Dissolved organic sulphur in soil water under *Pinus sylvestris* L. and *Fagus sylvatica* L. stands in northeastern Bavaria, Germany – variations with seasons and soil depth

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Abstract. Organically bound species have been identified as prominent and mobile forms of nitrogen and phosphorus in soils. Since a large portion of sulphur (S) in soil is bonded to carbon (C) also dissolved organic S likely is a significant constituent in soil water. To investigate the role of dissolved organic forms in leaching and cycling of S in forest soils, we examined concentrations, fluxes, and chemical composition of organic S in forest floor leachates and in soil solutions of Rendzic Leptosols under 90-year-old European beech (*Fagus sylvatica* L.) and Haplic Arenosols under 160-year-old Scots pine (*Pinus sylvestris* L.) for 27 months. These soils are low in adsorbed SO_4^{2-} and receive little atmospheric S depositions at present. The chemical composition of organic S was estimated by fractionation with XAD-8 and wet-chemical characterisation (HI reduction) of binding forms. Although not as prominent as the organic forms of other nutrient elements, organic S proved to be an important contributor to S dissolved in forest floor leachates and in mineral soil solutions. Dissolved organic matter contained on average 29% of total S in forest floor leachates at the pine site and 34% at the beech site. The largest portion of organic S occurred in the subsoil solutions under beech in summer and autumn (up to 53%). Mean concentrations of organic S peaked (up to 1.1 mg l^{-1}) in summer after rainstorms that followed dry periods. Fluxes with forest floor leachates and at 90 cm soil depth were largest in autumn because of huge amounts of rainfall. Organic S contributed significantly to the fluxes of S in the subsoils under beech comprising on average 39% of total dissolved S at 90 cm depth. Organic S produced in the forest floor layers was mainly in the hydrophilic fraction of dissolved organic matter (62 ± 6% at the pine site, 85 ± 4% at the beech site). The major binding form of organic S in the hydrophobic fraction was C-bonded S while in the hydrophilic fraction ester sulphate S, possibly associated with carbohydrates, was more prominent. Since the hydrophobic fraction increased in summer and autumn, C-bonded S was of greater importance during that time of the year than in winter and spring. With depth, concentrations and composition of organic S (and also of C) hardly changed at the pine site because of little retention of dissolved organic matter, presumably because of the small sorption capability of that soil. At the beech where organic C showed a marked decrease with depth, only a slight decrease in organic S, exclusively from the hydrophobic fraction, was found indicating that organic S was mobile compared with organic C. This was probably due to the concentration of S in the hydrophilic fraction of dissolved organic matter. Because of being concentrated in the mobile hydrophilic fraction, ester sulphate S was more mobile in the soil under beech than C-bonded S.

Introduction

Dissolved organic matter receives increasing attention as a significant link in cycling and as a vehicle for the leaching of nutrients from forest and arable land. The importance of dissolved organic matter in the export of nutrients from soil, although suggested in the late eighties (Schoenau and Bettany 1987), has been proven recently by studies on streams draining catchments under undisturbed native forests where nitrogen (N) was primarily transported in organic form (Hedin et al. 1995; Perakis and Hedin 2002). Most of the studies on soluble organic nutrients focused on N and a smaller number on phosphorus (P) (summarised by Kalbitz et al. 2000). Compared with the interest in those two elements, organically bound sulphur (S) in ground, surface and soil water is rarely considered in investigations. This may be surprising because, like N and P, S in most soils is predominantly bonded to organic matter (Zhao et al. 1996) and is essential for plant growth (Stevenson and Cole 1999). Incorporation into organic matter is an important pathway to retain S that the soil receives SO_4^{2-} form by fertiliser application or atmospheric deposition (Autry et al. 1990; Prietzel et al. 2001).

The few studies on dissolved organic S in soil and surface waters, which are exclusively from Northern Hemisphere forests on cambic and podzolic soils, showed that organic forms can represent a significant portion of dissolved S (up to 46%; Homann et al. 1990). However, the contribution of organic matter to total S in soil and surface waters is mostly lower (10–20%; Mitchell et al. 1986, 1989; Houle et al. 2001; Nilsson et al. 2001). For lakes, Houle et al. (1995) assumed that small portions of dissolved organic S are due to the large atmospheric depositions of SO_4^{2-}. The same might be true also for soil water.

Soluble organic S and carbon (C) and SO_4^{2-} seem to be intimately related, suggesting that production of dissolved organic matter and mineralisation of SO_4^{2-} are regulated by the same factors (Valeur et al. 2000). The production of soluble organic S seems to be highest in summer (Gorham et al. 1998) which supports the idea that its formation relates to microbial activity (Strickland and Fitzgerald 1987). Once produced, dissolved organic S is mobile with soil water and prone to leaching (Kaiser et al. 2000; Nilsson et al. 2001), possibly due to its enrichment in the hydrophilic fraction of dissolved organic matter which shows only a weak sorptive retention in soil (Kaiser 2001).

Little is known about the chemical composition of dissolved organic S in soil. The available results are those of David et al. (1987) who found ester SO_4^{2-} to be more important than carbon-bonded S in the soil waters of a Spodosol (Podzol) under a northern hardwood forest.

This brief summary shows that there is a lack of information on production and fate of dissolved organic S in soil. Therefore the first objective of our study was to broaden the perspective by considering soils other than Cambisols and Podzols. The second aim was to identify possible seasonal variations in production and sources of dissolved organic S. We approached this by analysing amounts and chemical composition of dissolved organic S leached from

organic forest floor layers. The third aim was to estimate the possible contribution of dissolved organic S to the leaching losses of S from soil. To do so, we compared the changes in concentration and fluxes of dissolved organic S with depth with those of organic C and SO_4^{2-}. Further, changes in the chemical composition of dissolved organic S with depth were investigated and utilised to distinguish between abiotic and biotic retention in the mineral soil.

The study was part of a 27-month-field experiment on dissolved organic matter (Kaiser et al. 2000, 2001a, b) that was carried out on Arenosols under Scots pine (*Pinus sylvestris* L.) and Leptosols under European beech (*Fagus sylvatica* L.). We determined concentrations and fluxes of dissolved organic S and estimated its composition by XAD-8 fractionation (Aiken and Leenheer 1993; Raastad and Mulder 1999) and HI reduction (Kowalenko 1993). The chosen sites currently receive relatively little atmospheric SO_4^{2-} and are low in extractable SO_4^{2-} (Table 1). So S stored is primarily in organic binding. This offers the opportunity to study dissolved organic S with less influence of inorganic SO_4^{2-} than is normally common.

Materials and methods

Field experiments

Sites

The experiments were carried out in NE Bavaria, Germany. One site was a 160-year-old Scots pine (*Pinus sylvestris* L.) forest near Seybothenreuth (49°53′N,

Table 1. Organic carbon (OC), total sulphur (Stot), sulphate sulphur (SO_4^{2-}–S), carbon-bonded sulphur (C–S), ester sulphate sulphur (ester sulphate S), organic sulphur (OS) in the studied soils (samples sieved to < 2 mm)

Horizon	Thickness (cm)	OC (g kg^{-1})	Stot (g kg^{-1})	SO_4^{2-}–S (g kg^{-1})	C–S (g kg^{-1})	Ester sulphate S (g kg^{-1})	OS (g kg^{-1})	OC/OS
Pine forest (Haplic Arenosol)								
Oi	2	498	1.92	0.03	1.66	0.23	1.89	263
Oe	4	476	2.18	0.07	1.65	0.46	2.11	226
Oa	4	377	2.27	0.09	1.63	0.55	2.18	173
A	5	15	0.28	0.06	0.13	0.09	0.22	68
C1	10	1	0.04	0.02	0.02	nd	0.02	50
C2	80 +	1	0.01	0.01	nd	nd	nd	nd
Beech forest (Rendzic Leptosol)								
Oi	≤ 5	481	2.54	0.05	2.06	0.43	2.49	193
A1	10	112	1.45	0.09	0.89	0.47	1.36	82
A2	15	69	1.07	0.11	0.55	0.41	0.96	72
C	70 +	11	0.40	0.16	0.14	0.10	0.24	46

Data on organic C taken from Kaiser et al. (2001b). Sulphur fractions were determined on ground subsamples as outlined by Kowalenko (1993).
nd: not detectable

11°41′E, 490 m above sea level). The ground vegetation was dominated by
Vaccinium myrtillus L. with small patches covered with *Deschampsia flexuosa*
(L.) Trin. and various moss species. The soils, Haplic Arenosols (FAO–Unesco
1990), were derived from an Upper Triassic sandstone low in cementing agents
and were strongly acidic, low in nutrients and in organic C, and characterised
by sandy texture. The organic forest floor layer was mor-type. The mean an-
nual precipitation during the experimental period accumulated to 587 mm and
the mean annual temperature was 8.3 °C. The second site located near Bet-
zenstein (49°44′N, 11°23′E, 520 m above sea level) was in a 90-year-old
European beech (*Fagus sylvatica* L.) stand. Ground vegetation was little
throughout the year and was dominated by *Anemone nemorosa* L. in early
spring and later on by *Mercuralis perennis* L. The soils, deriving from Upper
Kimmeridgian dolomite, were strongly aggregated Rendzic Leptosols (FAO–
Unesco 1990) with loamy texture and large contents of organic C. The organic
forest floor layer was mull-type and covered the soil at variable thickness
throughout the entire experimental period. The mean annual temperature
during the study period was 8.2 °C and the mean annual precipitation was
956 mm. At both sites, snowfall contributed < 5% of the precipitation during
the experimental period. A detailed description of the sites, the organic forest
floor layers, and the climatic conditions during the experimental period is given
in Kaiser et al. (2001a).

