PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Methane and Carbon Dioxide Production in, Transport through, and Efflux from a Peatland [and Discussion]

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Methane and carbon dioxide production in, transport through, and efflux from a peatland

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The top 5–50 cm of a peat deposit above the water table are predominantly oxic while below that the peat is anoxic. The concentrations of CH_4 and CO_2 in the peat below 50 cm do not change with the seasons. The concentrations are greatest at or near the base of the peat and decrease quadratically upwards, consistent with a gas production rate ($CH_4 + CO_2$) of 0.03 μmol cm^{-3} a^{-1} and movement by diffusion. The upward efflux of CH_4, calculated from the concentration profile in deep peat, is 1, and of CO_2 is 17 μmol m^{-2} h^{-1}. Just below the water table there is a small peak in CH_4 concentration. The peak concentrations are greater in summer than in winter. This indicates a second, seasonal and local, but not yet quantified source of CH_4. Effluxes of CH_4 from the peatland surface range from ordinary summer maxima of about 200 down to winter values less than 10 μmol m^{-2} h^{-1}, and at times negative values. The efflux from hummocks is usually about a third of that from hollows. These results indicate that methane oxidation may be important in hummocks.

1. Introduction

Peatlands cover about 3% of the Earth's land surface (Matthews & Fung 1987) mostly in the Northern Hemisphere. Boreal and Sub-Arctic peatlands alone contain about 460 Gt of carbon (Gorham 1991). The peat, which is 1–10 m deep, is the partially decayed remains of the plants which grew on the surface. A typical peatland surface is dominated by *Sphagnum* (bog-moss), ericaceous shrubs, and linear-leaved sedges.

(*a*) *The peat accumulation process*

Sphagnum moss grows indefinitely from the apex and forms a porous mass. The apex and topmost branches are green and photosynthetic, and it is here that new organic matter is added. Though porous, the canopy is surprisingly opaque and less than 1% of incident radiation penetrates more than 2–4 cm (Clymo & Hayward 1982). Below this depth most of the plant dies and aerobic decay by fungi and bacteria begins. The main gaseous product is CO_2. Meanwhile the apex grows on and the load above, mainly of associated capillary water, increases. At first the porous structure survives, just as a wall with a few bricks removed does. But eventually the structure collapses. The dry bulk density increases abruptly

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from about 0.02 to about 0.08 g cm^{-3}, the space between structural elements diminishes to about a quarter, and the hydraulic conductivity decreases, in inverse proportion to a power (approximately 4), by about 250-fold. Most of the water that has hitherto flowed easily downward is now forced to flow laterally, while a very small amount replaces what has percolated through the underlying peat with its low hydraulic conductivity. It is this process that keeps the peat waterlogged as long as precipitation exceeds losses by evaporation and percolation: capillary phenomena are incidental. After heavy rain the water table rises into a layer of increasing hydraulic conductivity, analogous to a V-notch weir, so the whole system is self-regulating and for most of the time the water table stays within 2–3 cm of the mean (figure 1*b*). Microorganisms in the centimetre or so below the water table use up the oxygen faster than it can be replaced by diffusion from above – the rate of diffusion of most gases in water is about 10^{-4} that in air. The peat thus becomes anoxic and the consequent bacterial decay processes are anaerobic and are much slower than the aerobic ones. In these conditions the main gaseous products are CH_4 and CO_2.

In the top 5–50 cm it is useful to recognize four structural layers, and four process zones which move up and down over days and years amid the layers (figure 1). The structural layers are: green, light brown litter-peat, collapse, and dark brown peat-proper. The process zones are euphotic, oxic (aerobic decay), transitional, and anoxic (anaerobic decay). The green layer and the euphotic zone coincide for most of the time, but the aerobic and transitional zones follow the water table down during the summer, and somewhat reduce the much more extensive anaerobic zone beneath. As figure 1 shows, this summer drop is greater than the occasional temporary rise.

This model has been described for a *Sphagnum* carpet, but can be adapted to include those linear leaved plants, herbs, shrubs and trees, together with their roots, that are common on peatlands.

