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Micro-scale CO₂ and CH₄ dynamics in a peat soil during a water fluctuation and sulfate pulse

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Abstract

We investigated the response of CO₂ and CH₄ production to a water table fluctuation and a SO₄²⁻ pulse in a bog mesocosm. Net gas production rates in the mesocosm were calculated from concentration data by diffusive mass-balances. Incubation experiments were used to quantify the effect of SO₄²⁻ addition and the distribution of potential CO₂ and CH₄ production rates. Flooding of unsaturated peat resulted in rapid depletion of O₂ and complex patterns of net CH₄, CO₂, and H₂S production. Methane production began locally and without a time lag at rates of 3–4 nmol cm⁻³ d⁻¹ deeper in the peat. Similar rates were determined after a time lag of 10–60 days in the surface layers, whereas rates at lower depths declined. Net CO₂ production was largest immediately after the water table position was altered (100–300 nmol cm⁻³ d⁻¹) and declined to –50–50 nmol cm⁻³ d⁻¹ after a few weeks. SO₄²⁻ addition (500 mM) significantly increased potential CH₄ production rates in the surface layer from an average of 132–201 nmol cm⁻³ d⁻¹ and reduced it below from an average of 418–256 nmol cm⁻³ d⁻¹. Our results suggest that deeper in the peat (40–70 cm) under in situ conditions, methanogenic populations are less impaired by unsaturated conditions than in the surface layers, and that at these depths after flooding the substrate availability for CH₄ and DIC production is significantly enhanced. They also suggest that methanogenic and SO₄²⁻-reducing activity were non-competitive in the surface layer, which might explain contradictory findings from field studies.

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Keywords: Peatlands; Carbon dioxide; Methane; Sulfate; Pore water

1. Introduction

Northern peatlands function as long term sinks for atmospheric carbon dioxide (CO₂) (Gorham, 1991; Botch et al., 1995) and as sources of atmospheric methane (CH₄) (Barlett and Harriss, 1993; Bubier et al., 1993, 1995). About 5–10% of the global CH₄ emissions to the atmosphere have been attributed to peatlands (Fung et al., 1991). Due to the important role of peatlands in the global carbon cycle their response to environmental change is currently investigated. Recent observations suggest for example that CO₂ may be net released due to changes in environmental conditions, such as drought and permafrost melting (Oechel et al., 1993; Moore et al., 1998; Griffis et al., 2000; Turetzky et al., 2002).

The production of CO₂ and CH₄ depends on the microbial activity in the peat, the soil temperature, plant

community structure, the chemical characteristics of the peat, and the position of redox boundaries associated with the water table (Bubier et al., 1993, 1995; Whiting and Chanton, 1993; Yavitt et al., 1997). Both CO₂ and CH₄ production rates are controlled by the availability of oxygen in the peat, which is influenced by the position of the water table. Strictly anaerobic conditions are a prerequisite for CH₄ production and generally reduce CO₂ production rates from peat (Moore and Dalva, 1993). Methane production and emission might also be influenced by the reduction of SO₄²⁻ (Dise and Verry, 2001; Nedwell and Watson, 1995; Watson and Nedwell, 1998; Wieder et al., 1990) because SO₄²⁻ reducers can compete with methanogens for organic substrates and H₂ (Kristjanson et al., 1982; Lovley and Klug, 1983). SO₄²⁻ availability in peatlands is influenced by atmospheric input and by the reoxidation of reduced inorganic organic sulfur compounds during water table fluctuations (Bayley et al., 1986; Devito and Hill, 1999; Shannon and White, 1996). Carbon dioxide and CH₄ production rates in peatlands are therefore affected by the seasonal water table pattern, typically at its lowest level

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during mid-summer. This pattern might become more pronounced in the future, with changes in the frequency and intensity of droughts resulting from climate change (Wetherald and Manabe, 1995; IPCC 1997; Moore et al., 1998).

Previous studies on the effects of water table position on C turnover in peat soils have focused mostly on the potential production rates in disturbed samples (Kettunen et al., 1999; Öquist and Sundh, 1998; Yavitt et al., 1987, 1990, 1997) and on the net exchange of trace gases with the atmosphere (Aerts and Ludwig, 1997; Moore and Dalva, 1993; Moore and Knowles, 1989). Spatially detailed information about production rates of CO₂ and CH₄ in intact peat soils, and about the effects of SO₄²⁻ pulses during water table fluctuations is missing.

The primary objective of this study is to identify cm-scale response of below-ground CO₂ and CH₄ dynamics to a large water table fluctuation. We also examined the response of CH₄ production to a pulse of SO₄²⁻. We based the study on a mass balance approach to estimate net production rates from concentration data in a mesocosm. We also conducted incubation experiments with peat with additions of SO₄²⁻ to obtain information about the effects of SO₄²⁻ on CH₄ production rates.

2. Materials and methods

2.1. Site

The Mer Bleue site near Ottawa, eastern Ontario, Canada, is an open, slightly domed, oligotrophic peatland that is dominated by mosses (e.g. *Sphagnum capillifolium*, *Sphagnum angustifolium*, *Sphagnum magellanicum* and *Polytrichum strictum*) and shrubs (e.g. *Ledum groenlandicum*, *Chamaedaphne calyculata*, *Kalmia angustifolia*, *Vaccinium myrtilloides*). The peat was about 4 m deep. Decomposition on the von Post scale, which encompasses ten grades of decomposition based on peat color and structure, increased from 2 to 3 in the upper 10 cm to about 6–10 at a depth of 70 cm.

2.2. Definitions and conventions

The terms mesocosm and core are used for the subsequently described experimental setting. The term incubation is used for vacutainer experiments. Rates in the mesocosm that were obtained from mass balances are referred to as in situ, whereas rates in vacutainer incubations are referred to as potential production rates. CO₂ is used synonymously with dissolved inorganic carbon (DIC), because dissolved CO₂ was, at pH values of below 3–5, the predominating carbonic species. Water table refers to the depth at which water could be extracted from samplers by suction with a syringe without extracting significant amounts of gas. Losses of CO₂ and CH₄ from the peat to

the atmosphere or due to drainage have been given a positive sign. All indicators of variability in the text and figures are standard deviations. All rates and reservoirs are given in molar units. All production rates are based on dry weight or volume of peat, and represent net rates.

2.3. Experimental setup

A sampling tube (20 cm diameter × 75 cm depth) was prepared that consisted of two half-tubes that could be disassembled. After coring of the peat, one half of the tube was removed and a transparent plexi-glass cover was attached with 77 pore water samplers (perforated Bev-Line IV tubing, Cole Parmer, 3 cm length, 7 mm outer diameter, 3 mm inner diameter, closed with a rubber stopper on the outside) on a 66 × 17.5 cm² grid. The core was initially kept at an air temperature of 12 °C day and 8 °C night, about representing average summer soil temperatures and fluctuations. The water table depth was kept at 66 cm for 4 months, and then raised to 3–5 cm below the moss surface and 1–3 cm above the first sampling depth for 103 days. The core was drained again and kept unsaturated for 94 days and finally flooded again and kept saturated for 32 days. About halfway into the second unsaturated period the temperature was raised to 20–22 °C to test the effect of temperature changes on CO₂ and CH₄ production. The duration of the first cycle of unsaturated–saturated–unsaturated conditions was chosen to represent the adjustment of the peat soil to a large water table fluctuation as it might occur in peatlands on a seasonal basis. The duration of the second flooding was chosen to examine whether patterns in CH₄ production that were observed initially after the first flooding were replicable.

