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Sulfate reduction and S-oxidation in a moorland pool sediment

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Abstract. In an oligotrophic moorland pool in The Netherlands, S cycling near the sediment/water boundary was investigated by measuring (1) SO_4^{2-} reduction rates in the sediment, (2) depletion of SO_4^{2-} in the overlying water column and (3) release of ^{35}S from the sediment into the water column. Two locations differing in sediment type (highly organic and sandy) were compared, with respect to reduction rates and depletion of SO_4^{2-} in the overlying water.

Sulfate reduction rates in sediments of an oligotrophic moorland pool were estimated by diagenetic modelling and whole core $^{35}SO_4^{2-}$ injection. Rates of SO_4^{2-} consumption in the overlying water were estimated by changes in SO_4^{2-} concentration over time in *in situ* enclosures. Reduction rates ranged from 0.27–11.2 mmol m^{-2} d^{-1}. Rates of SO_4^{2-} uptake from the enclosed water column varied from −0.5, −0.3 mmol m^{-2} d^{-1} (November) to 0.43–1.81 mmol m^{-2} d^{-1} (July, August and April). Maximum rates of oxidation to SO_4^{2-} in July 1990 estimated by combination of SO_4^{2-} reduction rates and rates of *in situ* SO_4^{2-} uptake in the enclosed water column were 10.3 and 10.5 mmol m^{-2} d^{-1} at an organic rich and at a sandy site respectively.

Experiments with $^{35}S^{2-}$ and $^{35}SO_4^{2-}$ tracer suggested (1) a rapid formation of organically bound S from dissimilatory reduced SO_4^{2-} and (2) the presence of mainly non SO_4^{2-}-S derived from reduced S transported from the sediment into the overlying water. A $^{35}S^{2-}$ tracer experiment showed that about 7% of $^{35}S^{2-}$ injected at 1 cm depth in a sediment core was recovered in the overlying water column.

Sulfate reduction rates in sediments with higher volumetric mass fraction of organic matter did not significantly differ from those in sediments with a lower mass fraction of organic matter.

Introduction

Sulfur cycling in aquatic and terrestrial ecosystems has received increasing attention due to concern about the potential impact of atmospheric S-decomposition. Many oligotrophic moorland pools, which are widely spread over The Netherlands, are acidified due to atmospheric inputs of anthropogenically derived sulfur and nitrogen (Van Dam 1987). Oligotrophic and mesotrophic moorland pools possess a variety of characteristic fauna and flora. Due to anthropogenic activity many of these moorland pools have lost their original character. Most moorland are sensitive to acid loading because their underlying and surrounding soils are low in chemical buffering capacity. Therefore biological processes in the sediment like denitrification and SO_4^{2-} reduction are of major importance to internal alkalinization necessary to neutralize the atmospheric input of potential acidifying N and S components. In two of the three moorland pools studied by Van Dam (1987), where littoral sediment was exposed to the atmosphere during the dry summer of 1976, water SO_4^{2-} concentrations increased and pH decreased due to oxidation of reduced sulfur. In subsequent years, however, SO_4^{2-} reduction resulted in an increased pH and alkalinity of the pool water (Van Dam 1987). The role of SO_4^{2-} reduction in alkalinity generation of acidified lakes is well documented (e.g., Rudd et al. 1986a; Giblin et al. 1990). Cook et al. (1986) reported that nearly 60% of alkalinity generation in littoral sediments in lake 223 (northwestern Ontario) was accounted for by net loss of SO_4^{2-} through SO_4^{2-} reduction. For every equivalent of SO_4^{2-} reduced an equivalent alkalinity is generated:

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S \tag{1}$$

Subsequently the alkalinity is removed again when reduced S is reoxidized. For long-term or permanent alkalinity production by SO_4^{2-} reduction therefore, reduced sulfur must be immoblilized by reaction with Fe or organic matter and be buried in the sediment (Giblin et al. 1990; Rudd et al. 1986a) or removed by leaching or volatilization. The net gain of alkalinity is equivalent to the removal or permanent burial of S.

In Gerritsfles, an acidified moorland pool in the Netherlands, fluxes over the sediment water interface were calculated from dissolved porewater ΣH_2S and SO_4^{2-} concentration profiles (Feijtel et al. 1989). The ΣH_2S flux over the sediment water interface may have been overestimated, however, because part of the ΣH_2S may be oxidized to S species of intermediate oxidation state, and leave the sediment unnoticed. So the S flux from the sediment to the overlying water involves partly oxidized S-species in addition to dissolved ΣH_2S. The primary aim of this study was to assess the S flux from the sediment into the water column and to estimate reoxidation rates of S to SO_4^{2-} in the overlying water.

In Gerritsfles the thickness of the detrital layer overlying quarzitic sands varies considerably. There is a large spatial variability of organic matter mass fraction and the size of the pools of reduced S in the upper

10 cm of the sediment (Marnette & Stein, submitted) where SO_4^{2-} reduction takes place. The second aim of this study was to test the hypothesis that in organic sediments with a high mass fraction of reduced S, reduction rates were higher than in sandy sediments with a low mass fraction of reduced S.

Methods and materials

Study site and sample collection

Experiments were carried out in Gerritsfles (5°49′E, 52°10′N, 40 m above mean sea level), a shallow freshwater lake in the centre of The Netherlands. The pool has a simple hydrology, characterized by a small catchment area and a perched water table due to an impermeable iron pan (Schimmel & Ter Hoeve 1952). The surface area of the pool is about 5 ha and the mean depth 0.65 m. The mean pH and SO_4^{2-} concentration of the lake water are 4.4 and 102 μM respectively. Gerritsfles is located in a heath-dominated ecosystem. The sediments are unconsolidated quartz sand covered with a detrital layer. The detrital layer varies in thickness (0—50 cm) over the sediment area and mainly originates from peat moss (*Sphagnum*).