The top three layers used to be called 'active' and the fourth below them 'inactive'. This was misleading: the peat-proper is not inactive. Ingram (1978) introduced the neutral terms 'acrotelm' for the peat above the depth to which the water table sinks in a dry summer, and 'catotelm' for that below it (figure 1).

The surface of most peatlands is heterogeneous on a scale of about 10 m, with alternating hummocks whose tops are perhaps 10–50 cm above the water table, hollows which in winter contain standing water but in summer have the water table just below the surface, and pools which contain permanent standing water.

The idea that CH_4 is produced during decay in waterlogged conditions is not new (Dalton 1802), with Websky (1864) and Rigg *et al.* (1927) showing that CH_4 and CO_2 are produced specifically in peatlands. Seasonally and spatially changing effluxes of both gases were reported by Clymo & Reddaway (1971), and crude concentration profiles were measured in 1981 by Claricoates (1990) who also showed that if other carbon containing gases are present they are so in very small concentrations. Shotyk (1989) reviews early work, and Fowler (this volume) summarizes the reasons for current interest in the efflux of CH_4 from peatlands to the atmosphere. There are numerous more recent reports of effluxes, using a variety of methods, at different sites, and yielding a bewildering variety of results, but with no attempt to locate or to quantify the sources of the CH_4 below the surface.

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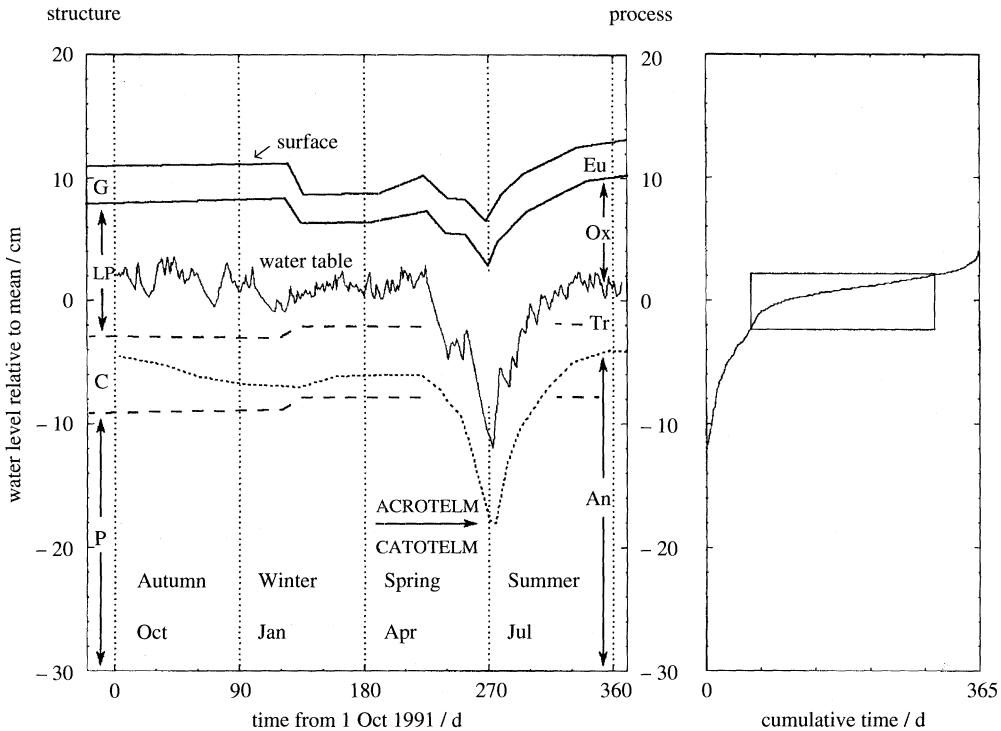

