

Interpretation of sulfur cycling in two catchments in the Black Forest (Germany) using stable sulfur and oxygen isotope data

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Abstract. The isotopic composition of SO_4^{2-} in bulk precipitation, canopy throughfall, seepage water at three different soil depths, stream water, and groundwater was monitored in two forested catchments in the Black Forest (Germany) between November 1989 and February 1992. Isotope measurements on aqueous sulfate were complemented by $\delta^{34}\text{S}$ -analyses on SO_2 in the air, total sulfur and inorganic sulfate in the soil, and bedrock sulfur, in order to identify sources and biogeochemical processes affecting S cycling in catchments with base poor, siliceous bedrock. Stable S isotope data indicated that atmospheric deposition and not mineral weathering is the major source of S in both catchments since $\delta^{34}\text{S}$ -values for sulfate in the soil, in seepage water, and in stream water were generally found to be similar to the mean $\delta^{34}\text{S}$ -values of precipitation SO_4^{2-} (+2.1‰). However, $\delta^{18}\text{O}$ -values of seepage water SO_4^{2-} at 30 cm and especially at 80 cm depth were depleted by several per mil with respect to those of the atmospheric deposition (+7.5 to +13.5‰). This indicates that in both catchments a considerable proportion of the seepage water SO_4^{2-} is derived from mineralization of carbon-bonded soil S and must therefore have cycled through the organic soil S pool. $\delta^{34}\text{S}$ -values for different S compounds in the solid soil were found to differ markedly depending on S fraction and soil depth. Since atmospheric S deposition with rather constant $\delta^{34}\text{S}$ -values was identified as the dominant S source in both catchments, this is interpreted as a result of *in situ* isotope fractionation rather than admixture of isotopically different S. The differences between the $\delta^{34}\text{S}$ -values of seepage water and soil sulfate and those of organic soil S compounds are consistent with a model in which SO_4^{2-} uptake by vegetation and soil microorganisms favours $^{34}\text{SO}_4^{2-}$ slightly, whereas during mineralization of organic soil S to aqueous SO_4^{2-} , ^{32}S reacts preferentially. However, the data provide evidence for negligible isotope fractionation during physico-chemical S transformations such as adsorption/desorption in aerated forest soils.

Key words: Catchment, isotope fractionation, sulfur cycling, stable isotopes, $\delta^{34}\text{S}$, $\delta^{18}\text{O}_{\text{sulfate}}$

Introduction

Mass balances in small experimental catchments is an important approach for studying the effects of atmospheric deposition on the biogeochemical

cycling in terrestrial ecosystems. This approach determines input/output ratios for elements for different compartments and fluxes including atmospheric deposition and runoff, and provides information about the response of the ecosystem to external influences such as atmospheric inputs or management practices. Since SO_4^{2-} is often the predominant anion associated with atmospheric deposition in forest ecosystems in Europe and Northern America (e.g. Führer et al. 1988; Binkley et al. 1989), the biogeochemical S cycle has been investigated in numerous studies in the last decade, some of which have been critically reviewed by Krug (1991).

A major problem associated with the input/output approach is the estimation of the actual total deposition for a whole catchment. Even though dry S deposition for an individual plot (e.g. forest stand) can be easily derived from the difference of the S fluxes in canopy throughfall and bulk precipitation, the up-scaling from the plot-level to the landscape-level may represent distinct uncertainties. But within the ability to accurately quantify both atmospheric input and stream export of S, a number of catchments are characterized by more or less balanced S budgets, whereas others were found to be unbalanced (e.g. Rochelle et al. 1987). Within the latter, catchments exist in which more S is imported than exported because significant amounts of S are retained over many years (e.g. Meiwes & Khanna 1981; Buell & Peters 1988; Swank & Crossley 1988). In others, higher S output was observed than input indicating a significant mobilization of S within the ecosystem (e.g. Likens et al. 1977; Johnson et al. 1986; Mitchell et al. 1992). Most of this variation in S retention or mobilization has been attributed to differences in the relative importances of various soil processes among sites.

Processes and patterns of S cycling in forest ecosystems have been reviewed by Johnson (1984) and Mitchell et al. (1992). In general, four transformation processes account for either retention or mobilization of S-containing compounds in well-aerated forest soils: (1) Deposited atmospheric SO_4^{2-} is assimilated (occasionally also accumulated) by vegetation and soil microorganisms, with carbon-bonded sulfur (C-S) and organic sulfate (C-O-S-O $_3^-$) being the major end products. (2) Organic S compounds can be mineralized and hydrolyzed to SO_4^{2-} preferentially in the topsoil. (3) Adsorption and occasionally precipitation of aluminium sulfate minerals may retain SO_4^{2-} in the subsoil, whereas (4) desorption and dissolution are the reverse mechanisms supplying SO_4^{2-} to the soil solution. Although in some catchments mass balances indicate considerable gains or losses of S over several years, the gross retention and mobilization processes cannot be ascertained if only atmospheric inputs and hydrological losses are known.

The analysis of natural abundance ratios of stable isotopes provides another approach to elucidate the biogeochemical S cycle. However, very few system-

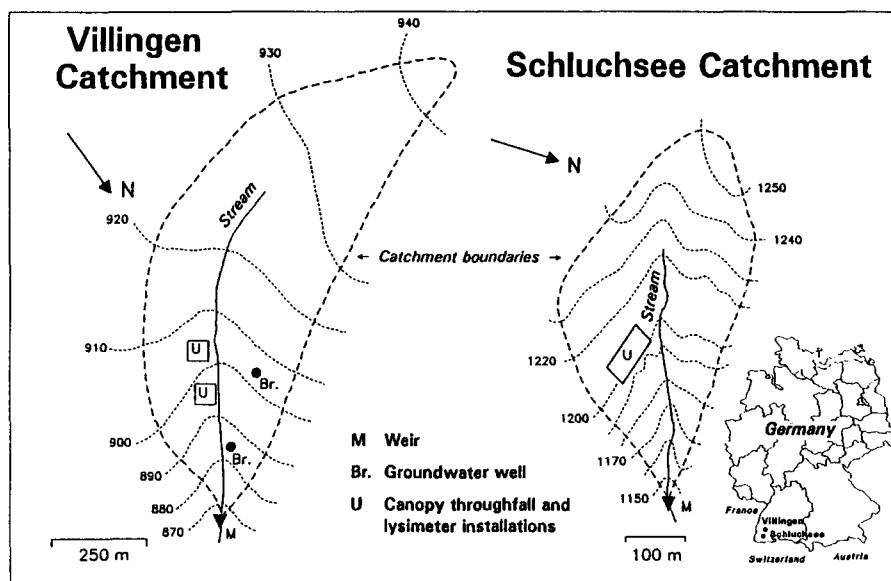


Fig. 1. Location and instrumentation of the ARINUS experimental catchments Schluchsee and Villingen in the Black Forest (Germany).

atic investigations of sulfur (Fuller et al. 1986; Hesslein et al. 1988; Stam et al. 1992) and oxygen isotopes in SO_4^{2-} (Gélineau et al. 1989; Van Stempvoort et al. 1992, 1994) on the catchment scale have been conducted so far. None of them have determined the isotopic compositions of all S sources. This proved to be problematic since both, the admixture of S with a different isotope composition, and isotopic fractionation during transformations can alter the isotope composition of S constituents within the ecosystem. Limited knowledge about the importance of isotope discrimination during transformations in the S cycle can therefore cause erroneous conclusions.

The purpose of this study was to determine the isotope compositions of S compounds in two forested catchments, for which S fluxes and pool sizes of all major S sources were known. Whereas S isotope measurements should allow the identification of S sources in different ecosystem compartments, oxygen isotope ratios in SO_4^{2-} were used as a potential indicator for redox-reactions. It was expected that the combination of flux and isotope data would allow us to distinguish whether alterations of the isotope composition of a given S compound throughout the catchment were caused by mixing of S from different sources or isotopic fractionation during S transformations in the ecosystem.

Description of catchments

The two study sites, Schluchsee (47° 49' N, 8° 6' E) and Villingen (48° 3' N, 8° 22' E) are located in the higher altitudes of the Black Forest, Germany (Fig. 1). Both catchments are completely forested and have not been affected by agricultural activities, fertilization, or road salts. Catchment Schluchsee (S1) is located between 1145 and 1253 m elevation and has an average slope of 22%. The total watershed (11 ha) is covered with 45 to 65 year old planted Norway spruce (*Picea abies* (L.) Karst.). Meteorological data have been obtained on adjacent forest openings continuously since 1987. The climate is cool and humid with a mean annual temperature of 5 °C and a mean annual precipitation of about 1900 mm, of which approximately 50% falls as snow. The bedrock is Bärhalde granite covered by well-drained Podzols (Typic Haplohumod). The thickness of the soil ranges from 60 cm to 100 cm. Between soil and solid granite exists a highly permeable layer of fine gravel with variable thickness ranging from a few centimeters to about 3 m. This gravel derived from both the physical in situ weathering of the granite during the last deglaciation (Würm) and the surficial deposits of a local glaciation. Hence, the mineralogical composition of the soils and the regolith zone is fairly homogeneous.