Sulfate reduction rates were estimated by 1) diagenetic modelling of SO_4^{2-} porewater profiles, and 2) whole core injection with radiolabelled SO_4^{2-} in the laboratory. Sulfate uptake of the sediment from the overlying water was measured from SO_4^{2-} depletion in *in situ* enclosures. Release of sulfur from the sediment into the pool water was assessed by whole core injection with radiolabelled S^{2-} in the lab. Sediment was collected by means of a coring device using Acrylic liners (5 or 7 cm diameter, 30 cm long). For diagenetic calculations, triplicate cores (5 cm diameter) were collected on November 14, 1990. Water temperature at the sediment-water interface was 8 °C. The cores contained securely taped (Scotch tape no. 471) 3-mm holes at 0.5—1 cm intervals. Sediment samples were obtained in the field from every core by inserting hollow stainless steel tubes through the holes. The sediment was transferred into mini-vials (maximum volume 1.5 ml) which were completely filled to minimize possible oxidation. Samples were stored at −5 °C and immediately centrifuged (6000 rpm) upon return to the laboratory.

For experiments involving radiolabelled sulfate, 2 cores (7 cm diameter) were collected on July 9, 1990 at sites with either a thin surface layer (1—2 cm) of detrital material or a thick (> 8 cm) detrital layer.

To assess release of sulfur to the water column, we used sediment sampled in August 1989 from an organic-rich part of the sediment. Water temperature at the sediment-water interface at time of sampling in July and August was 20 °C. All cores collected at the specific sites were taken within less than 1.5 m distance from each other.

Estimating rates of sulfate reduction and sulfate uptake

1. *Diagenetic modelling*

Berner's (1964, 1980) diagenetic model describes the change of sulfate concentration with time as a function of diffusion, sediment accumulation and bacterial sulfate reduction:

$$\frac{\partial C}{\partial t} = D_S * \frac{\partial^2 C}{\partial x^2} - \omega * \frac{\partial C}{\partial x} - f(x) \tag{2}$$

where C represents the SO_4^{2-} concentration (μM), D_S the whole sediment molecular diffusion coefficient ($m^2\ s^{-1}$), ω the sedimentation rate ($m\ s^{-1}$) and $f(x)$ the depth dependent sulfate reduction rate ($\mu mol\ m^3\ s^{-1}$). Measured sulfate concentrations were fit to the form

$$C(x) = (C_0 - C_\infty) * \exp(-b * x) + C_\infty \tag{3}$$

where C_0 is the sulfate concentration at the sedimeter-water interface ($x = 0$) and C_∞ is the sulfate concentration at a depth below which no further concentration change occurs.

Assuming a steady state situation at the time of sampling ($\partial C/\partial t_x = 0$) with time-independent D_s, ω and $f(x)$, the sulfate reduction rate can be expressed as

$$f(x) = (C_0 - C_\infty) * (D_S * b^2 + \omega * b) * \exp(-b * x) \tag{4}$$

D_S was determined independently using the ^3H_2O technique described by Rudd et al. (1986b) and modified by Sweerts et al. (1991). The mean ^3H_2O diffusion coefficient of the upper 4-cm sediment was obtained graphically using an error function (Duursma & Bosch 1970). Experiments were executed with non-asphyxiated (with bioturbation) cores. The measured value refers to the effective or apparent diffusion coefficient in water, D_e which is the sum of D_S and the increased diffusion due to faunal activity. The diffusion coefficient of SO_4^{2-} and ^3H_2O in water (D_0) are related through

$$D_0(SO_4^{2-}) = D_0(^3H_2O) * 0.5 \tag{5}$$

(Li & Gregory 1974). D_0 was corrected for temperature (Li & Gregory 1974). The change of porosity in the sediment with depth is considerable (0.95 at the sediment water interface, 0.75 at 3—4 cm depth) so using a single D_S as a mean value for the top 4 cm is not justified. D_S was estimated at 0.5 cm depth-intervals by the following procedure:

$$\theta^2 = \frac{D_0}{D_S} \qquad \text{Berner, 1980} \tag{6}$$

$$\theta^2 = \phi * F \qquad \text{Andrews \& Bennet, 1981} \tag{7}$$

$$F = \frac{1}{\phi^m} \qquad \text{Archie, 1942} \tag{8}$$

where θ denotes the tortuosity [dimensionless], F the formation factor [dimensionless] (i.e. the ratio of the electrical resistivity in pore water and in whole sediment) and ϕ the sediment porosity [dimensionless].

Equations (6), (7) and (8) yield

$$D_S = D_0 * \phi^{m-1} \tag{9}$$

The mean measured diffusion coefficient was fitted by averaging D_S of each individual sediment layer calculated by eq. (9) over 4 cm depth with a single value of m for the whole column, yielding $m = 1.788$.

Porosity used in eq. (9) was estimated from the mass fraction of water (1 g water equals 1 ml) and the dry bulk density of the sediment. Dry bulk density of the sediment was estimated from the organic dry mass, the inorganic dry mass (1.2 g/ml and 2.6 g/ml respectively: Rudd et al. 1986b) and the water content. The organic dry mass was estimated by loss of mass upon ashing at 430 °C.

For the sedimentation rate 1 mm yr^{-1} was used (Van Dam, 1988). The model is not sensitive to variations in sedimentation rates in the range of 0—5 mm yr^{-1}. A five-fold increase in the sedimentation rate would result in an increase in the calculated SO_4^{2-} reduction rate of $< 6\%$.

2. *$^{35}SO_4^{2-}$ core injection*

Sulfate reduction was estimated by $^{35}SO_4^{2-}$ core injection in two ways: 1) from the activity of the formed chromium reducible (inorganic) sulfur pool (Fossing & Jørgensen 1989), 2) by depletion of radioactive sulfate in the sediment (Hordijk et al. 1985).