Figure 1. (*a*) Structural layers (at the left) and process zones (at the right) in the surface of a peatland. The irregular line shows the measured movement of the water table at Ellergower Moss SW Scotland in 1991–92; all the other lines are inferred. Structural layers: G, green; LP, litter peat; C, collapse; P, peat proper. Process zones: Eu, euphotic; Ox, oxic; Tr, transition; An, anoxic. Any specific piece of plant matter begins at the top. Its physical movements are relatively small, but as it dies and decays so the perceived structural layers very gradually move upwards. The decay processes are related to the position of the water table, and to the attendant anoxia, so the transition zone moves up and down relatively rapidly through the structural layers as the water table does. As the water table drops so does the support it provides, and there is consequent reversible physical contraction of the structural layers above. This is distinct from the permanent collapse as a result of decay. (*b*) Cumulative frequency of the time spent by the water table at various heights, derived from the time-course in figure 1. Zero height is the mean water table position. The box encloses frequency from 0.16 to 0.84, equivalent to a spread of 1 SD about the mean of a Gaussian distribution. The corresponding amplitude is 5 cm.

Here we present measurements of profiles of concentration through the catotelm and through the acrotelm, and of effluxes, all measured with the same equipment, in the field, at a single site. From these we infer something of the location and nature of the processes of production, movement and disappearance of gases in peat.

2. Field site

Ellergower Moss is an elliptical raised bog at the northeast end of Loch Dee (National Grid reference: NX4880) near New Galloway in southwest Scotland. The axes are about 600 and 500 m long. In section the profile is close to hemi-elliptical (Ingram 1987) and about 6 m deep at the centre, close to which the measurements were made. Most of the bog centre has a fairly continuous carpet

of *Sphagnum* of several species. The surface is patterned with hummocks 5–10 m across which rise to about 50 cm above the water table occupying 67% of the area, and hollows covering 10%. There are few pools but about 23% of an intermediate habitat: flat lawns a few centimetres above the water table. On the hummocks grow the dwarf shrubs *Erica tetralix* and *Calluna vulgaris*, while on the lawns the linear-leaved *Eriophorum vaginatum* is abundant, and in the hollows *Rhynchospora alba*. The measurements reported here are for hummocks and hollows.

3. Methods

(*a*) *Gas concentration measurements*

All measurements were made on site with a VG Quadrupoles mass spectrometer (QMS) fitted with a membrane inlet and triple filter. Gas samples were brought to the mass spectrometer in a helium carrier gas stream or, for fluxes at the surface, in a syringe.

(*b*) *Deep peat profiles*

A 55 μm thick cylindrical silicone membrane was slightly stretched over an aluminium cylinder on the surface of which ran a spiral groove of 1 mm square cross section, with a 1 mm wall between turns. Most of the groove was filled by a 0.8 mm diameter stainless steel wire which gave extra support to the membrane. The part of the cylinder occupied by the groove was 40 mm diameter by 50 mm long. The membrane was sealed onto the cylinder beyond the limits of the spiral groove. Helium gas could be passed through the groove and then through 1 mm diameter stainless steel tubing to the QMS. The cylinder was attached to the end of standard peat-borer rods and pushed down to the required depth in the peat. Gas diffused from the water-saturated peat through the membrane into the gas space in the groove. Three modes were used. In static mode the sampler was left for 24 h or more with no flow through it to allow the peat gases to reach near-equilibrium with the carrier gas. Then the carrier gas flow was started and the 'slug' of equilibrated gas pushed to the QMS. In restricted mode the carrier gas was static for 60 min, and was then moved to the QMS. The value which would have been reached at equilibrium was calculated from the separately measured response time for the particular gas and temperature. (The response time is the time needed for the concentration inside to have reached $1/e = 0.37$ of a stepwise change outside the sampler.) Response times for CH_4 and CO_2 were about 1 h. In proportional mode a constant accurately measured flow of about 1 ml min^{-1} was maintained and the equilibrium value obtained from a flow-dependent calibration.

(*c*) *Shallow profiles*

Concentration profiles in the top 50 cm were measured by similar methods but the sampler was flat, with the groove chased on both sides on an area 50 mm wide by 20 mm deep.

