



Support for an anaerobic sulfur cycle in two Canadian peatland soils

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[1] Sulfur cycling in peatlands may affect global CH₄ emissions by suppression of methanogenesis through bacterial sulfate reduction (BSR). We sought evidence for anaerobic sulfur cycling in four peat mesocosms irrigated with sulfate at a loading of 0.8 and 3.3 g S m⁻² yr⁻¹. To this end we obtained concentration profiles of dissolved O₂, C, S, and Fe, and determined ³⁴S/³²S ratios of sulfate, reduced inorganic sulfur (TRIS), and total sulfur. To estimate the importance of BSR for anaerobic respiration, peat was incubated with molybdate as inhibitor of BSR. In the mesocosms, pore water concentrations of dissolved sulfate and H₂S adjusted to 5–20 μmol L⁻¹ and 0–9 μmol L⁻¹, respectively, whereas concentrations of CO₂, CH₄, and DOC reached millimolar levels. CO₂ production was not explained by methanogenesis and net reduction of inorganic electron acceptors. In the shallow peat, H₂S was produced and ³⁴S in sulfate enriched by 3.6 to 6‰, indicating occurrence of BSR. Sulfate reducers also accounted for much of the metabolic activity. Addition of molybdate suppressed CO₂ production by 20 to 50%. Deeper into the peat, the sulfate pool was apparently replenished from the peat matrix as sulfate became enriched in ³²S, likely stemming from TRIS or organic sulfur in the peat. Sulfur was thus anaerobically cycled between oxidized and reduced pools. An electron acceptor capable of driving this cycle could not be conclusively identified. Regardless of this uncertainty, the results suggest that anaerobic S cycling can maintain BSR and potentially contribute to low methane production in soils of ombrotrophic bogs.

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1. Introduction

[2] The fate of sulfur (S) deposited on the surface of wetlands and peatlands and its effects on carbon (C) cycling has seen a resurgence in interest, owing to the possible ramifications for greenhouse gas emissions from such environments [Gauci *et al.*, 2002; Vile *et al.*, 2003b]. Sulfate is important for rates and pathways of anaerobic carbon mineralization because its presence may decrease methane production through competition of anaerobic bacteria for substrates, such as acetate, alcohols, and hydrogen [Conrad, 1999; Kotsyurbenko *et al.*, 2004; Shannon and White, 1996]. Rates of bacterial sulfate reduction (BSR) have been reported to exceed rates of methane production in freshwater peats, on the basis of samples of peat soil incubated in vitro with tracer amounts of ³⁵S-sulfate [Nedwell and Watson, 1995; Vile *et al.*, 2003a, 2003b; Wieder *et al.*, 1990]. These findings have been used to conclude that

sulfate deposition inhibits methanogenesis through competitive suppression of methanogens by sulfate reducers [Gauci *et al.*, 2002; Nedwell and Watson, 1995]. A net decrease of cumulative emissions of atmospheric methane has been verified in sulfate deposition experiments [Dise and Verry, 2001; Gauci *et al.*, 2002].

[3] This hypothesis is not without caveats, though. The sum of methanogenesis and BSR often only explains a small fraction of anaerobic CO₂ production in ombrotrophic peats [Vile *et al.*, 2003a]. Electron accepting processes other than BSR may, therefore, be more important for anaerobic CO₂ production, which raises the question why a large effect of sulfate deposition on methanogenesis should be expected. Uptake of sulfate by plants, most of which was absorption by *Sphagnum* mosses, was furthermore reported to be about 0.9 g S m⁻² yr⁻¹ in a central continental bog, which exceeds moderate atmospheric sulfate deposition rates [Urban *et al.*, 1989]. Active sulfate reduction, which has still been reported from similar peatlands, should thus be primarily fueled by mineralization of organic S in the peat rather than sulfate deposition. Further problems arise from mass balance considerations. Sulfate pools are small in ombrotrophic peatlands and turn over rapidly [Nedwell and Watson, 1995; Wieder *et al.*, 1990]. The only established mechanism to allow for S recycling in saturated environments poor in ferric iron hydroxide involves reoxidation of reduced S with oxygen in the rhizosphere of plants capable of aerenchymatic transport [Wind and Conrad, 1997]. This

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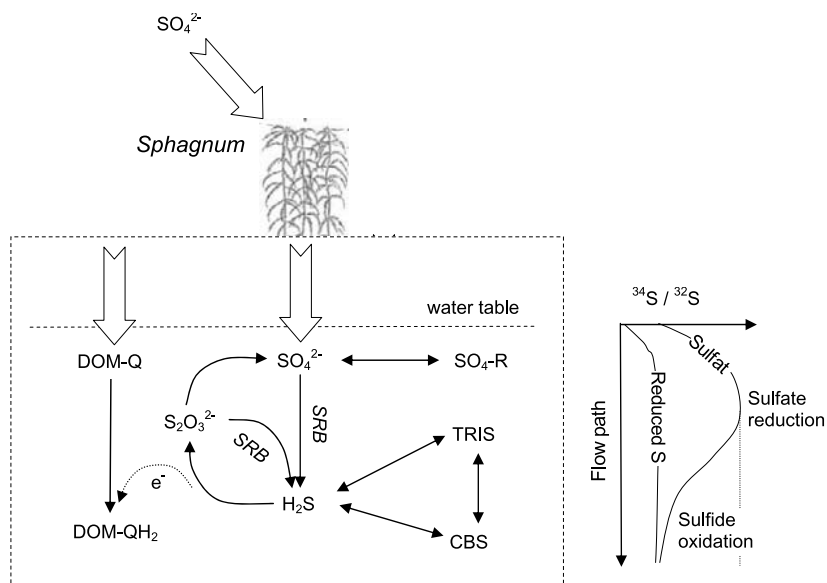


Figure 1. Schematic of some S transformations in saturated peat soils with vertical water flow, and expected shifts in $^{34}\text{S}/^{32}\text{S}$ ratios associated with them. Sulfate passing the *Sphagnum* moss canopy may form organic sulfate esters ($\text{SO}_4\text{-R}$) or be reduced by sulfate reducing bacteria (SRB). Hydrogen sulfide may subsequently be chemically incorporated into reduced inorganic sulfur (TRIS) or carbon-bonded sulfur (CBS), or be chemically or microbially reoxidized to thiosulfate ($\text{S}_2\text{O}_3^{2-}$), for example by quinone moieties (DOM-Q) contained in dissolved organic matter that leaches from vegetation and the unsaturated zone. Sulfate reduction leaves the remaining sulfate enriched in ^{34}S and the produced H_2S , TRIS, and CBS depleted in ^{34}S along the flow path (strong isotope fractionation [Canfield, 2001a]). Replenishment of the sulfate pool from H_2S , TRIS, and CBS will reduce the ^{34}S content of sulfate along the flow path (small isotope fractionation [Canfield, 2001b]), and indicate sulfur recycling.

mechanism, however, is of little significance in *Sphagnum* and shrub dominated continental bogs. We clearly need to gain better insight into the fate of sulfate in peatlands, especially with respect to our understanding of CH_4 production and emission.