The chemical and physical properties of the mineral soils are summarised in
Kaiser et al. (2000, 2001b). Sulphur fractions in the soils were determined
according Kowalenko (1993) except that the inorganic soluble and adsorbed
SO_4^{2-} extracted by 0.02 M KH_2PO_4 was measured using ion chromatography
(DX-100, Dionex Corp., Sunnyvale, CA). Additionally, we extracted the
mineral horizons of the Rendzic Leptosols with 0.1 M $NaHCO_3$ in order to test
for possibly incomplete extraction of SO_4^{2-} by KH_2PO_4 upon precipitation of
the added phosphate. However, no differences between the two extractions
were found.

Instrumentation and sampling
At each site, three plots of 50×50 m were selected at a minimum distance
between each other of 200 m. In each plot, we installed four stainless steel
zero-tension lysimeters ($\varnothing$ = 127 mm, mesh size 0.01 mm) directly beneath
the organic forest floor layer, four disk tension lysimeters (inner diameter
90 mm) at 15 and 30 cm depth, and four ceramic suction cups (Simplex K-
100, UMS GmbH, München, Germany) at 90 cm depth. The sampling devices
were fitted to 2-l glass bottles. Additionally, the plots were equipped with each
four tensiometers (Simplex T-100, UMS GmbH, München, Germany) at 10,
20, 60, and 100 cm depth. The pre-treatment and installation of the instru-
ments is given in greater detail in Kaiser et al. (2001b). Tensions were meas-
ured weekly using a pressure conductor (Infield 5, UMS GmbH, München,
Germany) and the vacuum of the suction cups was regulated according to
the measured tension of soil water. We collected soil water from August 1997

to November 1999 at 7-day intervals during the growing season (April–November) and at least at 14-day intervals during the dormant season (December–March). The samples were measured for volume, filtered through 0.45-μm polysulphone membrane filters (Supor-450, Pall Gelman Science, Ann Arbor, MI), and stored frozen at -18 to -30 °C. Preliminary experiments proved that this procedure had no effect on the concentrations and composition of C and S. The amount of seepage water from the forest floor was calculated by normalising the volume of the sample to the area of the lysimeter.

The amount of rainfall was determined using 12 rainfall collectors made of plastic funnels ($\varnothing = 200$ mm) fitted to 2-l bottles placed on clearings close to the experimental plots (< 400 m). The amount of throughfall was determined using 12 rainfall collectors placed in each plot. The volume of rainwater and throughfall was measured at the same intervals as the lysimeters and suction cups were sampled. The amount of rain and throughfall was calculated by normalising the volume of rainwater to the area of the rainfall collectors.

Dissolved organic matter sample treatment

Organic matter in soil water samples

Aliquots of the bulk solution samples were analysed for organic C using Pt-catalysed, high-temperature combustion (680 °C) followed by infrared detection of CO_2 (TOC-5050, Shimadzu Corp., Tokyo, Japan). Before determination of organic C, the inorganic C was removed by adjusting the pH of the solution to 2 using concentrated H_3PO_4 and sparging with CO_2-free synthetic air at a flow rate of 50 ml min^{-1} for 2 min. No flocculation of organic matter was observed on acidification of the samples. Untreated bulk solution samples were analysed for total S by inductively coupled plasma-optical emission spectrometry (ICP-OES, Integra XMP, GBC Scientific Equipment Pty Ltd., Dandenong, Victoria, Australia) and SO_4^{2-} (photometrically, RFA-300, Alpkem Corp., Clackamas, OR, or SAN Plus, Skalar Analytical B.V., Breda, The Netherlands). Organic S was estimated as the difference between total S and inorganic SO_4^{2-}.

A part of the bulk solution samples (40 ml) was acidified to pH 2 with 1 M HCl, then pumped through small glass columns (4 ml) filled with Amberlite XAD-8 resin (Rohm & Haas Co., Philadelphia, PA) to determine the distribution of organic C and S among two operationally defined fractions, the so-called hydrophilic fraction and the so-called hydrophobic fraction (Aiken and Leenheer 1993; Raastad and Mulder 1999). The effluent of the columns, representing the hydrophilic fraction, was analysed for organic C and S (see above), and the amount of organic C and S in the hydrophobic fractions was calculated by difference between organic C and S in the bulk sample and in the hydrophilic fraction. Tests showed that acidification to pH 2 had no effect on the distribution of S forms in the bulk sample.

Volume-weighted portions of the bulk solution samples were combined into 1- and 3-month samples. The latter represented the following periods: September to November 1997 (Autumn 97), December 1997 to February 1998 (Winter 98), March to May 1998 (Spring 98), June to August 1998 (Summer 98), September to November 1998 (Autumn 98), December 1998 to February 1999 (Winter 99), March to May 1999 (Spring 99), June to August 1999 (Summer 99), September to November 1999 (Autumn 99). The sample designation follows the meteorological definition of seasons. The combined samples were treated with a strongly acidic cation exchanger (AG-MP 50, BioRad Laboratories, Richmond, CA) in order to remove all other cations than H^+, and a portion was freeze-dried and then homogenised by grinding.

Preparation of hydrophilic and hydrophobic dissolved organic matter fractions
Combined bulk dissolved organic matter samples from autumn 1997 were separated into hydrophilic and hydrophobic fractions (Aiken and Leenheer 1993). The solutions were acidified to pH 2 with 1 M HCl, analysed for organic C and S, and pumped through 200-ml columns filled with XAD-8. In the effluent of the columns, representing the hydrophilic fraction, the concentrations of organic C and S were determined. Organic C and S in the hydrophobic fraction was calculated by difference. After passage of the samples, the columns were rinsed with water adjusted to pH 2 with 1 M HCl. The rinse water was combined with the hydrophilic fraction, freeze-dried and homogenised by grinding. The hydrophobic fraction was eluted from the columns with 0.1 M NaOH and the eluates were analysed for organic C and S. Mass-balance calculations showed that $>97\%$ of the C and $>95\%$ of the S in the hydrophobic fraction was recovered from the XAD-8 resin. Thus, the contribution of hydrophobic neutral compounds, equivalent to the loss, was little in the samples used. The hydrophobic fractions were protonated with a strongly acidic cation exchanger (AG-MP 50), acidified to pH 2 with 1 M HCl, and finally freeze-dried and homogenised by grinding.

Wet-chemical analyses of sulphur binding forms
Freeze-dried bulk solution samples (1- and 3-month) and hydrophilic and hydrophobic dissolved organic matter fractions from autumn 1997 were analysed for the chemical binding forms of S following to the experimental procedure of Kowalenko (1993). Briefly, HI-reducible S, consisting primarily of ester sulphate S and inorganic sulphate S, was analysed by direct reduction to sulphide with hydroiodic acid (HI). Sulphide was determined photometrically as bismuth sulphide colouring complex (Kowalenko 1993). The difference between HI-reducible S and inorganic sulphate S (determined photometrically, see above) was considered as ester sulphate S. Based on the finding of Strickland et al. (1987) that C–S (amino acid) or C–SO_3 (sulphonate) linkages will not be cleaved by HI, C-bonded S was considered to be total organic S minus HI-reducible S. The analyses were carried out in triplicate.

Calculation of fluxes

We calculated fluxes of the dissolved organic C and S from the forest floor into the mineral soil from the amounts of seepage water sampled by the zero-tension lysimeters beneath the forest floor layer and the concentrations therein.

Fluxes in the mineral soil were calculated from soil solution concentrations and simulated water fluxes. The simulation of water fluxes was carried out using two soil water transport models: WHNSIM (Huwe and Totsche 1995) and HYDRUS-2D (Simunek et al. 1996). WHNSIM calculates the water budget for a given increment on base of Richard's equation. We used as input transport parameter the measured unsaturated hydraulic conductivity as a function of the matric potential of the soils. Further input variables were meteorological data of the sites, root distribution and density estimated from soil pits. The potential evapotranspiration was estimated from the meteorological data using the classical Penman equation. The actual evapotranspiration of the vegetation cover was either calculated by WHNSIM according the approach of Beese et al. (1977) or estimated from literature data on beech and pine stands of the region (Peck and Mayer 1996; Köstner 2001) in combination with the measured leaf area index. In case of the beech stand, only the leaf area index of the trees was estimated; for the pine site also the leaf area index of the shrub layer was included. Both estimates of the actual evapotranspiration were fairly comparable (differences $<20\%$). In case of HYDRUS-2D, the water fluxes from the organic forest floor layer instead of precipitation were used as input data. In both cases, capillary rise was excluded due to deep groundwater tables (>10 m below the surface). The validation of the models was done according to measured soil water tensions. The simulated water fluxes were cross-checked by calculating the water fluxes from the measured tension gradients. All three methods gave comparable water fluxes for the mineral soils. To be consistent with previously published data we present fluxes of dissolved organic C and dissolved S calculated on base of the water fluxes as simulated with WHNSIM.