(*d*) *Expression of profile results*

The solubility of gases in peat is similar to that in water, in which it ranges from a few percent by volume (CH_4 5, N_2 2, Ar 5, O_2 4, all % V/V at 5 °C) to 140% for CO_2 and 400% for H_2S. Gas in deep water-saturated peat was collected into the gas phase for measurement. At the bottom of shallow profiles the peat was

water-saturated but the top was in the capillary fringe, with a mixed gas and water phase outside the sampler. All the profile results are therefore reported as equilibrium partial pressure of gas in the carrier stream at 1 atm (10^5 Pa) pressure and about 10 °C. In deep profiles at Ellergower Moss, where the mean annual temperature is 8 °C, the solubility of CH_4 in peat was taken to be 4.6%, for CO_2 133%. All that can be said for the shallow profiles is that for most gases the result is dominated by the gas phase around the sampler, but for CO_2 both liquid and gas phases contribute significantly.

(*e*) *Flux measurements*

The bottom of cylindrical polythene bins, 30 cm diameter by 40 cm deep, were cut off and the bottomless bin pushed down into a cylindrical cut in the peat, leaving about 10 cm above the surface. These flux boxes were left in place permanently. When in use, a tightly fitting lid was snapped on, thus defining a headspace. From the lid a 1 mm diameter nylon tube ran 10–20 m to the QMS. Samples were sucked through this tube into a syringe and then injected into the QMS sample chamber. After the initial fitting of the lid it was unnecessary to go near the flux boxes. Efflux was calculated from the time-course of concentration in, and the volume of, the headspace. The lid transmitted 0.05 of the incident visible radiation.

4. Results

(*a*) *Partial pressure of gases in the waterlogged catotelm*

Randomly ordered depths within a 5 m radius were measured on 13 different occasions at 1–3 month intervals over two years. There was no sign of seasonal variation so the mean values are shown in figure 2. The concentration of CH_4 inferred at 4–5 m depth was about 0.9 μmol cm^{-3}, compared with about 0.8 (Claricoates 1990) and about 1.0 (Nilsson & Bohlin 1993), though Shotyk (1989) using unspecified sampling methods found partial pressures equivalent to about 0.1 μmol cm^{-3}. In all four cases the concentration decreased from the base upwards. The repeated measurements in figure 2 indicate a fairly smooth somewhat convex decline toward the surface.

(*b*) *Partial pressure of gases in the top 50 cm*

The results in figure 3 show a general decrease in partial pressure toward the surface, continuing that in figure 2, though the values are rather smaller than those recorded by Dise (1993) for peatlands in Minnesota (around 200 μmol l^{-1} at 40 cm, equivalent to a partial pressure in the gas phase of about 10%). The Ellergower CH_4 profiles show an additional small 'hump' about 10–20 cm below the water table. This CH_4 hump is more conspicuous in the warmer months and in hummocks. The porous peat in the hummocks allows a gradient of partial pressure to develop in oxic conditions within the unstirred gas in the hummock. The hollow has no such overlying structure, however, and gases diffusing to the water table mix almost at once with the atmosphere. The hummock profiles in figure 3 are aligned on the water table at the time of sampling. The top of the hummock was at least 15 cm above the water table and, in midsummer, about 25 cm above it. The partial pressure of CH_4 becomes as low as that in the atmosphere at least 10 cm below the top of the hummock, and in summer appears often to be rather