Catchment Villingen (V1, 46 ha) has an average slope of 6%. It is covered mainly with 80 to 110 year old Norway spruce (*Picea abies* (L.) Karst.) mixed with silver fir (*Abies alba* Mill.) and Scots pine (*Pinus sylvestris* L.). Due to the lower elevation of 810 to 945 m, the mean annual precipitation is lower (1040 mm), and the mean annual temperature is higher (6 °C) than at Schluchsee; 40% of the annual precipitation falls as snow (Feger et al. 1990). The bedrock consists of triassic, quartz-rich, red sandstones (Buntsandstein) with clay interlayers. Soils are sandy to loamy and imperfectly drained due to the high clay content in the subsoil. Prevailing soil types are acid Brown-earths (Typic Dystrochrepts) and Stagnogleys (Histic Dystraquepts), the latter especially at lower hill-slope positions. Both catchments are drained by perennial (first order) streams.

Physical and chemical soil properties are described in detail by Feger et al. (1990). The soils in Schluchsee and Villingen are characterized by low pH-values (3.5–4.4 in CaCl₂ for S1, 2.4–4.7 in CaCl₂ for V1) and low base saturation (<10%) even in the deeper mineral soil. Whereas the Podzol at Schluchsee is highly permeable throughout the entire soil profile, higher clay contents in combination with elevated bulk densities in the subsoil of the Brown-earth Villingen cause a decrease in coarse pore volume and saturated hydraulic conductivity. Consequently, a perched water table is a common phenomenon in the Villingen catchment resulting in predominantly lateral superficial drainage during storm runoff (Brahmer & Feger 1991).

Methods

Gaseous sulfur compounds

The major gaseous input of S to forests occurs in the form of SO₂ (Lindberg et al. 1986). In order to trap SO₂ in the form of sulfate, ambient air was sampled over four-week intervals using alkaline impregnated glass fibre filters (Dämmgen et al. 1985). These were exposed at about 1.8 m height in the openings adjacent to the forest so that air had free access to the filter surfaces. The filters were returned to the laboratory and sulfate from the filter surfaces was extracted with hot double distilled (dd) water. For S isotope analysis, the SO₄²⁻ in the extractant was then precipitated as BaSO₄ as described below. Since mean SO₂ concentrations in the ambient air in this region of the Black Forest are typically below 5 µg m⁻³ (LfU Baden-Württemberg 1992), the amount of S trapped on the filters was frequently not enough to allow for reliable δ³⁴S-measurements. At the beginning of the study in 1989 and 1990, samples had to be combined to obtain δ³⁴S-values. The number of filters exposed per four week sampling period was increased in spring 1991 to overcome this problem.

Aqueous sulfate

Bulk precipitation, canopy throughfall, and soil seepage water at three different depths were collected as weekly or biweekly composites. In the same time intervals, stream water and groundwater were sampled throughout the study period. All water samples were returned to the laboratory for volume determination and chemical analysis. Water and element fluxes were determined for all compartments in both catchments. A description of methods used to estimate S fluxes to and within the catchments has been reported elsewhere (Feger 1993, 1995).

In openings or meadows adjacent to the forest, bulk precipitation was sampled 1 m above ground using five 1-L polyethylene darkened bottles covered by a funnel (450 cm² area) with a polyester screen (2×2 mm mesh) to avoid contamination. Since this device is permanently open to the atmosphere, it collects wet and the part of the dry deposition which is caused by sedimentation of coarse particles. Using the same type of rain gauges, canopy throughfall was sampled within representative stands in the catchments. Ten collectors were installed equidistant (5 m) along a transect. During the winter, the funnels were replaced by snow buckets (660 cm² area). All precipitation samples collected during the same period were bulked after measuring pH and electric conductivity. Since stemflow has been shown by Bücking et al. (1983) to represent a negligible proportion of throughfall in Norway spruce forests, neither the quantity nor the chemistry of stemflow was monitored.

Soil seepage water was sampled at three different depths: underneath the forest floor, at 30 cm depth (bottom of the intensively rooted A-horizon), and at 80 cm depth (bottom of the solum). Five plate lysimeters with a permanent suction of 200 hPa were used to collect soil solution samples underneath the forest floor. In the mineral soil, five suction cups were installed in 30 and 80 cm depths, respectively, with permanent suctions ranging from 300 to 500 hPa. The five samples obtained from each depth were combined to one sample per sampling event. Low water fluxes, however, especially in the summer periods did not always provide enough SO_4^{2-} for isotope analysis.

Streamflow was permanently recorded at the base of each catchment using 60° Thompson weirs (Feger et al. 1990). At Schluchsee streamflow represents the entire runoff of the catchment, whereas at Villingen subsurface runoff by groundwater contributes also to water and element export. Groundwater at the Villingen site was sampled in two water wells of a municipal drinking water supply. The accuracy of the hydrological budgets is discussed in detail by Brahmer (1990).

After filtration (0.45 μm membrane filter), SO_4^{2-} concentrations were determined by ion chromatography on aliquots of all water samples. The remaining water was bulked to give 2 to 4 monthly samples yielding 5 to 10 L solutions. This bulking was necessary to obtain sufficient SO_4^{2-} for isotope measurements.

Low SO_4^{2-} concentrations in all water samples required pre-concentration of SO_4^{2-} prior to precipitation as BaSO_4 for isotope analysis. Moist, fresh ion exchange resin (Baker ANGA 542, 16–50 mesh, OH^- -form) was placed in a column (1 cm diam., 25 cm length). Solution samples were passed through the column at 10 ml min^{-1} by a peristaltic pump followed by double distilled (dd) water rinse for 2 to 3 resin bed volumes. The ion exchange resin was eluted with 150 ml 0.5 M NaCl followed by 100 ml dd water at the same flow rate to obtain the SO_4^{2-} . Since the resins were rapidly contaminated by dissolved organic matter, fresh resin was used for each sample. The eluate was heated and 25 ml of 0.5 M BaCl_2 -solution were added to precipitate BaSO_4 . After standing overnight, the solutions were acidified to pH 3 in order to remove BaCO_3 . After several washings with dd water, BaSO_4 was recovered on a 0.45 μm membrane filter, air-dried overnight, weighed, and removed from the filter paper.

Soil and bedrock sulfur

In addition to concentration and isotope measurements on SO_4^{2-} , concentrations and $\delta^{34}\text{S}$ -values of different soil S compounds and of bedrock S were determined. In both catchments, forest floor and mineral soil samples at six different depths were collected, oven-dried at 105 °C, sieved (2 mm),

and ground prior to analysis. The spatial variability of concentrations and S isotope compositions for total S and inorganic sulfate was inferred by analyzing samples from six different soil cores. Total S concentrations were determined on a LECO SC 132 automated S analyzer. Total inorganic sulfate (adsorbed and soluble SO_4^{2-}) was extracted from soil samples with 0.016 M KH_2PO_4 solution (5:1, solution:soil ratio), followed by SO_4^{2-} analysis by ion chromatography. Organic S was calculated as the difference between total S and inorganic sulfate-S, since reduced inorganic S was found to be negligible in these forest soils (Kurth et al. 1989). Methods used to estimate pool sizes for vegetation, forest floor, upper (0–30 cm) and lower (30–80 cm) mineral soil have been reported by Feger (1993, 1995).

For S isotope measurements on total S, soil samples were mixed with Eschka mixture (MERCK Art. 3162) in a ratio 1:4 and ignited at 800 °C (ASTM 1993). The sulfate produced was dissolved in hot dd water and precipitated from the solution as BaSO_4 as described above. Sulfate from the phosphate extraction was also precipitated as BaSO_4 after boiling down the extraction solution to 250 ml. Barium phosphate was coprecipitated using this preparation.

Total S from fine ground granite (S1) and sandstone (V1) was reduced by Kiba-reagent (Kiba et al. 1955) to H_2S and precipitated as CdS . After conversion to Ag_2S , total S concentrations were determined gravimetrically. The Kiba reagent method (Sasaki et al. 1979) was also used to convert S from the mixed $\text{BaSO}_4 / \text{Ba}_3(\text{PO}_4)_2$ precipitate resulting from the phosphate extraction to Ag_2S .

Isotope measurements

With BaSO_4 from Eschka oxidation and filter SO_2 , 0.45 mg of BaSO_4 were combusted in a Carlo Erba Elemental Analyzer in presence of V_2O_5 at 1100 °C with a flush of oxygen in a He stream. The product SO_2 was separated from other gases by gas chromatography and carried with the He stream through a mass spectrometer (Giesemann et al. 1994). For all other preparations, SO_2 for $\delta^{34}\text{S}$ -measurements was produced by high temperature reaction of BaSO_4 or Ag_2S with V_2O_5 and SiO_2 (Yanagisawa & Sakai 1983; Ueda & Krouse 1986). $\delta^{34}\text{S}$ -values for organic S were calculated by mass and isotope balances from concentration and isotope data for total and inorganic S.

For ^{18}O -measurements on SO_4^{2-} , CO_2 was produced through thermal decomposition of BaSO_4 with pure graphite (ratio 17:6 by weight) in molybdenum foil under vacuum at more than 1000 °C followed by a high voltage conversion of CO to CO_2 in a discharge chamber (Holt 1991). $\delta^{18}\text{O}$ -values of water were determined using standard equilibration techniques (Epstein & Mayeda 1953).

