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CH_4 emission from a hollow-ridge complex in a raised bog: The role of CH_4 production and oxidation

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Abstract. The aim of this study was to correlate magnitude and controls of CH_4 fluxes with the microtopography and the vegetation in a hollow-ridge complex of a raised bog. High CH_4 emission rates were measured from hollows and mud-bottom hollows, while hummocks consumed atmospheric CH_4 at a low rate. The highest emissions were measured from plots with *Eriophorum vaginatum* and *Scheuchzeria palustris*. CH_4 emission ceased after *Scheuchzeria* had been clipped below the water table, indicating the importance of this aerenchymatic plant as a conduit for CH_4.

Peat in the upper catotelm of hollows was younger and less decomposed than in hummocks. Potential CH_4 production *in vitro* was higher and the methanogenic association was better adapted to higher temperatures in hollow than in hummock peat. Higher temperatures in hollows resulted in a stronger CH_4 source in hollows than in hummocks. Negative fluxes from hummocks indicated that even in wetlands methanotrophic bacteria exist that are able to oxidize CH_4 at atmospheric mixing ratios, and that oxidation controls CH_4 emission completely. The CH_4 mixing ratio was low in the acrotelm, but it increased within the catotelm. Comparing fluxes measured in static chambers with fluxes calculated from the porewater CH_4 profiles it was deduced that the zone of methane oxidation was located close to the water table.

In hollows, CH_4 production at *in situ* temperature was far higher than emission into the atmosphere, corresponding to an oxidation rate of nearly 99%. The CH_4 flux between the catotelm and the acrotelm of hollows was also higher than the emission, indicating the importance of CH_4 oxidation in the aerobic acrotelm, too. CH_4 microprofiles showed that CH_4 oxidation in mud-bottom hollows was confined to the topmost 2 mm, and that in *Sphagnum*-covered hollows CH_4 oxidation occurred at the lower edge of green *Sphagnum*-parts.

Introduction

During the Holocene, northern wetlands have accumulated huge amounts of organic carbon (Gore, 1983). However, peatlands are not only sinks for

atmospheric CO_2 but also sources for CH_4, another greenhouse gas. The contribution of CH_4 to climate forcing during the past 150 years has been about 35% of the climate forcing by CO_2 and about 22% of the forcing by all long-lived greenhouse gases (Lelieveld et al. 1998). Natural wetlands account for about 20% of global CH_4 emission (e.g. Bartlett & Harriss 1993; Matthews & Fung 1987). Emission rates of CH_4 from a wetland depend on two microbial processes, CH_4 production and CH_4 oxidation, and on physical accumulation and transport. CH_4 is produced by strictly anaerobic archaea and may be oxidized by a highly specialized group of proteobacteria that depends on CH_4 as the sole source of energy and carbon. Anaerobic CH_4 oxidation by an unknown microbial process has been repeatedly reported to occur in marine and saline habitats (Iversen & Joergensen 1985), but not from mires or other freshwater ecosystems (Nedwell & Watson 1995; Yavitt et al. 1988). Oxidation may be as important as production in controlling CH_4 emission. In rice fields, 30–90% of the CH_4 formed in the anoxic soil is oxidized while passing the oxic surface layer or the oxic rhizosphere of rice plants (Bosse & Frenzel 1998; Denier van der Gon & Neue 1996; Holzapfel-Pschorn et al. 1985). In freshwater sediments 80–90% of the CH_4 that is produced in deeper parts may be oxidized in a surface layer that is not deeper than a few millimeters (Frenzel et al. 1990; Kuivila et al. 1988).

Countless CH_4 fluxes have been measured during the past decades, but surprisingly few studies have focused on the underlying processes. The occurrence of CH_4 oxidation in peat has been demonstrated repeatedly (e.g. Dunfield et al. 1993; Krumholz et al. 1995; Watson et al. 1997; Yavitt et al. 1990) and some studies have addressed CH_4 oxidation in an ecological context (Fechner & Hemond 1992; Lien et al. 1992; Sundh et al. 1992; Sundh et al. 1995). However, the surface of bogs shows typically a small-scale pattern with hummocks, hollows, and mud-bottom hollows. Within the peat, the environment changes at the water table, with aerobic processes concentrated in the part above the water table (acrotelm: Ingram 1978) and anaerobic ones in the part below (catotelm). The acrotelm may be only a few millimeters to centimeters thick in hollows, but may be more than 20 cm in hummocks. The objective of our study was to clarify the role of CH_4 oxidation as a control of CH_4 emission in raised bogs with special attention to the influence of the microtopography. Our measurements cover the entire range from fluxes through processes to porewater CH_4, and from the microtopography (meter scale) down to microprofiles (millimeter scale).

Material and methods

Field measurements were carried out in June and July 1997 in Männikjärve Bog, a raised bog (320 ha, maximum peat depth 7.5 m, N 58°52.55′, E 26°14.87′) in Central Estonia. Männikjärve Bog is part of the Endla mire system (25,100 ha). Mire initiation in this area started during praeboreal when shallow parts of the ancient lake Endla became overgrown with Bryales-peat. In Männikjärve Bog, the eutrophic stage of the mire changed to oligotrophic during the Atlantic period when *Sphagnum magellanicum*, *Eriophorum-Sphagnum* and *Pinus-Sphagnum* peat started to form (Veber 1974).

Männikjärve Bog is a convex raised bog characterized by a well developed hollow-ridge and pool complex in its center. The moss layer was dominated by *S. fuscum* and *S. rubellum* on hummocks and ridges, and by *S. cuspidatum* and *S. balticum* in hollows and along the sides of the pools. The annual productivity of *Sphagnum* hummock communities is 1.4–2.4 g dryweight dm^{-2}, that of hollows 0.9–1.2 g dryweight dm^{-2} (Ilomets 1982). Dominating vascular plants on ridges were *Calluna vulgaris*, *Empetrum nigrum* and *Ledum palustre.* Along the edges of hollows and pools grew *Rhynchospora alba* and *Scheuchzeria palustris*. *E. vaginatum* and *Rhynchospora alba* dominated in lawns. Mud-bottom hollows were sparsely vegetated with the bare peat covered by a thin layer of algae (mainly *Zygogonium ericetorum*) or by remnants of decaying *Sphagnum* shoots. Water table was about 15–20 cm deep below hummocks and ridges, but only 1–2 cm below hollows and even less in mud-bottom hollows. The pH varied between 3.4 and 4.2.

