralized (Fuller *et al.*, 1986b; Mitchell *et al.*, 1992b). These reactions are normally in a steady state condition but the amounts of S cycled through these fractions may be substantial (Fuller *et al.*, 1986b). The secondary SO_4^{2-} is produced mainly in the upper soil horizons (Nriagu *et al.*, 1991; Mitchell *et al.*, 1992b). Sulfate adsorption and desorption occurs mainly in the B-horizon (Mitchell *et al.*, 1992b). The main question is whether or not the formation of organic S and its mineralization are in a steady state. It has been shown at the acidification reversal experiment at Risdalsheia in Norway that a steady state is not reached immediately (Wright *et al*, 1993). Mitchell *et al.* (1989) showed that whole tree harvesting did not significantly change the sizes of the organic S pools. Since a clear-cut would have a marked impact on the amount of S deposited, this result suggests that net transformations of organic S due to changes in deposition would be small or none. It is, therefore, unclear if reductions in SO_4^{2-} deposition will result in net mineralization of organic S. This has to be further investigated.

6. Conclusions

The isotope data suggest that fractionation of S isotopes within the roofed catchment is not significant. Therefore, $\delta^{34}S$ values in runoff and groundwater wells are a function of the deposited S and S fixed in the catchment. Variations and response time to changes in the deposition of SO_4^{2-} reflect transfers or mixing between different S pools. These pools of SO_4^{2-} in the soil are sufficiently large to control the isotopic composition of the runoff SO_4^{2-}.

The O isotopes of the SO_4^{2-} suggest that less than one third of the SO_4^{2-} in runoff has been acquired from mineralized organic S fractions. This is, however, no evidence for net mineralization of S. Sulfate in runoff can therefore be modelled as a mixture of S from adsorbed SO_4^{2-}, mineralized organic S and SO_4^{2-} from the sprinkler water. The relative contribution of these S sources within the catchment controls the turnover time for S in the catchment. Because the size of individual S pools in the catchment is large, the turnover time will be in the order of decades rather than years.

During an acidification reversal, output exceeds input and desorption of SO_4^{2-} and base cations previously adsorbed are leached from the soil. Calculations based on isotope data indicate that the turnover time of S within the catchment is on the order of decades. As S isotope data indicate that adsorption of SO_4^{2-} could be a reversible process, an acidification reversal will take much longer time than the decrease in concentration of SO_4^{2-} in runoff would suggest.

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