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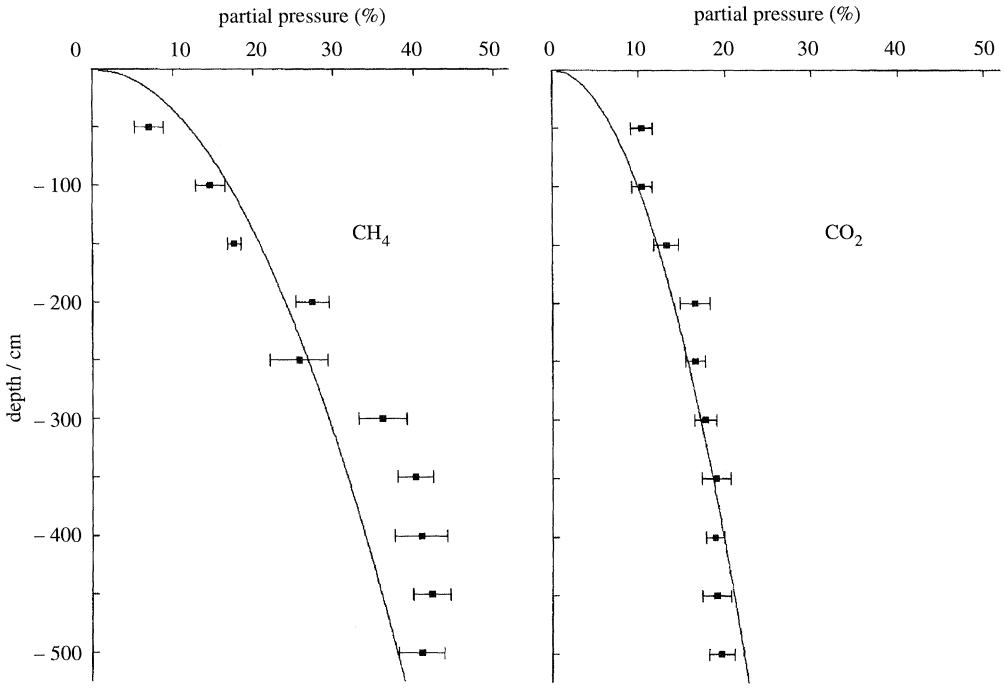

Figure 2. Partial pressure of CH_4 and CO_2 in equilibrium with the peat at a particular depth in Ellergower Moss. Bars are 1 SE ($n = 13$) on either side of the mean. The lines are fitted by equation (5.1); see text.

less than that in the atmosphere, suggesting that CH_4 is being removed within the hummocks.

(c) *Methane efflux from the peatland surface*

Figure 4 summarizes the median and range ($n = 6$) of efflux measurements over hummocks and hollows throughout the seasons. First, there is a clear seasonal cycle. Secondly, the efflux of CH_4 from hummocks is less than it is from hollows, although with CO_2 it is the other way around, with the efflux of CO_2 being greater from hummocks than it is from hollows. Thirdly, in late winter and early spring the fluxes of CH_4 are sometimes negative. There is, however, an asymmetry here: measured effluxes are real while influxes can occur only if there is CH_4 available in the atmosphere immediately above the surface.

5. Discussion

(a) *Processes in the catotelm*

In general the gas partial pressures decrease upwards (figure 3) and this is consistent with continued production at all depths in the peat. What exact shape and position might one expect the concentration profiles to have? Assume, simplistically, that decay continues at a constant proportional rate at all depths, that the gases produced remain in solution and move only by diffusion, that the concentration at the surface is maintained (effectively) at zero, and that the base is impermeable. The peat at Ellergower Moss has been growing slowly, probably for about 9000 years. This is a moving boundary problem, but the diffusion co-