In each of four sediment cores (two cores with a thick organic top layer and two with a thin detrital layer), 10 μl of $^{35}SO_4^{2-}$ solution (Amersham, $17.1 * 10^4$ Bq ml^{-1}) were injected from four directions at 1, 3, 5, 7 and 9 cm sediment depths. After a 19 to 22 hr incubation at *in situ* temperature (20 °C) the cores were sliced into 2-cm segments. The segments were transferred immediately to 40 ml 20% (w/v) zinc acetate (ZnAc) and frozen to terminate bacterial activity and to fix sulfides. The segments were weighed before and after addition of zinc acetate and subsamples were taken for the determination of the water content. The homogenized sediment was centrifuged and 1 ml of the supernatant and 3 ml Millli-Q water were transferred into a scintillation vial for determining radioactivity. The sediment pellet was washed twice with demineralized water to remove $^{35}SO_4^{2-}$. A subsample (2—3 g) was transferred to a reaction flask and reduced sulfur was then distilled as H_2S from the sediment into two ZnAc traps (cf., Canfield et al. 1986). The traps were pooled and a 5 ml subsample was transferred into a scintillation vial for measurement of the radioactivity.

Sulfate concentrations were determined by HPLC. Because SO_4^{2-} analyses by HPLC is interfered by zinc acetate, two parallel cores at each site were collected to assess SO_4^{2-} concentration in porewater. They were sliced in 2-cm segments, centrifuged (6000 rpm) and porewater SO_4^{2-} was measured.

Sulfate reduction rates (SRR) based on the activity of reduced inorganic sulfur were calculated according to the equation:

$$SRR = \frac{(SO_4^{2-}) * a * 24 * 1.06}{A * h} \text{ nmol } SO_4^{2-}\text{ cm}^{-3}\text{ d}^{-1} \qquad (10)$$

where a is the total radioactivity of ZnS, A is the total injected radioactivity, h is the incubation time in hours, (SO_4^{2-}) is the initial sulfate concentration in the sediment in nmol per cm^3 sediment, and 1.06 is a correction factor for the expected isotope fractionation (Jørgensen & Fenchel 1974).

SRR based on depletion of $^{35}SO_4^{2-}$ was calculated from (Hordijk et al. 1985):

$$SRR = \frac{(SO_4^{2-}) * \ln\left(\frac{A}{A_{rest}}\right) * 24 * 1.06}{h} \text{ nmol } SO_4^{2-}\text{ cm}^{-3}\text{ d}^{-1} \qquad (11)$$

where A_{rest} is the rest activity of SO_4^{2-} after incubation.

To estimate abiotic removal of SO_4^{2-} in Gerritsfles sediment like SO_4^{2-} adsorption to the solid phase, Feijtel et al. (1989) measured $^{35}SO_4^{2-}$ depletion in slurries after inhibition of SO_4^{2-} reduction with Na_2MoO_4. A 96 ± 4% recovery of $^{35}SO_4^{2-}$ was found, suggesting no SO_4^{2-} adsorption to the solid phase.

3. *In situ enclosure experiment*

Although methods to assess sulfate uptake rates in underwater sediments exist (e.g. Jørgensen 1978; Berner 1964; Fossing & Jørgensen 1989), SO_4^{2-} uptake measurements *in situ* are scarce (Kelly & Rudd 1984). Enclosures have been used to manipulate lake water conditions (e.g. Kelly & Rudd 1984; Schiff & Anderson 1987). To our knowledge, *in situ* enclosure experiments for measuring SO_4^{2-} depletion in the water column under ambient field conditions have never been done before.

A change of the SO_4^{2-} concentration in the water column can result from several processes. Dissimilatory SO_4^{2-} reduction in the sediment and assimilatory SO_4^{2-} uptake by algae, microorganisms and living *Sphagnum* can remove SO_4^{2-} from the overlying water. Abiotic processes that may remove SO_4^{2-} play a minor role in Gerritsfles sediment. On the other hand, SO_4^{2-} may be released by mineralization (conversion of carbon bonded S to SO_4^{2-} or release of SO_4^{2-} by cleavage of ester sulfates) or by bacterial or chemical oxidation of reduced inorganic S to SO_4^{2-}.

Pool water SO_4^{2-} concentrations in *in situ* enclosures were monitored to estimate net sulfate consumption rates. The enclosures were constructed from two acrylic columns with different dimensions (Fig. 1). The enclosures

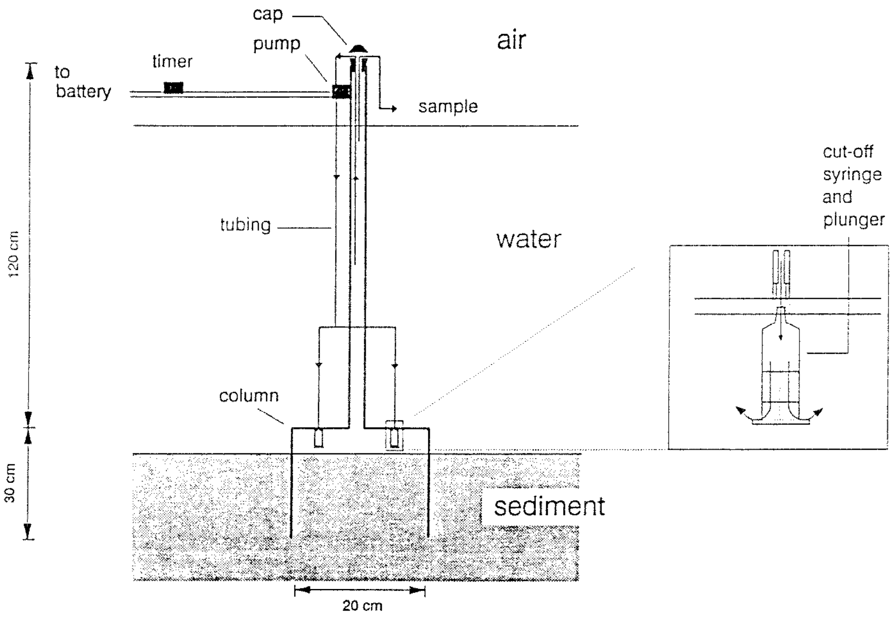

Fig. 1. In situ enclosure for monitoring SO_4^{2-} concentration in the overlying water column.

were placed in the sediment and reached above the pool water. The wide bottom part of the column protruded 5 to 10 cm into the overlying water. The upper part of the column was narrower to reduce the water volume — sediment area ratio in the enclosure so that changes in sulfate concentration due to SO_4^{2-} reduction could be measured more accurately. Water in the enclosure was open to the atmosphere. To obtain homogeneous water samples and to avoid development of anaerobic conditions above the sediment, water in the enclosure was mixed by pumping it down from the top of the column to just above the sediment. In lab installations a methylene blue dye was used to determine minimum pumping rates giving complete mixing (within 20 minutes) without disturbing the sediment. Redox potentials measured by a Pt electrode just above the sediment-water interface indicated that permanent aerobic conditions were maintained (E_h = 724 ± 3 mV at pH = 4.6). Without pumping the Eh dropped to −59 mV within 24 hours. Resuspension of the sediment was avoided through the use of cut-off syringes and plungers (Fig. 1) that directed the water flow away from the sediment.