[4] Several processes have to be considered regarding the fate of S in the saturated zone of organic rich soils (Figure 1). Sulfate may form organic sulfate esters, which may hydrolyze under sulfate-poor conditions [Wieder and Lang, 1988; Mandernack et al., 2000]. Following BSR, some H_2S is generally incorporated into iron sulfides or organic matter [Brown, 1985, 1986], for example by Michael's addition reaction with aromatic quinone moieties [Perlinger et al., 2002]. Carbon-bonded S has often been found to be the primary sink for H_2S stemming from BSR in peat soils, whereas metal sulfides were generally less important [Spratt and Morgan, 1990; Vile et al., 2003a; Wieder and Lang, 1988]. Both pools of S can be unstable in the saturated zone in the long term, and slow exchange among them and H_2S has been suggested [Spratt and Morgan, 1990].

[5] A mechanisms allowing for a more rapid cycling of S than through organic forms is the chemical oxidation of H_2S by dissolved organic matter (DOM) to thiosulfate (Figure 1). The process is likely driven by a two-electron transfer from H_2S to quinone or other polyphenolic moieties, which are reduced to hydroquinones [Scott et al., 1998]. In batch experiments with peat humic acid, the reaction diverted H_2S from incorporation into organic matter and proceeded on timescales of hours [Heitmann and Blodau, 2006]. Thio-sulfate can be disproportionated into sulfate and H_2S ,

utilized by sulfate reducing bacteria (SRB) and may thus maintain their dissimilatory activity [Jorgensen, 1990; Jorgensen and Bak, 1991]. Oxidation of H_2S by DOM could be important because peat pore waters are particularly rich in dissolved organic carbon (DOC). Concentrations of DOC typically range from 2 to 10 mmol L^{-1} , of which 70–90% fall in the subfraction of humic substances [Thurman, 1985]. Peat humic acids are also particularly rich in quinone moieties [Scott et al., 1998].

[6] We studied S cycling and its role for C metabolism in two peat soils at the upper and lower end of atmospheric S deposition in North America. The soils included the moss canopy, were contained in mesocosms, and subjected to water flow and sulfate deposition. Our specific objectives were (1) to examine BSR activity in the peat, (2) to seek evidence for a renewal of the dissolved sulfate pool along the flow path, and (3) to identify potential mechanisms by which the sulfate pool was maintained. BSR was inferred from concentration changes of sulfate and H_2S and enrichment of ^{34}S -sulfate along the flow path (Figure 1) and incubation experiments in which BSR was chemically suppressed. Depth profiles of total reduced inorganic sulfur (TRIS) were examined in separately taken peat cores. Renewal of the sulfate pool was indirectly inferred from depth profiles of sulfate and H_2S concentrations and ^{34}S contents in relevant S pools. The potential importance of DOM as an oxidant for reduced S was assessed from production rates of dissolved C in the mesocosms. We expected to find, regardless of soil origin and treatment, a retention of sulfate by the vegetation, low sulfate concen-

trations in the water saturated peat, and evidence for sulfate reduction and production from changes in ^{34}S in sulfate, TRIS, and total S with depth as outlined in Figure 1.

2. Sites, Methods, and Materials

2.1. Sites

[7] We sampled peat cores from two peatlands in central and eastern Canada, which have been exposed to different long-term deposition of S. Mer Bleue (MB), near Ottawa, eastern Ontario, Canada, is an open, slightly domed, acidic, and oligotrophic peatland that is dominated by mosses (e.g., *Sphagnum capillifolium*, *S. angustifolium*, *S. magellanicum* and *Polytrichum strictum*) and shrubs (e.g., *Ledum groenlandicum*, *Chamaedaphne calyculata*, *Kalmia angustifolia* and *Vaccinium myrtilloides*). The second site in the Experimental Lakes Area (ELA), near Kenora, northwestern Ontario, Canada, is a small acidic and oligotrophic peatland located in the northwestern watershed of Lake 239 on the Precambrian Shield [Bayley et al., 1986]. The peatland is dominated by black spruce (*Picea mariana*) and mosses (*S. magellanicum*, *S. angustifolium* and *S. fuscum*).

[8] Wet atmospheric deposition of S from 1990 to 1996 was approximately $0.22 \text{ g m}^{-2} \text{ yr}^{-1}$ (ELA) and $0.82 \text{ g m}^{-2} \text{ yr}^{-1}$ (MB), taking data from the nearest station reported (R. Vet. C. U. Ro, D. Ord., National Atmospheric Chemistry Database and Analysis Facility, Environment Canada, SOE Bulletin No 99-3).

2.2. Mesocosm Experiments

[9] We investigated the fate of S within a more comprehensive study covering C dynamics and the fate of deposited nitrogen (N) [Blodau et al., 2006, 2004]. To examine the fate of S we used 4 peat cores (MB 1, 2; ELA 1, 2), 20 cm in diameter and 75 cm long, sampled in PVC tubes from moss dominated hollows in the autumn of 1999. The vegetation was preserved. Following extraction, the peat cores ("mesocosms") were fitted with a mesh allowing drainage at the bottom, capped and sealed. A tube equipped with a stopcock was inserted through the bottom cap to allow for removal of water by suction. Pore water suction samplers of 15 cm length, perforated to sample the inner 10 cm of the cores, were horizontally inserted at 2-cm intervals through holes in the PVC tube. To seal samplers and cap we used a two-component glue and silicone. The mesocosms were then transferred to a growth chamber and kept under controlled conditions of light, humidity, and temperature for approximately 280 days. The water table was adjusted with deionized water to 2–6 cm below the moss cover for the experiment. Temperature was kept at 20°C for 60 days and then adjusted to 12°C (day) and 8°C (night) for ~ 220 days before termination of the experiment.

[10] The mesocosms were irrigated with a sprinkler 5 to 6 days a week at 4 mm d^{-1} , or 125 mL d^{-1} . Pore water was manually retrieved in the same intervals at the bottom of the mesocosms at 3, later at 1.9 mm d^{-1} (58 mL d^{-1}). Evapotranspiration amounted to about 0.32 mm d^{-1} (100 mL d^{-1}). To keep the water table constant, we added additional deionized water with the sprinkler. Application of bromide as conservative tracer suggested that most pore water had been exchanged by the end of the experiment [Blodau and Moore, 2002]. The irrigate contained either 26 or $104 \mu\text{mol L}^{-1}$

of sulfate, representing a deposition of S at 0.83 and $3.33 \text{ g S m}^{-2} \text{ yr}^{-1}$. Two mesocosms were exposed to high (MB1, ELA 1) and two to low (MB 2, ELA 2) levels of S loading. The precipitation also contained H_3O^+ ($92\text{--}358 \mu\text{mol L}^{-1}$), NO_3^- ($40\text{--}120 \mu\text{mol L}^{-1}$), NH_4^+ ($40\text{--}120 \mu\text{mol L}^{-1}$) and Ca^{2+} ($30 \mu\text{mol L}^{-1}$), Mg^{2+} ($15 \mu\text{mol L}^{-1}$), Na^+ ($50 \mu\text{mol L}^{-1}$), K^+ ($5 \mu\text{mol L}^{-1}$), and Cl^- ($150\text{--}265 \mu\text{mol L}^{-1}$).