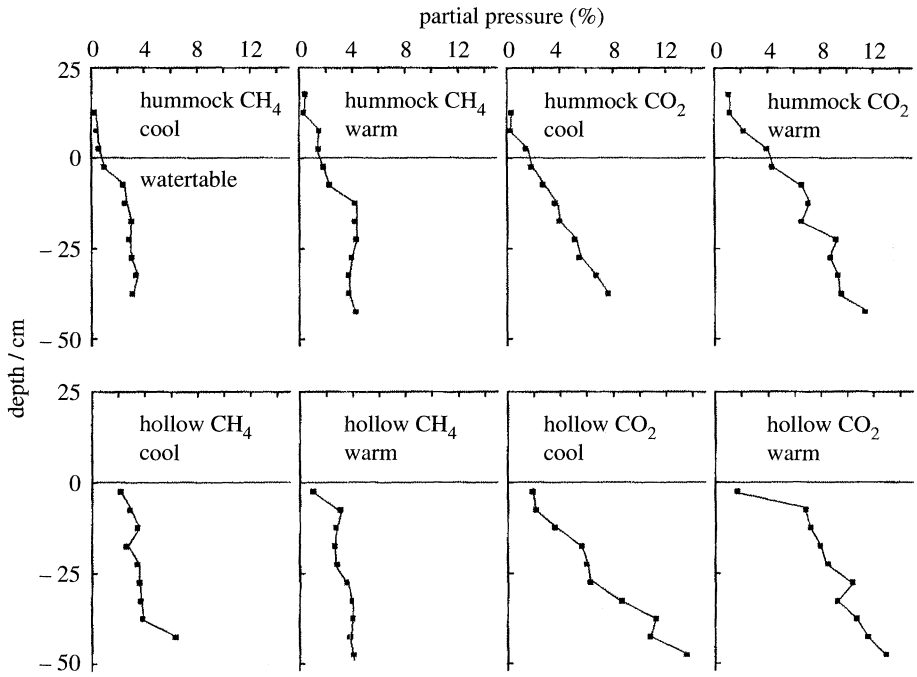

Figure 3. Partial pressure of CH_4 (left half) and CO_2 (right half) in shallow profiles of hummocks (upper half) and hollows (lower half) at Ellergower Moss. Within each quarter the left graph shows the median of measurements on six to nine occasions during the seven cooler months (October–April) and the right graph is the median of 7–11 occasions during the five warmer months (May–September). The results for hummocks are shown relative to the water table at the time of sampling.

efficient of gases in water (close to that of gases in peat) is about 315 $cm^2\ a^{-1}$ (= $10^{-5}\ cm^2\ s^{-1}$) and this implies effective movements of gases on a time scale much shorter than that of peat accumulation, so one can ignore the moving boundary and treat the problem as the equivalent of heat-flow in a slab with internal heat production. The solution (Carslaw & Jaeger 1959, 3.14:7) is complicated but 9000 years is, in the context, about 95% towards the much simpler state at infinite time when the concentration of gas, C, is given by

$$C = \frac{G}{2D}(Z_p^2 - z^2), \tag{5.1}$$

where Z_p is the depth of the whole peat column, z is the distance up from the peat base, G is the rate of gas production on a volume basis, and D is the diffusion coefficient. The curves in figure 2 show equation (5.1) fitted to the points. The inferred rate of production of gas (G above) for CH_4 is 0.0022 and for CO_2 is 0.029 $\mu mol\ cm^{-3}\ a^{-1}$. The corresponding effluxes of CH_4 and CO_2 from the top of the 500 cm catotelm in the steady state are then 1.1 and 17 $\mu mol\ m^{-2}\ h^{-1}$.

The term 'efflux from the catotelm' should be understood merely as the rate at which gas is being supplied to the acrotelm by the processes considered so far. It is not the rate at which gas reaches the atmosphere.

The rate of decay can also, in principle, be inferred from the convexity of an age