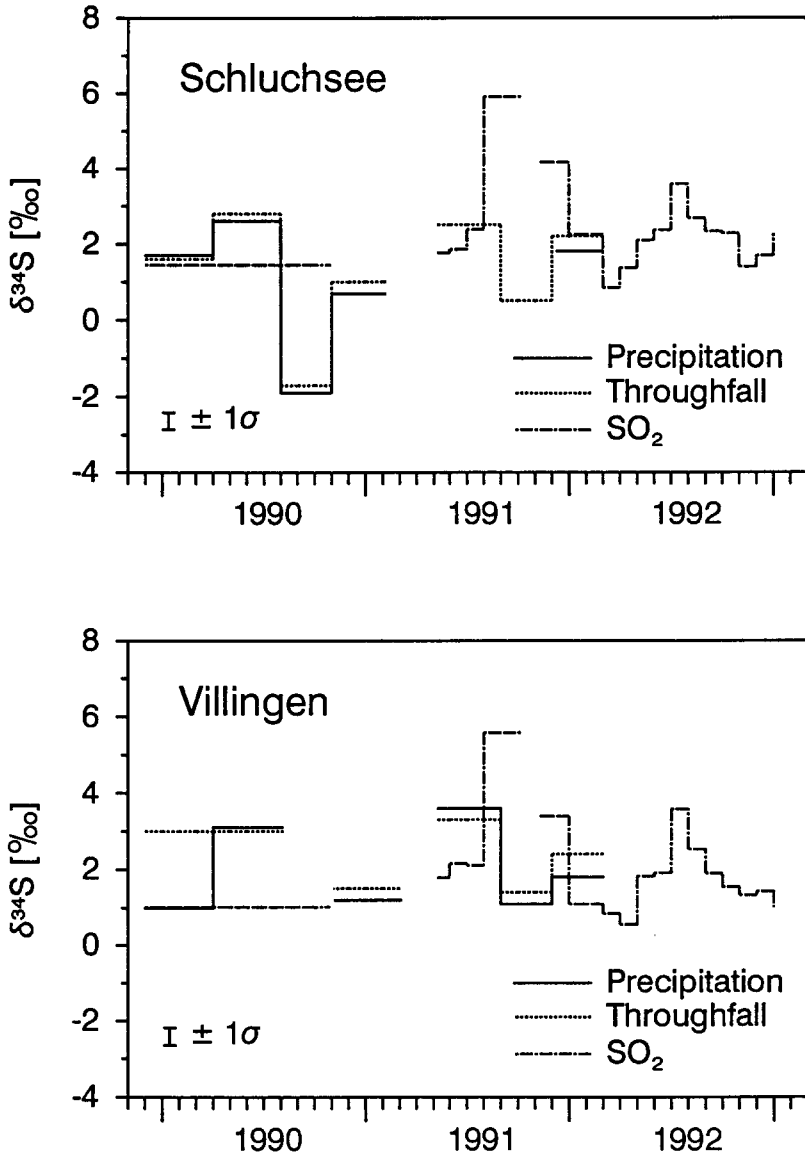


Fig. 2. $\delta^{34}\text{S}$ -values of SO_2 and SO_4^{2-} in bulk precipitation and canopy throughfall in the catchments Schluchsee and Villingen between November 1989 and December 1992.

Stable isotope compositions are reported in the conventional δ -notation in parts per thousand:

$$\delta_{\text{Sample}}(\text{‰}) = \frac{R_{\text{Sample}} - R_{\text{Standard}}}{R_{\text{Standard}}} \cdot 1000,$$

where R is the abundance ratio $^{34}\text{S}/^{32}\text{S}$ or $^{18}\text{O}/^{16}\text{O}$ in either the sample or a standard. The standard for S isotope measurements is Cañon Diablo Troilite (CDT) and Vienna Standard Mean Ocean Water (V-SMOW) for O isotope measurements. The precision ($\pm 1\sigma$) of S isotope measurements was within $\pm 0.2\text{‰}$, and ± 0.5 and $\pm 0.15\text{‰}$ for oxygen isotope measurements on SO_4^{2-} and water, respectively.

Results and discussion

Sulfur sources

Atmospheric deposition

Sulfur deposition in the Black Forest is low compared to that of other areas in Central Europe with similar amounts of precipitation (Führer et al. 1988). For the period June 1987 through May 1992 a rate of $9.8 \text{ kg S ha}^{-1} \text{ a}^{-1}$ was calculated for total deposition from measurements of bulk precipitation ($7.4 \text{ kg S ha}^{-1} \text{ a}^{-1}$) and canopy throughfall ($10.1 \text{ kg S ha}^{-1} \text{ a}^{-1}$) at the Schluchsee site (Feger et al. 1993). At Villingen, the S deposition rate was similar (total: $10.9 \text{ kg S ha}^{-1} \text{ a}^{-1}$; bulk precipitation: $7.2 \text{ kg S ha}^{-1} \text{ a}^{-1}$; canopy throughfall: $11.1 \text{ kg S ha}^{-1} \text{ a}^{-1}$). With the exception of significantly depleted $\delta^{34}\text{S}$ -values in Schluchsee between July and September 1990 for both bulk precipitation and canopy throughfall SO_4^{2-} , the $\delta^{34}\text{S}$ -values for precipitation samples varied only from $+0.5$ to $+2.8\text{‰}$ at Schluchsee and from $+1.0$ to $+3.6\text{‰}$ at Villingen (Table 1). No striking seasonal trends were observed.

Although total S fluxes in throughfall were 1.4 (S1) and 1.6 (V1) times higher than in bulk precipitation, significant differences in $\delta^{34}\text{S}$ -values were rarely observed due to the similarity of S isotope ratios in precipitation and throughfall sulfate (Fig. 2). For S, canopy-internal processes such as foliar leaching and uptake of S are only of minor importance (Lindberg & Garten 1988). Therefore, the similarity in $\delta^{34}\text{S}$ -values between precipitation and throughfall SO_4^{2-} suggests, that dry deposition of S compounds, isotopically similar to those of bulk precipitation, is the reason for the observed increase in S fluxes. This is confirmed by $\delta^{34}\text{S}$ -measurements on SO_2 (Fig. 2). Between November 1989 and September 1990, the mean S isotope composition of ambient air SO_2 at Schluchsee was with $+1.4\text{‰}$ very similar to that of bulk precipitation ($+1.4\text{‰}$) and throughfall SO_4^{2-} ($+1.6\text{‰}$) for the same period of time. The mean S isotope composition of air SO_2 at Villingen was $+1.0\text{‰}$ between November 1989 and September 1990. Better resolution throughout the year 1991, due to the increased number of filters, showed seasonal variation in the $\delta^{34}\text{S}$ -values of the SO_2 at both locations with an increase by about 4‰ from spring to summer followed by a decrease towards the winter

Table 1. Precipitation and throughfall (in mm), volume weighted SO_4^{2-} concentration, and isotopic composition of SO_4^{2-} and water oxygen in bulk precipitation and canopy throughfall in both catchments during November 1989 and February 1992 (n.d. = not determined).

Catchment	Sample type	Period		[mm]	[SO_4^{2-} -S] [$\mu\text{g l}^{-1}$]	$\delta^{34}\text{S}$ [‰]	$\delta^{18}\text{O}_{\text{sulfate}}$ [‰]	$\delta^{18}\text{O}_{\text{water}}$ [‰]
		From	To					
Schluchsee 1	Precipitation	Nov 89	Feb 90	814	230	1.7	10.4	-11.3
		Mar 90	Jun 90	546	740	2.6	n.d.	n.d.
		Jul 90	Sep 90	378	420	-1.9	n.d.	-9.1
		Oct 90	Jan 91	840	200	0.7	11.9	-8.3
		Feb 91	Mar 91	182	430	n.d.	n.d.	n.d.
		Apr 91	Jul 91	484	590	n.d.	n.d.	-7.4
		Aug 91	Oct 91	243	410	n.d.	9.1	-8.9
		Nov 91	Feb 92	681	200	1.8	n.d.	-11.1
	Throughfall	Nov 89	Feb 90	717	380	1.6	9.3	-10.5
		Mar 90	Jun 90	459	1180	2.8	n.d.	n.d.
		Jul 90	Sep 90	324	590	-1.7	n.d.	n.d.
		Oct 90	Jan 91	752	450	1.0	13.1	-8.5
		Feb 91	Mar 91	158	1290	n.d.	n.d.	n.d.
		Apr 91	Jul 91	380	1020	2.5	n.d.	-7.3
		Aug 91	Oct 91	199	660	0.5	7.5	-8.9
		Nov 91	Feb 92	537	370	2.2	9.4	-9.8
Villingen 1	Precipitation	Nov 89	Feb 90	593	240	1.0	n.d.	-11.4
		Mar 90	Jun 90	352	970	3.1	n.d.	-7.7
		Jul 90	Sep 90	259	640	n.d.	n.d.	n.d.
		Oct 90	Jan 91	497	210	1.2	n.d.	-7.6
		Feb 91	Mar 91	121	630	n.d.	n.d.	n.d.
		Apr 91	Jul 91	362	920	3.6	n.d.	-10.2
		Aug 91	Oct 91	159	440	1.1	n.d.	-6.7
		Nov 91	Feb 92	448	260	1.8	n.d.	-10.9
	Throughfall	Nov 89	Feb 90	468	570	3.0	n.d.	-11.6
		Mar 90	Jun 90	246	1850	3.0	13.9	-7.5
		Jul 90	Sep 90	166	1060	n.d.	n.d.	n.d.
		Oct 90	Jan 91	412	910	1.5	n.d.	-8.5
		Feb 91	Mar 91	93	3240	n.d.	n.d.	n.d.
		Apr 91	Jul 91	211	1720	3.3	n.d.	-10.4
		Aug 91	Oct 91	94	830	1.4	10.9	-8.0
		Nov 91	Feb 92	361	950	2.4	n.d.	-10.1

period (Fig. 2). This pattern was repeated in 1992 with seasonal variations of less than 3‰. These shifts are not expressed in the $\delta^{34}\text{S}$ -values of the 2 to 4