Statistical evaluation

The concentrations of bulk dissolved organic C and S, of organic C and S in the hydrophobic fraction of dissolved organic matter, and of sulphate as well as the C/S ratios of dissolved organic matter were not normally distributed. Differences between these variables in forest floor leachates and soil water in the mineral soil at various depths, since dependent, were evaluated using the Friedman test. The same procedure was applied for proportions of organic and inorganic S in bulk soil solutions. Rank correlations between variables were calculated according to Spearman.

For evaluation of seasonal trends, the volumetric weighted mean concentrations and cumulated fluxes calculated for the 9 seasons studied were tested,

since normal distributed, for differences using one-way analyses of variance (ANOVA) and the Scheffé test. The same procedure was applied for testing the differences in the slopes of the relations between dissolved organic C and S at the different sampling positions and for testing differences in organic and inorganic S fluxes from the forest floor and at 90 cm depth in the mineral soil. On base of the 1-month samples, the normally distributed differences in the distributions of C-bonded and ester sulphate S in forest floor leachates and subsoil solutions was evaluated using the paired t-test. All statistical analyses were performed using the software package STATISTICA 5.0 for Windows (StatSoft, Inc., Tulsa, OK).

Results and discussion

Water percolation through the forest floor and mineral soil

The amounts of seepage water from the forest floors reflected the course of rainfall at both sites (Kaiser et al. 2001a). On average, seepage water equalled about 75% of the rainfall at the beech site and about 73% at the pine site. The mean portions of throughfall that passed the forest floor were 93% under beech and 79% under pine. This suggests that the amount of seepage water collected by the zero-tension lysimeters were largely representative for the water inflow into the mineral soil at both sites. The smaller portion of throughfall that passed the forest floor at the pine site is most likely due to water-uptake by the ground vegetation which rooted almost exclusively in the organic layers and by the moss. Also the tree roots were concentrated in the forest floor. In contrast, the litter layer at the beech site contained no roots at all. The largest amounts of seepage water, especially at the beech site, occurred in autumn 1998 (Tables 2 and 3) because of huge amounts of rainfall (Kaiser et al. 2001a).

In summer and early autumn, the calculated amount of percolation water in the subsoil was far less than that of the seepage water from the forest floor and comprised $< 30\%$ of the rainfall most of the time because of the large consumption of water by the vegetation (Tables 2 and 3). On monthly base, in October–November, the amount of percolation water in subsoil approached the amount of seepage from the forest floor and during the rest of the dormant period (November–April), subsoil percolation water and forest floor seepage water were fairly similar. On average, the portion of the bulk precipitation that reached the subsoil during the experimental period was 37% at the pine site and 46% at the beech site.

Dissolved organic sulphur concentrations and fluxes

The concentrations of organic S in forest floor leachates of both sites showed strong temporal variations (Figures 1–4) that resembled those of dissolved

Table 2. Fluxes of water, sulphate sulphur (SO_4^{2-}–S) and organic sulphur (DOS) in seepage waters from the forest floor and in the mineral subsoil at 90 cm depth under a 160-year-old Scots pine (*Pinus sylvestris* L.) forest on Haplic Arenosols. In addition, the annual fluxes for the periods December 1997 to November 1998 (1997/1998) and December 1998 to November 1999 (1998/1999) are given

Sampling period	Forest floor			Subsoil at 90 cm depth		
	Water[a] (mm)	SO_4^{2-}–S (mg m^{-2})	DOS (mg m^{-2})	Water[b] (mm)	SO_4^{2-}–S (mg m^{-2})	DOS (mg m^{-2})
Seasonal fluxes						
December 1997–February 1998	42	11	4	36	12	5
March–May 1998	73	35	14	67	41	10
June–August 1998	118	122	53	41	54	16
September–November 1998	155	58	31	91	34	15
December 1998–February 1999	49	12	2	41	11	2
March–May 1999	71	38	12	59	39	9
June–August 1999	107	88	34	29	14	10
September–November 1999	111	41	23	72	33	19
Annual fluxes						
1997/1998	388	226	103	235	131	46
1998/1999	338	179	71	201	97	40

[a]Measured.
[b]Calculated (WHNSIM).

Table 3. Fluxes of water, sulphate sulphur (SO_4^{2-}–S) and organic sulphur (DOS) in seepage waters from the forest floor and in the mineral subsoil at 90 cm depth under a 90-year-old European beech (*Fagus sylvatica* L.) forest on Rendzic Leptosols. In addition, the annual fluxes for the periods December 1997 to November 1998 (1997/1998) and December 1998 to November 1999 (1998/1999) are given

Sampling period	Forest floor			Subsoil at 90 cm depth		
	Water[a] (mm)	SO_4^{2-}–S (mg m^{-2})	DOS (mg m^{-2})	Water[b] (mm)	SO_4^{2-}–S (mg m^{-2})	DOS (mg m^{-2})
Seasonal fluxes						
December 1997–February 1998	110	37	12	95	33	11
March–May 1998	102	49	20	91	40	16
June–August 1998	118	210	88	42	57	30
September–November 1998	433	116	101	280	71	71
December 1998–February 1999	153	39	13	131	32	12
March–May 1999	165	64	24	116	50	18
June–August 1999	115	160	48	23	9	11
September–November 1999	154	72	66	103	41	46
Annual fluxes						
1997/1998	873	412	221	565	202	128
1998/1999	587	335	151	373	132	87

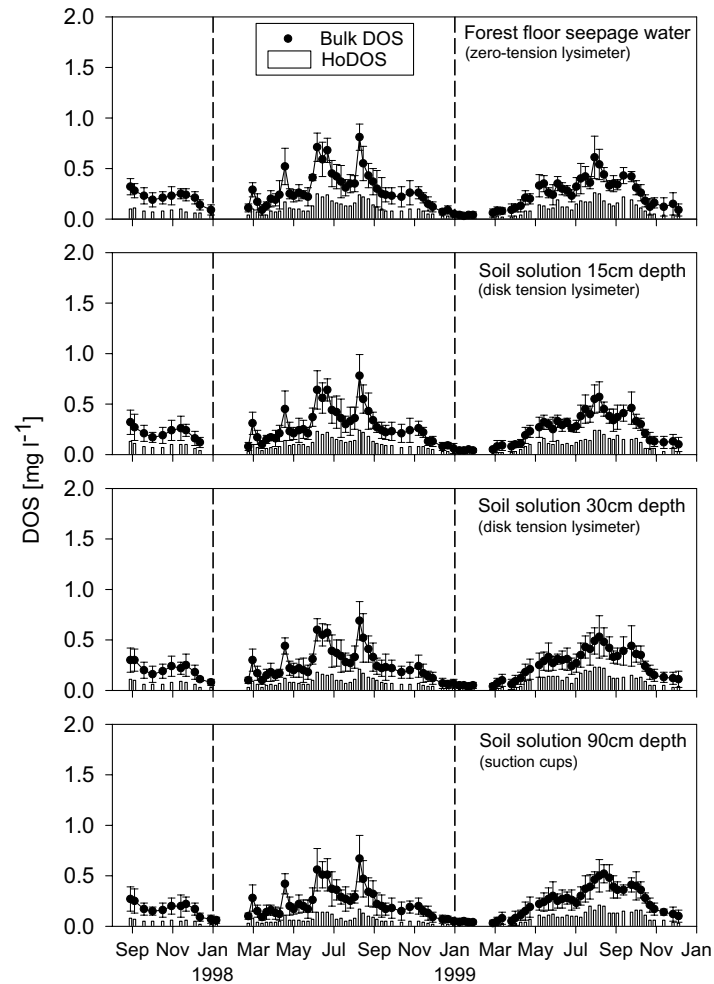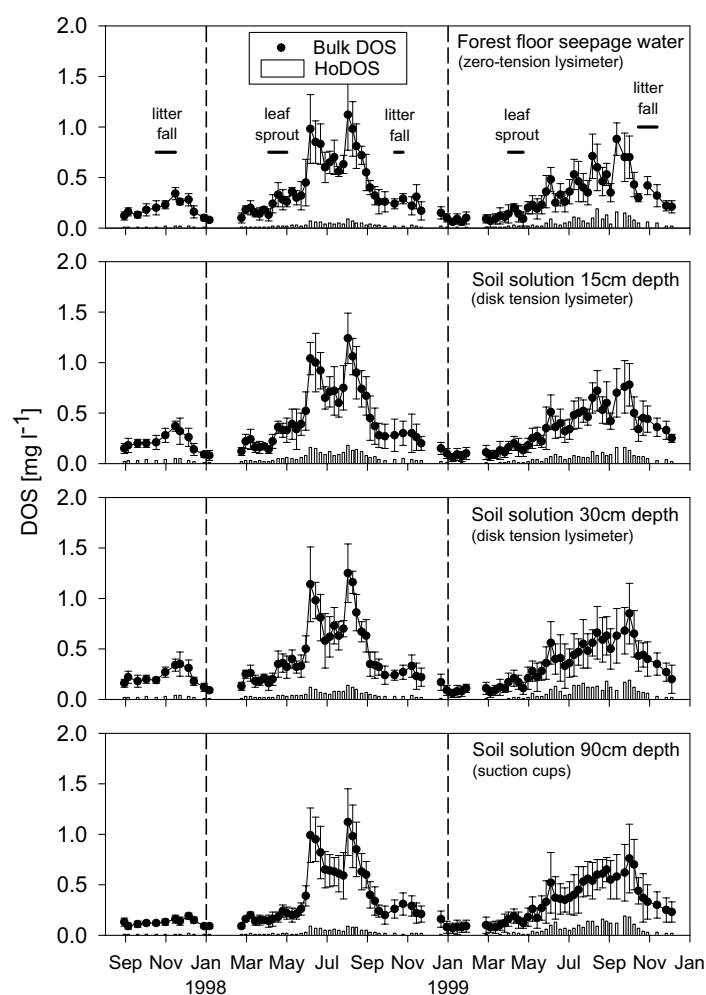[a]Measured.
[b]Calculated (WHNSIM).