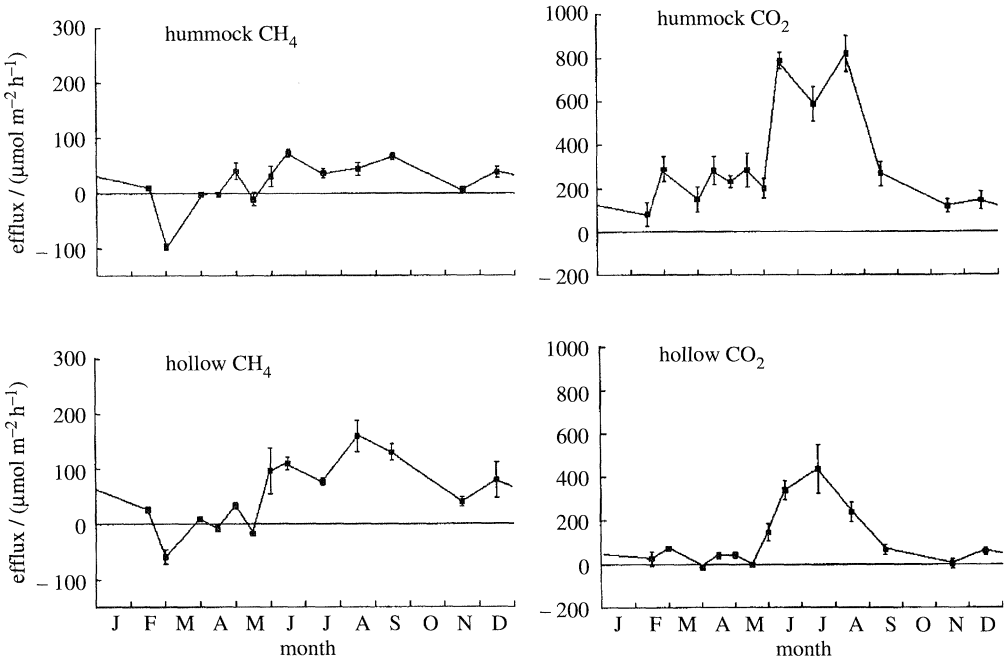

Figure 4. Measured efflux of CH_4 (left) and CO_2 (right) from hummocks (upper) and hollows (lower) at Ellergower Moss. Bars are 1 SE ($n = 6$). The measurements spanned 30 months but have been assembled here as if in a single year. The scale for CH_4 is 2.5 times greater than that for CO_2.

vs depth (as cumulative mass) curve (Clymo 1984, 1991, 1992), but the necessary measurements are not yet available for Ellergower Moss.

(*b*) *Efflux to the atmosphere*

The overall average effluxes of CH_4 and CO_2 to the atmosphere (table 1) are about 40 and 200 μmol m^{-2} h^{-1}, with maxima during the period of a specific measurement of about 200 and 1000 μmol m^{-2} h^{-1}. The CH_4 maxima are similar to those reported for sites in arctic tundra in Alaska in the years 1987–89 by Whalen & Reeburgh (1992), apart from three exceptionally high values recorded by them at the same type of site in one year only. The mean of four tundra site types and four years (excluding the egregious three values) was 300 mmol m^{-2} a^{-1} compared with the present measurements (converted from table 1) of 200 mmol m^{-2} a^{-1} for hummocks and 540 for hollows. Corresponding measurements at Marcell peatland in Minnesota were similar: 220 and 860 mmol m^{-2} a^{-1} (Dise *et al.* 1993). Weighting the values at Ellergower for these two microhabitat types by the proportion of the total area they occcupy at Ellergower (and splitting the lawn area equally between hummocks and hollows) gives a value for the whole Ellergower peatland of 270 mmol m^{-2} a^{-1}. Fowler (this volume) has used micrometeorological methods to estimate CH_4 effluxes at other sites in Scotland. He uses the temperature response at such sites and the measured temperature record for Ellergower Moss to derive a value for CH_4 efflux for the whole Ellergower peatland of 225 mmol m^{-2} a^{-1}. The agreement (270:225) of estimates made by such different methods seems encouraging.

There is a burgeoning literature of efflux measurements. The field evidence

Table 1. *Peatland gas production rates and fluxes*
(The gases move upwards and the table should be read from the bottom.)

location and basis of assessment	net rate of production (μmol cm^{-3} a^{-1})			upward flux (μmol m^{-2} h^{-1})		
	CH_4	CO_2	sum	CH_4	CO_2	sum
measurement						
hummocks				23	310	333
hollows				62	125	187
transition zone	?	?	?	?	?	?
catotelm gas profile	0.002	0.029	0.031	1.1[a]	17[a]	18

[a]Calculated for 500 cm depth of peat, using equation (5.1).