Fluxes were measured with static chambers (25 × 25 cm^2, height 25 or 50 cm) made from Plexiglas. The lower edge of the chambers reached below the water table. The effective chamber volume was calculated from the average height from the *Sphagnum* surface to the top of the chamber. Chambers were installed with the top lid open at least 2 h before the measurement began. The top lid was kept open by a rope and closed from a distance (2–5 m) before taking the first sample. The chamber atmosphere was mixed by a built-in fan to prevent the formation of gradients. Gas samples were taken with a syringe through a Teflon capillary (diameter 2 mm) from some distance (2–5 m) to avoid disturbance of the site by the operator. Five to six samples were taken during one hour. Fluxes were calculated from linear regressions. For storage, the gas samples were injected through a butyl rubber stopper into glass bottles (12.5 ml). The bottles had been pre-filled with a saturated NaCl solution (J. Heyer, pers. comm.; Heyer & Suckow 1985). Excess salt solution was expelled through an additional needle while the gas sample was injected. The bottles were stored upside down at ambient temperature and measured one to three months after sampling. According to experiments by J. Heyer

(pers. comm.) gas samples can be stored by this method without loss of CH_4 for at least six month. CH_4 mixing ratios were measured on a SRI-9300A gas chromatograph with a FID. Before taking a 1-ml gas sample, 1 ml of saturated NaCl solution was injected into the headspace.

Fluxes from mud-bottom hollows were also measured with circular chambers made from Plexiglas. The diameter of these chambers was 19 cm with a net volume of 0.96 l. The sampling procedure and sample treatment was as described above for the larger chambers. During five flux measurements an electronic thermometer was installed at the level of the peat surface. Average temperature increase until the end of the measurement was 1.04 °C.

To estimate the role of CH_4 oxidation in the acrotelm we measured fluxes from intact plots and from the same plots with the acrotelm removed. After removal of the acrotelm the chambers were flushed with N_2 and darkened with a black plastic sheath to prevent photosynthetic production of O_2. In some experiments, the upper 5 cm of the catotelm were also removed.

Plant-associated methane oxidation was measured *in-situ* by injecting C_2H_2 into the chamber to a final concentration of 1%. C_2H_2 is a suicide inhibitor of methane monooxygenase, the key enzyme of CH_4 oxidation (Prior & Dalton 1985). It diffuses through the aerenchyma of the plants into the roots the same way as does O_2. If CH_4 oxidation occurs, the flux is expected to increase and the oxidation rate as a fraction of potential CH_4 emission can be calculated from (flux with inhibitor - flux without inhibitor)/(flux with inhibitor). Potential CH_4 emission gives an approximation for CH_4 production. C_2H_2 was purified by bubbling it through 5 M H_2SO_4 and 5 M NaOH (Hyman & Arp 1987). We measured fluxes first without inhibitor for one hour and after adding C_2H_2 for another 1.5–2 h. The same experiment was done in the small circular flux chambers to measure CH_4 oxidation in mud-bottom hollows.

The role of vascular plants (*Scheuchzeria, E. vaginatum*) as conduits for CH_4 transport from the water-saturated peat to the atmosphere was studied by measuring the flux as described above before and after clipping the shoots below the water table. The number of shoots was 15 to 30 per flux chamber.

CH_4 may also be released by ebullition mainly from pools. In addition, CH_4 mixing ratio in bubbles reflects the porewater concentration in the layer from which the bubble is released. Hence, gas bubbles were collected from the edge of pools. Water-filled funnels (diameter 19 cm, height 8 cm) were installed upside down and sealed at the upper end with silicone septa. Care was taken not to stir up bubbles during installation. The funnels were kept in position for 18 to 66 h. The gas volume was measured and a sample was taken with a syringe. It was injected immediately into a stoppered glass vial and analyzed as described above. After removing all gas that had been freed

by natural ebullition the peat below the funnel was stirred with a stick down to a depth of about 30 cm and a sample of these stirred-up gas bubbles was collected as described above.

Potential CH_4 oxidation was measured in the field by placing 1–2 g dryweight peat from the acrotelm of a hummock into 150-ml glass bottles. The bottles were sealed with a rubber septum. CH_4 was injected to make mixing ratios from 1,400 to 18,000 ppm_v. A total of 15 bottles were incubated at *in situ* temperature (17 °C). Gas samples were taken for 20 h and preserved for later measurement as described above.

Potential CH_4 production rates were measured in peat samples from the acrotelm of a hummock and from the top 20 cm of a hummock and of a *Sphagnum*-hollow, respectively. The samples were transported in a temperature-insulated box at $\leq$ 10 °C to Germany and stored for two weeks at 4 °C until the experiment was started. Peat was mixed with N_2-bubbled demineralized water (1:1 by weight) and homogenized in a blender while continuously bubbled with N_2. Glass bottles (150 ml) were filled with 40 ml of this slurry, closed with rubber-stoppers and flushed with N_2. The bottles were incubated in temperature-controlled water baths at different temperatures. The bottles were not agitated during incubation, but shaken before gas sampling to equilibrate porewater and headspace CH_4. Gas samples (1 ml) were taken from the headspace with a gas-tight syringe and analyzed as described above. The increase of CH_4 mixing ratio was followed for 90 h (40 °C) to 210 h (4 °C). The experiment was done in triplicate.

To measure CH_4 concentration profiles, gas samples from the acrotelm and porewater samples from the catotelm were taken with a 10-ml syringe equipped with a steel capillary (length 1 m, outer diameter 1.5 mm). Gas samples were stored as described above. Water samples were injected into glass bottles (12.5 ml) flushed with CH_4-free N_2 and with enough solid NaCl to make up a saturated salt solution from the porewater. Gas samples were taken from the headspace and analyzed as described above. The headspace volume was measured gravimetrically after replacing the gas with water. Temperature profiles were measured with a thermocouple temperature probe mounted in a stainless steel tube (length 62 cm, diameter 0.5 cm) and a microprocessor thermometer (Omega, Newport).