monthly precipitation samples probably due to the longer sampling period, and since rainfall events are not equally distributed over time. However, for comparable sampling periods the $\delta^{34}\text{S}$ -values of SO_2 , bulk precipitation, and throughfall SO_4^{2-} agree reasonably well. Therefore, temperature-dependent isotope fractionation during oxidation of SO_2 to SO_4^{2-} (Caron et al. 1986) or seasonal variability in homogeneous and heterogeneous atmospheric oxidation reactions of SO_2 to SO_4^{2-} (Saltzman et al. 1983) seem not to be the main reason for the observed variations in $\delta^{34}\text{S}$ -values of atmospheric S over time. More likely, seasonal variabilities in S sources with different isotopic signatures such as burning of oil and coal (Nielsen 1974), emissions from automobile exhaust (Grey & Jensen 1972), or marine S sources (Nriagu et al. 1991; Newman et al. 1991; Wadleigh et al. 1994) are believed to cause the slight variations in $\delta^{34}\text{S}$ -values of atmospheric S constituents over time. The significantly depleted $\delta^{34}\text{S}$ -values for bulk precipitation and canopy throughfall SO_4^{2-} between July and August 1990 (observed only at the Schluchsee site) are also interpreted to be the result of admixture of isotopically different S from another source, namely biogenic S gas emissions. Local emission of volatile reduced S species enriched in ^{32}S from the forest floor or a nearby wetland (Eschenmoos) are considered to cause the depleted $\delta^{34}\text{S}$ -values in precipitation SO_4^{2-} during the summer 1990. Due to their short lifetime, most reduced S compounds emitted from soils (e.g. H_2S , DMS, COS, CS_2 ; Lovelock et al. 1972, Staubes et al. 1989) undergo rapid oxidation in the atmosphere ending up as sulfuric acid and particulate sulfate, which is redeposited to the ecosystem by dry and wet deposition processes (Andreae & Jaeschke 1992). Although emissions of reduced S from vegetation and soils play a minor role in the continental S cycle, they can temporarily and locally contribute to precipitation S and thereby lower its $^{34}\text{S}/^{32}\text{S}$ ratio.

The mass weighted mean $\delta^{34}\text{S}$ -value for bulk precipitation and throughfall SO_4^{2-} in both catchments was $+2.1\text{‰}$ ($n = 24$) over the entire observation period. This value is interpreted as the isotopic signature of long-range transported S of anthropogenic and natural origin, since the study sites in the Black Forest are remote with only minor emissions from local industrial sources.

Whereas $\delta^{34}\text{S}$ -values in precipitation SO_4^{2-} are dependent upon the S sources, the $\delta^{18}\text{O}$ -values of rainfall SO_4^{2-} depend upon the oxidation conditions of SO_2 in the atmosphere and the ^{18}O -content of water, which is involved in the oxidation of SO_2 to SO_4^{2-} . The $\delta^{18}\text{O}$ -values of precipitation ($n = 3$) and throughfall SO_4^{2-} ($n = 6$) varied between $+7.5$ and $+13.9\text{‰}$ with the higher values associated with the heavier $\delta^{18}\text{O}$ -values in the precipitation water (Table 1). Only after sampling periods of 3 to 4 months was enough SO_4^{2-} obtained for $\delta^{18}\text{O}$ -measurements on sulfate oxygen resulting in a lack of seasonal resolution. Secondary effects within the canopy influencing through-

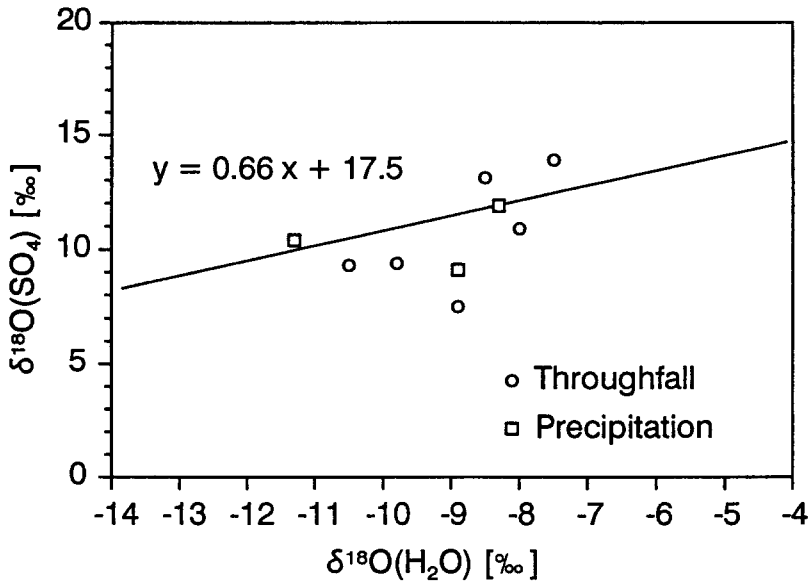


Fig. 3. $\delta^{18}\text{O}_{\text{sulfate}}$ -values versus $\delta^{18}\text{O}_{\text{water}}$ -values for nine precipitation samples collected in the two catchments between November 1989 and December 1992 compared to a general regression line for $\delta^{18}\text{O}$ -values of precipitation sulfate and precipitation water for Southern Germany (Mayer et al. 1995).

fall sulfate could be another reason why only a weak correlation ($r = 0.51$; $n = 9$) was observed between $\delta^{18}\text{O}$ -values of SO_4^{2-} and those of associated precipitation water. Using monthly precipitation samples, Mayer et al. (1995) however showed that the $\delta^{18}\text{O}$ -values of precipitation SO_4^{2-} in SE Germany exhibit a significant linear relationship with the $\delta^{18}\text{O}$ -values of precipitation water, having a slope of $+0.66 \pm 0.14$ and an intercept of $+17.5 \pm 1.4\text{‰}$. Based on annual mean $\delta^{18}\text{O}$ -values for precipitation water at the meteorological station at Mt. Feldberg (W. Graf, pers. comm.) which is located only 10 km from the Schluchsee site, the mean $\delta^{18}\text{O}$ -value of precipitation SO_4^{2-} in the study area is $+11.1 \pm 2.7\text{‰}$ using above relationship. Since most measured field data fall within the expected range (Fig. 3), it is likely that the strong dependence of the $\delta^{18}\text{O}$ -values of SO_4^{2-} on the $\delta^{18}\text{O}$ -values of the precipitation water found for SE Germany is also valid for the Black Forest region. Therefore, the given value is considered as a reasonable estimate for mean $^{18}\text{O}/^{16}\text{O}$ -ratios in precipitation SO_4^{2-} at the two study sites.

Lithogenic sulfur

Sulfur concentrations and $\delta^{34}\text{S}$ -values for bedrock samples in both catchments are summarized in Table 2. Gravimetrically determined S concentrations

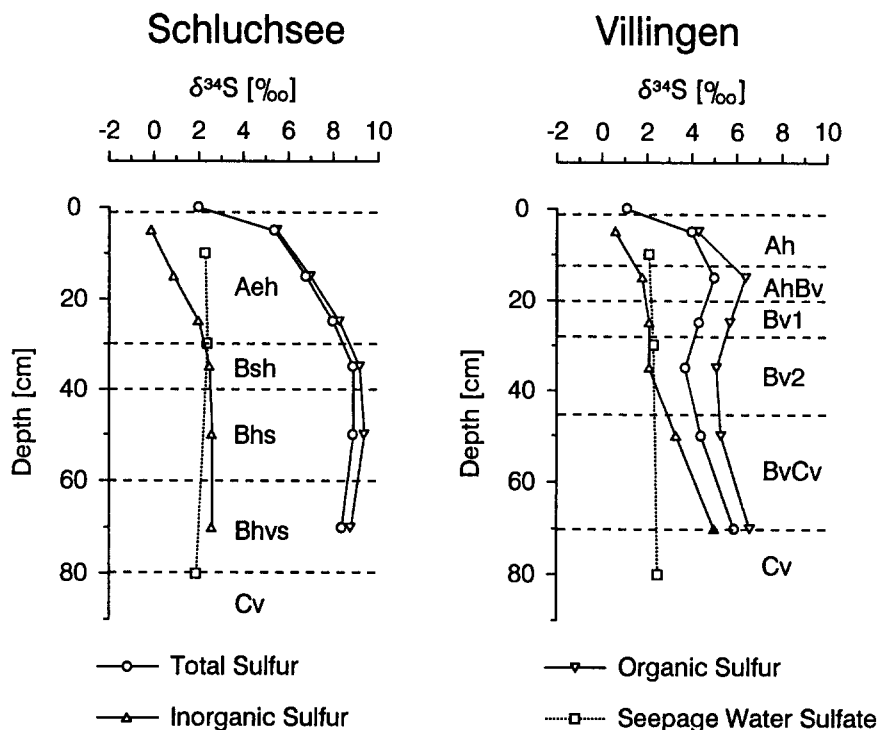


Fig. 4. Mean $\delta^{34}\text{S}$ -values for total S, inorganic S and organic S in the solid soil (six soil cores, sampled according to depth intervals in summer 1990) and mean $\delta^{34}\text{S}$ -values for seepage water SO_4^{2-} (November 1989 to February 1992) for the Schluchsee Podzol and Villingen Brown-earth.

for the granite from the Schluchsee catchment and the quartzitic sandstone from the Villingen catchment were found to be lower than $30 \mu\text{g g}^{-1}$ dwt. Therefore, no significant weathering contribution to the S cycle is expected in contrast to watersheds with S-rich bedrock such as shales (e.g. Mitchell et al. 1986). The mean $\delta^{34}\text{S}$ -values ($n = 2$) for the granite and the sandstone were $+6.5\%$ and $+11.8\%$, respectively.