Enclosures were placed at highly organic, intermediate and low organic (sandy) sediment sites (23, 10 and 4% mass fraction organic matter, respectively). The water circulation in the enclosures was interrupted for one hour after each one hour of pumping to minimize battery use. Every two or three days 10-ml samples were withdrawn from the enclosures with a syringe (10 ml) and filtered through a 0.45 μm millipore filter for SO_4^{2-} analysis. Three columns were installed on July 5, 1990 and were monitored for a 26 days period. A second and third series of two columns each started on July 31 and November 5, 1990, respectively and were monitored for 9 days. At April 15, 1991, one more column was monitored for 9 days.

Release of sulfur from the sediment into the overlying water column

The release of sulfur from the sediment into the overlying water column was assessed by whole core injection of $^{35}S^{2-}$ (added as a Na_2S solution) followed by monitoring the activity of ^{35}S in the (oxygenated) overlying water. After incubation, several sulfur species were analyzed in the water column to characterize sulfur transported from the sediment. In the radioactive cores $^{35}SO_4^{2-}$ and acid volatile ^{35}sulfur (^{35}AVS) was measured.

In total three cores, which were collected on August 14, 1989 were used. To assure that $^{35}S^{2-}$ would not be injected in the oxic layer, the oxygen penetration depth in the top sediment layer of one core was assessed by means of an oxygen microelectrode as described by Sweerts et al. (1989). Oxygen did not penetrate deeper than 2.5—3.5 mm into the sediment. In the two other cores 20 μl 4.42 $*$ 10^6 Bq/ml Na_2 ^{35}S solution (Amersham) was injected from four directions at 1 cm sediment below the sediment-water interface (total injected activity: 3.53 $*$ 10^5 Bq). The cores were incubated for about 72 h at *in situ* temperature (20 °C). The overlying water was gently stirred (4 rpm) with a motor driven impeller to maintain an aerobic, well mixed water column and a fixed diffusive boundary layer (Sweerts et al. 1989). At 2—8 hours time intervals, two 5-ml portions of the overlying water from the ^{35}S-injected cores were transferred into scintillation vials and radioactivity was counted.

Analyses

Sulfate concentrations were determined by ion chromatography (Hordijk et al. 1984).

Inorganic S in sediments was assessed using the single step chromium reduction method (Fossing & Jørgensen 1989). Chromium reducible sulfur comprises ΣH_2S, S^0, FeS and FeS_2.

Radioactivity was counted after addition of 10 ml Instagel II (Packard) in Packard Tri Carb 4530 liquid scintillation spectrometer for 10 minutes at a window width of 4—167 KeV. Quench corrections were made by means of the external-standard channel-ratio method using chloroform as quencher.

Radiolabelled SO_4^{2-} was measured after separation from other dissolved S species by HPLC and ^{35}AVS was determined after separation through microdistillation (Hordijk et al. 1985).

Results

Sulfate reduction and sulfate uptake

1. *Diagenetic modelling*

The ^3H_2O sediment diffusion coefficient, D_e (in non-asphyxiated cores) of the 4-cm sediment top layer was measured as $1.26 \cdot 10^{-5}$ cm^2 s^{-1} at 7 °C. Sweerts et al. (1991) reported in an asphyxiated core a D_S of $0.93 \cdot 10^{-5}$ cm^2 s^{-1} at 7 °C (corrected for temperature). The difference of $0.3 \cdot 10^{-5}$ cm^2 s^{-1} is relatively large compared to studies in other lakes (Sweerts, 1991), but may not be significant. Sulfate reduction rates calculated with D_S (Sweerts et al. 1991) and D_e, however differed by less than 12%. Diagenetic modelling of three SO_4^{2-} profiles in Gerritsfles (eq. 4) yielded sulfate reduction rates of 0.27, 0.66, and 0.38 mmol m^{-2} d^{-1}, linearly integrated over the upper 10 cm sediment (Fig. 2a, b, c).

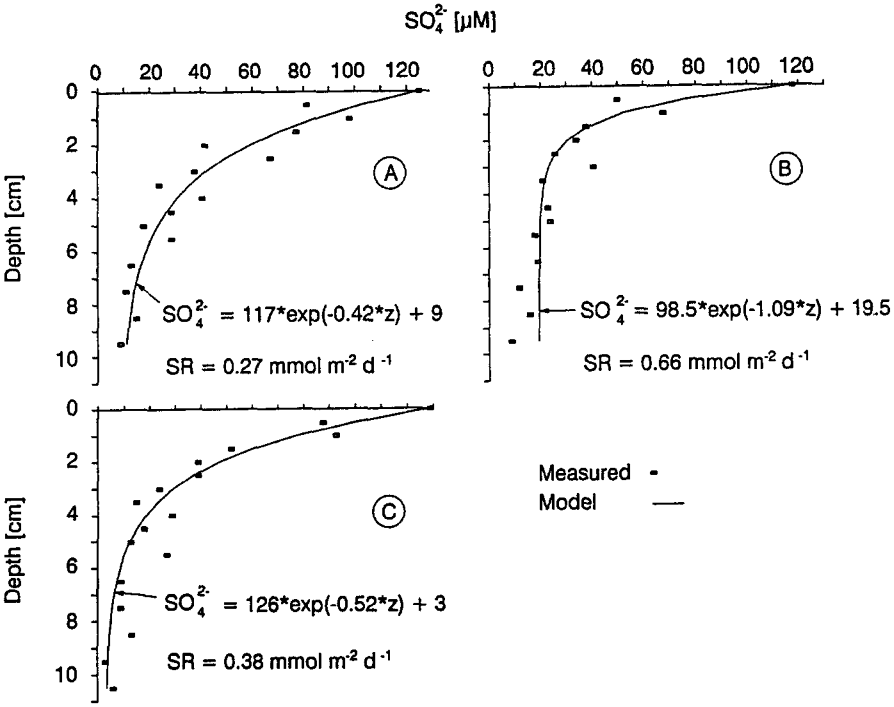

Fig. 2. Porewater SO_4^{2-} concentration profiles of three organic rich sediment cores, (measured and exponentially fitted, where z is depth below the sediment-water interface in cm) and integrated modelled SO_4^{2-} reduction rates (SR).