[11] Pore water (5 to 10 mL) was extracted from the suction samplers with stoppered syringes shortly before terminating the experiment and used to analyze dissolved inorganic carbon (DIC), DOC, CH_4 , sulfate, H_2S , Fe^{2+} and pH. The mesocosms were then transferred to the laboratory, closed on top by a cap and nitrogen was flushed through using a tube attached to the cap. After about 10 min, the mesocosms were drained through the horizontally inserted pore water samplers by gravity and N_2 pressure, while continuously flushing with N_2 . Beginning with the uppermost soil, a depth increment of 6–12 cm was allowed to complete draining. Then the next depth increment further down was drained. This procedure minimized mixture of pore water from different depths. The pore water was frozen and stored at -18°C until analyzed. The peat core was transferred to a glove box that was subsequently filled with nitrogen. Then the cap was removed and the core extruded, dissected and peat sampled for incubation and solid phase analyses.

2.3. Analyses

2.3.1. Pore Water

[12] DOC was determined after filtration of extracted pore water with a syringe microfilter ($0.45 \mu\text{m}$, nylon) on a Shimadzu 5050 TOC analyzer. Dissolved inorganic carbon (DIC) and CH_4 were determined on a Shimadzu Mini 2 gas chromatograph with methanizer in the gas phase of 1.8 mL vials, as described by Blodau et al. [2004]. Dissolved O_2 was determined amperometrically with a low-current electrode, and H_2S and pH potentiometrically ($\text{Ag}_2\text{S}/\text{glass-electrode}$, Watertest) on 0.5 to 3 mL of sample with a conventional meter (Orion). The sulfide electrode was conditioned with H_2S ($\sim 100 \mu\text{mol L}^{-1}$) prior to use. Dissolved O_2 contamination due to the sampling procedure was $\sim 0.5 \text{ mg L}^{-1}$. Sulfate was determined by ion chromatography (Metrosep Anion Dual 1, at 0.5 mL min^{-1} flow rate and chemical suppression). In a number of samples from the mesocosms, concentrations of formate, acetate, propionate, and butyrate were determined by HPLC at the end of the experiment. Dissolved Fe(II) and Fe(total) were photometrically determined at 512 nm with the phenanthroline method and addition of ascorbic acid (Fe(total)) [Tamura et al., 1974].

2.3.2. Solid Phases

[13] We collected additional peat cores from the Mer Bleue peatland for the analysis of inorganic solid phase Fe and S. Reactive iron was determined after cold extraction for 24 hours with 1M HCl [Wallmann et al., 1993], using the phenanthroline method. Iron(III) was calculated as the difference between Fe(tot) and Fe(II). The content of total inorganic reduced sulfur compounds (TRIS: FeS_2 , FeS , S^0) was determined using the method of [Fossing and Jorgensen, 1989]. Frozen peat samples were freeze dried and the material boiled with HCl ($c = 5 \text{ mol L}^{-1}$) and CrCl_2

($c = 0.15 \text{ mol L}^{-1}$) under a constant nitrogen stream. The H_2S released into the nitrogen stream was trapped in 50 mL of NaOH ($c = 0.15 \text{ mol L}^{-1}$) solution. The sulfide was precipitated by addition of zinc acetate and determined photometrically. S^0 was extracted from freeze dried sediment by methanol and measured by HPLC with UV detection [Ferdelman *et al.*, 1991].

2.3.3. Sulfur Isotope Analyses

[14] $^{34}\text{S}/^{32}\text{S}$ ratios were determined for sulfate contained in pore water, and TRIS and total S in the peat. For analysis of $^{34}\text{S}/^{32}\text{S}$ ratios in sulfate, we filtered pore water (100–300 mL per depth) obtained from the incremental drainage of the mesocosms ($\sim 1 \mu\text{m}$, Whatman paper filters). A volume of 5 mL of BaCl_2 solution (10%) was added to precipitate BaSO_4 and the solution was filtered again. The filters were dried at 70°C and kept in closed PE vials before analysis. For analysis of $^{34}\text{S}/^{32}\text{S}$ ratios in TRIS, the samples were boiled with 40–60 mL 1M CrCl_2 solution and 20 mL 6M HCl . TRIS was released as H_2S and trapped as CdS in CdAc . After 90 min, the CdAc trap was removed from the distillation apparatus and CdS was converted to Ag_2S by addition of 0.1 M AgNO_3 solution, followed by filtration of the AgNO_3 precipitate. The Ag_2S precipitate was dried, weighed, and stored for subsequent isotopic analysis. For analysis of $^{34}\text{S}/^{32}\text{S}$ ratios in total peat, the peat was dried at 70°C and finely ground. The sulfur isotope ratio of sulfate, total S, and TRIS was determined by converting either BaSO_4 , the peat sample, or Ag_2S into SO_2 in an elemental analyzer (EA 1500) coupled to a mass spectrometer (VG Prism II) in continuous flow mode. Sulfur isotope ratios are reported on the usual δ -scale in parts per thousand deviation relative to the internationally accepted standard V-CDT (troilite from the Canyon Diablo meteorite),

$$\delta^{34}\text{S}[\text{‰}] = \left[\frac{{}^{34}\text{S}/{}^{32}\text{S}_{\text{sample}}}{{}^{34}\text{S}/{}^{32}\text{S}_{\text{reference}}} - 1 \right] \cdot 1000.$$

[15] Sulfur isotope data were calibrated with the international reference materials IAEA-S1 ($\delta^{34}\text{S} = -0.3$) and IAEA-S2 with an assigned $\delta^{34}\text{S}$ value of $+21.7\text{‰}$. The reproducibility for sulfur isotope measurements on aqueous sulfate was better than $\pm 0.3\text{‰}$. Not all samples had enough sulfate to complete the analysis.

2.4. Calculations

[16] Net production rates of DIC and CH_4 in the mesocosms were estimated by mass balance on the basis of change in concentration with depth, the known vertical mass flow of water, i.e., advection, and diffusion (equation (1)). Diffusion of DOC could be neglected, as diffusion coefficients of macromolecular DOM are very small [Cornel *et al.*, 1985]. A preliminary calculation suggested that diffusive transport of DOC was negligible. Model calculations further showed that the assumption of advective-diffusive transport was adequate to describe water movement in the mesocosms [Blodau and Moore, 2002]. Net production rates were thus calculated by equation (1), not considering dispersion.

$$R = \Delta S_A / \Delta T - (D_{s,\text{in}} \Delta C_A / \Delta x)_{\text{in}} + (D_{s,\text{out}} \Delta C_A / \Delta x)_{\text{out}} - v(C_{A,\text{in}} - C_{A,\text{out}}) / \Delta x, \quad (1)$$

where

- R net production rate, $\text{nmol cm}^{-3} \text{ d}^{-1}$;
- C_A concentration of species A, $\mu\text{mol L}^{-1}$, with subscript “in” at upper boundary and “out” at lower boundary of depth segment;
- $\Delta S_A / \Delta T$ change in storage of species A in a segment, $\text{nmol cm}^{-3} \text{ d}^{-1}$;
- D_s whole sediment diffusion coefficient, $\text{cm}^2 \text{ d}^{-1}$, with subscript “in” at upper boundary and “out” at lower boundary of depth segment;
- $\Delta C_A / \Delta x$ concentration gradient of species A, nmol cm^{-4} ;
- v advection rate, cm d^{-1} .