Soil sulfur

In Table 3, concentrations for total S, inorganic SO_4^{2-} , and organic S, and the respective $\delta^{34}\text{S}$ -values are reported for six randomly sampled soil profiles. Total S decreased in both soil profiles from about $1350 \mu\text{g g}^{-1}$ dwt ($\pm 20\%$) in the forest floor to $100 \mu\text{g g}^{-1}$ dwt ($\pm 35\%$) at 80 cm depth. Organic S predominates in the entire profile at Schluchsee. This is also true for the forest floor and the upper mineral soil of the Brown-earth Villingen, but inorganic (phosphate-extractable) SO_4^{2-} represents a significant proportion of total S (up to 45%) in the mineral soil.

Table 2. Concentrations and $\delta^{34}\text{S}$ -values of total S in bedrock samples from the catchments Schluchsee (Bärhalde granite) and Villingen (quartzitic sandstone).

Catchment	Rock type	Sample amount [g]	S-content [$\mu\text{g S g}^{-1}$]	$\delta^{34}\text{S}$ [‰]
Schluchsee 1	Granite	30.9	15	+6.9
		50.3	16	+6.0
Villingen 1	Sandstone	23.2	27	+11.8
		29.9	18	+11.8

$\delta^{34}\text{S}$ -values of total S were lowest in the forest floor at both sites (Fig. 4). They increased by 5‰ (V1) to 6‰ (S1) within the A-horizons of both soils and remained more or less constant in the B-horizons. At the bottom of the solum, $\delta^{34}\text{S}$ -values for total S tend to shift towards those of the bedrock. There is no information on the $\delta^{34}\text{S}$ -value of total S in the debris zone between soil and solid granite at Schluchsee but it is expected to be similar to that of the bedrock. The general trend of increasing $\delta^{34}\text{S}$ -values with depth can be explained by a two-source mixing model, where S from one source (the bedrock) is constant in concentration and isotope composition, and that from a second source of another $\delta^{34}\text{S}$ -value varies spatially in concentration (Krouse 1980; Rolland et al. 1991). The second source is the litterfall contributing needles with $\delta^{34}\text{S}$ -values of +2.8‰ (S1) and +1.3‰ (V1) to the forest floor. Nevertheless, such a model cannot explain the markedly high $^{34}\text{S}/^{32}\text{S}$ ratios in the A-horizons especially in Schluchsee, where $\delta^{34}\text{S}$ -values for total S were found to be higher than those of the bedrock (Fig. 4).

To interpret these shifts in more detail, the isotope compositions of inorganic and organic soil S were determined. For a given horizon and S compound from six different cores, the spatial variability of the $\delta^{34}\text{S}$ -values was found to be low with standard deviations usually $< \pm 1\%$ (Table 3). Larger variabilities were realized only for $\delta^{34}\text{S}$ -values in the BvCv and Cv horizon of the Brown-earth Villingen. Nevertheless, the spatial variabilities of the $\delta^{34}\text{S}$ -values were in all other horizons small enough to identify processes and different sources of S using stable isotope techniques.

The $\delta^{34}\text{S}$ -values for inorganic and organic S in the soil differed markedly throughout the profiles. $\delta^{34}\text{S}$ -values for organic S were always higher than $\delta^{34}\text{S}$ -values for inorganic SO_4^{2-} (Fig. 4). At Schluchsee, the $\delta^{34}\text{S}$ -values for inorganic SO_4^{2-} remained rather constant between 20 and 80 cm depth and are identical to those of the atmospheric deposition. This is also true for the upper 40 cm of the Villingen Brown-earth, where only in the BvCv and Cv horizons did the $\delta^{34}\text{S}$ -values increase slightly towards those of the bedrock.

Table 3. Mean concentrations ($n = 6$) and mean $\delta^{34}\text{S}$ -values ($n = 6$) for total, inorganic, and organic S from six soil cores in each catchment (n.d. = not determined).

Catchment	Depth [cm]	S-concentration [$\mu\text{g g}^{-1}$ dwt]			$\delta^{34}\text{S}_{\text{CDT}}[\text{‰}] (\pm\text{SDV})$		
		Total	Inorganic	Organic	Total	Inorganic	Organic
Schluchsee 1 (Podzol)	Forest floor	1380 \pm 266	n.d.	n.d.	2.0 \pm 0.2	n.d.	n.d.
	0–10	352 \pm 54	9 \pm 2	343 \pm 54	5.4 \pm 0.5	-0.1 \pm 0.3	5.5 \pm 0.6
	10–20	226 \pm 33	9 \pm 1	217 \pm 33	6.8 \pm 0.4	0.9 \pm 0.5	7.0 \pm 0.6
	20–30	201 \pm 34	9 \pm 2	192 \pm 34	8.0 \pm 0.4	2.0 \pm 0.6	8.3 \pm 0.7
	30–40	169 \pm 22	8 \pm 1	161 \pm 22	8.9 \pm 0.7	2.5 \pm 0.2	9.2 \pm 0.7
	40–60	147 \pm 27	10 \pm 3	137 \pm 27	8.9 \pm 0.7	2.6 \pm 0.4	9.4 \pm 0.8
60–80	104 \pm 34	7 \pm 3	97 \pm 34	8.4 \pm 0.9	2.6 \pm 0.4	8.8 \pm 0.9	
Villingen 1 (Brown-earth)	Forest floor	1316 \pm 237	n.d.	n.d.	1.1 \pm 0.4	n.d.	n.d.
	0–10	222 \pm 40	16 \pm 5	206 \pm 40	4.0 \pm 0.5	0.6 \pm 0.4	4.3 \pm 0.6
	10–20	137 \pm 60	42 \pm 26	195 \pm 65	5.0 \pm 0.7	1.8 \pm 0.3	6.4 \pm 0.8
	20–30	166 \pm 50	66 \pm 37	100 \pm 62	4.3 \pm 0.7	2.1 \pm 0.3	5.7 \pm 0.8
	30–40	189 \pm 45	89 \pm 34	100 \pm 56	3.7 \pm 0.6	2.1 \pm 0.6	5.1 \pm 0.8
	40–60	154 \pm 36	69 \pm 19	85 \pm 41	4.4 \pm 1.9	3.3 \pm 2.1	5.3 \pm 2.8
60–80	110 \pm 40	48 \pm 16	62 \pm 43	5.9 \pm 2.5	5.0 \pm 3.1	6.6 \pm 4.0	

Hence, S isotope data indicate that atmospheric deposition is the dominant source of SO_4^{2-} throughout the mineral soil horizons of the Podzol Schluchsee and the Brown-earth Villingen, whereas lithogenic S derived from mineral weathering is rather insignificant.

In contrast to the $\delta^{34}\text{S}$ -values of inorganic S, the calculated $\delta^{34}\text{S}$ -values for organic S in the A-horizons increased by several per mil with increasing depth and decreasing organic S contents. Within the B-horizons, the $\delta^{34}\text{S}$ -values remained rather constant, with $\delta^{34}\text{S}$ -values for organic S being up to 7.9‰ heavier than those of inorganic sulfate in the same horizon. Since there is apparently only one major S source in both catchments and under the assumption that S inputs were isotopically similar since the last glaciation, the systematic differences in the $\delta^{34}\text{S}$ -values of different forms of S must be interpreted as *in situ* isotope fractionation during S transformations in the soil. After organic S compounds enter the soil via litterfall and turnover of roots and microbial biomass, they are mineralized to SO_4^{2-} by a number of different pathways (Freney 1967, Bremner & Steele 1978; Trudinger & Longhlin 1981; Germida et al. 1992). Our data suggest that ^{32}S is favoured in the aqueous sulfate during the mineralization process and in gaseous S compounds during biogenic S gas release. Consequently, the remaining organic S fractions in the A-horizons get increasingly enriched in ^{34}S as the organic S contents decrease during decomposition and humification of organic matter. Even very small fractionation factors can cause cumulative ^{34}S enrichment in the remaining organic compounds and explain differences of several per mil between $\delta^{34}\text{S}$ -values of coexisting inorganic and organic S in the humic mineral soil horizons. The fact that the elevated $\delta^{34}\text{S}$ -values occur also in the deeper subsoil implies that organic S compounds from the topsoil are leached further down to the subsoil as suggested by other studies (David et al. 1987, Schoenau & Bettany 1987, 1989).

Sulfur dynamics

Seepage water and groundwater sulfate

Figure 5 summarizes $\delta^{34}\text{S}$ -values for SO_4^{2-} in bulk precipitation, canopy throughfall, soil seepage water underneath the forest floor and at 30 and 80 cm mineral soil depth, and groundwater (only Villingen) for both catchments between November 1989 and February 1992. $\delta^{34}\text{S}$ -values in seepage water SO_4^{2-} did not differ significantly from those of the precipitation SO_4^{2-} in both catchments.