For flooding and the replacement of evaporative losses during the saturated periods an aqueous solution was sprinkled on top of the core. This solution was also used during unsaturated conditions at an inflow rate of 5 mm d⁻¹ to maintain constant moisture conditions. Excess water was removed from the bottom through a drainage tube. In the initial flooding and during unsaturated conditions, the inflow contained H₃O⁺ (328 μmol l⁻¹), SO₄²⁻ (104 μmol l⁻¹), NO₃⁻ (120 μmol l⁻¹), NH₄⁺ (120 μmol l⁻¹), Ca²⁺ (30 μmol l⁻¹), Mg²⁺ (15 μmol l⁻¹), Na⁺ (50 μmol l⁻¹) and K⁺ (5 μmol l⁻¹) and Cl⁻ (265 μmol l⁻¹), representing precipitation strongly affected by acid rain. In the second flooding, 500 μmol SO₄²⁻ l⁻¹ was applied to test the effect of a SO₄²⁻ pulse on the CH₄ dynamics. This concentration is well above levels in precipitation but regularly occurs in soil solution (e.g. Shannon and White, 1996)

Carbon dioxide and CH₄ concentrations were determined on 23 occasions by extracting pore water or gas with a syringe. On some occasions, we also determined pH, and concentrations of O₂, H₂S and SO₄²⁻. The core contained *C. calyculata*, *L. groenlandicum*, *S. capillifolium* and *P. strictum* and a small *Eriophorum virgicum* that

developed several roots along the transparent cover; root distribution was mapped after the end of the experiment. The living vascular above-ground biomass (dry weight) was 31 g m^{-2} (graminoid), and 34 g m^{-2} (shrubs), with a below-ground biomass of ca. 18 g m^{-2} . The total moss biomass was ca. 200 g m^{-2} . With an average bulk density of ca. 0.1 g cm^{-3} (Blodau, unpublished data) the total dry peat mass in the core was ca. 1000 g , or 66 kg m^{-2} . The pH of the pore water was between 3.4 and 3.8 at the surface and 4.5 at 66 cm and changed little over time.

2.4. Incubation experiments

Incubations were carried out in 12 ml Vacutainers with three sub-samples of peat (2–3 g wet) from the sampling ports of the core after the end of the experiment, which was 36 days after the second flooding. To these ends the water table was successively lowered by removing the rubber stoppers from each row of samplers until the water of that depth increment had drained. Then the core was horizontally placed on a work bench and the front plate was removed. Samples were taken by cutting out a little cube of material around the port with a knife and placed in a vacutainer as quickly as possible and repeatedly evacuated and flushed with N_2 . Two milliliters of a solution were added and the headspace was adjusted to 500–800 ppm CH_4 in order to determine potential production or consumption of CH_4 . The treatments were (I) distilled water, (II) $500 \mu\text{M Na}_2\text{SO}_4$, or (III) $500 \mu\text{M Na}_2\text{SO}_4$ and 10 mM 2-bromoethanesulfonic acid (BES), which selectively inhibits methanogenesis (Oremland and Capone, 1988). In another set of samples, encompassing 11 sub-samples from one depth profile, 1 mM sodium acetate was added. From another location eight sub-samples were taken to obtain information about the variability of CH_4 production rates within the treatments and replicate samples.

Potential CH_4 production rates were determined from volume-corrected linear regressions of headspace concentration changes over a period of 11 days (regression over four measurements) replacing the extracted volume (1 ml each) with N_2 . We determined CH_4 production rates immediately after setting up the incubations to compare potential rates of CH_4 production in incubations with rates calculated from concentration changes in the cores. The CH_4 concentration in the headspace increased in most samples linearly with time. After a 30-day equilibration period and flushing of the incubation vessels with N_2 , carbon dioxide production rates were determined on the subsamples filled with distilled water over a period of 8 days (regression of three measurements). This was done to avoid the inclusion of the typically observed ‘flush’ of CO_2 production after redox disturbance and to obtain potential CO_2 production rates under constantly anaerobic conditions.

Methane loss rate of spiked controls (Vacutainer) was smaller than the analytical error over the incubation

period, and experimental variability of CH_4 production rates within treatments was small (172 ± 17 and $400 \pm 6 \text{ nmol g d}^{-1}$, st. dev., $n = 4$). All rates were based on dry weights of peat and recalculated for volumes using average bulk densities.

2.5. Analytical procedures

DIC and CH_4 were determined on a Shimadzu Mini 2 gas chromatograph with methanizer in the gas phase of 1.8 ml GC autosampler vials closed with Teflon coated rubber septa after addition of $20 \mu\text{l}$ of 4 M HCl and 0.5 ml sample. Losses of CO_2 and CH_4 from the GC vials were corrected with exponential loss functions ($n = 16$, $R^2 = 0.99$; concentration of CO_2 : $C = C_0 10^{(-0.0264t)}$ and concentration of CH_4 : $C = C_0 10^{(-0.00635t)}$ with t : (h). The original dissolved concentration was reconstructed using the headspace concentrations, the volumes of headspace and water phase and Henry’s law ($K_H = 10^{-1.5} (\text{mol l}^{-1} \text{atm}^{-1})$ for CO_2 and $K_H = 2 \times 10^{-3} (\text{mol l}^{-1} \text{atm}^{-1})$ for CH_4 . In the unsaturated zone, CO_2 and CH_4 were directly determined on gas samples that were extracted from the sampling ports with syringes. O_2 was determined amperometrically with a low-current electrode (Orion) and H_2S and pH potentiometrically (AgS/glass-electrode, Watertest) on $0.5\text{--}3 \text{ ml}$ of sample with a conventional meter (Orion). O_2 contamination due to the sampling procedure was ca. 0.5 mg l^{-1} . SO_4^{2-} was determined by ion chromatography (Dionex, Metrosep Anion Dual 1, at 0.5 ml min^{-1} flow rate and chemical suppression).

2.6. Calculation of in situ production rates

Advection being zero, the net production of a compound A in a given volume is given by:

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

in which

R : production rate ($\text{nmol cm}^{-3} \text{d}^{-1}$),

C_A : concentration of compound A,

$\Delta S_A / \Delta T$: change in storage of compound A in a segment ($\text{nmol cm}^{-3} \text{d}^{-1}$),

D : whole peat diffusion coefficient ($\text{cm}^2 \text{d}^{-1}$),

$\Delta C_A / \Delta x$: concentration gradient of compound A (nmol cm^{-4}).

Mass balances of dissolved CH_4 and CO_2 were accordingly calculated for each sampling port between sampling dates. To obtain concentration gradients the circumference of each port was divided into eight triangles covering the area between the port and all neighboring ports. For each of these segments concentration gradients and diffusional lengths were used to estimate a diffusive flux at the sampling date i and all fluxes added up. The change in concentration over time at each port was calculated between

sampling dates $i - 1$ and $i + 1$. Diffusive mass balances and change in concentration over time were then used to calculate an average net production at sampling date i according to Eq. (1).