Peat cores were taken with Plexiglas-corers (inner diameter 80 mm) and transported to the laboratory. In these cores microprofiles of CH_4 were measured with a microprobe as described previously (Rothfuss et al. 1994). In brief, a steel capillary (outer diameter 1 mm) with four membrane-covered openings (diameter 0.5 mm) was flushed with N_2 and placed in the peat for 2 min to allow dissolved CH_4 to diffuse into the tip of the probe. The gas sample was flushed out of the tip with 1 ml of N_2 and trapped in a collecting

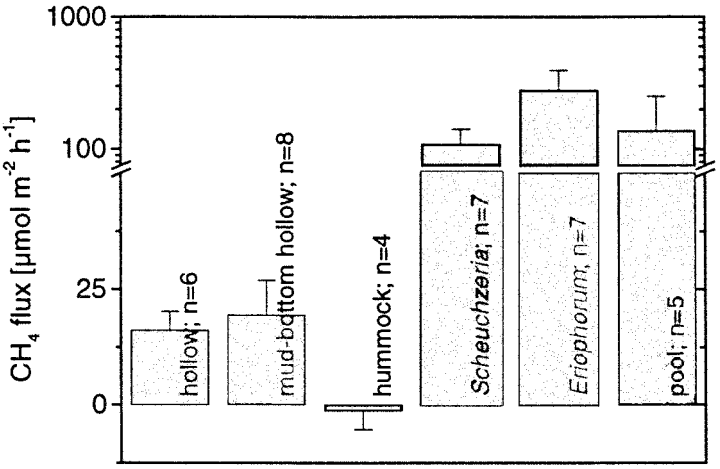

Figure 1. CH_4 fluxes from different microsites in Männikjärve Bog; mean ± SE. Positive and negative values represent emission and deposition (in hummocks), respectively.

vessel, then analyzed by gas chromatography for CH_4. The detection limit was ≤ 5 μM CH_4.

Results

Fluxes

CH_4 was taken up from intact hummocks at an average rate of 1.3 μmol CH_4 m^{-2} h^{-1} (Figure 1). However, in two experiments we removed the acrotelm from the hummocks and measured fluxes that reached values of 11.6 and 49.6 μmol CH_4 m^{-2} h^{-1}, respectively.

Hollows and mud-bottom hollows emitted CH_4. Removing the acrotelm from hollows had no effect on CH_4 emission (Figure 2). Only after the upper layer of the catotelm including all green *Sphagnum*-parts had been removed CH_4 emission did increase slightly. *In-situ* inhibition experiments in mud-bottom hollows (n = 4) showed consistently higher fluxes after addition of C_2H_2. However, the calculated oxidation rates varied between 5% in bare peat and 65% in a site with a well-developed algal mat. In one experiment the C_2H_2 mixing ratio was increased first from 1 to 3% and after that to 10%. Compared to the flux measured before, these changes resulted in an increase of flux by 17% and a decrease of 28%, respectively.

The highest CH_4 emissions were observed from plots with *E. vaginatum* or *Scheuchzeria* (Figure 1). In inhibition experiments with *Scheuchzeria* (n = 5) the CH_4 mixing ratio in the flux chamber was followed for two hours after

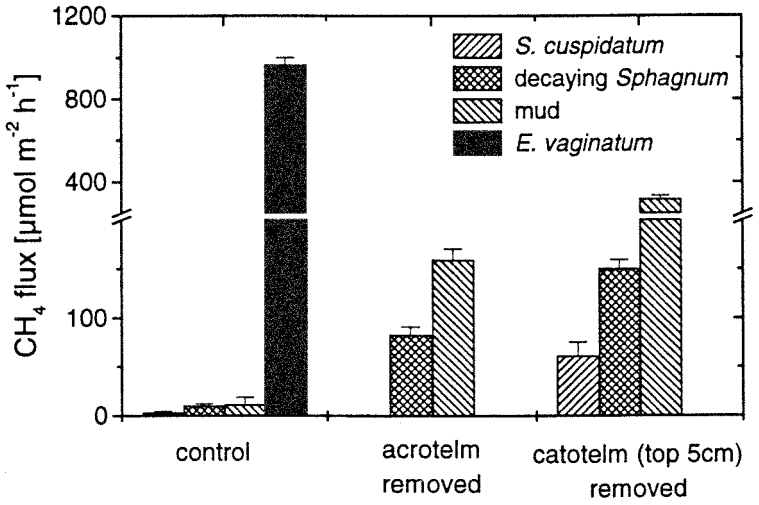

Figure 2. The effect of successive removal of acrotelm and top layer of catotelm on CH_4 emissions from hollows with different vegetation. Emission (± SE) from a tussock of *E. vaginatum* is given for comparison.

Table 1. CH_4 bubble fluxes from the edge of pools with different vegetation.

Vegetation	Duration [h]	Naturally emitted [% CH_4]	Stirred up [% CH_4]	CH_4 flux [μmol m^{-2} h^{-1}]
Scheuchzeria, S. cuspidatum	66	0.2	0.5	0.8
Scheuchzeria, S. cuspidatum	66	2.0	6.2	4.0
Decaying *Sphagnum*	18	18.7	43.2	44.5
Decaying *Sphagnum*	18	37.1	41.5	588
S. cuspidatum	25	23.5	24.2	54.8

adding the inhibitor. CH_4 flux dropped by 21 to 52% compared to the flux measured without C_2H_2. After venting two chambers the flux recovered to nearly the same value as prior to C_2H_2 addition. In the three remaining plots the shoots were clipped below the water table. The chambers were closed again and fluxes were measured for another hour, showing a reduction of $\geq$ 97% of the value with intact plants.