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Figure 1. Temporal course of the concentrations of bulk dissolved organic sulphur (bulk DOS) and of organic sulphur in the hydrophobic fraction of dissolved organic matter (HoDOS) in the forest floor leachates and in soil solutions (15, 30, and 90 cm depth) under a 160-year-old Scots pine (*Pinus sylvestris* L.) forest on Haplic Arenosols during the sampling period August 1997 to November 1999. Error bars for bulk DOS represent the standard deviation of at least three samples.

organic C (Kaiser et al. 2001a). Concentrations of organic S were largest in summer and autumn and peaked after rainstorms that followed short dry periods (Figures 1 and 2). Maximum concentrations at the pine site were around 0.8 ± 0.1 and 1.1 ± 0.3 mg l^{-1} at the beech site. These values are at the upper end of the published concentrations of organic S in forest floor leachates (Homann et al. 1990; Nilsson et al. 2001). The average concentrations

Figure 2. Temporal course of the concentrations of bulk dissolved organic sulphur (bulk DOS) and of organic sulphur in the hydrophobic fraction of dissolved organic matter (HoDOS) in the forest floor leachates and in soil solutions (15, 30, and 90 cm depth) under a 90-year-old European beech (*Fagus sylvatica* L.) forest on Rendzic Leptosols during the sampling period August 1997 to November 1999. Error bars for bulk DOS represent the standard deviation of at least three samples.

of organic S in summer and autumn exceeded those in winter and spring by a factor of 4 at the pine site and by a factor of 5 at the beech site (Figures 3 and 4; Kaiser et al. 2000). Close correlations between organic C and S (Figure 5) suggest that the production of soluble organic S was directly linked to that of soluble organic C at both sites.
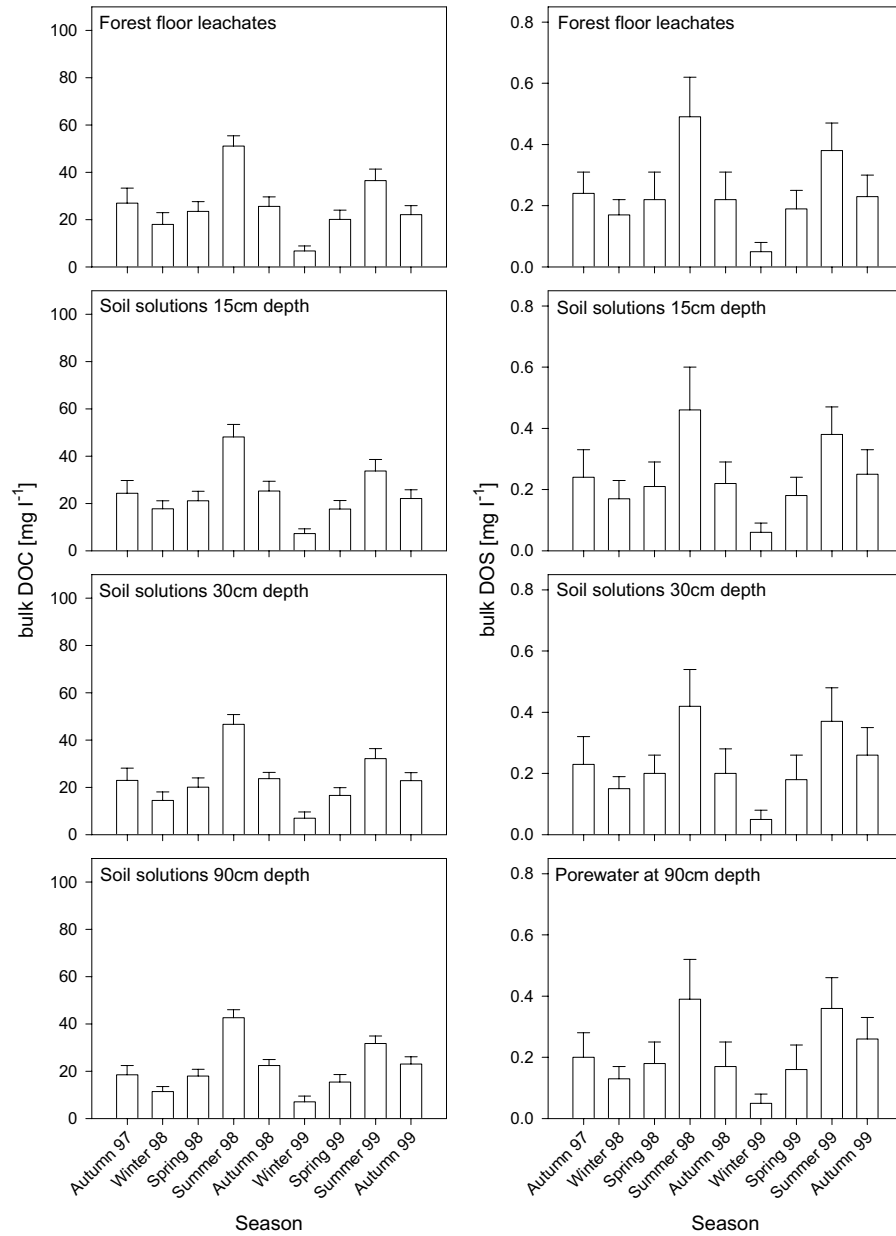
Figure 3. Mean bulk concentrations of dissolved organic carbon (DOC) and dissolved organic sulphur (DOS) in the forest floor leachates and in soil solutions (15, 30, and 90 cm depth) under a 160-year-old Scots pine (*Pinus sylvestris* L.) forest on Haplic Arenosols. The error bars represent the standard deviation as a measure of temporal variation of each 3-month period ($n \geq 6$).
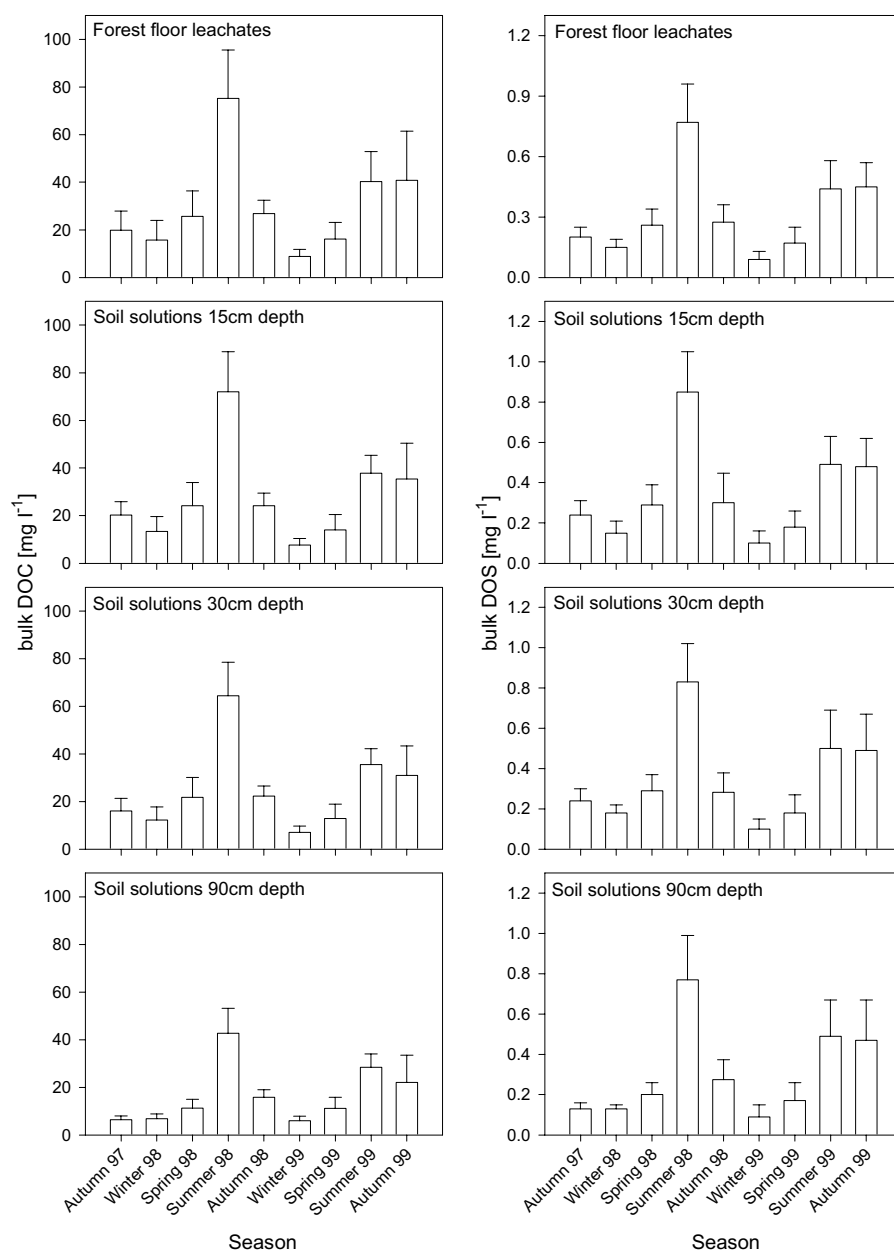
Figure 4. Mean bulk concentrations of dissolved organic carbon (DOC) and dissolved organic sulphur (DOS) in the forest floor leachates and in soil solutions (15, 30, and 90 cm depth) under a 90-year-old European beech (*Fagus sylvatica* L.) forest on Rendzic Leptosols. The error bars represent the standard deviation as a measure of temporal variation of each 3-month period ($n \geq 6$).
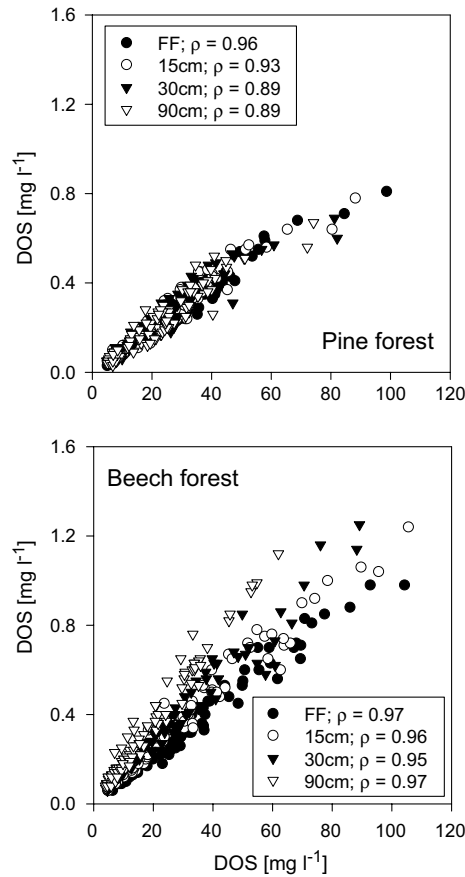
Figure 5. Relationship between bulk dissolved organic carbon (DOC) and bulk dissolved organic sulphur (DOS) in the forest floor (FF) leachates and in soil solutions (15, 30, and 90 cm depth) under a 160-year-old Scots pine (*Pinus sylvestris* L.) forest on Haplic Arenosols and a 90-year-old European beech (*Fagus sylvatica* L.) forest on Rendzic Leptosols ($n \geq 91$). Since the data were not normally distributed, Spearman correlation coefficients are given for each soil compartment.