Temperature-corrected diffusion coefficients for dissolved CO_2 , CH_4 and O_2 were taken from Lerman (1979). The effect of bulk density on diffusion coefficients was taken into account by using separately determined bulk density profiles, which were fitted against a power function ($B_d = 0.0107 \times 10^{0.567}$ with $B_d =$ bulk density (g cm^{-3}); x depth (cm); $R^2 = 0.79$; Blodau and Moore, 2002). Diffusion coefficients were adjusted to porosity by reducing the molecular diffusion coefficient by a factor (porosity)² (Lerman, 1979). Porosity was calculated from bulk density assuming a specific density of the peat solids of 1.5 g cm^{-3} (Weiss et al., 1998). Diffusive exchange with the atmosphere

was calculated using Fick's 1st law. For this calculation, it was assumed that gaseous concentrations 1–2 cm above the water table were in equilibrium with the dissolved concentration at the water table.

To estimate production rates under unsaturated conditions, we separately determined water contents of the depth segments in three separate cores under identical conditions as used in this experiment and fitted the data to a linear function ($R^2 = 0.97$). Porosity was calculated as described above. Eq. (2) (Jin and Jury, 1996; Millington and Quirk, 1961), and gaseous, temperature-corrected diffusion coefficients taken from Lerman (1979) were used to estimate unsaturated diffusion coefficients in the peat:

$$\alpha(a) = a^2 \beta^{-2/3} \quad (2)$$

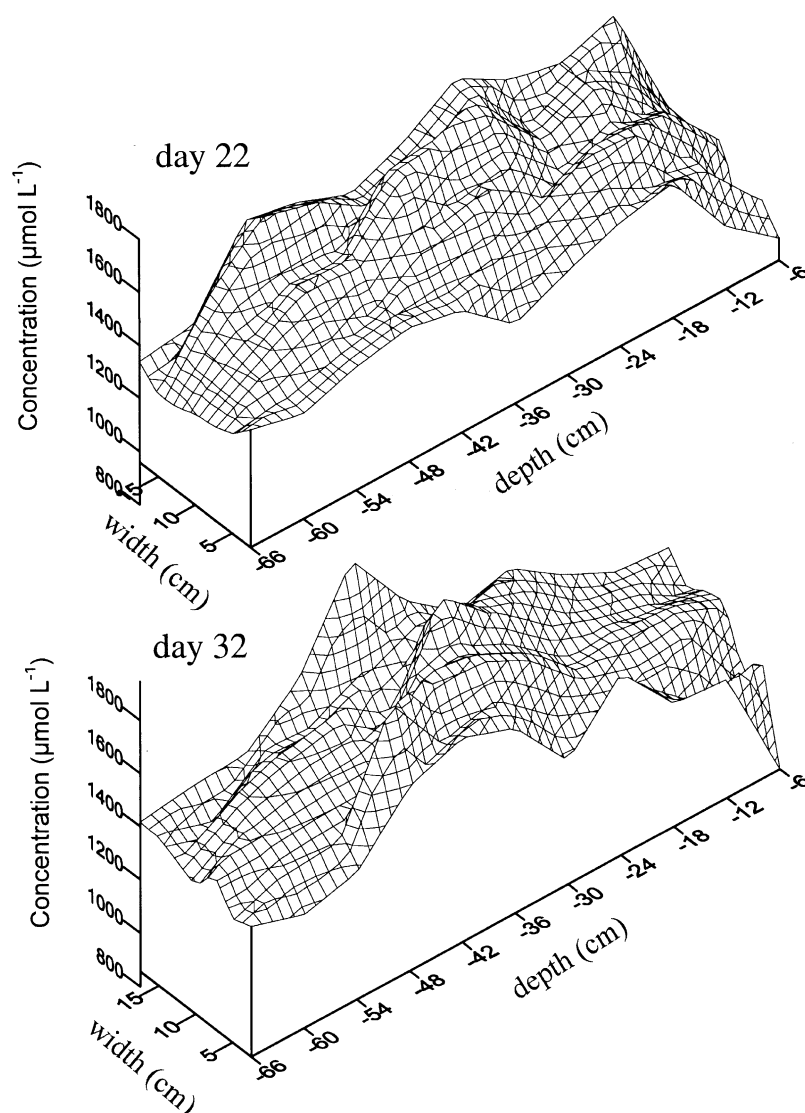


Fig. 1. Concentrations of DIC 22 and 32 days after the 2nd flooding as an example for partly increasing, partly decreasing DIC concentrations in the peat matrix.