We measured bubble fluxes from the margins of pools. In three sites without vascular plants the CH_4 mixing ratio in the collected gas was

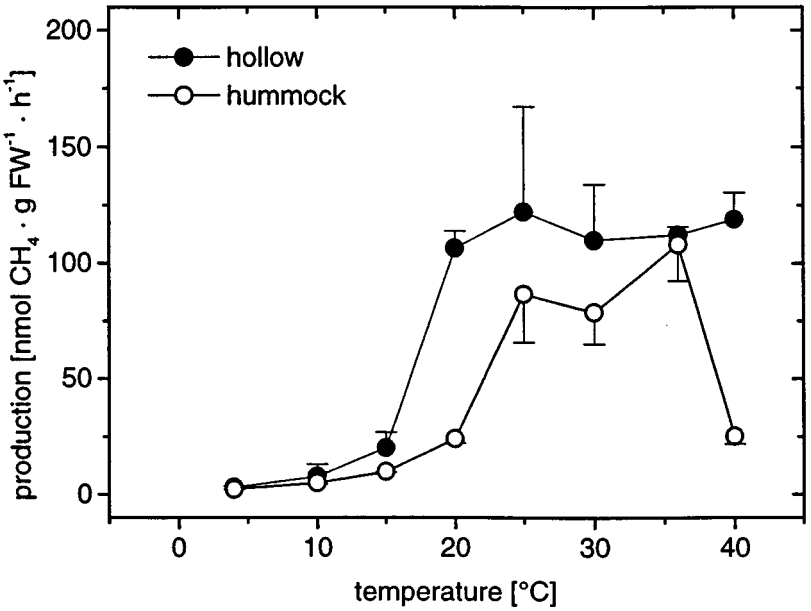

Figure 3. Temperature dependency of CH_4 production in hollow- and in hummock peat from the upper catotelm; mean ± SE, $n = 3$.

significantly higher than in gas from sites with *Scheuchzeria* ($p < 0.01$; Mann-Whitney U-test; Table 1). The mixing ratio in naturally emitted bubbles was always lower than in bubbles that had been stirred-up.

Processes

In vitro, mixed peat from the acrotelm of hummocks showed no detectable CH_4 oxidation over a wide range of mixing ratios (1,400–18,000 ppm_v; $n = 15$) and potential CH_4 production was barely detectable (data not shown).

The influence of temperature on CH_4 production was measured *in vitro* in peat from the upper catotelm of a hummock and from the corresponding layer of a hollow (Figure 3). The $Q_{10;4-25\,°C}$ was 4.5 and 6.8 for hummock- and hollow-peat, respectively. The production rates for the hollow-peat at temperatures $\leq 15\,°C$ in Figure 4 are conservative estimates, because they were taken from the CH_4 accumulations that were measured after an initial equilibration phase of about two days. During this time methanogenesis was extraordinarily high, even at a temperature as low as 4 °C (Figure 4). However, CH_4 production was nearly constant in the hummock-peat during the duration of the experiment.

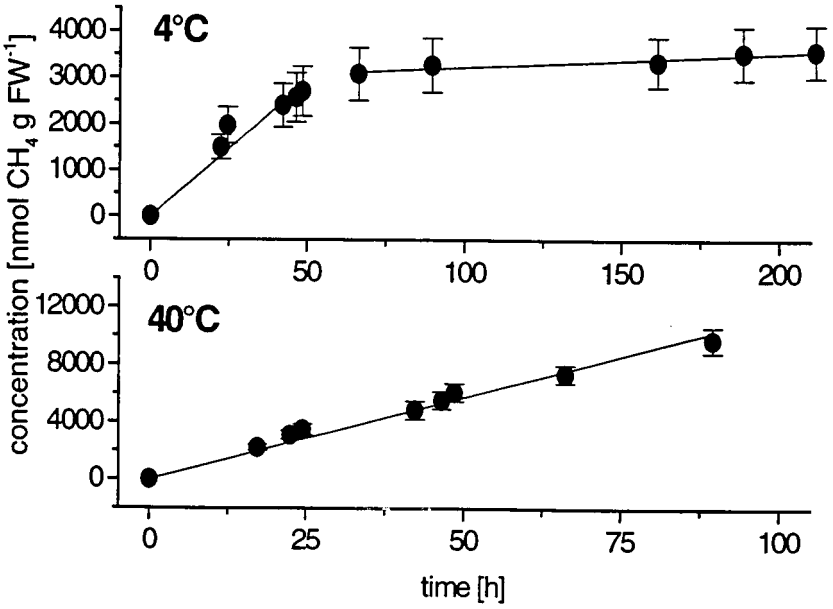

Figure 4. CH_4 production in hollow-peat from the upper catotelm at 4 ° and 40 °C; mean ± SE, $n = 3$.

Porewater

The CH_4 mixing ratio and the equivalent porewater CH_4 concentration was low in the acrotelm of hummocks but increased sharply in the catotelm (Figure 5). In a mud-bottom hollow we measured a CH_4 porewater-profile that had nearly the identical shape as that in the catotelm of a hummock (Figure 5). Porewater CH_4 concentrations in a *Sphagnum*-hollow with no obvious occurrence of vascular plants increased with depth and reached values of about 300 μM at 40 cm depth reaching a maximum of 900 μM in 80 cm depth (Figure 6). Porewater CH_4 concentrations in a *Scheuchzeria*-stand at the edge of a pool were $\leq$ 50 μM down to a depth of 40 cm (Figure 6). The shape of four other profiles from hollows and mud-bottom hollows was in between that of the two profiles shown in Figure 6. An influence of vascular plants on these profiles could not be ruled out. Temperatures below hummocks were significantly lower than temperatures below hollows (Figure 7).

In a core from a *Sphagnum*-covered hollow we measured a high-resolution porewater profile (Figure 8). The water table in this core was at the surface, and down to the lower limit of the green parts of the mosses at 7 cm depth nearly no CH_4 could be detected. In the peat below this zone of active plants the CH_4 concentration increased to 750 μM CH_4.