The temporal pattern of the concentrations in the mineral soil followed that in forest floor leachates (Figures 1 and 2). The concentrations of dissolved organic S in soil solutions remained fairly constant with depth at the pine site (Figures 1 and 3) as well as at the beech site (Figures 2 and 4), suggesting little retention.

At both sites, dissolved organic C and S were correlated throughout the entire mineral soil as strongly as in the forest floor leachates (Figure 5). Similar to organic S, concentrations of dissolved organic C remained largely unchanged with depth at the pine site and so the relationship between organic C and S in soil water from all depths did not differ from that in the forest floor

leachates. This indicates that there was little interaction of dissolved organic matter and the mineral matrix, possible due to the low content of clay and pedogenic Al and Fe (Kaiser et al. 2001b), and also no pronounced microbial decay during the passage through the mineral soil.

In contrast to the pine site, concentrations of dissolved organic C at the beech site decreased significantly ($p < 0.01$) in the subsoil. This is in agreement with the stronger retention of dissolved organic C by the soils of the beech site as compared with those of the pine site observed in sorption experiments (Kaiser et al. 2001b). The slope of the relation between organic C and S became steeper ($p < 0.05$) towards the subsoil (Figure 5) which means that organic matter in soil water became richer in S while passing through the mineral soil. This confirms the results of Nilsson et al. (2001) who observed that organic S is more mobile in soil than organic C. We explain the mobility of organic S by its concentration in the non-sorptive and thus largely mobile hydrophilic fraction of dissolved organic matter (Kaiser 2001). In summary, transport of organic S in soil resembles that of other organically bound nutrients such as N and P (Qualls and Haines 1991; Andersson et al. 1999).

Although a significant constituents in forest floors leachates and mineral soil solutions, organic S was not the dominant contributor to dissolved S. On average, in forest floor leachates it comprised 29% of total dissolved S at the pine site and 34% at the beech site. The respective values for the subsoils at 90 cm depths were 28% under pine and 39% under beech. Proportions of organic S were generally lowest during winter and spring and highest in summer and autumn. Highest proportions of organic S (up to 53% of total dissolved S) occurred in subsoils under beech during summer and autumn which probably resulted from the large production of soluble organic matter in the forest floor at that time of the year (see Kaiser et al. 2001a) and strong uptake of SO_4^{2-} by plants. The observed values correspond to the upper end of published portions of organic S in forest floor and soil seepage waters (David et al. 1987; Mitchell et al. 1989; Homann et al. 1990; Houle et al. 2001) and in leachates of soil columns in laboratory experiments (Valeur et al. 2000). They also reflects the low contents of SO_4^{2-} in the studied soils (Table 1) and the relatively little annual inputs of inorganic S by atmospheric depositions which were about 0.36 g m^{-2} at the pine site and 0.32 g m^{-2} at the beech site during the study period. These values are rather low compared to the depositions many European forests received a decade ago (Prechtel et al. 2001).

At the beech site, the proportions of total dissolved S in soil solutions at 90 cm depth being in organic form were significantly ($p < 0.05$) larger than those in the forest floor leachates. This is in agreement with the previously observed mobility of organic S (Kaiser 2001; Nilsson et al. 2001) and other organically bound nutrients such as N and P (Qualls and Haines 1991; Andersson et al. 1999). Reasons for the decreasing contribution of SO_4^{2-} in the mineral soil could be uptake by the deep-rooting beeches, sorption to Al and Fe hydrous oxides, and precipitation as $CaSO_4$. However, sorption to Al and Fe oxides is negligible at pH values > 6 (Nodvin et al. 1986). The high solution

pH (7.2–8.0) throughout the mineral soil given, sorption of SO_4^{2-} to hydrous oxides seems unlikely. Also precipitation can be ruled out since all solutions were undersaturated with respect to $CaSO_4 \cdot 2H_2O$ despite the large concentrations of Ca^{2+} ($\geq$11 mg l^{-1} at 90 cm depth). The contribution of SO_4^{2-} to total S in the subsoil solutions under beech at 90 cm depth was significantly ($p < 0.05$) smaller during summer and autumn 1999 than during winter 1998/1999 and spring 1999 (Table 3). A similar but not significant trend was observed when summer and autumn 1998 where compared with winter 1997/1998 and spring 1998. This seasonality in the contribution of SO_4^{2-} to total S in the subsoil suggests that the reduction in SO_4^{2-} was mainly due to uptake by roots. At the pine site, the proportions of organic S in soil solutions remained largely unchanged with depth. This might be caused by little uptake of SO_4^{2-} by plants since the roots of the vegetation were concentrated in the organic forest floor layer and from the poor capability of the mineral soil to adsorb dissolved organic matter (Kaiser et al. 2001b, 2002) and presumably also SO_4^{2-} due to small concentrations of Al and Fe hydrous oxides (Kaiser et al. 2001b).