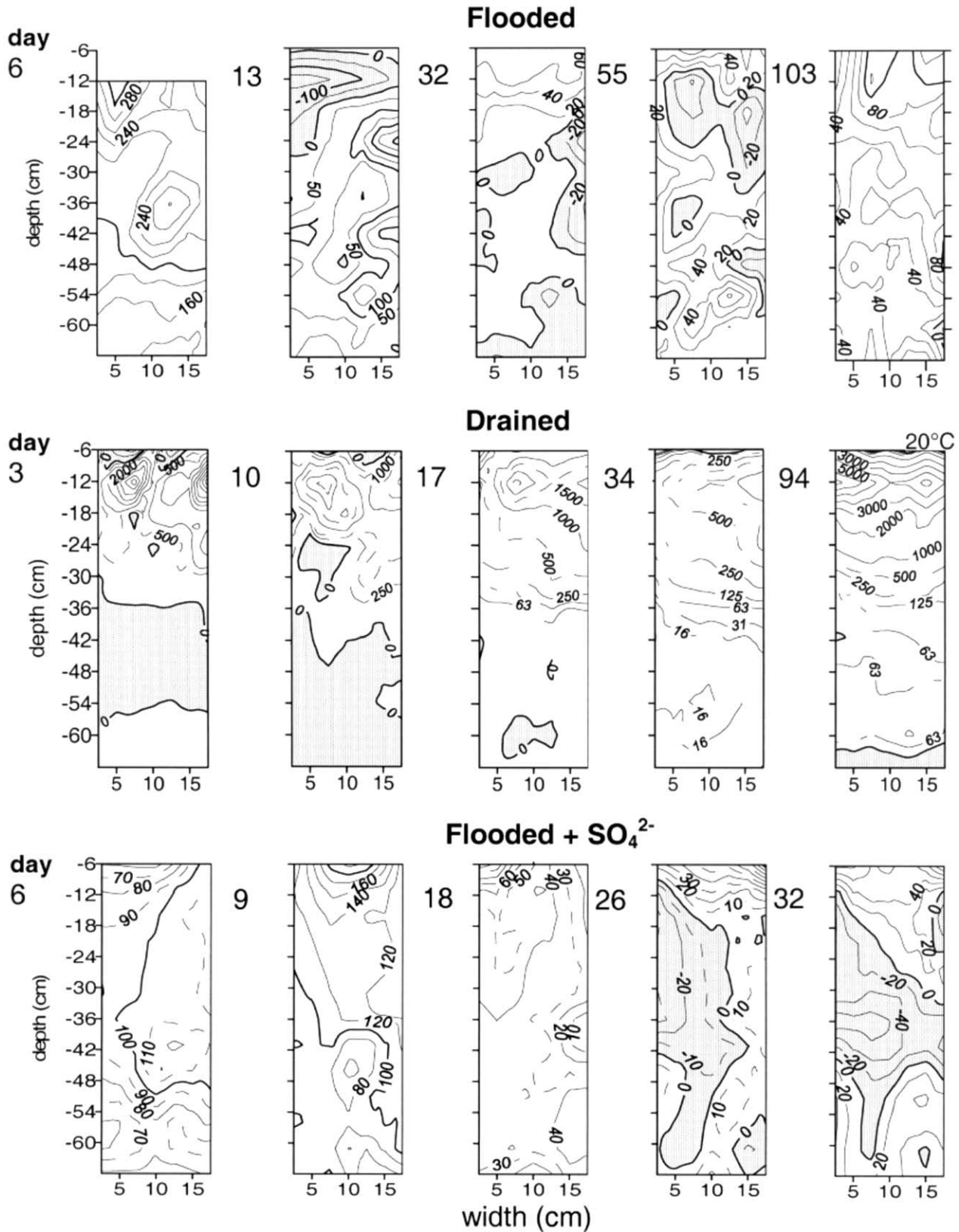


Fig. 2. Spatio-temporal patterns of net DIC/CO₂ production (nmol cm⁻³ d⁻¹) after flooding, subsequent drainage and repeated flooding in the grid core. The time scale refers to the time after disturbance. Between day 34 and 94 (drained) the temperature was increased from 12/8 to 20–22 °C. Here and thereafter, shaded areas indicate net consumption. Note the development of local sinks after flooding (e.g. second flooding, day 26 and 32), and of initially in- then decreasing CO₂ production rates after drainage.

in which

α : diffusion coefficient correction factor (–), a : volumetric air content (–),

β : soil porosity (–); empty brackets indicate the absence of units.

Ambient atmospheric concentrations, diffusive mass balances and changes in storage were used to calculate production and exchange rates of CO_2 and CH_4 with the atmosphere. A few sampling locations with elevated CH_4 concentrations, indicating anaerobic pockets, were discarded from the unsaturated rate calculations. In these locations water contents were obviously much larger than on average, which interferes with the calculation of rates according to Eq. (2). Since these data points were excluded the calculated net CH_4 consumption is an upper estimate.

Production rates were visualized using isoline plots in WinSurf, release 5.00. Isolines of concentration and production rates were plotted using a Kriging procedure. Linear interpolation provided similar results. For the analysis of the isoline plot data in this study it should be kept in mind that only spatially broad or temporally consistent trends in the data can be interpreted.

3. Results

3.1. In situ concentrations and production rates

Flooding of the grid core resulted both times in rapid depletion of dissolved O_2 to background levels (about 0.5 mg l^{-1}) followed by the development of a steep concentration gradient with average consumption rates between 20 and $50 \text{ nmol cm}^{-3} \text{ d}^{-1}$ in the 6 cm depth segment below the water table (data not shown).

DIC concentrations rapidly increased throughout the core to 1500 – $2000 \text{ } \mu\text{mol l}^{-1}$ within the first 2–4 weeks after each flooding (Fig. 1), reaching maximum concentrations of 3000 – $5000 \text{ } \mu\text{mol l}^{-1}$ at day 103 (data not shown). In some areas of the core DIC concentrations decreased after the initial pulse of DIC production, whereas in other areas DIC concentrations continued to rise (Fig. 1). Accordingly, DIC net production rates were initially high everywhere (50 – $300 \text{ nmol cm}^{-3} \text{ d}^{-1}$) and decreased later to values of below $50 \text{ nmol cm}^{-3} \text{ d}^{-1}$, with some areas showing net consumption of DIC on the order of 20 – $50 \text{ nmol cm}^{-3} \text{ d}^{-1}$ (Fig. 2).

After the first flooding CH_4 production began at depths of 48 – 60 cm and formed a distinct and replicable production ‘hot spot’ of 3 – $4 \text{ nmol cm}^{-3} \text{ d}^{-1}$ within 5–6 days. This hot spot continued developing till day 32 with CH_4

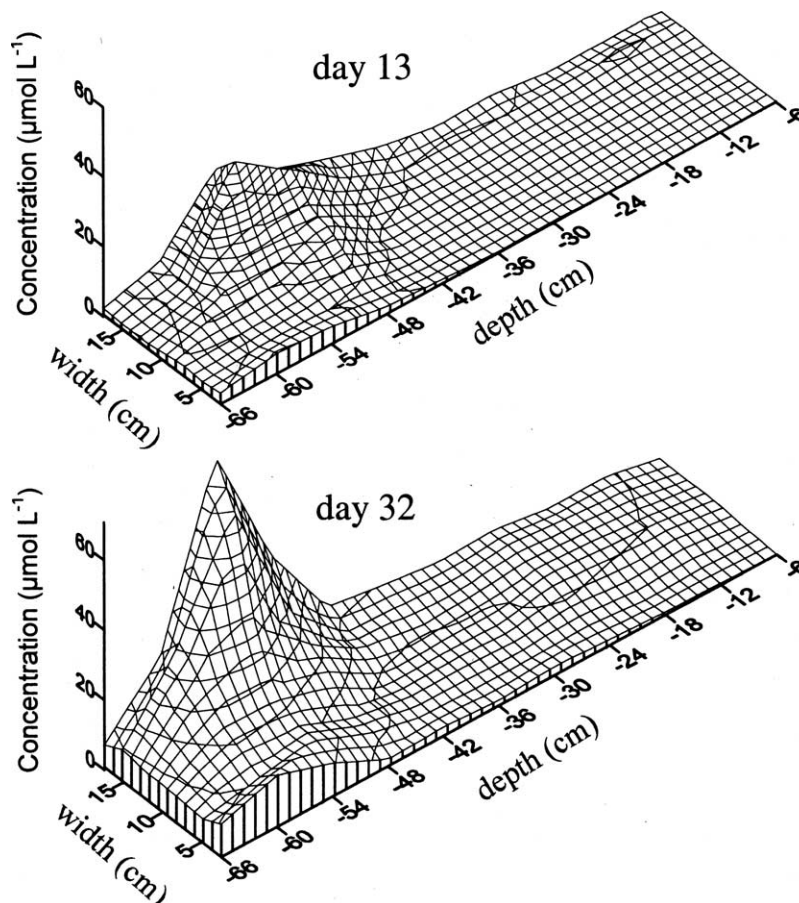


Fig. 3. Concentrations of dissolved CH_4 13 and 32 days after the first flooding, illustrating the development of a CH_4 concentration hot spot after flooding.

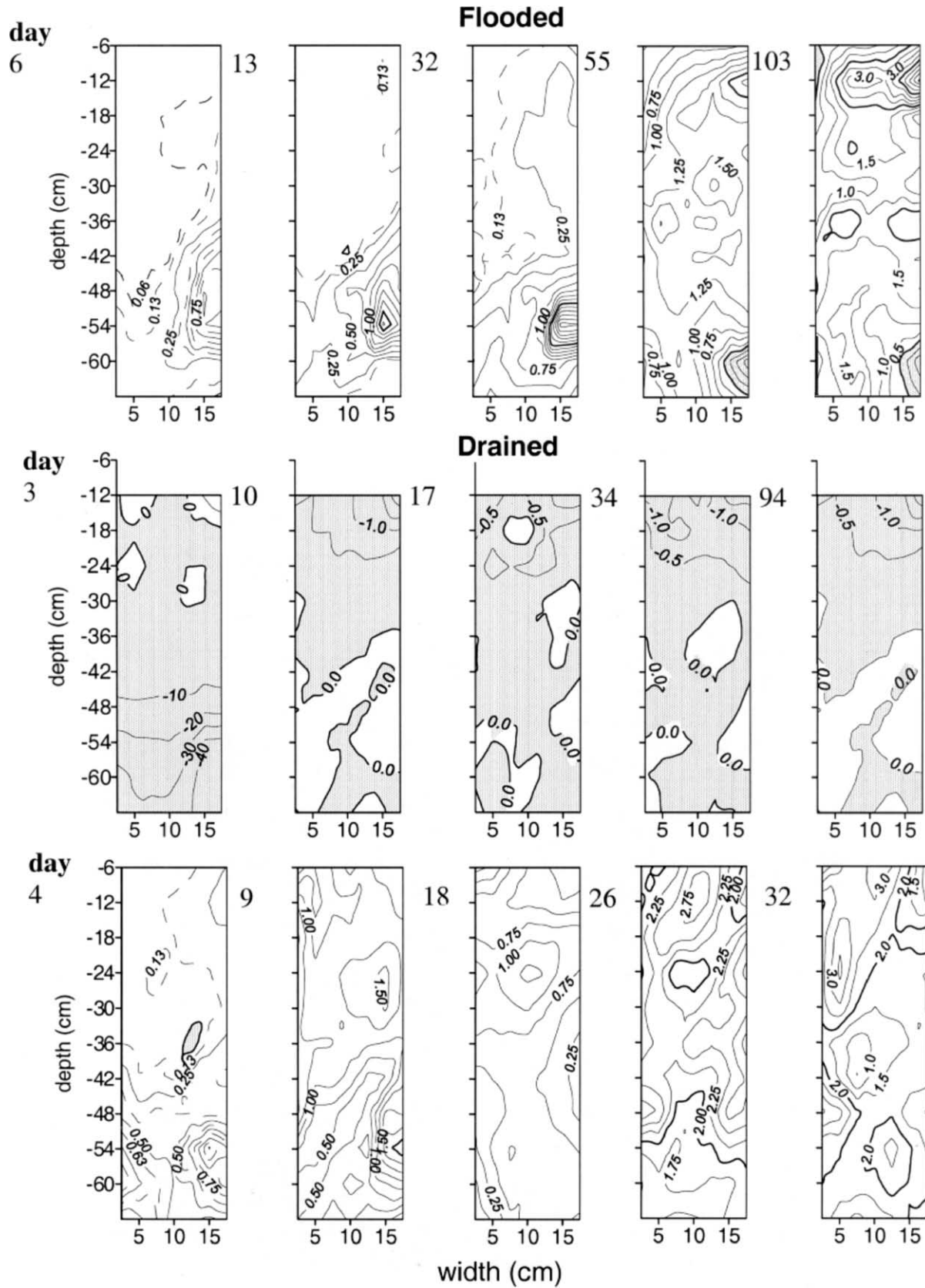


Fig. 4. Spatio-temporal patterns of net CH_4 production ($\text{nmol cm}^{-3} \text{d}^{-1}$) after flooding, subsequent drainage and repeated flooding in the grid core. The time scale refers to the time after disturbance. Between day 34 and 94 (drained) the temperature was increased from 12/8 to 20–22 °C. Note the development of CH_4 production hot spots.

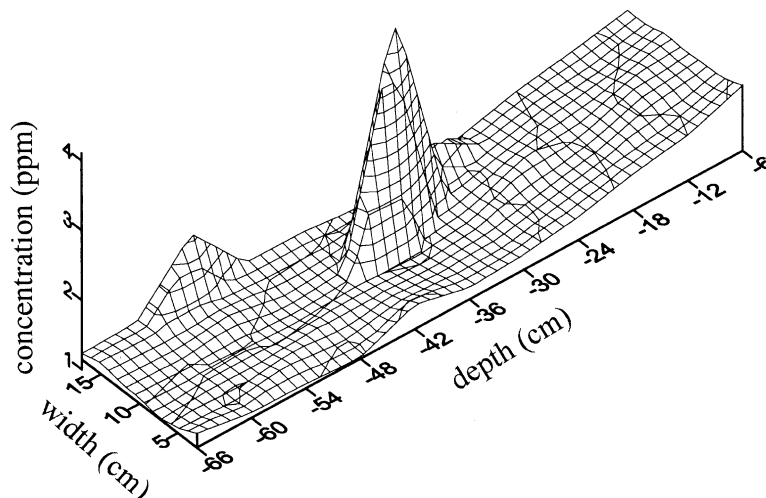


Fig. 5. Concentrations of CH_4 in the gas-phase during unsaturated conditions 34 days after drainage.

concentrations reaching $70 \mu\text{mol l}^{-1}$ (Fig. 3). In the more shallow peat CH_4 production rates picked up only after day 32. After day 32 rates in the hot spot location began to decrease, and later on the maximum of production rates ($2\text{--}5 \text{ nmol cm}^{-3} \text{ d}^{-1}$) was recorded in the surface layers (Fig. 4, day 55 and 103). After the second flooding, with addition of SO_4^{2-} ($500 \mu\text{M}$) and at a temperature of ca. 20°C , the hot spot occurred again but in much weaker intensity. Also the CH_4 production picked up more quickly in the rest of the core than after the first flooding at the lower temperature ($8/12^\circ\text{C}$). Towards the end of the saturated periods, CH_4 concentrations reached $40\text{--}160 \mu\text{mol l}^{-1}$ between 12 and 66 cm below water table (data not shown).

After drainage, the estimated in situ CO_2 production rates initially reached $1000\text{--}5000 \text{ nmol cm}^{-3} \text{ d}^{-1}$ in the surface layers and then decreased to $350\text{--}1400 \text{ nmol cm}^{-3} \text{ d}^{-1}$ at day 34 (Fig. 2). Increasing the temperature by $10\text{--}12^\circ\text{C}$

resulted in an increase of the maximal rates to $3000\text{--}6000 \text{ nmol cm}^{-3} \text{ d}^{-1}$ (Fig. 2). At larger depths (36–66 cm) rates were much smaller ($0\text{--}250 \text{ nmol cm}^{-3} \text{ d}^{-1}$) than in the upper layers. Methane was consumed in most of the peat core, at $0\text{--}1.8 \text{ nmol cm}^{-3} \text{ d}^{-1}$, but in some locations CH_4 continued to be produced. This was clearly indicated by the elevated concentrations of CH_4 at some sampling ports in the peat matrix (Fig. 5). Since hot spot locations, such as in Fig. 5, were excluded from the diffusive rate calculation due to the uncertainty about the water content in this location, CH_4 production rates as shown in Fig. 4 might be an underestimate of the CH_4 production rate in the unsaturated core.