Due to low amounts of leachates collected underneath the forest floor, only four water samples from this depth yielded enough BaSO_4 for isotope analyses. $\delta^{34}\text{S}$ -values were generally depleted between 0.4‰ (April to July 1991, V1) and 1.0‰ (November 1991 to February 1992, V1) with respect to

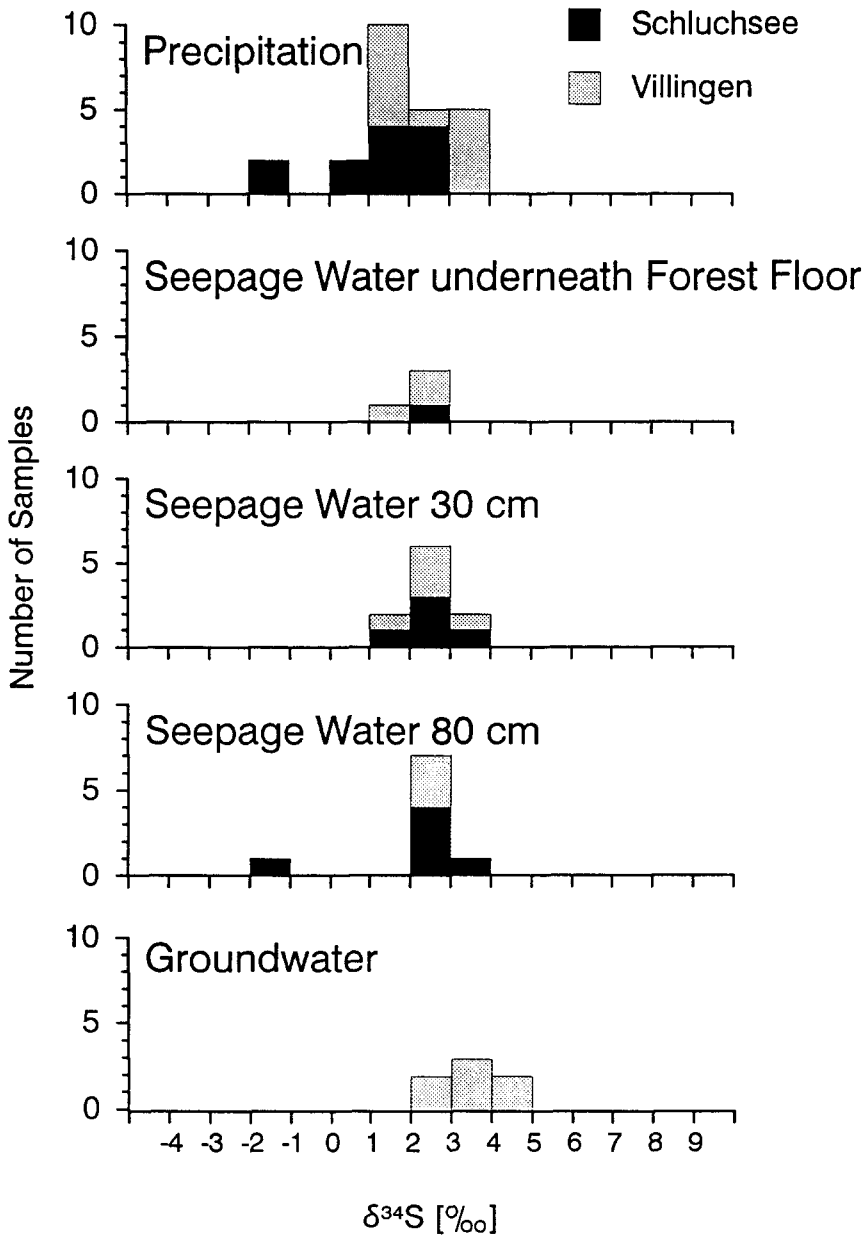


Fig. 5. Histograms of $\delta^{34}\text{S}$ -values for SO_4^{2-} in bulk precipitation, canopy throughfall, soil seepage water underneath the forest floor, at 30 cm and at 80 cm depths, and groundwater (only Villingen) in the catchments Schluchsee and Villingen between November 1989 and February 1992.

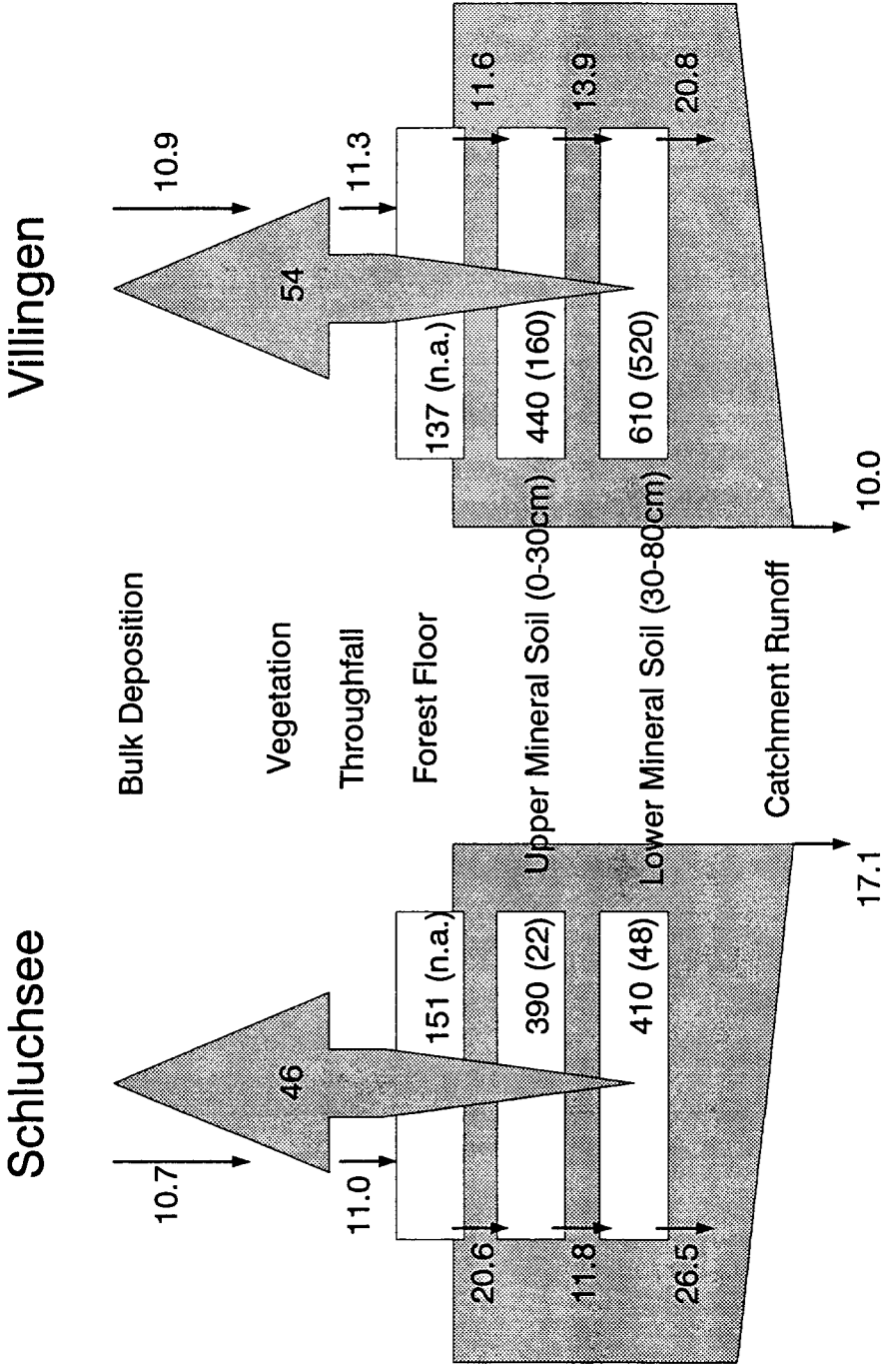


Fig. 6. Pools of total S and inorganic (exchangeable) SO_4^{2-} (in brackets) in vegetation, forest floor, upper and lower mineral soil, and S fluxes determined for the observation period November 1987 through October 1990 (modified from Feger 1993).