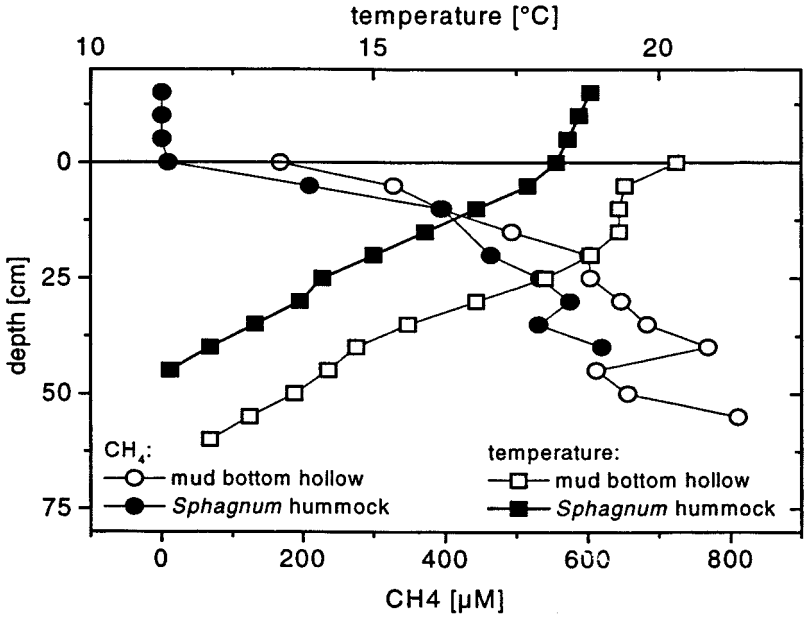

Figure 5. CH_4 and temperature profiles in a mud-bottom hollow and in an adjacent hummock. The depth is given relative to the water table; the acrotelm lies above and the catotelm below the zero-line.

In mud-bottom hollows, CH_4 porewater profiles sampled in the field did not resolve an oxidizing surface layer (Figure 5). A microprofile measured in a core from a mud-bottom hollow showed a high porewater CH_4 concentration below a layer only 2.5 mm thick, where CH_4 concentration was below the detection limit (Figure 9). Two rather high CH_4 values in 30–35 mm depth indicated the presence of gas bubbles (Rothfuss et al. 1996).

Discussion

Hummocks

CH_4 was taken up in intact hummocks, but after the acrotelm had been removed the hummocks emitted CH_4. This indicates that CH_4 oxidation in the acrotelm fully controls CH_4 emission. The CH_4 mixing ratio and the equivalent porewater CH_4 concentration was low in the acrotelm of hummocks but increased sharply in the catotelm (Figure 5). A similar CH_4 profile has been reported in a Scottish mire (Benstead & Lloyd 1996). Applying Fick's 1st law to the topmost linear part of the CH_4 profile we calculated a diffusive flux of 660 μmol $CH_4 \cdot m^{-2} \cdot h^{-1}$ from the catotelm into the acrotelm. We assumed

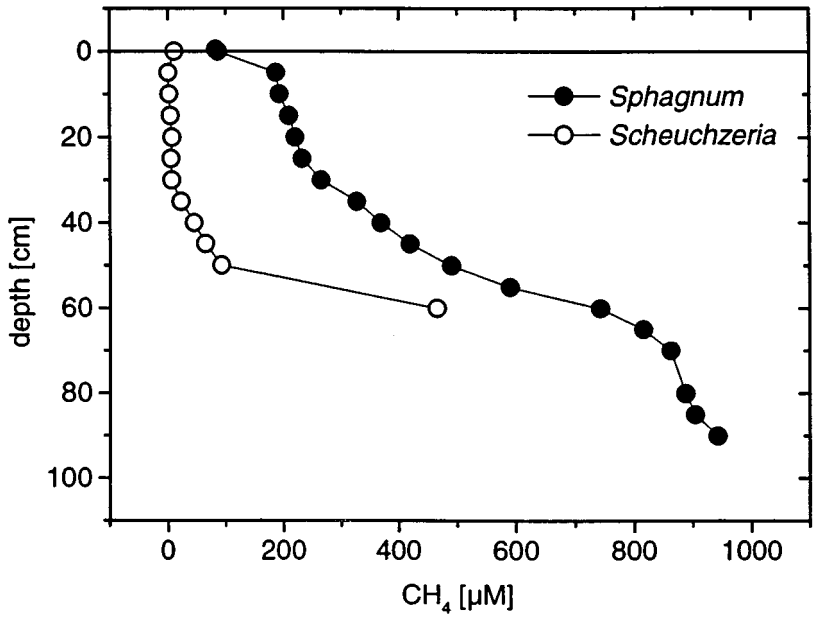

Figure 6. CH_4 profiles in a hollow with a *Sphagnum*-carpet and in a hollow with *Scheuchzeria*. The depth is given relative to the water table; the acrotelm lies above and the catotelm below the zero-line.

a diffusion coefficient of $5 \cdot 10^{-8}$ m^2 sec^{-1} for water-saturated peat (Benstead & Lloyd 1996; Stephen et al. 1998) and a porosity of 0.95 (Walter et al. 1996). The experimental removal of the acrotelm together with the shape of the porewater profile in the catotelm indicate that the zone of CH_4 oxidation is closely associated with the water table.

In vitro, peat from the acrotelm of hummocks showed no detectable CH_4 oxidation over a wide range of mixing ratios. This is in accordance with observations in a Finnish pine fen, where potential CH_4 oxidation in hummock peat was negligible in the acrotelm but increased sharply in the top layer of the catotelm (Saarnio et al. 1997).

From the different experiments it becomes evident that in these hummocks CH_4 is largely oxidized at the transition between cato- and acrotelm. The depth of maximal potential CH_4 oxidation has been found to be positively correlated with the depth of the water table (Sundh et al. 1995), and CH_4 fluxes are inversely related to the depth of the water table (Bubier et al. 1995; Saarnio et al. 1997). In general, CH_4 fluxes are lower from topographically elevated structures like hummocks or ridges than from lower ones (Waddington & Roulet 1996). To summarize, control of CH_4 emission by oxidation seems to be a general feature in hummocks and ridges.