[17] For simplicity, we assumed $\Delta S_A / \Delta T = 0$. Diffusion coefficients of CO_2 ($1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and CH_4 ($1.73 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) at 25°C were corrected for temperature using linear interpolation and for the effect of porosity ϕ by $D_s = D \times \phi^2$ [Lerman, 1988]. Porosity was estimated from bulk density reported by Blodau and Moore [2002]. A caveat of equation (1) is the negligence of ebullition of CH_4 , which may occur initially at partial pressures above 0.21 atm, or 358–389 $\mu\text{mol L}^{-1}$ at 8 to 12°C . With continuous stripping of N_2 by ebullition of CH_4 , higher partial pressures of CH_4 are required for the process to proceed [Fechner-Levy and Hemond, 1996]. Methane fluxes determined in chambers on top of the mesocosms were higher than calculated diffusive fluxes across the water table [Blodau *et al.*, 2004]. Methane production rates were thus likely underestimated.

2.5. Incubation Experiments

[18] Potential production rates of DOC, DIC, CH_4 , and H_2S were determined at four depths ($\sim 10, 24, 34,$ and 60 cm) under anaerobic conditions at the end of the experiment. Peat cores were extruded, dissected, and peat sampled under nitrogen in a glove chamber. The peat (50–100 g wet weight, $7.2 \pm 3.2 \text{ g}$ (s.d.) dry weight) was placed in 125–250 mL, rubber-stoppered Erlenmeyer flasks and fully immersed in deaerated water. All flasks were filled with solution containing 500 $\mu\text{mol L}^{-1}$ of Na_2SO_4 . One half of the flasks was prepared by adding 1000 $\mu\text{mol L}^{-1}$ of $(\text{NH}_4)_2\text{MoO}_4$, a specific inhibitor of BSR [Oremland and Capone, 1988]. The water was sampled through suction samplers inserted through the rubber stoppers that closed the flasks. Within 7 to 9 days, $\sim 10 \text{ mL}$ of water were extracted on five to six occasions and DOC, DIC, CH_4 , H_2S , Fe^{2+} concentrations and pH determined. The water was replaced with oxygen-free solution. Rates were determined from volume-corrected linear regression of concentration over time.

3. Results

3.1. Concentration Profiles and C Turnover

[19] Concentrations of dissolved sulfate in the irrigation water were 26 $\mu\text{mol L}^{-1}$ in the low S treatment and 104 $\mu\text{mol L}^{-1}$ in the high S treatment, which would increase to 47 and 191 $\mu\text{mol L}^{-1}$ after correction for evaporation. Sulfate concentrations below the water table were low, ranging from 10 to 20 $\mu\text{mol L}^{-1}$ (Figure 2). The majority

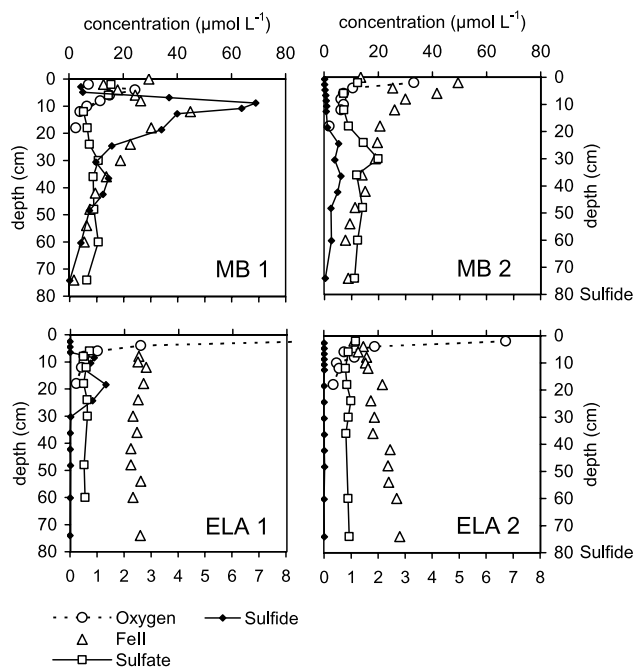


Figure 2. Depth profiles of dissolved oxygen, sulfate, ferrous iron, and hydrogen sulfide in mesocosms. The uppermost value indicates the position of the water table. Note different concentration scale for hydrogen sulfide (bottom).

of the deposited sulfur was thus retained by the *Sphagnum* canopy, capillary fringe, and at the water table. Oxygen concentrations decreased within three centimeters below the water table to background contamination levels $<15 \mu\text{mol L}^{-1}$ (Figure 2). Hydrogen sulfide concentrations ranged from non-detectable to $9 \mu\text{mol L}^{-1}$ in the MB 1 mesocosm (Figure 2). Maximum H_2S concentrations were detected at a depth of 10 to 30 cm, depending on the mesocosm. Ferrous iron concentrations ranged from <10 to $50 \mu\text{mol L}^{-1}$. In the MB mesocosms, Fe^{2+} was mobilized within the first 10 cm below the water table and immobilized deeper. Concentrations of Fe^{2+} were less variable in the ELA mesocosms.

[20] Dissolved C was dominated by the DOC fraction, with concentrations ranging from 1.4 to 9 mmol L^{-1} (Figure 3) and with the percolate from the *Sphagnum* canopy and thin unsaturated zone containing 1.4 to $3.5 \text{ mmol DOC L}^{-1}$. In the MB mesocosms, DOC concentrations continued to increase with depth, reaching a maximum at 30 to 40 cm, whereas this increase was small in the ELA mesocosms. DIC concentrations increased from 0.12 – 0.35 mmol L^{-1} at the water table to 1.7 – 2.3 mmol L^{-1} . Methane concentrations were much lower than DIC concentrations and increased from 0.009 – 0.08 mmol L^{-1} at the water table to 0.53 – 0.63 mmol L^{-1} at 20 to 60 cm. Acetate, propionate, and butyrate remained below the detection limit of $\sim 0.05 \text{ mmol L}^{-1}$ in the subset of samples analyzed. Maximum production of DIC was 21 to $93 \text{ nmol cm}^{-3} \text{ d}^{-1}$ and of CH_4 6.2 to $11.5 \text{ nmol cm}^{-3} \text{ d}^{-1}$. The fastest rates generally occurred in the surface peat for DIC and at depths of 15 to 30 cm for CH_4 (Table 1). The ELA 2 mesocosm was an exception, with the peat below 10 cm being fairly

inactive. Standardized to the peat surface, the magnitude of rates was similar among cores and decreased in the order $\text{DOC} > \text{DIC} > \text{CH}_4$ (Table 2). Production of DOC, however, was considerably faster in the MB soil.