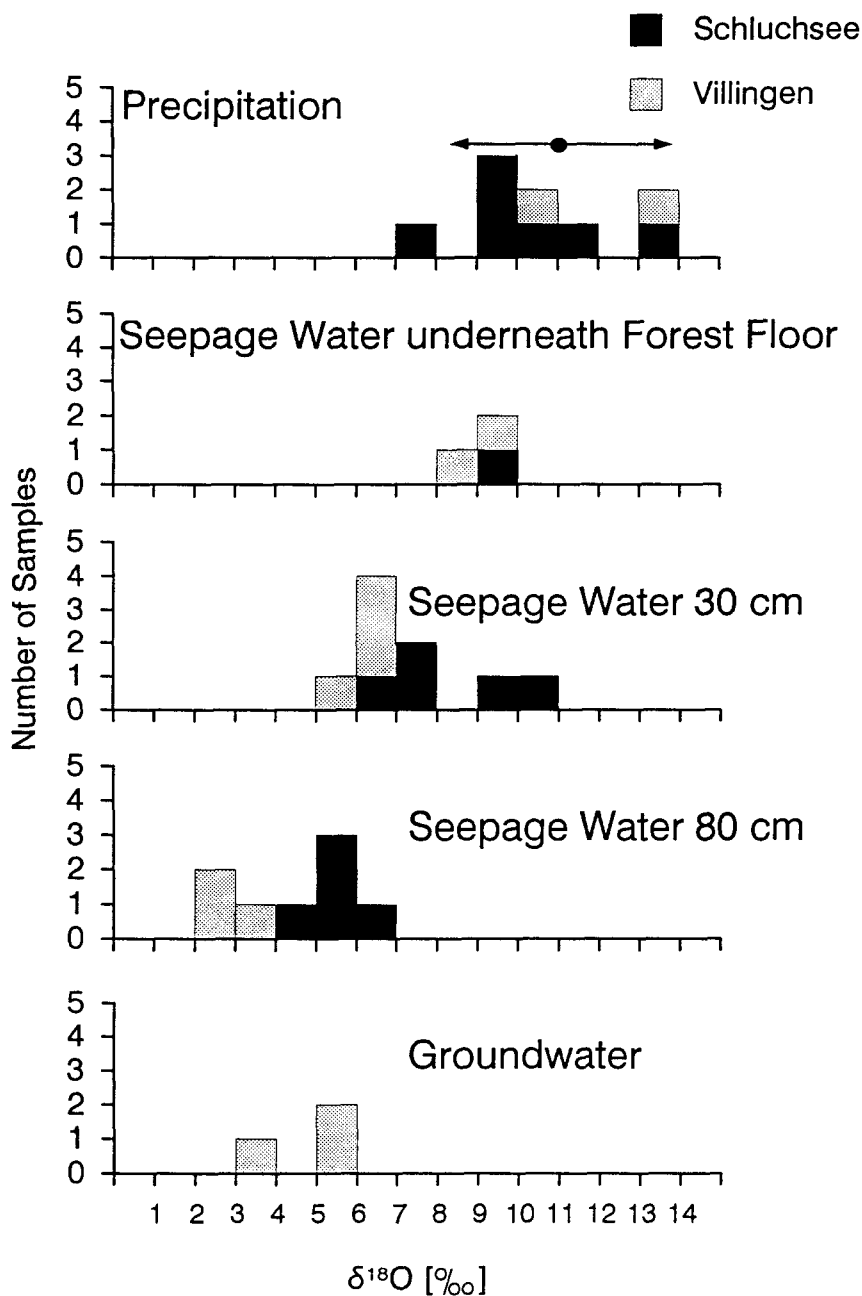


Fig. 7. Histograms of the $\delta^{18}\text{O}$ -values of SO_4^{2-} in bulk precipitation, canopy throughfall, soil seepage water underneath the forest floor, at 30 cm and at 80 cm depths, and groundwater (only Villingen) in the catchments Schluchsee and Villingen between November 1989 and February 1992.

throughfall SO_4^{2-} in a given observation period (not shown). This is consistent with the finding that inorganic sulfate extracted from topsoil horizons was also found to be depleted in ^{34}S with respect to throughfall sulfate (Fig. 4). If these shifts were caused entirely by mineralization of organic sulfur, a significant depletion in the $\delta^{18}\text{O}$ -value of aqueous sulfate with respect to that of throughfall sulfate would occur concurrently (see discussion below). Since this is not the case for topsoil horizons (Fig. 7), we propose that the observed depletion in ^{34}S for inorganic sulfate is caused during the immobilization process. Sulfate in soil solution with $\delta^{34}\text{S}$ -values of +2‰ is the central S pool, which is converted into organic S compounds by microorganisms and plants. The slightly depleted $\delta^{34}\text{S}$ -values for inorganic sulfate observed in seepage water underneath the forest floor and in SO_4^{2-} extracted from the A-horizons in both catchments indicate that the uptake of SO_4^{2-} during the immobilization process favours $^{34}\text{SO}_4^{2-}$ slightly, leaving the soil solution depleted in ^{34}S .

In both catchments, $\delta^{34}\text{S}$ -values for seepage water SO_4^{2-} at 30 cm (S1: $2.4 \pm 0.6\text{‰}$, $n = 5$; V1: $2.2 \pm 0.6\text{‰}$, $n = 5$) and 80 cm depth (S1: $1.9 \pm 1.3\text{‰}$, $n = 6$; V1: $2.5 \pm 0.1\text{‰}$, $n = 3$) did not deviate significantly from those of precipitation and throughfall SO_4^{2-} (Fig. 5). Even for the groundwater SO_4^{2-} at Villingen, mean $\delta^{34}\text{S}$ -values were $3.3 \pm 1.0\text{‰}$ ($n = 7$), only slightly enriched compared to that of atmospheric deposition. This confirms that atmospheric deposition and not mineral weathering is the major source of sulfate in the soil. Due to the high hydraulic conductivity in the Schluchsee Podzol, the same variability of $\delta^{34}\text{S}$ -values of about 5‰ was observed in seepage water sulfate at 80 cm depth as for precipitation SO_4^{2-} . For example, the significantly depleted $\delta^{34}\text{S}$ -values in precipitation SO_4^{2-} in summer 1990 (-1.9‰) were also observed in seepage water SO_4^{2-} at 80 cm depth (-1.0‰). In contrast, the variability of the $\delta^{34}\text{S}$ -values in precipitation SO_4^{2-} of about 3‰ is not reflected in the 80 cm seepage water at the Villingen site with its constant $\delta^{34}\text{S}$ -values of $2.5 \pm 0.1\text{‰}$ ($n = 3$). This pattern points to an internal process in this soil that buffers seasonal variations in $\delta^{34}\text{S}$ -values. Due to its high sesquioxide content (Kurth et al. 1989), adsorption / desorption processes seem to be responsible for controlling concentrations and isotope compositions of SO_4^{2-} in seepage water of the subsoil at the Villingen site. In contrast, a similar process is not apparent in the Schluchsee Podzol. In this humus-rich soil, SO_4^{2-} adsorption is blocked by organic anions even in the subsoil (Kurth et al. 1989) which does not allow the build up of a large sulfate pool in the deeper mineral soil. This is clearly confirmed by differences in adsorption isotherms of the subsoils (Feger 1995) and by the S pool sizes. Less than 12% of total S was found in the inorganic form in the mineral soil of the Podzol Schluchsee, whereas

more than 36% of total S occurred as inorganic sulfate in the Brown-earth Villingen (Fig. 6).

For the Schluchsee Podzol, mean $\delta^{34}\text{S}$ -values for phosphate-extractable SO_4^{2-} were nearly identical to $\delta^{34}\text{S}$ -values of seepage water SO_4^{2-} at 30 and 80 cm depths (Fig. 4). This is also true in the mineral soil of the Villingen Brown-earth (30 cm). This similarity in the $\delta^{34}\text{S}$ -values indicates rapid equilibration between adsorbed and solution SO_4^{2-} suggesting that SO_4^{2-} adsorption does not fractionate S isotopes significantly.

Figure 7 summarizes $\delta^{18}\text{O}$ -values for SO_4^{2-} in bulk precipitation, canopy throughfall, soil seepage water underneath the forest floor and at 30 and 80 cm depths, and groundwater (only Villingen) during November 1989 and February 1992. The $\delta^{18}\text{O}$ -values of SO_4^{2-} in the forest floor leachates varied for both sites between +8.4 to +9.9‰ ($n = 3$) and were within the range of the mean annual $\delta^{18}\text{O}$ -value of precipitation SO_4^{2-} of $+11.1 \pm 2.7\%$. At Schluchsee, the $\delta^{18}\text{O}$ -values of SO_4^{2-} at 30 cm depth varied between +6.6 and +10.0‰ ($n = 5$). At 80 cm depth, the $\delta^{18}\text{O}$ -values of SO_4^{2-} ranged between +4.7 and +6.6‰ ($n = 5$) being significantly depleted with respect to those of precipitation SO_4^{2-} . At the Villingen site, a similar depletion was already apparent at 30 cm depth ($+6.1 \pm 0.2\%$, $n = 4$). At 80 cm depth, the $\delta^{18}\text{O}$ -values of SO_4^{2-} ($+2.6 \pm 0.4\%$, $n = 3$) were depleted by 8 to 9‰ compared to those of mean annual precipitation SO_4^{2-} .

Since oxygen atoms do not readily exchange between H_2O and SO_4^{2-} under environmental conditions (Chiba & Sakai 1985), and soil sorption does not fractionate sulfate oxygen significantly (Van Stempvoort et al. 1990), changes of $\delta^{18}\text{O}_{\text{sulfate}}$ -values require SO_4^{2-} reduction and reoxidation in the soil. Mineralization of carbon-bonded S, during which four new oxygen atoms are incorporated with water or atmospheric oxygen as possible sources, is the only explanation for the markedly depleted $\delta^{18}\text{O}$ -values in SO_4^{2-} in aerated soils (Mayer et al. 1995). These authors expected negative $\delta^{18}\text{O}$ -values for mineralized SO_4^{2-} from carbon-bonded S under the environmental conditions in Southern Germany, whereas hydrolysis of organic (ester) sulfates is believed to cause only depletions of 2 to 3‰ in the $\delta^{18}\text{O}_{\text{sulfate}}$ -values with respect to those of precipitation sulfate. The depleted $\delta^{18}\text{O}_{\text{sulfate}}$ -values in soil leachates in both catchments provide evidence that a considerable portion of SO_4^{2-} in the subsoil seepage water must be derived from the mineralization of carbon-bonded S. This finding is supported by flux data revealing a 2.4 times higher rate of sulfur flux at 80 cm soil depth, than with the canopy throughfall in Schluchsee (Fig. 6). For the Villingen Brown-earth, the S fluxes at 80 cm depth increased by a factor of 1.8 with respect to the S input in the canopy throughfall. Since soil S constitutes predominantly of organic S in the topsoil of both catchments (Table 3), the increased S fluxes result from

a combination of residual atmospheric SO_4^{2-} and mineralized SO_4^{2-} from organic soil S. The $\delta^{18}\text{O}_{\text{sulfate}}$ data suggest that the latter is predominantly derived from the mineralization of carbon-bonded S. Based on flux data, mineralized sulfate constitutes at least 45% of the seepage water SO_4^{2-} . Since nearly half of the infiltrating deposition SO_4^{2-} is additionally subjected to uptake by the forest vegetation in both catchments (Feger 1993, 1995), the majority of the SO_4^{2-} entering the soil via canopy throughfall evidently cycles through the organic pool of soil and vegetation. Unfortunately, quantitative estimates based on $\delta^{18}\text{O}$ measurements on SO_4^{2-} remain difficult, as long as the $\delta^{18}\text{O}_{\text{sulfate}}$ -values of the end members (deposition SO_4^{2-} , mineralized SO_4^{2-} from carbon-bonded S and hydrolyzed organic sulfates) are not exactly known.