The seasonal fluxes of S varied greatly during the course of the year (Tables 2 and 3). At the pine site, the fluxes of SO_4^{2-} of organic S and in summer and autumn were up to 11 and 17, respectively, times larger than those in winter and spring. The differences between the fluxes in the dormant and growing season were less pronounced at the beech site. Here, the fluxes of SO_4^{2-} in summer and autumn were at maximum six times larger than those in winter and spring. For organic S, the fluxes in summer and autumn exceeded those of winter and spring by a factor of ≤ 8. The increase in both SO_4^{2-} and organic S in summer and autumn was presumably due to increased microbial activity resulting in increased production of soluble organic compounds (Kaiser et al. 2001) and mineralisation.

The annual fluxes of SO_4^{2-} with forest floor leachates of both sites (Tables 2 and 3) ranged at the lower end of SO_4^{2-} fluxes in forest soils observed, especially in polluted regions (Schulze et al. 1989; Ulrich 1989). At the pine site, they represented on average 56% of the atmospheric deposition of SO_4^{2-}. The mean annual fluxes of total S equalled about 80% of the mean annual deposition which means that the forest floor at the pine site was a net sink for atmospheric S during the experimental period. In contrast, the mean annual fluxes of SO_4^{2-} from the forest floor at the beech site exceeded the atmospheric depositions of SO_4^{2-} by a factor of about 1.2. This indicates that a part of the SO_4^{2-} in the forest floor leachates resulted from mineralisation of organic S. The mean annual fluxes of total S from the forest layer into the mineral soil at the beech site were about 1.7 times higher than the mean annual atmospheric deposition of sulphate S. The average organic S that was leached annually from the organic layers amounted to 0.09 g m^{-2} at the pine site and to 0.19 g m^{-2} at the beech site which was less than the annual fluxes of dissolved organic S estimated for the organic layers of non-limed and limed Norway spruce (*Picea abies* (L.) Karst.) stands (0.26 and 0.42 g m^{-2}; Nilsson et al. 2001).

Although organic S did not dominate the fluxes of dissolved S in the subsoils (Tables 2 and 3) as reported for organic forms of other nutrient elements such as N and P (Kaiser et al. 2000) it was a significant contributor, especially in summer and autumn. Therefore organic S can be considered to be important for the leaching of S from the rooting zone of the two studied soils. This supports findings of previous studies stressing the potential effects of organic species on the leaching of nutrients in forest ecosystems (Qualls and Haines 1991; Hedin et al. 1995; Qualls et al. 2000). The annual fluxes of dissolved organic S at 90 cm depth averaged 0.04 g m^{-2} under pine and 0.11 g m^{-2} under beech. At the pine, the fluxes of dissolved organic S at 90 cm depth represented 46% of those from the forest floor. The respective value for the beech site is 57%. These large portions of organic S leached in the two studied subsoils we assign to the small capability of the soils to sorb dissolved organic matter as compared to podzolic soils (Kaiser et al. 2000, 2002). Even larger subsoil fluxes have been estimated for non-limed and limed forests stands (0.18 and 0.36 g m^{-2}; Nilsson et al. 2001). In that study, the estimated subsoil fluxes represented 69–86% of the organic S leached from the forest floor.

Carbon-to-sulphur ratios of bulk dissolved organic matter

In the forest floor leachates and soil solutions of both study sites, bulk organic C and S were closely correlated (Figure 5) which suggested that production and transport of organic C and S relate to each other. This was especially true for the beech site where the C/S ratios of bulk dissolved organic matter in forest floor leachates were almost constant during the whole experimental period (Figure 6). Also at the pine site, the C/S ratios of dissolved organic matter in the forest floor leachates were constant except for autumn 1998 and winter 1998/1999 where the C/S ratios increased (Figure 6). The increase in C/S ratios at the pine site in autumn 1998 and winter 1998/1999 followed heavy storms in autumn which could have induces preferential leaching of C-rich compounds from the forest floor. However, the amount of rainfall at the beech site was much higher but no changes in C/S ratios of dissolved organic matter occurred. The constant C/S ratios and the close relationships between organic C and S (Figure 5) suggest simultaneous production of dissolved organic C and S in the forest floor.

At the pine site, the C/S ratios of dissolved organic matter in the mineral soil solutions remained fairly unchanged and followed the course of those in the forest floor leachates. This reflects the little changes in dissolved organic matter during the transport through that soil (see above).

In contrast, the C/S ratios of dissolved organic matter in mineral soil solutions under beech significantly ($p < 0.05$) decreased with depth (Figure 6). This resulted from the preferential removal of the C-rich but S-poor hydrophobic fraction of dissolved organic matter from soil water in the subsoils (see below). The decrease in the C/S ratios of dissolved organic matter is in contrast to the increase observed in a Douglas fir and a red alder forest where the ratios
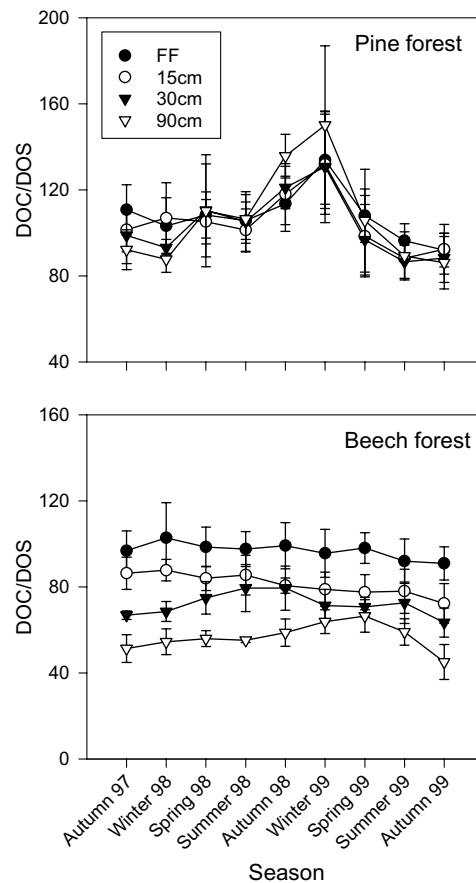
Figure 6. Seasonal mean ratios of dissolved organic carbon to dissolved organic sulphur (DOC/DOS) in the forest floor leachates and in soil solutions (15, 30, and 90 cm depth) under a 160-year-old Scots pine (*Pinus sylvestris* L.) forest on Haplic Arenosols and a 90-year-old European beech (*Fagus sylvatica* L.) forest on Rendzic Leptosols during the sampling period August 1997 to November 1999. The error bars represent the standard deviation as a measure of temporal variation during each 3-month period ($n \geq 6$).

of organic C to organic S in soil water from the upper mineral soil (A horizon) were equal or larger than the ratios of organic C to organic S in forest floor leachates (Homann et al. 1990).

The ratios of organic C to organic S in forest floor leachates at the pine site (84–167) as well as at the beech site (78–131) and in soil solutions at 90 cm depth under pine (64–230) were within the range of values of soil and surface waters (David et al. 1987; Homann et al. 1990; Houle et al. 1995; Nilsson et al. 2001). The ratios in soil solutions at 90 cm depth under beech (37–79) were clearly at the lower end of published values.
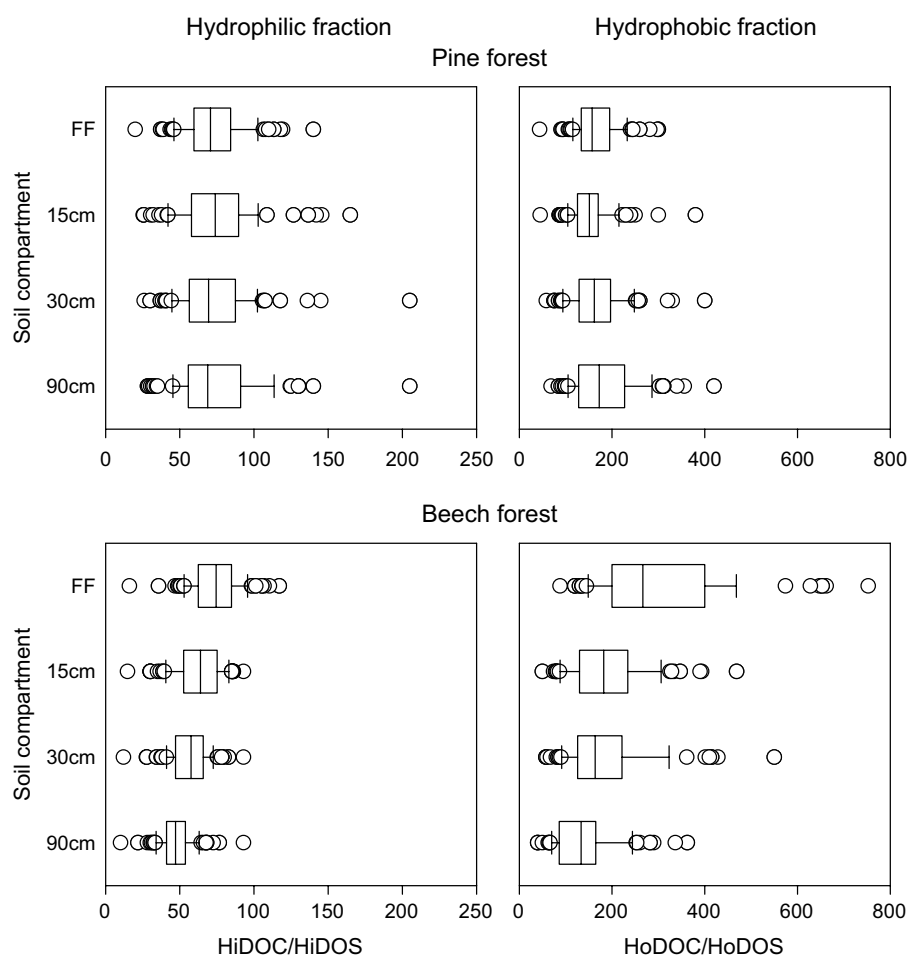
Hydrophilic fraction   Hydrophobic fraction