2. *$^{35}SO_4^{2-}$ core injection*

Sulfate profiles from the duplicate cores at the organic location were not significantly different ($p = 0.124$) while the difference between both SO_4^{2-} profiles at the sandy location ($p = 0.07$) was greater. An inventory study on spatial variability indicated that SO_4^{2-} concentrations in sandy top sediment (0—2 cm) of Gerritsfles did not vary more than 14% (SD in % of mean, N = 15, unpubl.). Since porewater SO_4^{2-} concentrations ((SO_4^{2-}), eq. 10, 11) and radioactivities of labelled S (a, A, A_{rest}, eq. 10, 11) were measured in separate cores, we calculated SO_4^{2-} reduction rates using combinations of labelled S profiles and SO_4^{2-} profiles.

Sulfate reduction rates invariably decreased with depth (Fig. 3). Depth-integrated SO_4^{2-} reduction rates calculated from production of inorganic reduced ^{35}S (eq. 10) were significantly ($p < 0.0001$) lower than those based on depletion of $^{35}SO_4^{2-}$ (eq. 11, Table 1). Mean depth-integrated SO_4^{2-} reduction rates in organic cores were lower than in sandy cores but the differences were not significant.

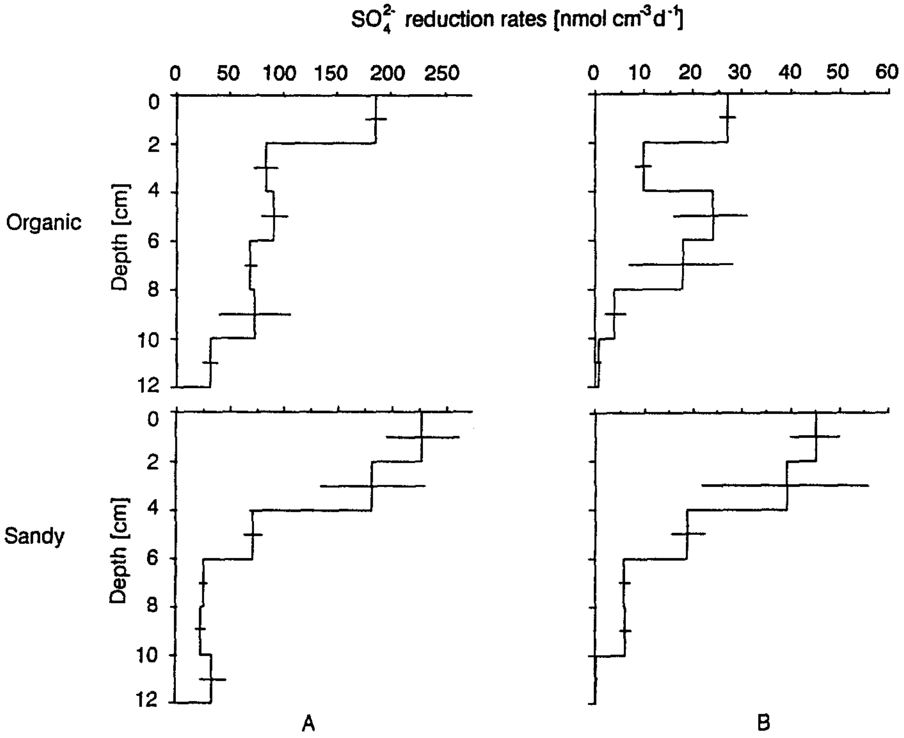

Fig. 3. Variation in sulfate reduction rates with depth in organic rich and sandy cores calculated from A) rest activity of $^{35}SO_4^{2-}$ and B) formation of inorganic ^{35}S. Note the differences between the scales. Bars indicate ± SD.

3. *In situ enclosure experiment*

Rates of uptake of SO_4^{2-} could be estimated by the slopes of the linear regression of changes in SO_4^{2-} concentration over time ($R^2 > 0.91$, Fig. 4).

An apparent decrease of SO_4^{2-} (expressed in mmol m^{-2}) was observed in the overlying water in July 1990 and April 1991 (Fig. 4a, b, d) while SO_4^{2-} increased in November 1990 (Fig. 4c). Rates of SO_4^{2-} uptake are given in Table 1.

Release of sulfur from the sediment into the overlying water column

Transport of reduced ^{35}S from the sediment into the water column is illustrated in Fig. 5. The duplicate results were very similar. Spatial variability between both cores did not lead to exceptional differences in ^{35}sulfur release. About 7% of the $^{35}S^{2-}$-label injected at 1 cm depth in the sediment was recovered in the overlying water after 60 hours incubation. The

Table 1. (Net) sulfate reduction rates calculated by diagenetic modelling, determined with labelled experiments and sulfate uptake rates measured *in situ*

	(Net) sulfate reduction and sulfate uptake rates (mmol m^{-2}) d^{-1})						
	diagenetic modelling	labelled experiments				*in situ* SO_4^{2-} uptake	
sediment type	org	org[1]	org[2]	san[1]	san[2]	org*	san*
Jul '90		10.7 ± 0.7	1.7 ± 0.4	11.2 ± 1.9	2.3 ± 0.5	0.43	0.73
Aug '90							1.81
Nov '90	0.27					−0.51	−0.30
	0.66						
	0.38						
Apr '91						0.94	

org = organic rich sediment, san = sandy sediment

[1] calculations based on rest activity of $^{35}SO_4^{2-}$ (± SD, $N = 4$)