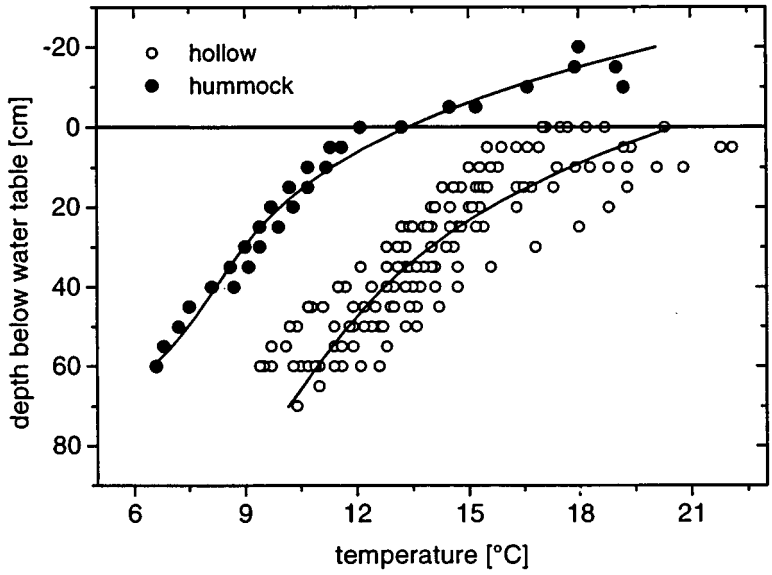

Figure 7. Temperature profiles in hummocks and hollows, 28 June–3 July. The depth is given relative to the water table; the acrotelm lies above and the catotelm below the zero-line.

During our experiment in Männikjärve Bog, temperatures below hummocks were significantly lower than temperatures below hollows (Figures 5, 7), indicating that the relatively dry acrotelm of hummocks was thermally insulating the water-saturated catotelm. Methanogenesis is highly temperature-sensitive (Figure 3). Potential CH_4 production was barely detectable in the acrotelm (data not shown), but became significant in the catotelm. The Q_{10} for peat from the upper catotelm of a hummock and from the corresponding layer of a hollow was 4.5 and 6.8 (4–25 °C), respectively. An even stronger temperature dependency of potential CH_4 production with Q_{10} values up to 20 has been observed in peat samples from other mires (Dunfield et al. 1993; Nedwell & Watson 1995).

The temperature difference in the upper catotelm of hummocks and hollows (Figure 5) may have influenced CH_4 emissions, too. For the top 20 cm of catotelm an *in situ* CH_4 production rate of 4.6 and 61.6 nmol $CH_4 \cdot$ g freshweight$^{-1} \cdot h^{-1}$ was calculated for hummock and hollow peat, respectively. Assuming an active CH_4 production in the top 20 cm of the acrotelm only, the production below a hummock would account for 920 μmol $CH_4 \cdot m^{-2} \cdot h^{-1}$. This is in fairly good agreement with the flux of 660 μmol $CH_4 \cdot m^{-2} \cdot h^{-1}$ that was calculated from the *in situ* porewater CH_4 profile. Peat below the water table in hummocks is more decomposed (8–15%) than peat in hollows (3–5%) (Ilomets 1979). In Männikjärve Bog, the residence

time of peat in the acrotelm of hummocks is about 20–30 years but only 1–3 years in the acrotelm of hollows (Ilomets 1979). Because aerobic and anaerobic mineralization in peat are correlated with the former being 2.5 times larger than the latter (Moore & Dalva 1997), a prolonged passage of the organic matter through the acrotelm of hummocks should reduce the amount of available substrates for methanogenesis. Together with a relatively low temperature in the catotelm, substrate availability and hence, CH_4 production may also be responsible for the small CH_4 emissions from hummocks. Nevertheless, CH_4 oxidation was definitively the controlling factor for CH_4 emissions from these hummocks.

Hollows

Surprisingly, hollows covered with *Sphagnum* and mud-bottom hollows showed approximately the same and relatively low CH_4 emissions (Figure 1). CH_4 production in peat from hollows *in vitro* was more stimulated by increasing temperatures than in hummock peat (Figure 3). CH_4 production was also less sensitive to high temperature (40 °C; Figure 3), indicating a better adaptation of the microbial biocoenosis to higher temperatures. This is in accordance with the higher *in situ* temperatures (Figure 7).

However, in hollow peat initial CH_4 production rates for temperatures ≤ 15 °C were much higher during the first two days when methanogenesis was extraordinarily high even at 4 °C (Figure 4). Because hummock peat showed a constant production rate at all temperatures (data not shown) one may argue that the different initial production rates are somehow correlated with a different substrate availability. However, we have no mechanistic explanation for this phenomenon, which was not observed at temperatures ≥ 20°C. To our knowledge such an effect has never been reported before.

At a bulk density of 1 for water-saturated hollow peat the *in situ* CH_4 production rate would have been 12.3 mmol $CH_4 \cdot m^{-2} \cdot h^{-1}$, if production had been confined to the topmost 20 cm of catotelm. Compared to an emission of 16.2 μmol $CH_4 \cdot m^{-2} \cdot h^{-1}$ from hollows (Figure 1), this is equivalent to an oxidation rate of 99%.

A porewater CH_4 profile measured in a *Sphagnum*-hollow showed an increase with depth as expected, but also some deviations that did not allow to calculate fluxes from a simple Fickian model (Figure 6). In other profiles an influence from roots and rhizomes was even more probable because the shape of the profile resembled more or less that from a profile measured in a *Scheuchzeria*-stand (Figure 6). The low CH_4 concentrations over a wide depth range in this profile indicate plant-mediated transport of $CH_4$from the porewater to the atmosphere and/or CH_4 oxidation.

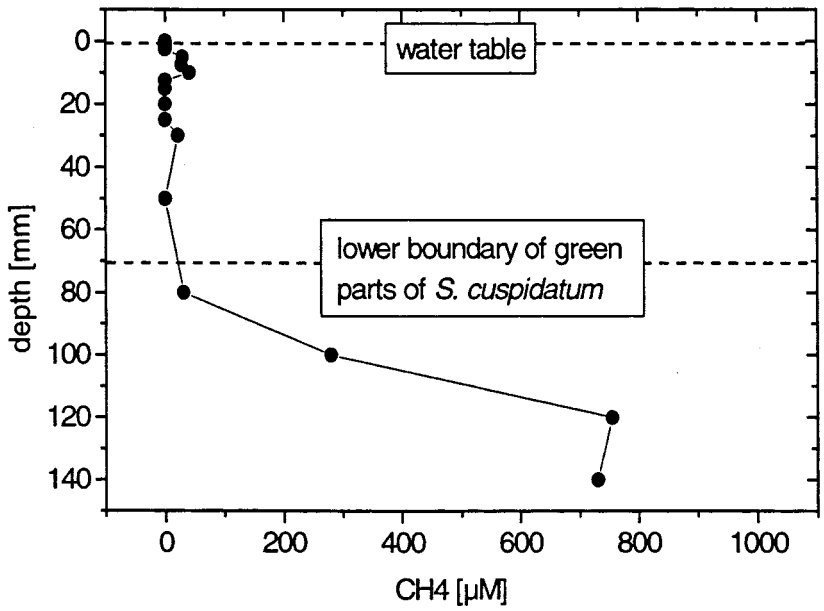

Figure 8. CH_4 microprofile in a core from a *Sphagnum*-covered hollow.