Runoff sulfate

At Schluchsee, S output with the stream water exceeded canopy throughfall input by a factor of 1.6 (Fig. 6) indicating that the ecosystem presently acts as a source rather than a sink for S. In contrast, the S input-output budget for the Villingen catchment is balanced. The nearly constant $\delta^{18}\text{O}$ -values for stream water in the Schluchsee catchment during the observation period (Table 4) indicate mean residence times of the water of more than one year, since seasonal variations in $\delta^{18}\text{O}$ -values of the precipitation water are nearly eliminated by hydrodynamic dispersion. Due to the high permeability of the soil and debris zone at Schluchsee, water follows vertical pathways and percolates through the subsoil into the groundwater (k_f -values for A-horizon: $3 \cdot 10^{-3} \text{ cm s}^{-1}$; C-horizon: $5 \cdot 10^{-2} \text{ cm s}^{-1}$; Feger et al. 1990). With respect to the $\delta^{18}\text{O}$ -values of precipitation sulfate, SO_4^{2-} in stream water during base flow and in seepage water in the deeper mineral soil are similarly depleted in ^{18}O . Only during the winter season, when most of the runoff from heavy rains and rapid snowmelts preferentially reaches the streams through the surface soil horizons, are $\delta^{18}\text{O}$ -values of stream water SO_4^{2-} similar to those of precipitation SO_4^{2-} . The $\delta^{34}\text{S}$ -values of stream water SO_4^{2-} were only slightly enriched with respect to those of seepage water at 80 cm depth ($+0.8 \pm 0.7\text{‰}$, $n = 6$) and those of canopy throughfall ($+0.9 \pm 1.6$, $n = 7$).

The more variable $\delta^{18}\text{O}$ -values of the streamwater at Villingen (Table 4) point to a short mean residence time of the water in the catchment. A hydrochemical hydrograph separation indicated a 70% proportion of direct flow versus indirect baseflow (Brahmer & Feger 1991) showing that the water flux is often restricted to superficial soil horizons. This is consistent with the differences in the permeability of the soils in the two catchments. In Villingen, k_f -values range between $2 \cdot 10^{-2} \text{ cm s}^{-1}$ (A-horizon) and $2 \cdot 10^{-4} \text{ cm s}^{-1}$ (C-horizon) in the Brown-earth, and $2 \cdot 10^{-4} \text{ cm s}^{-1}$ (A-horizon) and $5 \cdot 10^{-6} \text{ cm}$

Table 4. Mean daily runoff, mean SO_4^{2-} concentrations (volume weighted), and isotopic compositions of SO_4^{2-} and water oxygen in stream and groundwater (Villingen) of both catchments during November 1989 and February 1992 (n.d. = not determined).

Catchment	Sample type	Period		Mean runoff [l s ⁻¹]	[SO ₄ ²⁻ -S] [μg l ⁻¹]	δ ³⁴ S [‰]	δ ¹⁸ O _{sulfate} [‰]	δ ¹⁸ O _{water} [‰]
		From	To					
Schluchsee 1	Stream	Nov 89	Feb 90	7.42	1220	-0.5	8.6	-10.0
		Mar 90	Jun 90	4.28	1310	3.9	n.d.	-10.0
		Jul 90	Sep 90	2.54	1140	-1.6	5.9	-10.2
		Oct 90	Jan 91	7.09	1230	3.0	5.5	-9.3
		Feb 91	Mar 91	4.27	1250	1.6	5.6	-10.2
		Apr 91	Jul 91	2.67	1200	3.7	n.d.	-10.3
		Aug 91	Oct 91	1.29	1000	4.0	6.2	-9.9
		Nov 91	Feb 92	5.07	1260	3.0	9.5	-10.3
Villingen 1	Stream	Nov 89	Feb 90	12.64	2270	2.6	6.4	-9.7
		Mar 90	Jun 90	4.25	1970	4.0	5.8	n.d.
		Jul 90	Sep 90	1.11	1890	2.4	9.1	-9.4
		Oct 90	Jan 91	9.24	2050	1.9	10.1	-8.8
		Feb 91	Mar 91	2.28	1880	2.8	7.0	n.d.
		Apr 91	Jul 91	1.60	2030	3.9	5.8	-10.4
		Aug 91	Oct 91	0.31	1250	4.6	12.6	-9.7
		Nov 91	Feb 92	7.05	2330	3.1	9.0	-10.1
Villingen 1	Groundwater	Nov 89	Feb 90	1.32	1400	3.5	5.6	-10.0
		Mar 90	Jun 90	0.82	1320	4.3	n.d.	-9.9
		Jul 90	Sep 90	0.37	1160	2.0	n.d.	-10.1
		Oct 90	Jan 91	1.06	1340	3.2	n.d.	-9.4
		Feb 91	Mar 91	0.60	1170	2.2	3.6	-10.0
		Apr 91	Jul 91	0.43	1180	n.d.	n.d.	-10.0
		Aug 91	Oct 91	0.04	720	3.1	5.6	-9.8
		Nov 91	Feb 92	0.42	1280	4.8	n.d.	-10.2

s⁻¹ (C-horizon) in the Stagnogley, respectively (Feger et al. 1990). In some periods marginally depleted δ¹⁸O-values in stream water SO_4^{2-} compared to those of precipitation SO_4^{2-} are further evidence that a considerable amount of the drainage has not passed the subsoil with its significantly depleted δ¹⁸O_{sulfate}-values.

As in Schluchsee, the mean δ³⁴S-values of stream and groundwater SO_4^{2-} in Villingen were less than 1.0‰ heavier than those of canopy throughfall SO_4^{2-} . This also confirms at the most a small contribution of lithogenic S to the S export from both catchments.

Conclusions

The similarity of the $\delta^{34}\text{S}$ -values of SO_4^{2-} in precipitation, seepage water, and inorganic soil S indicates that atmospheric deposition and not mineral weathering is the dominant S source in both catchments regardless whether input/output calculations for S are balanced (Villingen) or unbalanced (Schluchsee). The atmospheric S input is low compared to other areas in Central Europe and thus may not largely exceed the nutritional demand of the forest. Feger (1993, 1995) calculated S uptake rates between 4 and 5 kg S ha⁻¹ a⁻¹ for both catchments whereas the incorporation of S by the microbial biomass is unknown. A considerable part of the deposited S is therefore taken up either by the stand or the soil microorganisms and is converted in S-containing amino acids and proteins. After these carbon-bonded S compounds are returned to the forest floor via litterfall and turnover of dead microbial biomass, they are mineralized to SO_4^{2-} . $\delta^{18}\text{O}$ -measurements on SO_4^{2-} together with S flux data indicate that the majority of the seepage water SO_4^{2-} in the subsoil of the two catchments originates from the mineralization of carbon-bonded S compounds. This is not only true for ecosystems with net S mobilization such as Schluchsee, where at the current stage mineralization seems to occur at a greater rate than immobilization of S, but also for Villingen with a balanced S budget. Thus, balanced S budgets and unchanged $\delta^{34}\text{S}$ -values for SO_4^{2-} percolating through the soil do not necessarily indicate negligible S transformations and conservative behavior of SO_4^{2-} in the catchment. If immobilization of SO_4^{2-} and mineralization of carbon-bonded S occur concurrently at a comparable rate, they do not change the S pools in the forest ecosystem and are therefore easily overlooked in a mass balance approach. Depleted $\delta^{18}\text{O}$ -values for seepage water SO_4^{2-} in the subsoil indicate however that the assimilation reoxidation sequence of S is an important pathway of S cycling through the organic pool in both catchments.

Microbial transformations are not only responsible for the depletion in the $\delta^{18}\text{O}$ -values of seepage water SO_4^{2-} but they also explain variations in the $\delta^{34}\text{S}$ -values of different S compounds in different soil horizons. These variations do not indicate multiple sources of S in this ecosystem but *in situ* isotope fractionation during S mineralization and immobilization in the soil. Since the investigated systems are not closed, it is difficult to express these phenomena quantitatively. However, fractionation factors for S isotopes in both processes are expected to be rather small under field conditions.

Stable isotope techniques are undoubtedly a useful tool for elucidating the S cycle on the catchment scale since they can indicate processes which are not detectable by mass balances alone. The determination of $^{34}\text{S}/^{32}\text{S}$ ratios in sulfur-containing environmental samples allows the delineation of

S sources if these are isotopically distinct. However, a better understanding of the extent of isotope fractionation during S transformations is required in order to more conclusively discern $\delta^{34}\text{S}$ trends caused by soil internal processes (such as mineralization and immobilization) from those caused by admixture of isotopically different sulfur from another source. The analysis of $^{18}\text{O}/^{16}\text{O}$ -ratios in sulfate can additionally serve as an indicator for redox reactions. However, a better knowledge of the $\delta^{18}\text{O}$ -values in SO_4^{2-} derived from mineralization of carbon-bonded sulfur and hydrolysis of organic sulfates under various environmental conditions is needed before this tool can be used as a quantitative estimate for sulfate fluxes in ecosystem research.

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