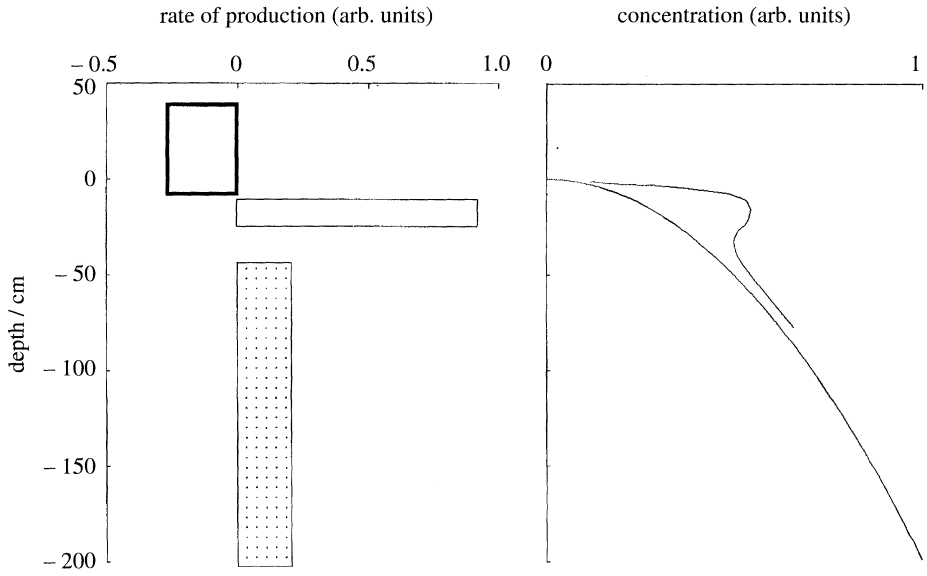

Figure 5. Scheme showing CH_4 production rates (left) and concentration profiles (right). The dotted area represents production at all depths in the catotelm. The open bar represents production in the transition zone just below the water table, which is at zero in the diagram. The thick-edged box represents oxidation in the acrotelm. In the concentration diagram the continuously declining line is that expected if equation (5.1) applies. The second line superimposes the consequences of production in the transition zone.

points strongly to the effects of temperature and water table depth on CH_4 efflux. There is also field evidence of the importance of gas spaces in vascular plants in expediting the upward transport of gases (see, for example, Whiting & Chanton 1992). These effects are confirmed in experiments, which also point to the effects of light and of SO_4^{2-} supply. Here all we need note is that the Ellergower measurements fit the general pattern for CH_4 efflux from northern peatlands.

(c) Processes in the acrotelm

The concentration profiles in the catotelm change little with the season (figure 2) probably because the temperature changes little: an annual cycle of about 2 °C at 400–500 cm depth. The upward flux is likely to be fairly constant. Yet the efflux from the surface (figure 4) is strongly seasonal and during the summer is at least two orders of magnitude greater than the estimate made from deep peat profiles (table 1). These facts strongly suggest a second source of CH_4 close to the surface, where its activity will be driven by large water table and temperature fluctuations. The results in figure 3 do give some credence to this suggestion, though the 'hump' in the CH_4 profile at 5–15 cm is not particularly pronounced even in the warm months. Gas produced in such a position has a relatively short path to the surface and simulations show that it disperses relatively rapidly. It may be that the active zone is no more than 1–2 cm deep at any one time. Its accurate location requires more detailed measurements than are practicable in the field. It seems to be located at or about the transition zone (figure 1).

Efflux of CH_4 from hummocks is about one third that from hollows, whereas the reverse is true for CO_2. There are periods in late winter and early spring when the net flux of CH_4 is (potentially) downward, suggesting that in hummocks at least there is the potential for CH_4 to be oxidized to CO_2. In addition Nedwell & Watson (personal communication) have shown that there is a population of facultatively anaerobic CH_4 oxidizing bacteria in the peat from Ellergower Moss in the anoxic transition zone. The eventual efflux of CH_4 may be controlled as much by these CH_4-destructive processes as by the productive ones in the catotelm and lower parts of the acrotelm.

Figure 5 is a pictorial summary of some of these possibilities. The biggest uncertainties are in the rate of production in the zone just below the water table and in the rate of oxidation of CH_4 in hummocks.

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Discussion

R. Conrad (*Max-Planck-Institut, Marburg, Germany*). Did Professor Clymo observe any gas bubbles in the peat and how much did ebullition events contribute to the CH_4 flux?

R. S. Clymo. Canadian colleagues have extracted large volumes of gas from some of their peatlands and believe there is a lot of gas in bubbles in the peat. I have occasionally come on pockets of gas several metres below the surface, and bubbles rise through pools almost whenever one treads near them. But these seem to come from just below the surface. Occasional jumps in concentration in flux boxes are probably the result of ebullition. In cores raised from peat below, say, 150 cm gas bubbles are not obvious and do not usually appear even when the peat is submerged in water and broken up. The concentrations we measured are containable in the dissolved state.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES