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# Mass spectrometric monitoring of gas dynamics in peat monoliths: effects of temperature and diurnal cycles on emissions

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**Abstract**

Membrane inlet mass spectrometry was used to monitor dissolved gas concentrations and gas exchange rates of $CO_2$, $CH_4$ and $O_2$ in peat cores from three very different locations in the Northern Hemisphere: Kopparås Mire (Sweden), Hestur Site (Iceland), and Ellergower Moss (Scotland). With an increase of temperature gas solubilities are reduced, and due to additionally increased microbial activities higher gas emission rates for both $CO_2$ and $CH_4$ were observed. Experimental alterations of temperature and photosynthetically active radiation (PAR) also drastically effect daytime carbon dioxide emission rates as a result of changes in microbial and plant physiology. The impact of ebullition on gas emission rates was indicated by continuous measurements of gas concentrations in the headspace of Icelandic and Swedish cores using two different experimental setups. For methane, up to $\frac{2}{3}$ of the total emission from cores from both sites is released by ebullition. Total gas emission rate measurements in this study were similar for both experimental setups, and revealed gas effluxes comparable with field measurements for Scottish and Icelandic peat.

*Keywords:* Methanogenesis; Methane oxidation; Membrane inlet mass spectrometry; Peat

## 1. Introduction

Northern wetlands account for approximately 3% of total land area in the Northern Hemisphere (Clymo, 1987), and contain one-third of the global terrestrial carbon pool accumulated over millennia by slow plant decomposition processes (Gorham, 1991). Recently, the importance of exchange of gases between terrestrial environments and the atmosphere has been studied with special reference to its impact upon climatic change (Bartlett and Harriss, 1993; Brimblecomb, 1998). Global warming would markedly increase the release of these potent greenhouse gases from wetlands, as $Q_{10}$ values $>3$ have been shown for both $CO_2$ and $CH_4$ efflux processes (Dunfield et al., 1993; Krumholz et al., 1995; Thomas et al., 1998).

Gas emission from wetlands is a complex function of surface vegetation and the circadian-controlled physiology of plant cover, nutritional sources, microbial activity, temperature, illumination and water levels (Thomas et al., 1998; Dedysh and Panikov, 1997; Moore

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and Roulet, 1993; Mikkelä et al., 1995; Whiting and Chanton, 1993; Conrad, 1996; Joabsson et al., 1999; King and Schnell, 1994; Fechner-Levy and Hemond, 1996). The potential impact of atmospheric change, particularly involving cycles within the terrestrial component of the biosphere, remain somewhat undefined (Conrad, 1996). The dynamics of gas emissions from wetlands are complicated further by the potential for increased atmospheric $CO_2$ levels to result in increased $CH_4$ emission rates.

We have previously applied the technique of membrane inlet mass spectrometry (MIMS) to studies of peat and soil cores (Lloyd et al., 1998; Beckman and Lloyd, 2001; Sheppard and Lloyd, 2002a-c). In this study we investigate how the complex interaction of different factors, including soil structure, surface vegetation, and depth of the oxic zone, affects ecosystem function in terms of ebullition, potential for methanotrophic/methanogenic processes and, ultimately gas emission rates ($CO_2$ and $CH_4$). Also we monitor effects of temperature and light/dark cycles on gas emissions from peat to atmosphere, in cores from three different locations. This information can improve understanding of gas dynamics in different peat types and the potential effect of climate change.

## 2. Material and methods

### 2.1. Peat cores

Gas emissions were examined from water-saturated peat cores (mesotrophic Kopparås, Mire Central Sweden in 1998; the less minerotrophic Hestur site, Iceland in 1999; and the ombrotrophic Ellergower Moss site (New Galloway, Scotland) in 1994. These differed in their covering surface vegetation. The water-logged Scottish cores (Hayward and Clymo, 1982) were dominated by vascular plant species (Eriophorum, Molinia, Carex and Calluna); the Swedish core was covered with a thick layer of mosses (*Sphagnum magellanicum*) and with a sedge (*Eriophorum angustifolium*), and the Icelandic cores with sparsely vegetated Eriophorum spp. shoots. Icelandic and Scottish peat cores were extracted using PVC cylinders (20 cm diameter, 35 cm depth), and Swedish cores were collected in aluminium containers (25 × 25 cm, 26 cm depth). In each case cores were sealed at the base immediately after removal, transported to Cardiff in cooler chests and maintained in constant temperature growth chambers (12 h light/dark cycle). Twelve 58 W fluorescent tubes (Thorn White Pluslux 3500), 50 cm above the soil surface were used. Photosynthetically active radiation (PAR) was measured at $110\,\mu mol\,s^{-1}\,m^{-2}$, using an integrated/quantum/radiometer phomometer (LI-188B equipped with a LI-190SB Quantum Sensor, LI-COR Inc.); an additional light source gave PAR values of $170\,\mu mol\,s^{-1}\,m^{-2}$. Experiments were carried out in a controlled-temperature chest freezer (21 °C) with a small orifice drilled in the perspex lid for the MIMS probe. Temperature probes were employed set at 3 cm depth and in the headspace. Multiple cores were collected (3–9) and replicate experiments ($\geqslant 3$) were carried out. Results presented are representative of data from multiple investigations.

### 2.2. Membrane inlet mass spectrometry (MIMS) system

Gases were monitored using a quadrupole mass spectrometry system (HAL 2/201, Hiden, Warrington, UK) (Benstead and Lloyd, 1994, 1996). A gas inlet probe, attached to the MS-system, consisted of stainless steel capillary tubing (1.56 mm OD, 0.5 mm ID, 100 cm length) which had an entry port (50 μm diameter) for gases 0.4 cm from the tip. The orifice was covered with a sleeve of silicone rubber (100 μm thickness). Calibration procedure was performed as previously described, to eliminate any ambiguity associated with the rate and magnitude of the instruments response (Lloyd et al., 2002; Sheppard and Lloyd, 2002a). Solubility data was from Wilhelm et al. (1977).

### 2.3. Monitoring gas exchange rates

Gas exchange rates in the headspace of peat cores were monitored using the same MIMS-system. The gas phase of the headspace was contained by a glass funnel (volume: 600 mL) in the case of Icelandic, and Scottish cores, and an perspex cover for the Swedish peat cores (volume: 6 L).

Two experiments were conducted in order to monitor changes in gas concentrations in the headspace of peat cores. In the experimental setup I, a static chamber closed system method was used adapted from well defined techniques (Gupta and Singh, 1981; Bowden et al., 1993; Toland and Zak, 1994; Marra and Edmonds, 1996). The MIMS probe was placed under the appropriate cover approximately 5 cm above the surface of the peat cores. A small leak (≈2 mm) in the headspace at the entrance port for the probe allowed for pressure compensation. Gas exchange rates for $CO_2$ and $CH_4$ between the peat and atmosphere were derived from continuous measurements of gas concentrations in the headspace of peat cores from 1.5 to 11 h. After each experiment the headspace and the incubator were manually flushed with ambient air to prevent moisture saturation of the chamber and build up of $CO_2$. In experimental setup II, a dynamic chamber open system method was used based on mehtods which have been used in numerous studies of soil gas dynamics (Kucera and Kirkham, 1971; Ewel et al., 1987; Hall et al., 1990; Norman et al., 1992; Luo et al., 1996). Gas exchange rates in a constant air stream through the headspace were monitored over a period of up to 6 days at 18.0 ± 0.3 °C. The air inlet was near the peat surface, and the probe of the MIMS-system was attached in the gas outlet (8 mm diameter) at the top of the headspace. A small fan (Papst, 12 V DC, operated at 3 V DC) near the surface of the cores ensured homogenous distribution of gases in the headspace. Measurable differential gas efflux signals were obtained with an inflow of 30 mL s$^{-1}$ (approximately one air change per minute). Air flow was controlled by varying the fan speed. Half hourly averages of ecosystem $CO_2$ and $CH_4$ flux were calculated by multiplying the inlet flow rate by the difference between inlet and outlet gas concentrations and then dividing by unit ground area (Lund et al., 1999). Net C uptake was calculated by integration of flux measurements over time.

## 3. Results

### 3.1. Headspace measurements of gas exchange rates: experimental setup I

Continuous monitoring of gas concentrations in the static headspace of Swedish and Icelandic peat over periods of up to 12 h (Fig. 1) revealed the effect of ebullition on total gas emission rates. Initial emission rates calculated for the first hour derived from 4 to 6 separate measurements are shown in Table 1. Ebullition rates are presented as an average per hour of all the single events during separate experiments. Icelandic cores released up to twice as much $CH_4$ as gas bubbles than is released by diffusion or gas transport through plants. In the Swedish peat ebullition occurred as an intermittent event on average once every 2 hours, once

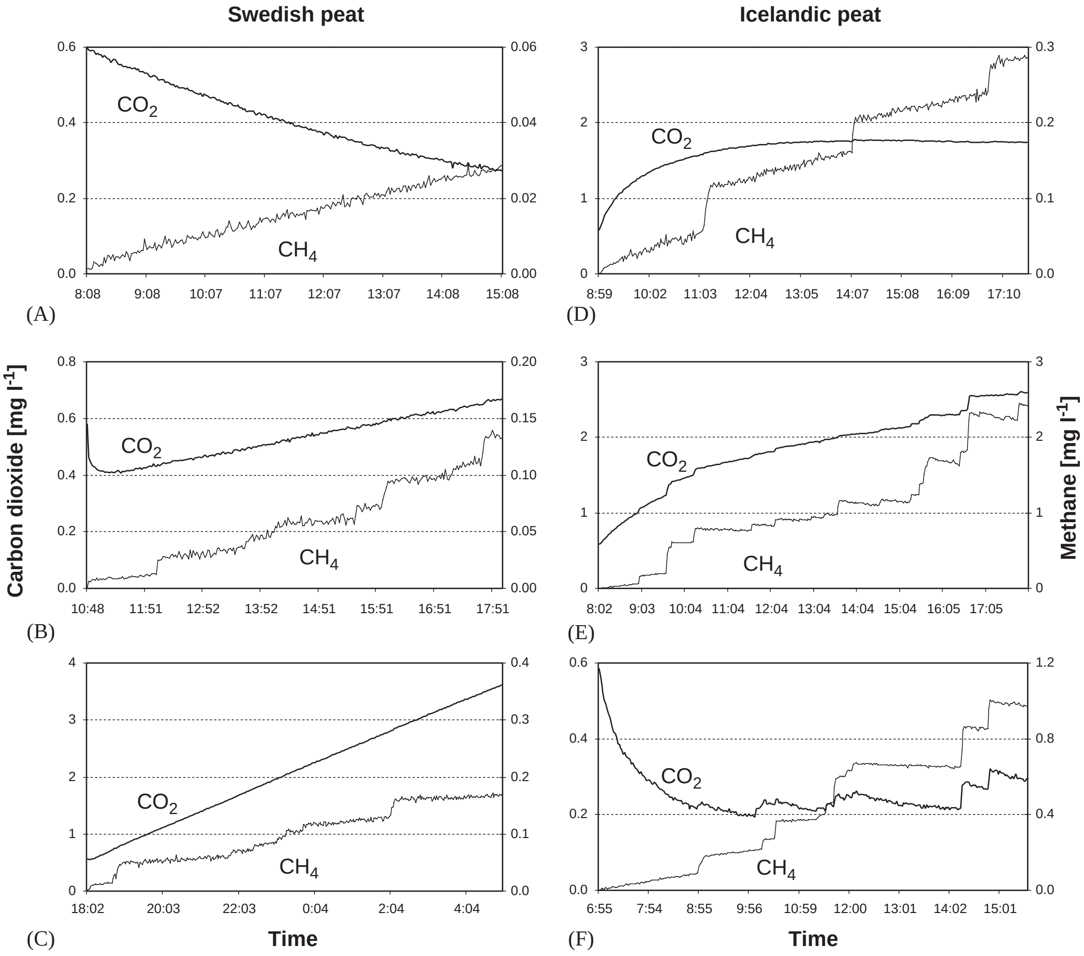

Fig. 1. Typical changes in headspace gases in cores of Swedish and Icelandic peat: (A) 9.4 ± 0.2 °C and (B) 20.3 ± 0.1 °C during daytime; (C) (20.3 ± 0.1 °C) during night in all cores and at all temperatures; (D) 9.3 ± 0.2 °C, (E) 15.3 ± 0.2 °C, and at subsequently decreased temperatures (F) 14.7 ± 0.2 °C. Steps in the graphs indicate the release of gas bubbles into the headspace.

Table 1
Gas exchange measured in the headspace above peat monoliths from mesotrophic Kopparås Mire (Sweden), minerotrophic Hestur Site (Iceland), and ombrotrophic Ellergower Moss (Scotland) during dark and light (85 μmol $s^{-1}$ $m^{-2}$) phases: *experimental setup I*

| | | | Diffusion rate[a] | | Ebullition rate[b] | |
|---|---|---|---|---|---|---|
| Source of cores | Phase | Temp (°C) | $CO_2$[c] (mg $h^{-1}$ $m^{-2}$) | $CH_4$ (μg $h^{-1}$ $m^{-2}$) | $CO_2$ (μg $h^{-1}$ $m^{-2}$) | $CH_4$ (μg $h^{-1}$ $m^{-2}$) |
| Sweden | Dark | 9.6 | 30.3 (3.0) | 592 (0) | n.o. | n.o. |
| | | 14.8 | 31.4 (1.6) | 592 (0) | n.d. | 529 (261) |
| | | 20.3 | 41.1 (4.3)[d] | 1973 (342) | 1221 (464) | 1068 (489) |
| | Light | 9.6 | −14.8 (0.8)[d] | 606 (30) | n.o. | n.o. |
| | | 14.8 | −19.8 (0.4) | 888 (419) | 419 (333) | 1176 (936) |
| | | 20.2 | 5.5 (0.6)[d] | 888 (342) | 1302 (170) | 2481 (334) |
| Iceland | Dark | 9.3 | 21.6 (2.3) | 624 (300) | n.o. | n.o. |
| | | 15.3 | 28.8 (12.6) | 2163 (577) | 2343 (56) | 4133 (1203) |
| | | 14.7 | 40.8 (19,4) | 2019 (540) | n.d. | 2964 (466) |
| | | 20.3 | 45.7 (4.3) | 4182 (408) | 4640 (494) | 7690 (1411) |
| | Light | 9.3 | 21.9 (9.8)[d] | 1154 (220) | 289 (16) | 763 (56) |
| | | 15.3 | 26.2 (9.2)[d] | 2740 (288) | 2977 (730) | 7730 (2790) |
| | | 14.7 | −18.2 (5.7)[d] | 1803 (102) | 2374 (2117) | 8145 (5412) |
| | | 20.3 | 30.8 (5.9) | 4218 (827) | 4250 (823) | 8176 (344) |
| Scotland | Dark | 8.9 | 3.8 (2.6) | 341 (192) | n.o. | n.o. |
| | | 13.2 | 19.8 (6.1) | 598 (375) | n.o. | n.o. |
| | | 12.2 | 22.5 (5.6) | 695 (652) | n.o. | n.o. |
| | Light | 8.9 | −0.9 (3.7) | 674 (574) | n.o. | n.o. |
| | | 13.2 | 18.9 (15.2) | 562 (426) | n.o. | n.o. |
| | | 12.2 | −16.8 (8.0) | 271 (157) | n.o. | n.o. |

Diffusion rates plus ebullition rates add up to total emission rates; figures in parentheses indicate (± S.D.); n.d.: not detected; n.o.: not observed.

[a] During the 1st hour of each experiment ($n = 4$); comprises diffusion of gases from cores and plants.

[b] Values derived from single events during continuous measurements (for up to 12 h, see Fig. 2).

[c] Negative values indicate $CO_2$ uptake.

[d] For example see Fig. 2.

an hour in the Icelandic peat, and not at all in Scottish peat.

Carbon dioxide accumulated in the headspace during the dark-phase up to 4 mg–$l^{-1}$ (Fig. 1(C)). At all experimental temperature settings, net $CO_2$ uptake rates by plants reached a maximum on re-illumination and accounted for 35.5 ± 4.2 mg $h^{-1}$ $m^{-2}$ in Swedish peat at the experimental PAR (85 μmol $s^{-1}$ $m^{-2}$). $CO_2$ emission depended on core temperature (Fig. 1(A) and (B), Table 1). In Icelandic peat cores maximal net $CO_2$ uptake rate was 21.4 ± 7.2 mg $h^{-1}$ $m^{-2}$ by plants on re-illumination at the elevated $CO_2$ concentrations that had accumulated in the headspace during nocturnal measurements.