3.2. Solid Phases

[21] In the cores extracted separately from the Mer Bleue peatland, TRIS occurred in all depth layers, even those (<20 cm) typically above the water table (Figure 4), indicating in situ formation of iron sulfides. A maximum of 10 to $19 \mu\text{mol g}^{-1}$ of TRIS was found at depths of 25 to 35 cm where elemental S reached a maximum of 1 to $2 \mu\text{mol g}^{-1}$. Reactive ferric and ferrous iron concentration peaked in the depth layer of 15 cm at low concentrations of 15 to $25 \mu\text{mol g}^{-1}$.

3.3. Sulfur Isotopes

[22] The $\delta^{34}\text{S}$ values of total sulfur decreased with depth in all cores, from 5.0–6.0‰ to 1.9–2.4‰ in ELA and 5.7–6.8‰ to 4.0–4.3‰ in MB mesocosms (Figure 5). In the lower layers of the MB cores, however, $\delta^{34}\text{S}$ values of total S increased. Sulfur isotope ratios in TRIS followed roughly the same trend, but the differences in $\delta^{34}\text{S}$ with depth were more pronounced. In MB 1, $\delta^{34}\text{S}$ values distinctly decreased from 7.2‰ (10 cm) to 1.4‰ (48 cm). The $\delta^{34}\text{S}$ value of sulfate in the irrigation water was 7.4‰ and 0.2 and 2.2‰ smaller just below the water table. In all four cores, sulfate was enriched in ^{34}S at depths of 10 to 25 cm, where $\delta^{34}\text{S}$ values reached 10.1‰ (MB 1 and 2), 11.8‰ (ELA 2) and 13.4‰ (ELA 1). Below that maximum, $\delta^{34}\text{S}$ values decreased but mostly remained well above values of total S and TRIS.

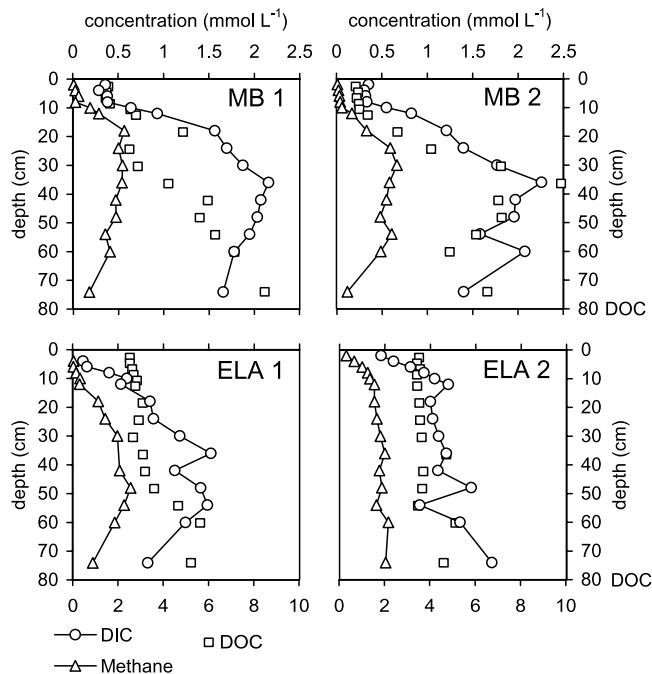


Figure 3. Depth profiles of dissolved inorganic carbon (DIC), CH_4 , and dissolved organic carbon (DOC) in mesocosms. Note different concentration scale for DOC (bottom).

Table 1. Net Production of DIC, CH₄, and DOC in Depth Segments of Peat Mesocosms^a

Core Depth	MB1			MB2			ELA1			ELA2		
	DIC	CH ₄	DOC	DIC	CH ₄	DOC	DIC	CH ₄	DOC	DIC	CH ₄	DOC
3	29	0.67	46	26	0.40	22	21	0.20	66.4	93	11.5	61
9	36	1.0	53	26	0.88	22	10	1.2	6.5	2.7	3.9	2.3
15	24	9.2	39	2.0	6.2	27	15	7.4	3.0	1.4	2.6	17
21	19	4.5	-22	15	7.2	54	13	5.7	-4.7	-2.8	1.1	1.5
27	7.1	-0.3	0.1	11	6.2	81	6.9	3.5	-2.7	0.0	0.6	8.6
33	11	1.4	57	10	0.9	119	11	0.6	8.8	1.2	0.7	9.9
39	7.4	0.0	49	19	-0.7	79	2.2	2.1	13.9	-0.8	-0.2	-6.0

^aNet production is in nmol cm⁻³ d⁻¹ and depth segments are in centimeters.

3.4. Incubation Experiments

[23] Dissolved carbon and H₂S concentrations increased steadily in most incubation flasks (see example in Figure 6), sometimes after an initial lag time (H₂S and CH₄). Ferric iron and proton concentrations mostly decreased or were without trends. The anaerobic potential DIC production rates mostly decreased with depth (Figure 7). Addition of MoO₄²⁻ decreased averaged DIC production rates by 20 to 50% (paired t-test, *P < 0.05; Figure 7 and Table 3). The potential CH₄ production rates peaked on average at 24 cm and 0.75 ± 0.32 μmol g⁻¹ d⁻¹ (Figure 7). Addition of MoO₄²⁻ decreased potential CH₄ production rates by a factor of 2–8 times (paired t-test, P < 0.05) at depths of 10 and 24 cm but not at greater depths (Table 3 and Figure 7). Potential rates were on average larger than the corresponding diffusive-advective in situ rates by a factor 2 (10 cm) to 26 (60 cm). Potential DOC production rates decreased on average from 17 to 4 μmol g⁻¹ d⁻¹ with depth. Addition of MoO₄²⁻ resulted in increased rates (factor 1.5 to 2.1) at depths of 10–24 cm, compared to the controls.

[24] Potential H₂S production rates ranged from 0.007 to 2.6 μmol g⁻¹ d⁻¹ (Figure 7). Production was fastest in the mesocosm and the layers that were characterized by the highest in situ concentrations of H₂S (MB1, 10 to 25 cm; Figure 2) and a similar pattern was found in ELA 1. In the surface layers of MB 2 and ELA 2, however, H₂S was also produced, although we were unable to detect the gas in situ. A statistical correlation between the variables could thus not be established. Addition of molybdate suppressed H₂S production completely.