A high-resolution CH_4 profile measured in a peat core without vascular plants (Figure 8) showed clearly that down to the lower limit of the green parts of the mosses at 7 cm depth nearly no CH_4 was present. In the peat below this zone of active plants the CH_4 concentration increased. Similar CH_4 profiles have been reported in another mire (Benstead & Lloyd 1996). Because diffusion of O_2 from the atmosphere down to this depth is very slow it becomes evident that CH_4 oxidation was mainly driven by photosynthetically produced O_2. Comparing this profile with the flux manipulation experiment (Figure 2) explains why removing the acrotelm may have had no effect on CH_4 emission. CH_4 oxidation occurs at the border between the living *Sphagnum* well below the water table in what we defined arbitrarily as catotelm. The abrupt change in the slope of the profile is also consistent with a nearly complete control of CH_4 emission by oxidation (Figure 2).

Measured emissions compared to CH_4 production at the actual *in situ* temperature together with the manipulation experiment and the porewater profiles demonstrated an effective CH_4 oxidation at the surface of *Sphagnum*-hollows. Using a different experimental approach, our conclusions agree with that of other authors (Fechner & Hemond 1992; Sundh et al. 1995).

In mud-bottom hollows, CH_4 porewater profiles sampled in the field did not allow the recognition of an oxidizing surface layer (Figure 5), but fluxes were low (Figure 1). However, with the flux manipulation experi-

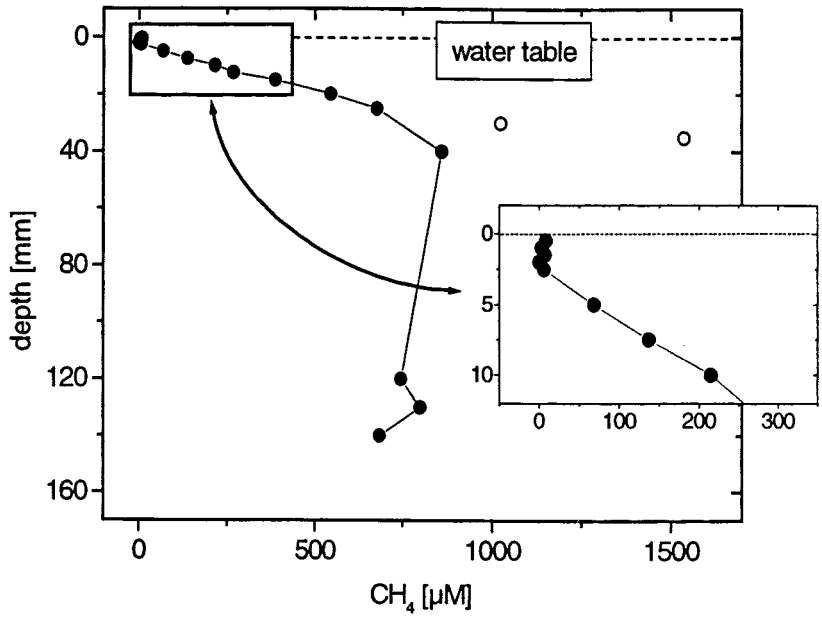

Figure 9. CH_4 microprofile in a core from a mud-bottom hollow. The top layer is shown enlarged in the inset. The open symbols represent outliers, probably caused by gas bubbles.

ment we observed an immediate increase of CH_4 emission after the acrotelm had been removed (Figure 2). The microprofile from a mud-bottom hollow showed a high porewater CH_4 concentration below a layer only 2.5 mm thick, where CH_4 concentration was below the detection limit (Figure 9). The nearly CH_4-free surface layer is clear evidence for CH_4 oxidation. In similar environments the O_2 supply depended on the development of an algal layer and on light availability for photosynthetic O_2 production (King 1990).

In mud bottom hollows, clear oxidation signals were observed with the inhibition experiments. However, the use of C_2H_2 in this environment may have some disadvantages, because at higher concentrations the CH_4 emission dropped down. This results from an inhibitory effect of C_2H_2 on methanogenesis (Oremland & Taylor 1975; Sprott et al. 1982). It indicates also that CH_4 production occurs within a few millimeters from the peat surface. From the shape of the porewater-profile (Figure 9) it can be deduced that highest CH_4 production occurred between 20 and 40 mm depth, but the data do not exclude CH_4 production closer to the surface. In other wetland studies CH_3F has been used as an inhibitor (Moosavi & Crill 1998). In spite CH_3F has been claimed to be a selective inhibitor of CH_4 oxidation it has been shown more recently that it inhibits acetoclastic methanogenesis, too (Frenzel & Bosse

1996; Janssen & Frenzel 1997). The perfect inhibitor to measure community CH_4 oxidation has to be found.

To summarize, temperatures *in situ* are higher in hollows and mud-bottom hollows than in hummocks. Also, CH_4 production rates *in vitro* are higher in hollow- than in hummock-peat and actual *in situ* production rates may have been tenfold higher in hollows than in hummocks. However, CH_4 emission may be controlled by CH_4 oxidation. In *Sphagnum*-hollows CH_4 oxidation is coupled immediately to photosynthetic O_2 production. This is in contrast to the hummocks, where diffusion through the catotelm supplies CH_4 oxidation with O_2. In mud-bottom hollows benthic photosynthesis may support a very effective CH_4 oxidation, too, but the very thin oxidizing surface layer may be affected by even minor environmental changes, explaining the large variation between different sites.

Vascular plants

Vascular plants have repeatedly been shown to form strong point sources of CH_4 in northern wetlands (Christensen 1993; Schimel 1995). Nevertheless, plant-associated CH_4 oxidation may reduce potential CH_4 emission by 20 up to 90% (Frenzel 1999).