[2] calculations based on formation of reduced inorganic ^{35}S (± SD, $N = 4$)

* %C; see Table 3

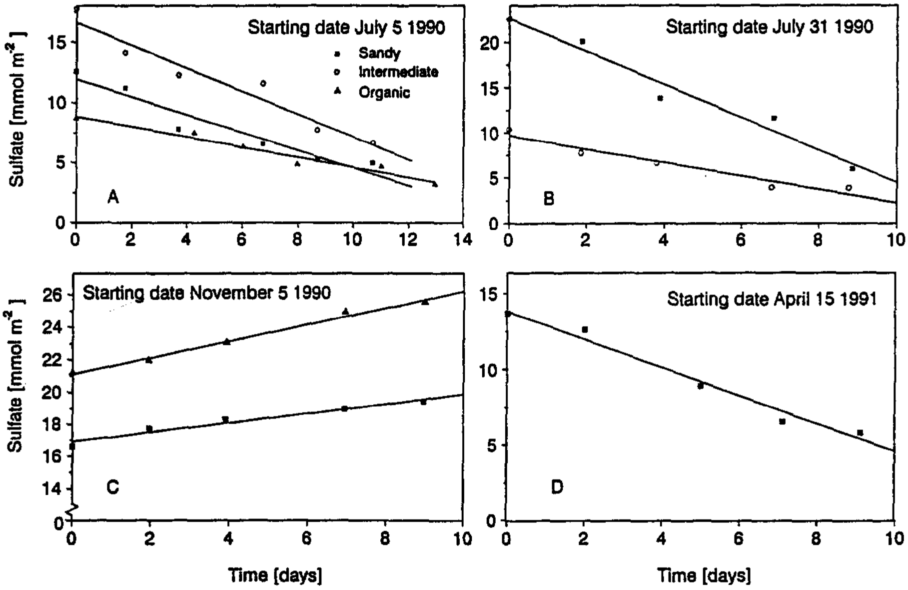

Fig. 4. Change of amount of SO_4^{2-} per m^{-2} in *in situ* enclosures on sediments with high, intermediate and low (sandy) organic matter mass fractions during different periods in 1990 and 1991.

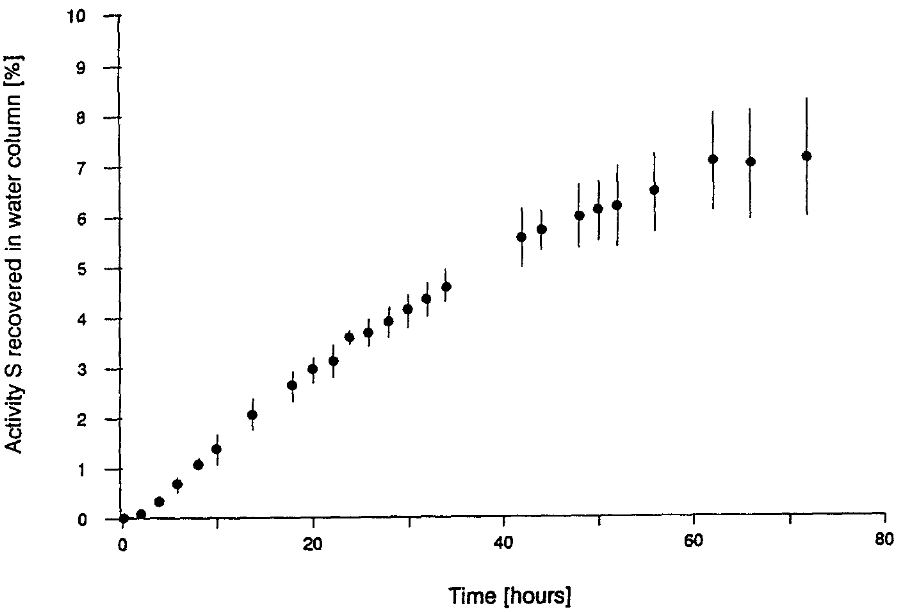

Fig. 5. Mean amount of activity recovered in the overlying water column of two sediment cores injected with $^{35}S^{2-}$ at 1 cm sediment depth versus time. The bars indicate the range of the two replicate cores.

curve shows a sigmoid shape with a short lag at the start of the incubation. There is a linear ($R^2 = 0.996$) increase of the fraction recovered activity in the water column and total injected activity during the first ca. 24 hours of 3.7% d^{-1}. Only a small fraction of the ^{35}S in the water column (about 3%) consisted of SO_4^{2-} and a negligible fraction (about 0.3%) consisted of ^{35}AVS.

Discussion

The value of 10.3 mmol m^{-2} d^{-1} determined by Feijtel et al. (1989) from $^{35}SO_4^{2-}$ depletion in sediment slurries from Gerritsfles agrees well with the results from the present study (10.7, 11.2 mmol m^{-2} d^{-1}). We reported a wide range of sulfate reduction rates (0.27–11.2 mmol m^{-2} d^{-1}) in Gerritsfles sediment. These rates are in the same order of magnitude as those reported for other sediments (Table 2). Sulfate reduction rates determined by $^{35}SO_4^{2-}$ depletion are somewhat higher than those estimated by Kuivila et al. (1989) and Ingvorsen et al. (1981) who calculated SO_4^{2-} reduction rates from formation of ^{35}AVS. However if also organic bound