4. Discussion

[25] Bacterial sulfate reduction in northern peatlands has been investigated in several studies using ³⁵S-radiotracer incubation techniques. On the basis of the incorporation of the tracer in iron sulfides and elemental S, BSR rates of 2.5 to 180 nmol cm⁻³ d⁻¹ have been reported from peats at temperatures of 20 to 25°C and across the gradient of S deposition of northern peatlands [Vile et al., 2003b]. Given the incorporation of ³⁵S in organic matter, BSR rates can be substantially higher [Vile et al., 2003a]. Sulfate reduction rates in peat bogs may overlap with rates in environments where sulfate is not limiting BSR, such as salt marshes [Howarth and Jorgensen, 1984], sediments of lakes polluted by acid mine drainage [Blodau et al., 1998], and marine sediments [Canfield et al., 1993]. On the basis of the small sulfate pools present, which usually range from 10 to 300 μmol L⁻¹ in peat bogs, a turnover time of sulfate

on the order of hours to weeks has been reported [Nedwell and Watson, 1995; Wieder and Lang, 1988]. This has led to the suggestion of an anaerobic recycling of sulfur to oxidized forms and subsequent repeated reduction [Nedwell and Watson, 1995; Wieder and Lang, 1988; Vile et al., 2003a]. It was our objective to find evidence for such a recycling process.

[26] The mesocosms were exposed to constant water tables for more than 200 days, in which the initial pore water had been mostly replaced by irrigation water [Blodau and Moore, 2002]. Anaerobic conditions and adjustment to input of sulfur was thus established for long periods of time before sampling. A reoxidation of reduced sulfur by water table fluctuations, to which a renewal of sulfate pools in peats has been frequently attributed [Bayley et al., 1986; Lazerte, 1992], can thus be discarded.

[27] Most of the deposited sulfur did not reach the anaerobic zone below the water table. Between 76 and 94% of the deposited sulfate was retained by the *Sphagnum* layer and unsaturated zone in the mesocosms when the water table was near the surface, as was previously reported by Moore et al. [2005]. The influence of long-term in situ loading with sulfur (MB high and ELA low) and the short-term sulfate loading in the experiments (MB1 and ELA 1 high, and MB2 and ELA2 low) thus seemed to be of minor importance for sulfate supply to BSR. Because of sulfate retention, sulfate concentrations typically ranged from 5 to 20 μmol L⁻¹ below the water table, long considered the lower boundary for dissimilatory activity of sulfate reducers [Ingvorsen et al., 1981, 1984; Lovley and Klug, 1983]. Still, sulfate was reduced in our peat mesocosms. Hydrogen sulfide was present in the pore waters of three of the four mesocosms, and TRIS accumulated at depths of 10 to 30 cm in situ at the Mer Bleue site. Evidence for BSR was further provided by the enrichment of ³⁴S in the sulfate pool at these depths in all cores (Figure 5). Using natural populations of SRB, sulfate reduction has resulted in isotopic fractionation with enrichment factors typically between 8‰ and 40‰, depending on temperature, substrate availability, and specific sulfate reduction rates [Canfield, 2001a]. Our results thus suggest that BSR remained an

Table 2. Depth-Integrated Production in Mesocosms^a

Depth	DIC	CH ₄	DOC
MB 1	5.2	0.68	17.2
MB 2	4.5	0.71	16.5
ELA 1	6.2	1.3	6.2
ELA 2	4.7	0.73	9.6

^aNumbers in depths are in centimeters. Production is mmol m⁻²d⁻¹.

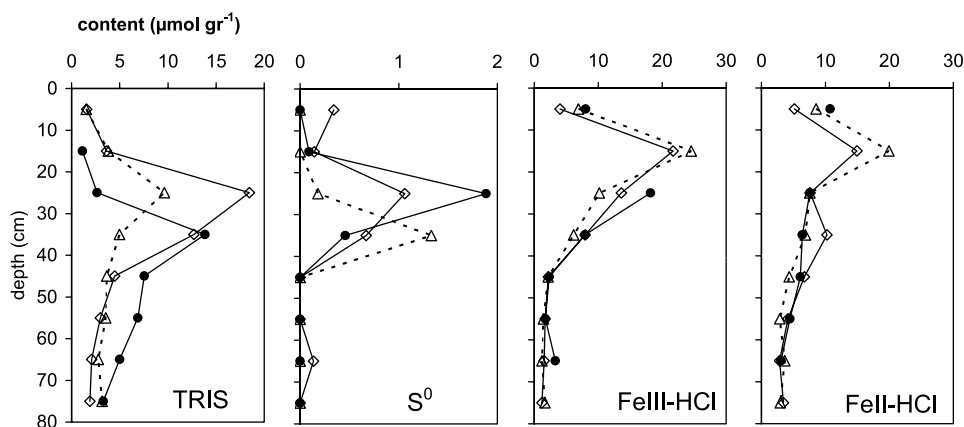


Figure 4. Depth profiles of total reduced inorganic sulfur (TRIS), elemental S, and HCl-dissolvable ferric and ferrous iron in cores sampled separately at the Mer Bleue site in May 2003.

active process even at very low sulfate concentrations, corroborating results by *Nedwell and Watson* [1995] from an ombrotrophic bog in Britain.

[28] The results further support the idea of sulfate reducers accounting for a substantial fraction of the anaerobic metabolic activity. We observed DIC production that could not be attributed to methanogenesis or the utilization of nitrate and ferric iron. Nitrate concentrations were $<5 \mu\text{mol L}^{-1}$ [Blodau et al., 2006; Moore et al., 2005]. Concentrations of ferrous iron, which mainly functioned as a scavenger for sulfide, remained low ($<50 \mu\text{mol L}^{-1}$) in the pore waters and solid phase. Incubation experiments with peat from the Mer Bleue site had shown only small rates ($<0.1 \mu\text{mol g}^{-1}\text{d}^{-1}$) of ferrous iron release, independent of sulfate and acetate availability in the slurries, and may have accounted for 0.3–0.4% of DIC production [Blodau et al., 2002]. In

contrast, addition of molybdate suppressed H_2S formation fully and DIC production by 20 to 50% in the experiments reported here. Molybdate blocks the activation of sulfate by ATP through formation of an unstable APMo analogue to APS within sulfate respiring bacteria [Oremland and Capone, 1988]. As sulfate respiring bacteria must first expend energy in form of ATP before generating energy from respiration, ATP pools are rapidly depleted in presence of molybdate, thereby likely causing cell death [Taylor and Oremland, 1979]. Such a process and associated cell lysis might have contributed to the increased net DOC production (Table 3), apart from physicochemical effects and the decrease in DIC production that occurred. Interestingly, suppression of BSR by addition of molybdate was accompanied by lower methane production rates (Table 3), suggesting that SRB and methanogens did not only compete for substrates. In agreement with this interpretation, also the addition of sulfate partly had little effect on methane production in incubation experiments with peats from the Mer Bleue bog [Blodau and Moore, 2003]. Both findings are not implausible assuming that a fraction of SRB used lactate as substrate and produced acetate, which is an important substrate for methanogenesis in peatlands [Avery et al., 2003; Hornibrook et al., 1997].