For the Icelandic peat (Fig. 1(D)), $CO_2$ emission rates tailed off from those initially observed in experiments conducted during daytime to final uptake rates of 1.8 mg $h^{-1}$ $m^{-2}$ in the afternoon. In Fig. 1(E), observed $CO_2$ emission rates tailed off in ongoing experiments during daytime and revealed final emission rates of 1.6 ± 1.1 mg $h^{-1}$ $m^{-2}$ in the afternoon. In Fig. 1(F), microbial activities were decreased, indicated by high $CO_2$ uptake rates, and decreased $CH_4$ diffusion rates (Table 1). We calculated decreased production rates of 83 ± 5% $CO_2$ and 30 ± 25% $CH_4$; ebullition accounted for the large standard errors in this experiment.

### 3.2. Headspace measurements of gas exchange rates: experimental setup II

The effect of doubling photosynthetically active light intensity is demonstrated in Figs 2(A) and (B). Due to the thick vegetation cover of the Swedish core higher illumination resulted in increased $CO_2$-uptake, whereas the comparatively sparse vegetation on the Icelandic cores attained only lower carbon dioxide production

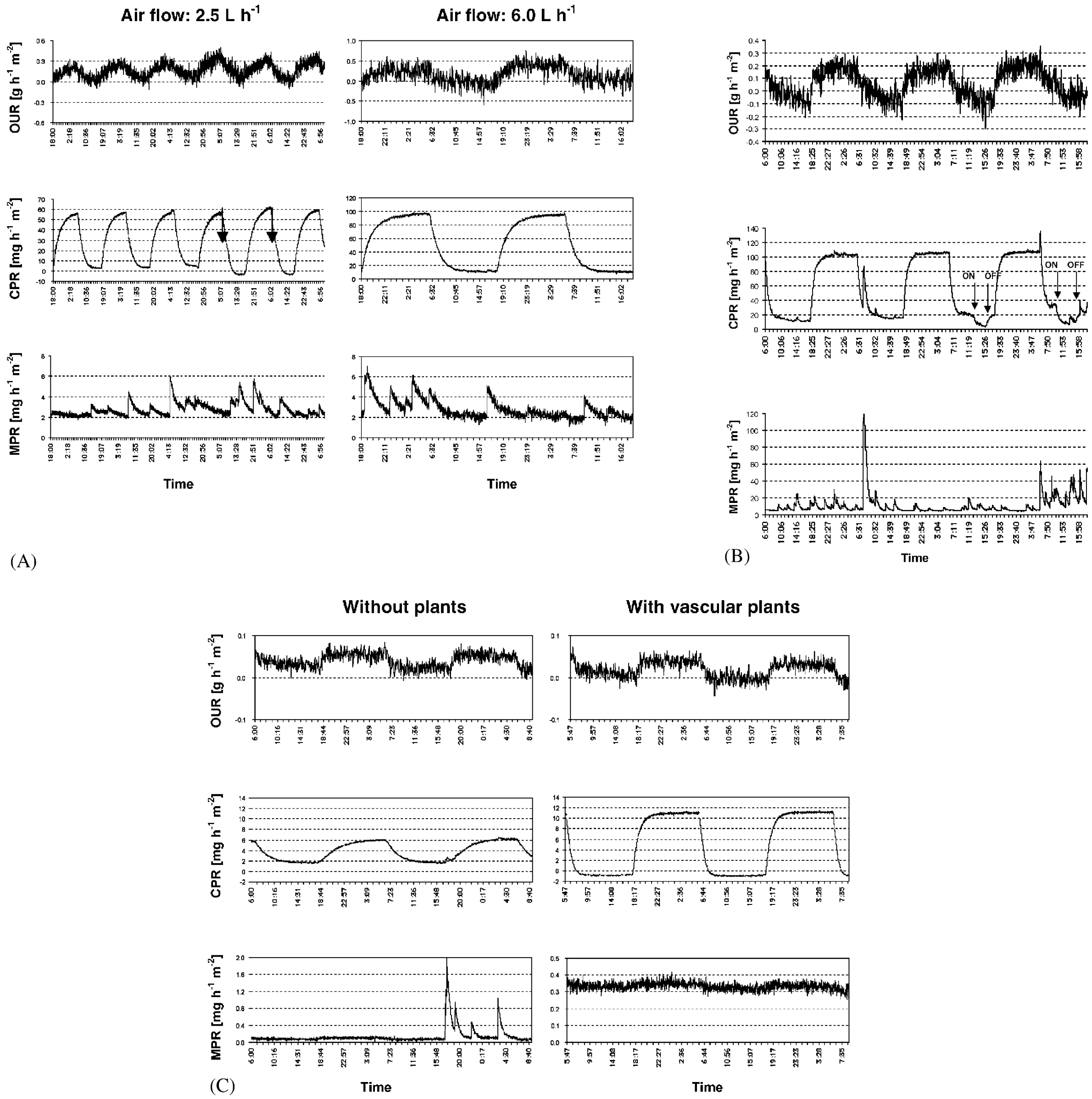

Fig. 2. Diurnal gas exchange rates of: (A) Swedish peat at 2.5 and 6 L h$^{-1}$ air flow, respectively (arrows indicate where an additional light source was switched on); (B) Icelandic peat at 600 mL h$^{-1}$ air flow (arrows indicate, where an additional light source was switched on and off); (C) water-logged Scottish peat, with, and without vascular plants at 600 mL h$^{-1}$ air flow. All experiments were at at 18 ± 0.2 °C. Graphs describe oxygen uptake rate (OUR), carbon dioxide production rate (CPR) and methane production rate (MPR).

rates. Different airflows through the headspace (Fig 2(B)) shows that gas volume of the headspace must be changed at least once an hour for reliable production rates (Table 1). Fig. 2(C) shows the effects of the presence of vascular plants on processes in peat. Gas emissions from different areas of a water-logged Scottish core were monitored; as this core showed patches of vascular plants, areas could be selectively measured by placing a glass funnel on sites on a single core with, and without plants. In replicated experiments, ebullition could be observed only on those sites on a core without plants.

## 4. Discussion

Changes in temperatures of the peat show effects on gas exchange rates both at night and at day caused by variations in microbial activities, as has been already shown for dissolved gas concentrations monitored at constant depth and temperature (Sheppard and Lloyd, 2002c; Beckmann and Lloyd, 2001). This effect is enhanced in situations where the surface is only partly covered with vegetation as for the Scottish (waterlogged) and