Table 2. Sulfate reduction rates in several freshwater systems

lake water SO_4^{2-} concn. (μM)	sulf. red. rate (mmol m^{-2} d^{-1})	method of determination	reference
105	0.12	a^1	Kuivila et al. (1989)
135	0.17—1.2	c	Sinke et al. (1990)
300	20.4	d*	Bak et al. (1991)
1200—2000	4.2	d	Herlihy & Mills (1989)
220	0.4—2.8	a^1	Ingvorsen et al. (1981)
105	0.27—0.36	d	Kelly & Rudd (1984)
200	3.6	a^3	Hordijk et al. (1985)
100	10.3	b	Feijtel et al. (1989)
100	1.7, 2.3	a^2	This study
100	10.7, 11.2	a^3	This study
100	−0.51—1.81	d	This study
100	0.27—0.66	e	This study

a : $^{35}SO_4^{2-}$ injection
[1] based on formed acid volatile ^{35}S
[2] based on chromium-reducible S
[3] based on rest activity of $^{35}SO_4^{2-}$
b : slurry incubation based on rest activity of $^{35}SO_4^{2-}$
c : based on SO_4^{2-} flux over the sediment-water interface
d : loss SO_4^{2-} from water overlying cores
e : from diagenetic calculations
* : over 10 cm sediment depth

S and pyrite are formed, SO_4^{2-} reduction rates based on formed ^{35}AVS are underestimated. Bak et al. (1991) reported extremely high SO_4^{2-} uptake rates (20.4 mmol m^{-2} d^{-1}) when measuring SO_4^{2-} depletion from the water column of Lake Constance sediment under anaerobic conditions, but 3.5 times slower rates under aerobic conditions.

Sulfate reduction rates estimated from $^{35}SO_4^{2-}$ depletion were 4—8 times higher than rates estimated from the accumulation of chromium-reducible (i.e. reduced inorganic) ^{35}S (Table 1). So only 12—25% of reduced $^{35}SO_4^{2-}$ is recovered as inorganic S. The remaining 75—88% is most likely transformed to organic S. Organic S was reported as a dominant initial product of dissimilatory sulfate reduction by Baker et al. (1989), Nriagu & Soon (1985) and Rudd et al. (1986a). S addition to humic substances during early diagenesis by chemical reactions between organic matter and H_2S or its oxidation products were found to be important mechanisms in marsh and marine sediments (Ferdelman et al. 1991; Francois 1987). Sediments high in sedimentary iron (> 20 mg g^{-1})

typically have a large fraction of sulfur bound in iron monosulfides, but even then organically bound S may be the main initial product of sulfate reduction (Baker et al. 1989). In Gerritsfles low sedimentary iron content (about 3.5 mg g^{-1}) and undersaturation of porewater with respect to iron sulfides (Marnette et al. in prep.) may explain the initial high formation rate of organically bound S.

Diagenetic calculation of SO_4^{2-} reduction rates obtained from porewater SO_4^{2-} concentrations ignore the possible effects of a diffusive flux of ΣH_2S over the sediment water interface followed by back oxidation of sulfide to SO_4^{2-} in the overlying water (Carignan 1988). Also possible oxidation of reduced S to SO_4^{2-} in the top sediment layer is not incorporated in the calculations and therefore diagenetic modelling may underestimate SO_4^{2-} reduction rates.

The change of SO_4^{2-} concentration in the *in situ* enclosures is a balance between several processes that consume and produce SO_4^{2-} in the sediment and water column. Some processes however are of minor importance in Gerritsfles. Sulfate consumption in sediment and overlying water is a combination of assimilatory and dissimilatory SO_4^{2-} reduction. Gerritsfles is a clear water pool without abundant growth of algae and assimilatory SO_4^{2-} uptake in the water column is negligible with respect to the observed changes of SO_4^{2-} in the enclosures. Also uptake of SO_4^{2-} by living *Sphagnum*, estimated from the annual detrital S burial flux of organic matter (15 μmol m^{-2} d^{-1}, Feijtel et al. 1989), is minor ($<5\%$) compared to the change of SO_4^{2-} in the enclosures. Assimilatory SO_4^{2-} uptake in the sediment is relatively low compared to dissimilatory SO_4^{2-} reduction (Brown, 1986) so dissimilatory SO_4^{2-} reduction must be considered as the main SO_4^{2-} consuming process in Gerritsfles sediment. Sulfate release in the enclosures is the result of oxidation of inorganic S and mineralization of organic S compounds to SO_4^{2-}. The inorganic (dissimilatory) reduced S pool is much more susceptible to oxidation than is the organic S pool (Wieder and Lang 1988) and therefore oxidation of inorganic S compounds is likely the main source of SO_4^{2-} release in the enclosed water column. Mineralization of organic S compounds may proceed under oxic and anoxic conditions, but the conversion to SO_4^{2-} requires a final oxidative reaction, except in case of mineralization of ester sulfates. The change of SO_4^{2-} in the enclosed water column therefore may be considered as the net result of dissimilatory SO_4^{2-} reduction, oxidation of reduced S compounds and mineralization of ester sulfates.

Differences in SO_4^{2-} removal rates between July and November sediments indicate that there might be a seasonal factor controlling SO_4^{2-} removal. Although we do not have seasonal replicated observations of removal rates of SO_4^{2-} at the specific sites, the difference between the negative SO_4^{2-} uptake rates (November) and the positive SO_4^{2-} uptake rates (July, August and April) are likely to be real, because during an incubation period trends of SO_4^{2-} removal at the specific sites were similar. In July, SO_4^{2-} removal from *in situ* enclosures was significantly lower than $^{35}SO_4^{2-}$ reduction (based on rest activity of $^{35}SO_4^{2-}$, Table 1) in the sediment. This indicates an apparent release of S into the water column. The SO_4^{2-} increase in the enclosure in November can be explained only by a net release of S due to oxidation and mineralization of S compounds. The rather steep SO_4^{2-} gradients at the sediment-water interface (Fig. 2) suggested that oxidation to SO_4^{2-} did not occur in the sediment. There was no clear subsurface peak of SO_4^{2-} that pointed to SO_4^{2-} formation from S oxidation or mineralization of ester sulfates in the sediment which could result in an upward SO_4^{2-} flux. Consequently there must have been a diffusive flux of reduced sulfur species from the sediment coupled with oxidation to SO_4^{2-} in the overlying water.