[29] DIC release unexplained by CH_4 production amounted to $0\text{--}81 \text{ nmol cm}^{-3} \text{ d}^{-1}$. In terms of electron

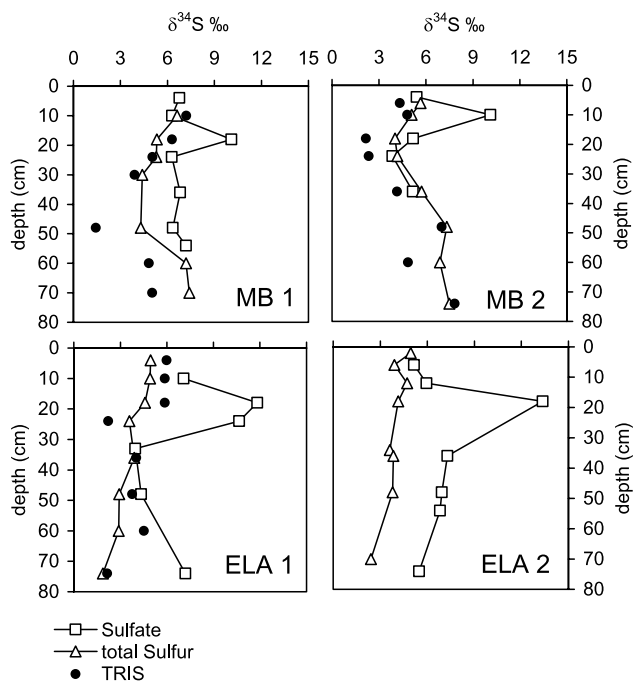


Figure 5. Isotopic signatures ($\delta^{34}\text{S}$) of sulfate, total S, and TRIS, as obtained from drained pore water (sulfate) and solid phase extraction.

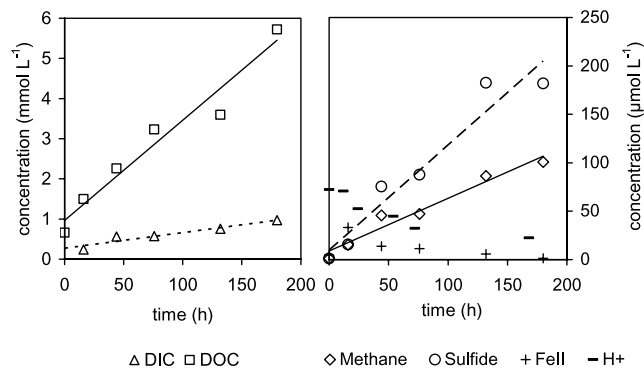


Figure 6. Time course of an exemplary incubation showing a high potential hydrogen sulfide production (MB1, depth 24 cm).

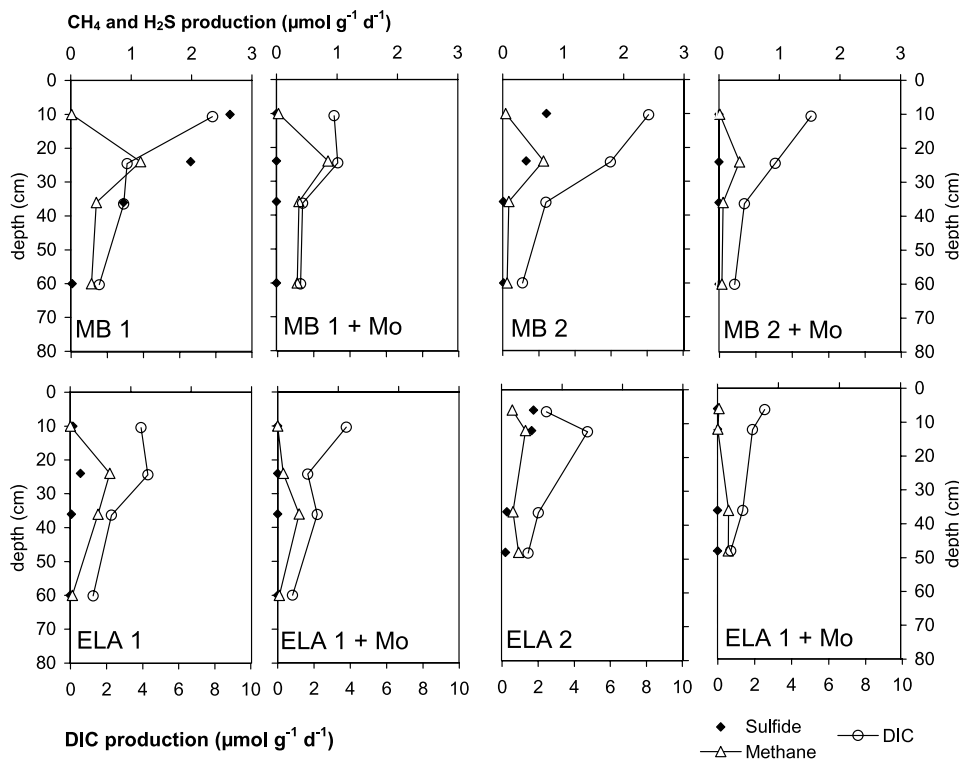


Figure 7. Potential production rates of DIC, CH₄, and H₂S. In all incubations sulfate (0.5 mM) and in one set ammonium molybdate (1 mM) was added to the incubation water. Note different scale for DIC production.

equivalents, unexplained CO₂ production rates were similar to BSR rates (7–38 nmol cm⁻³ d⁻¹) in a Cedar Swamp [Spratt and Morgan, 1990] and northern peatlands [Vile et al., 2003a, 2003b]. The calculated differences between net DIC and CH₄ production were probably underestimated as DIC is commonly reduced to CH₄ in peatlands [Avery et al., 2003; Hornibrook et al., 1997]. This holds true at least in the upper peat layers, where CH₄ concentrations were <358–389 µmol L⁻¹ and thus insufficient to allow for ebullition, a transport mechanism that we could not account for in the dissolved C mass balance approach.

[30] The occurrence and potential significance of BSR in the mesocosms raise the question whether and where sulfur recycling occurred and what processes may have been involved. Instructive in this respect is an examination of the δ³⁴S profiles (Figure 5). The δ³⁴S-sulfate values decreased after a maximum at a depth of 10 to 20 cm and roughly followed the δ³⁴S profiles of TRIS and total sulfur, with the exception of the deepest sample in ELA 1 (Figure 5). This pattern contradicts a Rayleigh distillation along a flow or diffusion path in a semi-closed system, which will result in progressively increasing δ³⁴S values with depth for sulfate, and a growing difference between δ³⁴S values of sulfate and reduction products, such as H₂S and TRIS [Jorgensen, 1979]. The decrease in δ³⁴S-sulfate values with depth thus requires replenishment of the sulfate pool from the peat matrix. Taking into account that the sulfate concentration profiles did not show a net mass loss in the zone of 10–20 cm (Figure 5), where ³⁴S-enriched sulfate accumulated and sulfate was reduced, recycling must already have occurred in the zone of active BSR near the surface.