Figure 7. Depth distribution of organic carbon to organic sulphur ratios in hydrophilic and hydrophobic fractions of dissolved organic matter (HiDOC/HiDOS and HoDOC/HoDOS) in the forest floor (FF) leachates and in soil solutions (15, 30, and 90 cm depth) under a 160-year-old Scots pine (*Pinus sylvestris* L.) forest on Haplic Arenosols and a 90-year-old European beech (*Fagus sylvatica* L.) forest on Rendzic Leptosols during the sampling period August 1997 to November 1999. The extents of the box indicate the 25th and 75th percentiles, the line inside the box the 50th percentile. Whiskers represent the 10th and 90th percentile and outliers are given as open symbols ($n \geq 91$).

Fractions of dissolved organic sulphur

At both study sites, the hydrophilic fraction of dissolved organic matter in forest floor leachates and in soil solutions comprised the major part of organic S (Figures 1 and 2). On average, $62 \pm 6\%$ of the organic S in forest floor
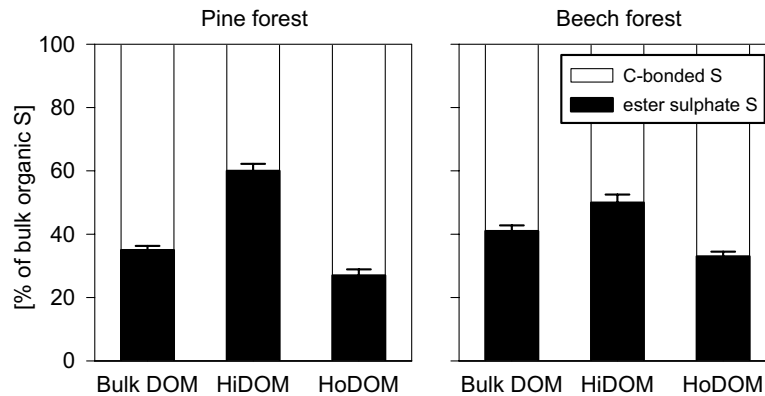
Figure 8. Distribution of binding forms of organic sulphur in bulk organic matter and hydrophilic and hydrophobic fractions of combined 3-month samples of forest floor leachates under a 160-year-old Scots pine (*Pinus sylvestris* L.) forest on Haplic Arenosols and a 90-year-old European beech (*Fagus sylvatica* L.) forest on Rendzic Leptosols. Samples were collected from September to November 1997. Error bars represent the standard deviation as a measure of the analytical precision ($n = 3$).

leachates under pine was in the hydrophilic fraction. The respective percentage at the beech site was $85 \pm 4\%$. In the soil solutions at 90 cm depth, the hydrophilic fraction contained $68 \pm 7\%$ of the organic S at the pine site and $89 \pm 7\%$ at the beech site. The average C/S ratio of the hydrophilic fraction in forest floor leachates at the pine site was 73 ± 20 and that of the hydrophobic fraction was 167 ± 44. The respective values at the beech site were 74 ± 16 and 313 ± 151. These values underline the concentration of S of the hydrophilic fraction.

The proportions of organic S in the hydrophilic fraction in winter and spring (54–78% at the pine site, 86–100% at the beech site) were significantly larger ($p < 0.01$) than those in summer and autumn (44–73% at the pine site, 75–95% at the beech site; Figures 1 and 2). The increase in organic S in the hydrophobic fraction in summer and spring paralleled the increase of organic C in the hydrophobic fraction (Kaiser et al. 2001a). The enrichment of organic S in the hydrophilic fractions is in accordance with previous results on other organically bound nutrients (e.g. Qualls and Haines 1991). The different proportions of organic S in the hydrophobic fraction at the two study sites compares well with the differences in the distribution of organic C between the hydrophilic and hydrophobic fraction.

Organic S in the hydrophobic fraction tended to decrease slightly with depth at the pine site. The decrease of organic S of the hydrophobic fraction was about equal to that of bulk dissolved organic S and went along with a slight decrease of organic C of the hydrophobic fraction. The decrease in both C and S of the hydrophobic fraction was probably due to some sorption by Al and Fe oxides (Kaiser 2001). This little sorption of dissolved organic matter contrib-
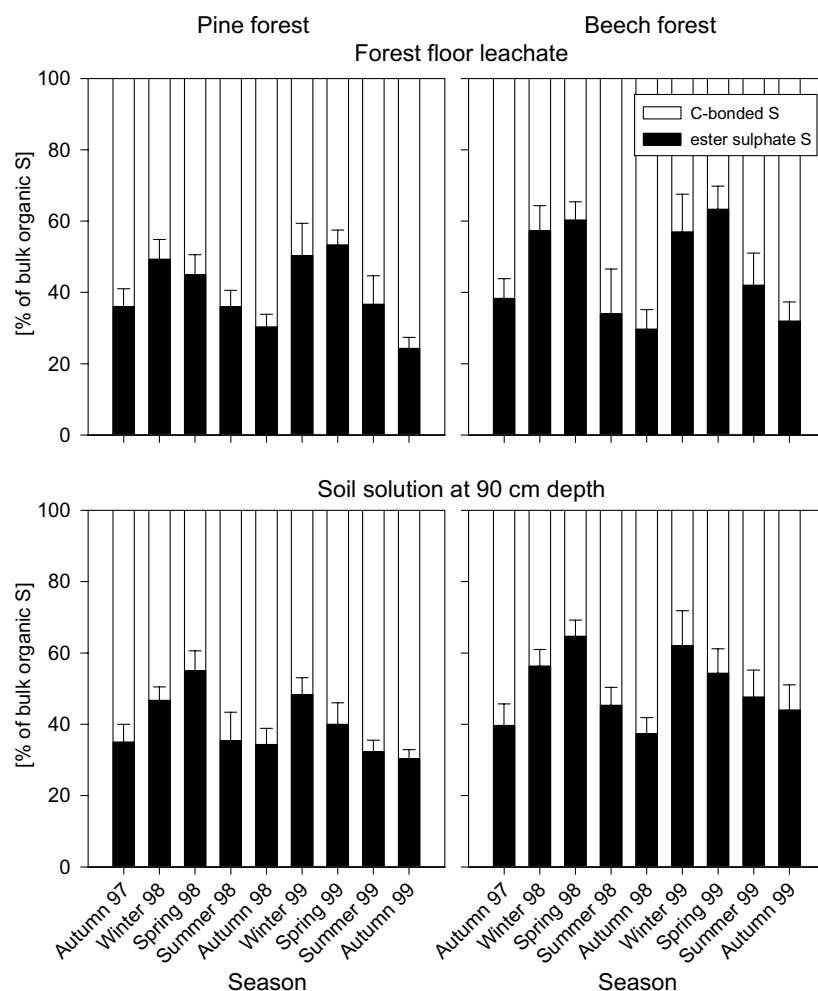
Figure 9. Seasonal volume-weighted mean distribution of binding forms of organic sulphur in forest floor leachates and soil solutions 90 cm depth under a 160-year-old Scots pine (*Pinus sylvestris* L.) forest on Haplic Arenosols and a 90-year-old European beech (*Fagus sylvatica* L.) forest on Rendzic Leptosols. Since the means were calculated based on the analyses of 1-month samples, the error bars represent the standard deviation as a measure of temporal variation during each 3-month period ($n = 3$).

utes, considering the small contents of hydrous oxides in those soils, probably to the little retention of SO_4^{2-} at the pine site. The hydrophobic fraction of dissolved organic matter typically outcompetes SO_4^{2-} for sorption sites on oxides (Gu et al. 1995). Since there were no changes in proportions of C and S in the hydrophilic fraction with depth and those in the hydrophobic fraction paralleled each other, the C/S ratios of both fraction remained largely
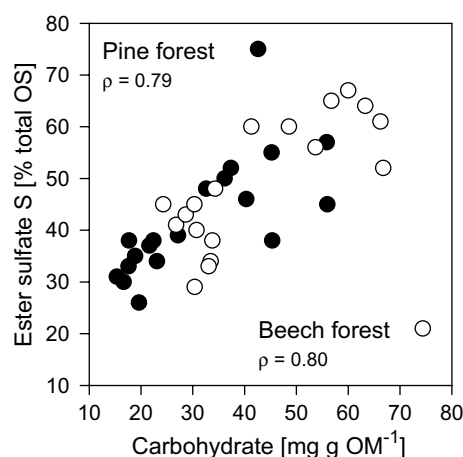
Figure 10. Relationship between concentrations of total hydrolysable carbohydrates and ester sulphate sulphur (S) in 3-month samples of forest floor leachates and soil solutions at 90 cm depth under a 160-year-old Scots pine (*Pinus sylvestris* L.) forest on Haplic Arenosols and a 90-year-old European beech (*Fagus sylvatica* L.) forest on Rendzic Leptosols. Carbohydrate data from Kaiser et al. (2001a). Carbohydrate concentrations are given on base of ash-free organic matter (OM) while ester sulphate S is given in percent of the total organic S (OS). Because the data were not normally distributed, Spearman correlation coefficients are given.

unchanged throughout the whole mineral soil (Figure 7). The average C/S ratio of the hydrophilic fraction at 90 cm depth was 75 ± 29 and that of the hydrophobic fraction was 176 ± 59.