the Icelandic peat (sprouting *Carex*). In contrast, the Swedish peat completely covered with a thick layer of mosses showed the highest photosynthetic activity per square-metre as indicated by high $CO_2$ uptake rates (Fig. 2(A)) or, at lowered temperature, comparatively low emission rates during illumination (Fig. 2(B)). Carbon dioxide uptake by plants during the day is much higher under natural conditions when photosynthetically active radiation exceeds the photon flux of $85\,\mu mol\,s^{-1}\,m^{-2}$ attained during headspace measurements in the laboratory.

Accumulating gas concentrations in the headspace of peat during these experiments may influence gas exchange rates over a period of more than 1 h. Higher than ambient $CO_2$ levels have been shown to increase the $CH_4$ efflux over much longer periods of several months (Saarnio et al., 1998), and will cause increased plant growth rates and photosynthetic activity. Although further work is necessary to confirm the impact of raised atmospheric $CO_2$ over such short time scales the latter effect would explain decreasing $CO_2$ emission rates in continuing light measurements from the Icelandic peat: maximal $CO_2$ uptake rates by photosynthetically active plants of $20.3 \pm 0.4\,mg\,h^{-1}\,m^{-2}$ were attained at approximately $0.08 \pm 0.01\%$ $CO_2$ in the headspace. In contrast, in the Icelandic peat, high $CH_4$ uptake rates ($4855 \pm 2532\,\mu g\,h^{-1}\,m^{-2}$) were observed when headspace concentrations exceeded the concentration of dissolved methane as a consequence of high methane ebullition rates (Fig. 2). This did not effect $CO_2$ production rates, as effluxes were almost constant at all temperatures during nocturnal measurements.

The deeper oxygen is transported into peat (e.g. open-meshwork of the decaying root material, vascular plants with hollow root systems), and the greater the thickness of the overlaying material (e.g. depth of oxic zone, layer of mosses, water table position), the greater the amount of methane is oxidised to carbon dioxide and the smaller the efflux of methane. Taking into account that falling water table levels in peat also increase the potential for $CH_4$ oxidation, wetland ecosystems have the ability to switch from being areas of net $CH_4$ production in spring to areas of net consumption after long periods of drought. Similarly, established thick plant covering can change peatlands from being areas of net $CO_2$ production during nights to net consumption during long summer days. However, ambient conditions at high latitudes, including low solar inclination, may still favour net respiration over net $CO_2$ uptake.

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