[31] The processes involved in the recycling cannot be unequivocally identified on the basis of our results but some insight can again be gained from combining concentration profiles, isotopes and incubations. Heitmann and Blodau [2006] have previously reported that peat DOM can reoxidize H₂S chemically to thiosulfate which can be used by SRB and thus support their dissimilatory activity and growth [Jorgensen, 1990; Jorgensen and Bak, 1991; Widdel, 1988]. Thiosulfate can further be disproportionated into H₂S and sulfate by microbial mediation, thus resupplying the sulfate pool [Habicht et al., 1998]. Although we cannot directly support such a mechanism by thiosulfate measurements and changes in electron accepting capacities of the DOM with depth, it seems likely that this process occurred in the uppermost peat layer, where DOM must have been leached in its oxidized form. There we determined the highest potential H₂S production rates (Figure 7) and observed the largest suppression of DIC production (Table 1 and Figure 7). Hydrogen sulfide was furthermore net consumed by some process as indicated by a decreasing concentration below a peak of maximum concentration (Figure 2).

Table 3. Change in Production With Molybdate Addition in Peat Incubations With MB Peat^a

Depth, cm	DIC	CH ₄	DOC
10	-50 ± 11	-37 ± 92	+74 ± 4
24	-22 ± 28	-47 ± 19	+98 ± 82
36	-42 ± 11	-42 ± 36	+19 ± 47
60	-29 ± 13	-7 ± 20	+27 ± 3

^aChange is given as percent ± s.d. Here n = 3.

[32] Mass balance considerations suggest that production of electron accepting capacity related to DOM alone could not account for the DIC production, even if a maximum of electron transfer capacities was assumed. The electron accepting capacity of fully oxidized Mer Bleue DOM toward H_2S may reach $6 \text{ mmol g}^{-1} \text{ C}$, or one electron transfer for 14 C atoms [Heitmann *et al.*, 2007]. Using this value, only 1.5 to 5% of DIC production unexplained by methane production can be accounted for in the uppermost layer. In deeper layers, this percentage was higher but it is not clear in what redox state DOM was released. This consideration leaves the capacity of the solid phase organic matter to reoxidize H_2S unaccounted for. Information about this capacity is not available yet and its contribution to respiration cannot be evaluated.

[33] A complete recycling of H_2S back to sulfate at depths of 10 to 20 cm would not produce a peak in ^{34}S -enriched sulfate as observed but would leave $\delta^{34}\text{S}$ values unchanged. Part of the reduced sulfate must have left the reoxidation cycle in the uppermost layers, leading to a net enrichment in ^{34}S (Figure 1). H_2S can be incorporated into organic matter [Brown, 1986; Heitmann and Blodau, 2006], for example by Michael's addition reaction with quinone moieties [Perlinger *et al.*, 2002]. Formation of CBS may often, but not always, predominantly follow the production of H_2S by BSR in peat soils [Spratt and Morgan, 1990; Vile *et al.*, 2003a; Wieder and Lang, 1988]. Incorporation of H_2S into DOM also occurred in pore water from the Mer Bleue peatland (T. Heitmann and C. Blodau, unpublished data, 2005).

[34] At greater depths, sulfate was depleted in ^{34}S and the sulfate pool must have been replenished either by a reoxidation process providing sulfate from hydrogen sulfide, or TRIS, or from organic sulfur, which had a much lower $\delta^{34}\text{S}$ signal than sulfate (Figures 1 and 5). A release of S deeper into *Sphagnum* peat has been inferred earlier on the basis of increasing ^{34}S values of peat with depth [Novák *et al.*, 1994]. Among the possible mechanisms for S release, hydrolysis of organic ester-bound sulfate is probably common in peatlands [Mandernack *et al.*, 2000]. It does not seem to be a viable explanation for the decreasing $\delta^{34}\text{S}$ values of sulfate, however, because at greater depths ester-bound sulfate should have been enriched in ^{34}S itself. It seems likely that at least part of the sulfate-sulfur stemmed from the TRIS fraction, because TRIS contents decreased below a maximum at 20 to 30 cm in peat cores from Mer Bleue (Figure 4), similarly as in other *Sphagnum* bogs [Novák *et al.*, 1994]. With burial, TRIS contents should increase owing to selective accumulation with C loss over time. This was not the case and suggests that TRIS was labile and reoxidized, as previously documented experimentally by Wieder and Lang [1988]. The same conclusion applies to elemental S, which is an important intermediate in the microbial reoxidation of hydrogen sulfide and can be both reduced and oxidized [Canfield and Thamdrup, 1996].

[35] In previous studies, the deposition of S has had a larger effect on CH_4 production and emissions than expected, on the basis of sulfate and CH_4 mass balances [Dise and Verry, 2001; Gauci *et al.*, 2002]. A continuous reoxidation of reduced sulfur to sulfate under anaerobic conditions should contribute to this large effect and is likely based on previous studies and our results. The addition of molybdate to peat furthermore showed that not much dis-

solved sulfate was needed to maintain a high activity of SRB. This is also in agreement with earlier work on this issue [Vile *et al.*, 2003a]. Very low sulfate concentration levels of 5 to $20 \mu\text{mol L}^{-1}$ were attained after equilibration of the mesocosms to the chosen conditions of water table and S deposition. Hence the activity of SRB in our peat soils must have been constrained by the kinetics of S oxidation or by the provision of electron accepting capacity that fuelled the oxidation. If this interpretation is correct, and if the rate of S oxidation is proportional to the size of reduced S pools, an increase in sulfur pool sizes by sulfate deposition may result in increased BSR rates, although the sulfate pool itself cannot maintain BSR for extended periods. We cannot refute or confirm this conclusion on the basis of the data obtained. It is in agreement with the observation that rates of BSR increase and methane production decrease with S loading, as documented by Vile *et al.* [2003b] and with the preferential retention and accumulation of atmospherically deposited S in ombrotrophic peatlands [Moore *et al.*, 2005].

5. Conclusion

[36] We examined sulfur cycling in intact peat mesocosms from two peatlands at natural background (ELA) and moderately elevated sulfate deposition (MB), and two levels of experimental sulfate deposition. Sulfate was reduced at sulfate concentrations $<20 \mu\text{mol L}^{-1}$ and SRB were important for the anaerobic electron flow, as their inhibition substantially lowered potential CO_2 production rates. We suggest that BSR was partly maintained by a recycling of reduced inorganic sulfur that was "leaky" with respect to organic S. In the upper peat layers, ^{34}S -enriched sulfate accumulated in the absence of net sulfate loss from pore water. This suggested a mode of S cycling in which sulfate was reduced and the sulfide produced only partly reoxidized, and partly incorporated into organic matter and TRIS. Deeper in the peat, release and reoxidation of S stemming from organic matter or TRIS became more important, as indicated by decreasing $\delta^{34}\text{S}$ values in sulfate. The results of this study thus support earlier investigations that documented high rates of BSR in presence of small sulfate pools and provide support for a reoxidation of reduced S in peats poor in inorganic oxidants.

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