H_2S was detectable but remained below $1 \mu\text{mol l}^{-1}$ during the first flooding event with $104 \mu\text{M SO}_4^{2-}$ solution. During the second flooding event, with addition of $500 \mu\text{M SO}_4^{2-}$, H_2S began accumulating 13–18 days after flooding

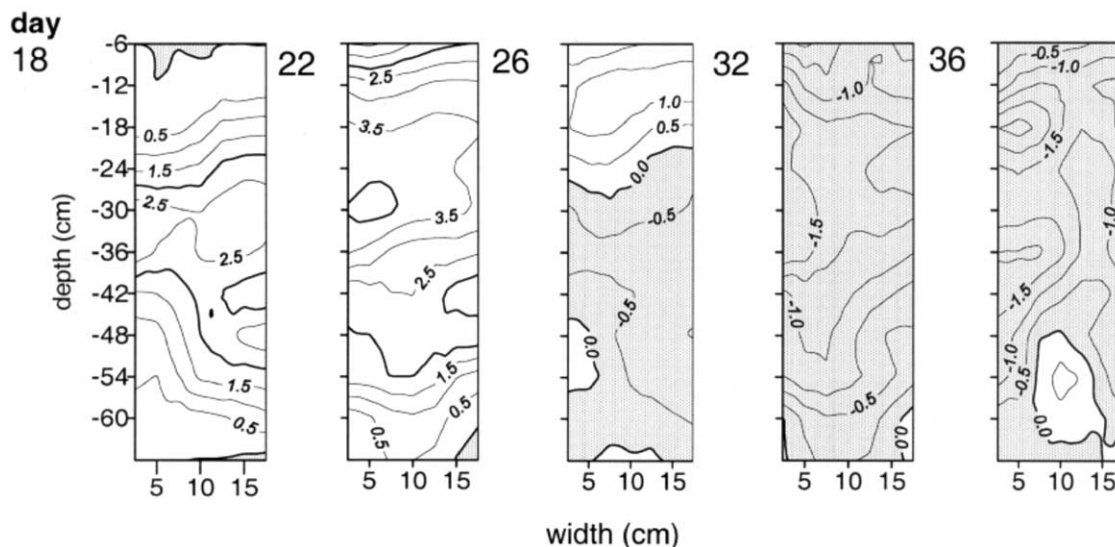


Fig. 6. Spatio-temporal patterns of net H_2S production ($\text{nmol cm}^{-3} \text{ d}^{-1}$) after the second flooding. Before day 18, no H_2S was detectable, net rates were therefore zero and are not shown. The time scale refers to the time after flooding.

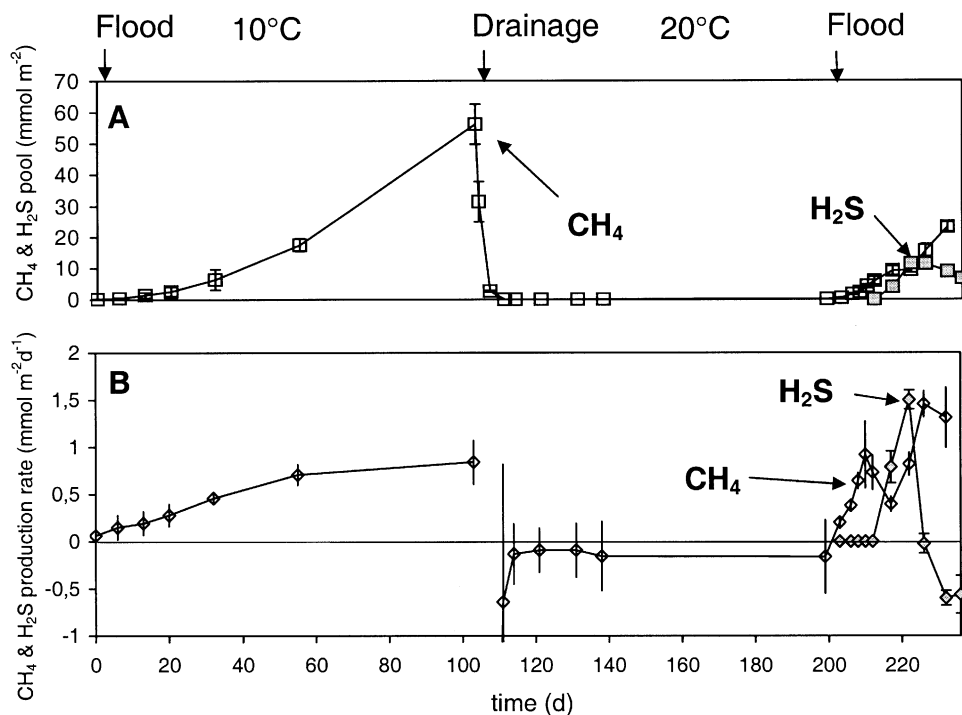


Fig. 7. The aggregated effect of water table fluctuation on CH₄ dynamics. Panel A shows measured pool sizes and panel B depicts calculated production of CH₄ and H₂S. Error bars represent standard deviations of the seven vertical rows of samplers over which production was depth-integrated. At day 150 the temperature was changed from 12/8 to 20–22 °C.

and net production rates reached 3–4 nmol cm⁻³ d⁻¹ at day 22 in the upper 30 cm of the peat core (Fig. 6). After day 22, H₂S was initially consumed in the deeper parts of the core and later at all depths (Fig. 6). Concentrations of H₂S peaked at 32 μmol l⁻¹ and declined to 0.5–10 μmol l⁻¹ by day 32, when the added SO₄²⁻ (500 μmol l⁻¹) had almost been fully consumed and SO₄²⁻ concentrations were between 10 (30–42 cm depth) and 30 μmol l⁻¹ at the water table.

A cumulative suppressive effect of SO₄²⁻ reduction that could not be inferred from the in situ-rates on the centimeter scale was suggested when the data set was integrated to an aerial basis (Fig. 7B). Net H₂S production began between day 210 and 217. At this time CH₄ production rates had decreased compared to before. At day 226 net H₂S production rates became negative and CH₄ production reached a new maximum (Fig. 7B). With respect to the pool of dissolved H₂S and CH₄ these changes were, however, barely visible (Fig. 7A).

There was no evident correlation between the in situ process rates and the distribution of Eriophorum roots or visual structural characteristics of the peat.