After addition of the gaseous inhibitor a very quick response is to be expected. E.g., O_2 diffuses within minutes from shoots to roots both in rice and bog plants (Armstrong 1964; Barber et al. 1962). In an inhibition experiment with rice, complete inhibition of CH_4 oxidation was observed within 15 min after addition of C_2H_2 (Gilbert & Frenzel 1995). However, in inhibition experiments with *Scheuchzeria* the CH_4 mixing ratio in the flux even dropped by 21 to 52% compared to the flux measured without C_2H_2. If CH_4 oxidation had a significant effect, fluxes should have been higher with the inhibitor. The observed response could have resulted from an inhibition of CH_4 production if production occurs near to or on the roots (Frenzel & Bosse 1996; Lehmann-Richter et al. 1999). One may also speculate that C_2H_2 had decreased the flux by affecting the stomatal openings of *Scheuchzeria*. Regardless of the reason, C_2H_2 is not appropriate to measure CH_4 oxidation rates with these plants *in situ*.

The clipping-experiment showed a reduction of CH_4 emission by 97% as compared to the control experiment with intact plants. This indicates that the main route for CH_4 to the atmosphere was through the vascular plant and not through *Sphagnum*. This is in accordance with findings in rice and in other wetland plants where it has been shown that about 90% of the CH_4 emission is mediated by the plants (Holzapfel-Pschorn et al. 1985; King et al. 1998; Muller et al. 1994; Waddington et al. 1996).

The role of vascular plants as conduits for CH_4 has been shown in a wide variety of wetlands (e.g. Chanton et al. 1991; Holzapfel-Pschorn et al. 1985; Whiting & Chanton 1992). In spite of many examples for a plant-associated CH_4 oxidation (Frenzel 2000) a few plants including *Eriophorum* sp. have been shown not to support CH_4 oxidation (Frenzel & Rudolph 1998; King et al. 1990). The reason for this is unknown. However, plant associated CH_4 oxidation was found *in vitro* in *Scheuchzeria* from a Siberian peatland (Bosse, pers. com.). For Männikjärve bog the role of CH_4 oxidation in *Scheuchzeria* could not be estimated because of the unexpected reaction to C_2H_2. However, *Scheuchzeria* has a significant impact on porewater CH_4, by oxidation, or by transport, or by both (Figure 7). The effect of this plant could also be observed with gas bubbles (see below).

Pools

We measured bubble fluxes from the margins of pools. CH_4 mixing ratios were lower in bubbles from sites with *Scheuchzeria* and lower in naturally emitted than in stirred-up bubbles (Table 1). The order of magnitude of bubble fluxes was in the range reported for other ecosystems (Kiene 1991; Muller et al. 1994). Vascular plants like *Scheuchzeria* drain off CH_4 from the porewater *via* their aerenchyma, but the low CH_4 content in bubbles from the *Scheuchzeria*-sites may also indicate that CH_4 is oxidized in the rhizosphere of these plants. Low bubble CH_4 mixing ratios have been observed in sites with other vascular plants, too (Muller et al. 1994; Holzapfel-Pschorn et al. 1985), and $\delta^{13}C$ signatures of bubble CH_4 gave a hint of oxidative losses *in situ* (Uzaki et al. 1991). Losses of CH_4 from the collection funnel back into the water have been shown to be not significant (Holzapfel-Pschorn et al. 1985). In the *Scheuchzeria*-site, no large difference in the CH_4 mixing ratio between naturally emitted and stirred-up bubbles could be expected, because the rooting depth is equal or greater than the depth from which the bubbles have been stirred up. The low CH_4 porewater concentrations throughout the rooted peat support the bubble data (Figure 7). Nevertheless, the mixing ratio in naturally emitted bubbles was always higher than in bubbles that had been stirred-up. At least the highest difference in one of the *Sphagnum*-sites is indicative for CH_4 oxidation, too. To summarize, the bubble data do not contradict the view of CH_4 oxidation as a control of emission. However, the magnitude of CH_4 oxidation in these sites has to be estimated in additional experiments.

Conclusions

From a combination of flux measurements, flux experiments with the acrotelm experimentally removed, *in-situ* CH_4 profiles and *ex-situ* high-resolution CH_4 profiles we conclude that CH_4 oxidation is a major control of CH_4 emission from hummocks and hollows. This has already been shown to some extent for hummocks, but the importance of CH_4 oxidation especially in mud-bottom hollows has not been reported as yet. Microprofiling using miniaturized sensors for porewater CH_4 was most helpful to establish the role of and to localize CH_4 oxidation in mud bottoms. The most stable conditions for CH_4 oxidation are to be expected in hummocks, where due to the insulation by the relatively dry hummock peat, temperature varies less than in hollows. On the contrary, mud-bottom hollows with an oxidizing layer only a few millimeters thick may be very sensitive to changes in ambient conditions.

The most significant hot spots of CH_4 emission are vascular plants and pools. Both *Scheuchzeria* and *E. vaginatum* emit CH_4 at high rates. The potential role of plant-associated CH_4 oxidation could not be clarified, and new inhibitor assays have to be developed to overcome the problems that we encountered with the application of C_2H_2. To quantify CH_4 oxidation in the field remains a major challenge. Ebullition was highest from pools without vascular plants. Our data indicate a potential impact of CH_4 oxidation on emission even in pools.

The structures that we have studied (hummocks, hollows, mud-bottom hollows and pools) are typical elements of the surface pattern of boreal bogs. However, the microtopography together with the plant cover does change with time. As shown by paleogeographical reconstructions, the ratio between hummock and hollow areas changes essentially during the bog development (Hulme 1986). The formation of hollows depends on external factors and on the developmental stage of a particular bog as well (Hulme 1986). A change in their area was found to be correlated with the paleoclimate: hollows became larger during wet and cool periods, while hummocks expanded during drier and warmer periods, respectively. This is of special interest regarding climate changes, because changes in the microtopography will influence the overall CH_4 source strength of a bog, too. Until recently, experimental work (Chapman & Thurlow 1996; Updegraff et al. 1995) as well as modeling studies (Cao et al. 1998; Christensen & Cox 1995) only took into account the changing temperature as a control of CH_4 production. However, structural changes in a bog will be important, too, and not at least by changing the role of CH_4 oxidation.

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