At the beech site, the proportions of organic S in the hydrophobic fraction in soil solutions at 15 cm depth exceeded significantly ($p < 0.05$) those in forest floor leachates, possibly due to release from decaying litter fragments transported into the upper mineral soil by earthworms. With further depth, the portions of organic C in hydrophobic fractions decreased considerably ($p < 0.01$) whereas the organic S in that fraction decreased only slightly. For the hydrophilic fraction, there was also a decrease ($p < 0.05$) in organic C with depth but not of organic S. We assign this to preferential retention of constituents poor in S. Consequently, the C/S ratios of both fractions increased towards the subsoil (Figure 7). The average C/S ratio of the hydrophilic fraction at 90 cm depth was 48 ± 10 and that of the hydrophobic fraction was 141 ± 66.

These results indicate that the vertical mobility of organic S in the studied soils resulted mainly from its concentration in the hydrophilic fraction of dissolved organic matter. However, there are also some indications for a preferential transport of organic S as compared with C within the two analysed fractions of dissolved organic matter. This points at a concentration of S in compounds that sorb weakly. Most mobile in soil are neutral hydrophilic

compounds such as non-charged carbohydrates (Qualls and Haines 1991; Guggenberger and Zech 1994).

Binding forms of dissolved organic sulphur

The distribution of the two binding forms of organic S, C-bonded S and ester sulphate S, in dissolved organic matter and its hydrophilic and hydrophobic fractions in forest floor leachates of the two studied sites is given in Figure 8. At both sites, C-bonded S comprised the bigger part of organic S of the bulk sample and also in the hydrophobic fractions while in the hydrophilic fractions a larger portion of organic S was found as ester sulphate S. Ester sulphate S is considered to derive mainly from microbial production while C-bonded S, which mainly represents S in amino acids and protein, can be found both in microbial and plant residues (Strickland et al. 1987; Zhao et al. 1996). Typically, fresh plant litter contains no ester sulphate S but it forms rapidly when microbial degradation and transformation starts (Strickland et al. 1987). Thus, the relative enrichment of ester sulphate S in the hydrophilic fractions is plausible because these fractions were strongly influenced by carbohydrates of microbial origin while the hydrophobic fractions consisted mainly of lignin degradation products (Kaiser et al. 2001a).

The distribution of C-bonded and ester sulphate S in dissolved organic matter showed strong seasonal variations (Figure 9). In summer and autumn, C-bonded S was by far the most important constituent of organic S in forest floor leachates at both sites. In contrast, the share of ester sulphate S was larger in winter and spring. This may seem paradox since one would assume that microbial products and thus ester sulphate S should become more prominent during the growing season. Instead, we found an increase in C-bonded S which suggest a larger contribution of plant-derived material to dissolved organic matter. However, this result is line with our former observation of increasing contribution of lignin degradation products during summer and autumn (Kaiser et al. 2001a). The relative increase in plant-derived products in summer and autumn was due to degradation of organic matter preferentially taking place during the warm growing season. Production of microbial metabolites was also greatly enhanced but overcompensated by the production of water-soluble degradation products of plant biomass. The large contribution of microbial products to dissolved organic matter in winter and spring was due to leaching of bacterial and, especially, fungal biomass, presumably disrupted by frost cycles.

Compared to the organic matter of the forest floor layers (Table 1), which were the major sources of dissolved organic matter in the studied forests, dissolved organic matter was richer in ester sulphate S. This confirms the importance of microbial activity in the production of dissolved organic matter shown also by analyses of biomarker compounds (Guggenberger and Zech 1994; Kaiser et al. 2001a).

With depth, there was no significant change in the distribution of bindings forms of organic S in the mineral soil under pine (Figure 9) which is in agreement with the little changes observed for the concentration of organic S and its distribution between dissolved organic matter fractions. On average, ester sulphates comprised $41 \pm 10\%$ of organic S in forest floor leachates and $40 \pm 8\%$ of organic S in soil solutions at 90 cm depth.

In contrast to the pine site, the portions of ester sulphate S at the beech site increased significantly ($p < 0.01$) with depth (Figure 9) which could be due to the preferential sorption of the hydrophobic dissolved organic matter fraction that was low in ester sulphate S (Figure 10). Thus, ester sulphate S seems to be the more mobile form of organic S because of its concentration in the weakly sorbing hydrophilic fraction. Ester sulphates comprised, on average, $47 \pm 14\%$ of organic S in the forest floor leachates and $51 \pm 10\%$ in soil solutions at 90 cm depth. The trend to larger retention of C-bonded S was possible caused by its concentration in the strongly sorbing hydrophobic fraction (Figure 8) but could also be due to direct sorption of S-containing amino acids by mineral surfaces (Aufdenkampe et al. 2001).

Being potentially labile, the increase in ester sulphate S with depth under beech underlines the little biodegradation of dissolved organic matter during its passage through the mineral soil as mentioned in several studies before (Qualls and Haines 1992; Boissier and Fontvieille 1993).

The observed distributions of C-bonded and ester sulphate S were in agreement with the distribution of organic S forms in seepage waters from a Podzol E horizon (David et al. 1987) and with spectroscopic analyses of organic S of isolated dissolved organic matter (Xia et al. 1998).

Figure 10 displays the relationship between ester sulphate S and total hydrolysable carbohydrates (Kaiser et al. 2001a) in 3-month samples of bulk dissolved organic matter in forest floor leachates and soil solutions at 90 cm depth. Both variables were closely correlated which supports the assumption that ester sulphate S is related to mobile carbohydrate structures and thus passes the mineral soil to a greater extent than C-bonded S and organic C itself.

Conclusive remarks

(1) Organic S is an important contributor of S dissolved in forest floor leachates and in soil solutions. Although not as prominent as the organic forms of other elements such as N and P (e.g. Kalbitz et al. 2000), it comprises up to about 50% of total dissolved S and proved to be equally or even more mobile in the studied mineral soils as SO_4^{2-}. Therefore organic S is important in cycling, transport, and leaching of S in forest soils, especially in such soils that contain little inorganic S and receive little

atmospheric inputs of SO_4^{2-}. This could mean that the importance of dissolved organic S will increase with ongoing decreases in atmospheric S deposition and depletion of adsorbed SO_4^{2-} pools in soil. Thus, in future research, organic S in soil should not only be considered as a potential source of soil and surface water SO_4^{2-} as emphasised by Alewell (2001) but has also to be considered as a contributor to leaching of S from soil.

(2) The strong changes in concentration and composition of organic S in forest floor leachates throughout the year suggest seasonal changes in the production of dissolved organic matter. The distribution of organic S between fractions of dissolved organic matter and binding forms reflects the seasonal changes in mechanisms that steer the contribution of microbial and plant-derived compounds to of dissolved organic matter (see Kaiser et al. 2001a): leaching of disrupted microbial biomass in winter and spring and microbial production of soluble compounds during the degradation of plant-derived organic material in summer and autumn.

The close relationship of C and S in forest floor leachates indicates that the production of soluble organic S is directly related to the turnover of organic matter. Astonishingly, the seasonal changes in sources of organic C and S did not result in pronounced seasonal changes in the C/S ratio of dissolved organic matter.

(3) Organic S is mobile in the mineral soil when in the hydrophilic fraction of dissolved organic matter or if the soil's capability to sorb dissolved organic matter, as in the present study, is small. Ester sulphate S is more mobile than C-bonded S because of being more prominent in the weakly sorbing hydrophilic fraction. Presumably, ester sulphate S is associated with carbohydrate structures.

Because of being potentially labile, the unchanged or even increased proportions of ester sulphate S with increasing soil depth suggest little microbial degradation of organic matter dissolved during the passage of water through soil.

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