3.2. Potential CO₂ and CH₄ production rates

Anaerobic potential CO₂ production from peat samples taken from the core was largely laterally stratified (Fig. 8) and reached up to 600 nmol cm⁻³ d⁻¹. The ratio of the sum

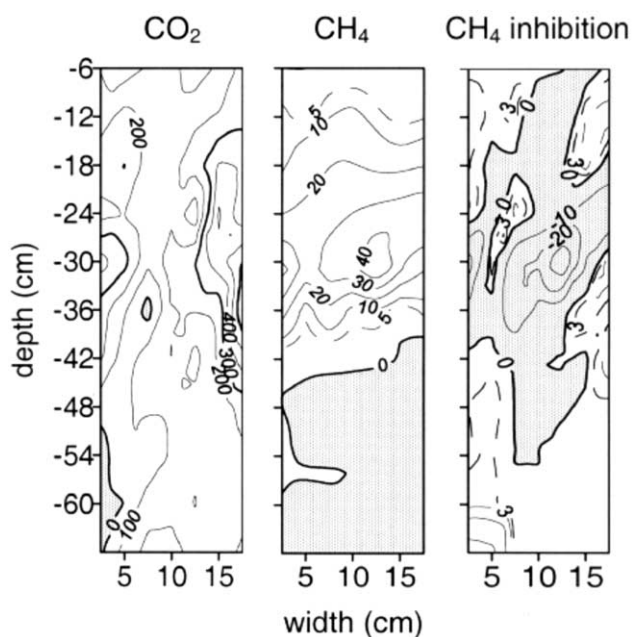


Fig. 8. Potential production rates of CO₂ and CH₄ (left-hand and central panels) and effects of SO₄²⁻ addition on potential production of CH₄ (right-hand panel) in anaerobic incubation experiments with peat from the grid core. Negative rates in the SO₄²⁻/CH₄ experiment indicate inhibition. Potential production rates were calculated on a volumetric basis, using separately determined average bulk densities of the peat.

of potential rates to in situ rates in the core was 5.5:1. Average in situ and potential CO₂ production rates from the port locations were not correlated.

Anaerobic potential CH₄ production was mainly stratified with depth and rates increasing from 0 to 25 nmol cm⁻³ d⁻¹ in the surface layer to 25–55 nmol cm⁻³ d⁻¹ at 24–30 cm (Fig. 8). At a depth of 42 cm, rates were near 0 nmol cm⁻³ d⁻¹ and below that depth, CH₄ was consumed from the headspace of the incubation vessels at rates between 0 and -5 nmol cm⁻³ d⁻¹ (Fig. 8). The sum of potential CH₄ production rates were larger than in situ rates by an average factor of 7, and potential rates were only weakly correlated with in situ rates (Pearson, $r = 0.18$, $*P < 0.05$). BES addition completely suppressed both CH₄ production and consumption.

In the incubations, SO₄²⁻ addition had spatially differentiated effects on the potential CH₄ production rate (Fig. 8). When the profile was separated in three vertical horizons, SO₄²⁻ addition significantly stimulated CH₄ production from 132 ± 147 to 201 ± 161 nmol g⁻¹ d⁻¹ close to the surface, and reduced it from 418 ± 210 to 256 ± 141 nmol g⁻¹ d⁻¹ in the zone below (paired *t*-tests, $*P < 0.05$). (These data were not converted to a volume basis to maintain the accuracy of rates.) These differences were significant because the effect was fairly homogeneous within the zones, despite rates being different between port locations. A stimulatory effect of SO₄²⁻ on CH₄ production apparently also occurred deeper in the profile (Fig. 8).

4. Discussion

The effect of water table fluctuations on CO₂ and CH₄ emissions from peat soils has been examined using peat cores (Aerts and Ludwig, 1997; Moore and Dalva, 1993), and there have been a few studies that have investigated the effect of fluctuations by incubating peat samples (Kettunen et al., 1999; Öquist and Sundh, 1998). Only in the latter studies were CO₂ and CH₄ production rates determined within the peat. There have been few attempts, if any, to characterize the in situ response of CO₂ and CH₄ production rates to disturbance, and to relate in situ rates to rates obtained from incubations of extracted peat. To undertake this is important, because exchange studies cannot localize the sources of variability in exchange rates, and because carefully controlled incubation studies cannot fully account for the complexity of factors that might influence production rates in situ.

As demonstrated for other environments, active populations of methanogens and SO₄²⁻ reducers can survive unsaturated conditions for extended periods of time (Peters and Conrad, 1996). Our spatially detailed approach revealed, in addition, that the activity remaining after drainage and flooding is locally very variable: some locations in the peat core, for instance, showed CH₄ production under unsaturated conditions. Also, CH₄

production after flooding began immediately in a distinct location at larger depths (Figs. 3 and 4). The in situ production rate at this location decreased later, possibly due to the exhaustion of substrate, and potential rates of CH₄ and CO₂ production were very small at that location after the experiment (Fig. 8). Methane production rates in the upper part of the profile began much later, after 10–30 days, but developed much faster rates (Fig. 4), probably due to the more decomposable quality of the substrate. A better substrate quality in these layers was indicated by the large potential CO₂ production rates (Fig. 8).

The occurrence of in situ CH₄ production rate maxima in different locations (Fig. 4) suggests that, under transient conditions, fairly large in situ differences in rates and fluxes might occur on the centimeter scale independently of the potentials for CO₂ production, which might be taken as an indicator of potential decomposability. These results suggest that after disturbance and in situ, rates might not relate as strongly to the spatial distribution of decomposable organic matter as they do in incubation studies (Wachinger et al., 2000).

Öquist and Sundh (1998) demonstrated that the onset of methanogenesis in surface layers of peat soils is delayed but not inhibited by oxic periods, a pattern that was also observed in this study (Fig. 4). In bacterial suspensions, oxygenation reduces potential production rates but not the viability of cells, and 0.5–10% of the active biomass might survive desiccation (Fetzer et al., 1993). Mayer and Conrad (1990) noted that the initiation of CH₄ production in paddy soils is retarded when soil is stored under aerated, but moist conditions. Our results also suggest that deeper in the peat (40–70 cm) under in situ conditions, methanogenic populations are less impaired by unsaturated conditions than in the surface layers even if they are more poorly adapted to aeration (Öquist and Sundh, 1998). This is explained by the maintenance of anaerobic pockets deep in the peat due to larger water potentials and small unsaturated diffusion coefficients. The maintenance of such anaerobic pockets in the peat was suggested by CH₄ production in some areas of the unsaturated peat core (Fig. 5).

The existence of CH₄ production hot spots after flooding is an interesting phenomenon, but is quantitatively unimportant compared to the production within depth increments, or the later, less variable, production in shallow layers, which contributed most to the accumulation of CH₄ in the mesocosm (Fig. 7). The lack of correlation between CH₄ concentrations and rates and the distribution of Eriophorum roots shows that, at this scale, roots do not control CH₄ production and consumption. Root density was very small in this experiment, and individual graminoid roots control biogeochemical processes only on the scale of a few millimeters (Wind and Conrad, 1997).

After flooding, a combination of initial conditions, such as pre-flooding water potentials and substrate availability, probably controlled CH₄ production rates in the Sphagnum-dominated peatland soil. Also, substrate availability for CH₄

and DIC production seemed to be enhanced after flooding at depths at which incubation-scale potential production rates are very small. This could be a consequence of advective DOC transport during flooding, leading to C mineralization deeper in the peat (Chanton et al., 1995). Even without such transport, however, CO₂ production rates might increase up to a factor 200 when stabilized, usually anaerobic peat from larger depths is incubated in flasks under aerobic conditions (Hogg, 1993). Thus, enhanced rates of CH₄ and DIC production may primarily be caused by enhanced substrate release due to redox-induced chemical breakdown and enhanced recycling of biomass (Aller, 1994; Kieft et al., 1987). Mineralization pulses after disturbance have also been observed in drying-wetting experiments with soils or as a result of regularly changing water tables (Aerts and Ludwig, 1997; Bottner, 1985; Clein and Schimel, 1994; Kieft et al., 1987), although they have not always led to an overall increase in C mineralization rates (Clein and Schimel, 1994).