Temperature may be an important factor by controlling processes that affect sulfate removal. Low temperature in November may have caused low microbial activity allowing oxygen to penetrate deeper into the sediment. Provided microbial reduction processes would have been hampered by low temperatures more strongly than oxidation processes, this should have resulted in a net flux of oxidized S into the water column. Since no subsurface SO_4^{2-} peak was observed, the mobilized S must have involved intermediate S species that were oxidized to SO_4^{2-} only after diffusion into the water column. In July, when sediment temperatures are high (20 °C), an extra S flux into the water column due to oxidation of the top sediment layer is probably not present.

A flux of reduced S into the overlying water column is supported by results of the $^{35}S^{2-}$ core injection experiment. The ^{35}S-time curve (Fig. 5) shows a sigmoid shape with a short lag at the start of the incubation (the time needed for the label to move from 1 cm depth to the water column). The asymptote beyond which no further net increase of label would occur can be attributed to the lack of a constant source of label in the sediment. About 7% of the activity injected as $^{35}S^{2-}$ in the reduced sediment at 1 cm depth, was recovered in the overlying water column after 60 hours (Fig. 5). It was not possible to quantify the absolute release of “cold” sulfur to the water column because $^{35}S^{2-}$ was present in heterogenous pools directly after tracer injection and therefore specific activities are not known. Only 3% of the 7% activity recovered in the overlying water column of Gerritsfles consisted of $^{35}SO_4^{2-}$ and 0.3% of ^{35}AVS. Although we do not have absolute data on reduced S release into the water, it is likely that the S flux must be much greater than the oxidation rate to SO_4^{2-} in water column and that a large part of sulfur in the water column is present in non-SO_4^{2-}

form. We do not know in which forms the remaining 97% of ^{35}S, that is not converted to ^{35}S, ends up in the overlying water.

The thickness of the detrital layer on the quarzitic bottom of Gerritsfles did not seem to be correlated with SO_4^{2-} reduction rates in these sediments. Rudd et al. (1986b) reported that in oligotrophic lakes highly flocculent-organic sediments are not as active microbially per unit volume as compact inorganic sediments because carbon content per unit volume is higher in the more compact sediments. In two lakes with about equal epilimnetic SO_4^{2-} concentrations, Rudd et al. (1986b) measured a much faster sulfate flux into highly inorganic Lake 320S sediments than into the organic sediments of lake 114. In Gerritsfles the carbon content per unit volume in the more compact, sandy sediments was also higher (Table 3). However, SO_4^{2-} reduction rates in the sandy sediments were not significantly different from reduction rates in organic rich sediments (Table 1). Changes in SO_4^{2-} in *in situ* enclosures were consequently smaller at the sandy sites than at sites with a thin organic layer, but the differences may not be significant.

Table 3. Organic C content per unit weight and volume and dry bulk density in Gerritsfles sediment at 0—2 cm and 4—6 cm depth

	Depth [cm]	C [g/g]	C [g/cm^3]	Dry bulk density [g/cm^3]
Organic rich sediment	0—2	0.137	0.025	0.18
Transition zone	0—2	0.058	0.019	0.33
Sandy sediment	0—2	0.027	0.021	0.76
Organic rich sediment	4—6	0.121	0.022	0.18
Transition zone	4—6	0.009	0.127	1.41
Sandy sediment	4—6	0.008	0.116	1.45

From real SO_4^{2-} reduction rates (based on depletion of $^{35}SO_4^{2-}$) and *in situ* SO_4^{2-} uptake (which is considered to be the result of SO_4^{2-} reduction, oxidation of organic and inorganic S to SO_4^{2-} and mineralization of ester sulfates) measured during a same period in July 1990 (Table 1), oxidation rates can be calculated at the two locations in Gerritsfles. The oxidation rate of reduced S to SO_4^{2-} at the organic site amounts 10.7—0.43 = 10.3 mmol m^{-2} d^{-1} and at the sandy site 11.2—0.73 = 10.5 mmol m^{-2} d^{-1}. These oxidation rates indicate that a large fraction (>90%) of reduced SO_4^{2-} is reoxidized again. We must notice however that these rates are overestimated because an unknown fraction of SO_4^{2-} is released by mineralization of ester sulfates, which is not an oxidative process. Also the unknown variation in determination of *in situ* SO_4^{2-} uptake is a factor of uncertainty, but even with a high variation of 200 or 300%, a large fraction of reduced SO_4^{2-} is reoxidized, since the net *in situ* SO_4^{2-} uptake is low compared to SO_4^{2-} reduction rates (Table 1). For a quantification of whole-lake fluxes associated with these oxidation and reduction processes on annual basis, more replicated samples at several times throughout the year would be necessary.

Conclusions

The tracer $^{35}S^{2-}$ study indicated that a part of reduced S introduced into the sediment was moved from the sediment into the overlying water. Only a small fraction of labelled S in the water column could be recovered as either SO_4^{2-} (3%) or S^{2-} (0.3%), indicating rapid transport of this mobile reduced S to organic S or S of intermediate oxidation state.

Results of whole core injections of $^{35}SO_4^{2-}$ and measurements on removal of SO_4^{2-} in overlying water in July 1990 demonstrated that there must be a (maximum) flux of reduced S from the sediment into the water column of which 10.3 (organic rich site) and 10.5 mmol S m^{-2} d^{-1} (sandy site) is oxidized to SO_4^{2-}. From SO_4^{2-} reduction rates and oxidation rates it could be calculated that >90% (this value may be overestimated) of reduced SO_4^{2-} was reoxidized to SO_4^{2-}.

With low temperature in November an additional flux of mobilized, non SO_4^{2-}-S from the sediment into the water column was observed. This result in increased SO_4^{2-} concentration in the pool water after complete oxidation.

Sulfate reduction rates in sediments with higher volumetric mass fraction of organic matter did not differ significantly from those in sediments with a lower mass fraction of organic matter.

$^{35}SO_4^{2-}$ core injections indicated that organically bound S is a major (75–88%) initial product of sulfate reduction in Gerritsfles.

An important conclusion of this study is that a model based on the SO_4^{2-} — S^{2-} redox couple and the appropriate transport equations gives a very simplified picture of S cycling in a moorland pool. In future research much more attention must be paid to inorganic S intermediates and organic S forms.

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