In our study, after the initial mineralization pulse, the calculated in situ DIC production was 5–6 times larger under unsaturated and aerobic conditions than under saturated and mostly anaerobic conditions, but this ratio is poorly constrained because of uncertainty about production rates in the unsaturated peat. It is similar, however, to results from several other incubation and column studies in which aerobic–anaerobic ratios typically ranged from 1.2 to 6 (Aerts and Ludwig, 1997; Moore and Knowles, 1989; Moore and Dalva, 1993; Öquist and Sundh, 1998; Updegraff et al., 1996; Yavitt et al., 1997).

Anaerobic DIC consumption, without an equivalent CH₄ production due to CO₂ reduction, occurred in the peat core (Fig. 2), in incubations after 7 days (not shown), and in other incubation experiments with these peats (C.L. Roehm, pers. communication). It is not clear what process is responsible for this pattern. It could possibly be explained by homoacetogenesis of H₂ and DIC to acetate. Observed large concentrations of DIC and H₂ (0.1–4 μmol l⁻¹, Blodau unpublished data) could make this a thermodynamically feasible and competitive process (Conrad, 1999; Conrad et al., 1989; Dieckert and Wohlfahrt, 1994). Anaerobic CO₂ consumption could then be understood as a thermodynamically controlled negative feedback mechanism in the mineralization process. Analyses of intermediate organic decomposition products were performed in one profile of the grid core on the last sampling date (courtesy R. Roy, Biotechnology Institute, Montreal) but did not show a substantial accumulation of acetate and other fatty acids. Only one sample, at a depth of 36 cm, was above the detection limit of 50 μmol l⁻¹ and this only for acetate. More data, however, would be necessary to refute or confirm the above hypothesis.

Reduction of methanogenesis due to atmospheric SO₄²⁻ deposition and internal cycling of S has been investigated in detail in several other studies (Nedwell and Watson, 1995; Segers and Kengen, 1998; Shannon and White, 1996;

Watson and Nedwell, 1998; Wieder et al., 1990). It has usually been assumed that methanogenic and sulfidogenic activity are competitive (e.g. Nedwell and Watson, 1995). If SO₄²⁻ is sufficiently available, SO₄²⁻ reduction dominates in such a scenario, as it is thermodynamically and kinetically favored (Achnich et al., 1995; Kristjanson et al., 1982). The lower SO₄²⁻ concentration threshold necessary for sulfate reducers being more competitive than methanogens has not been quantified in peatlands, but concentrations of 40 μmol l⁻¹ might be sufficient (Nedwell and Watson, 1995). In freshwater sediments it was demonstrated that sulfate reducers succeed at concentrations of 60–100 μmol l⁻¹ (Lovley and Klug, 1983). In this study the sulfate concentration (500 μmol l⁻¹) in water added to the unsaturated peat was well above this value, and also well above concentrations in rain, but not unrealistically large, since SO₄²⁻ concentrations in oligotrophic peatlands can temporarily increase to such concentration levels (Shannon and White, 1996).

Despite these SO₄²⁻ concentrations, which should be large enough to reduce rates of methanogenesis, the effect of SO₄²⁻ addition on CH₄ production rates was overall only slightly negative (–11%, not significant) in incubations. The response was also spatially complex: when all data were aggregated, in situ net CH₄ production rates were at a low when net H₂S production rates were at a maximum (Fig. 7B). The spatial pattern of H₂S production (Fig. 6), however, was very variable and not correlated to the pattern of CH₄ production (Fig. 4). Moreover, in the incubations the response of CH₄ production to SO₄²⁻ addition was positive or negative depending on the location within the profile (Fig. 8). In the surface layer, addition of SO₄²⁻ mostly stimulated CH₄ production. Deeper in the peat, CH₄ production was reduced by SO₄²⁻ addition.

This locally reversible response of potential CH₄ production rates to the addition of SO₄²⁻ on the centimeter scale is a finding which, to our knowledge, has only once been documented for peatlands (Yavitt et al., 1987). It suggests that the microbial communities differed in these zones and that methanogens and SO₄²⁻-reducing bacteria did not compete for substrate everywhere. This interpretation is confirmed by the fact that the suppression of SO₄²⁻ reduction by MoO₄²⁻ also strongly reduced methanogenesis in the upper layers whereas the effect of MoO₄²⁻ on CH₄ production rates was smaller deeper in the peat (Blodau, unpublished data).

It may be that thermodynamic and kinetic controls, as they are found in carefully controlled incubation experiments, are of little importance in the surface layers of peatlands that do not approach a steady state with respect to biogeochemical processes. Response times of sulfidogenic and methanogenic populations, even under optimal nutritional conditions, can be on the order of months (Raskin et al., 1996). Some SO₄²⁻ reducers can survive and even be more competitive in the absence of SO₄²⁻, probably due to their metabolic flexibility allowing them to gain energy by

acetogenesis and fermentation (Raskin et al., 1996). A 'cryptic presence' of SO_4^{2-} reducers has also been postulated by others (Conrad, 1999). The zonation found in this study may be an adaptation to SO_4^{2-} entering the peatland from the moss surface and being more rapidly recycled in the surface layers, for example due to small water table fluctuations and diurnal fluctuations of O_2 penetration from photosynthetic activity (Frenzel et al., 1992).

In the surface layers of peatlands, exposed to redox oscillations and SO_4^{2-} pulses from remineralization of organic S and reoxidation of iron sulfides (Bayley et al., 1986; Devito and Hill, 1999; Mandernack et al., 2000; Shannon and White, 1996), a coexistence between methanogenic and sulfidogenic activity may thus occur, whereas deeper in the peat, this would not be the case. This would be in agreement with ecological disturbance theory (Buckling et al., 2000). If common, a variable relationship between sulfate reducers and methanogens might help explain the contradiction that SO_4^{2-} reduction predominates in some oligotrophic peatlands (Nedwell and Watson, 1995) and coexists with methanogenesis in others (Wieder et al., 1990).

5. Conclusions

Disturbances, such as water table draw-downs and SO_4^{2-} pulses, alter biogeochemical patterns and net C production rates in peat soils. This investigation demonstrated that the production patterns and their controls are highly variable in space and time during a water table fluctuation. Under such conditions the often reported vertically oriented production patterns might be overruled by more complex temporal patterns, which are probably controlled by the pre-disturbance conditions in the peat. The net effect of disturbances on C dynamics will therefore be difficult to predict. A better quantitative understanding of the impact of environmental disturbances on biogeochemical cycling in peatlands may depend on a better appreciation of microbial dynamics, and on the factors that control the bioavailability of substrates after the disturbance. Our results suggest that deeper in the peat (40–70 cm) under in situ conditions, methanogenic populations are less impaired by unsaturated conditions than in the surface layers, and that at these depths after flooding the substrate availability for CH_4 and DIC production is significantly enhanced. They also suggest that methanogens and SO_4^{2-} -reducing bacteria were non-competitive in the surface layer of the peat soil, which might explain contradictory findings from field studies.

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