Methane oxidation in a peatland core

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Abstract. We made an experiment on a 30 cm diameter core of Sphagnum-dominated vegetation and peat to estimate the parameters controlling methane oxidation during movement to the ambient air: 13CH4 was added at the water table, and excess 13CO2 appeared in the gas space above the core. At 20°C in otherwise undisturbed conditions, ~22% of CH4 was oxidized to CO2 during passage up through the overlying 10-cm thick unsaturated peat and plants. We simulated the experiment, with seven parameters: transfer coefficients in water, in the gas phase, and through the container wall; the rate of CH4 and of CO2 generation; and the two parameters of a hyperbolic relation between CH4 concentration and the rate of CH4 oxidation. We optimized these parameters to fit the experimental results, and then were able to generalize to any temperature (0°–25°C) and any depth (0–55 cm) of water table. Changing temperature has important effects on the proportion of CH4 oxidized.

1. Introduction

Peatlands cover ~3% of the Earth's land surface [Clymo, 1984]. About 3.5 million km², enough to form a square of side 1800 km, are in the Boreal zone [Gorham, 1991], especially in the former USSR, Fennoscandia, Canada, and the northern parts of the United States. The vegetation of much of this Boreal peatland is dominated by Sphagnum that, because it decays unusually slowly, comes to form a disproportionately large part of the peat [Clymo, 1984].

The surface layers of a peatland including the live plants and down to the depth to which the water table drops in a dry summer are collectively called the acrotelm [Ingram, 1978]. Below this is the peat proper: the permanently waterlogged and permanently anoxic catotelm, throughout which the hydraulic conductivity is relatively lower, by several orders of magnitude, than it is in the acrotelm. In the acrotelm the water table moves up and down as the balance among precipitation, evaporation, runoff, and downward percolation dictate, and the attendant transition from predominantly oxic conditions above the water table to anoxic ones below also moves up and down [Clymo and Pearce, 1995]. In this article the unsaturated zone is considered to be the acrotelm, and the saturated zone is considered to be the catotelm.

The surface of most Boreal peatlands is patterned on a scale of 1–10 m. Hummocks, from 10 to 60 cm tall, alternate with hollows, whose water table is above the surface in winter and below it in summer, and pools, whose water table is at the surface at all times. Each of these microforms has its own characteristic vegetation whose properties contribute to the maintenance of the microform [Malmer et al., 1994]. Feedback mechanisms ensure the continued coexistence of hummocks and hollows [Belyea and Clymo, 1998].

At Ellergower Moss in southwest Scotland, a typical small rainwater-dependent raised bog, the concentration of CH4 in the permanently waterlogged and anoxic catotelm increases approximately hyperbolically with depth [Clymo and Pearce, 1995]. This is consistent with continued slow production of CH4 at all depths. The net upward flux can be inferred from the curve and is ~2% of the net efflux from the surface of hollows. Detailed measurements [Daulat and Clymo, 1998] show high peaks in CH4 concentration profiles 10–15 cm below the water table. These peaks are barely a few centimeters thick and move up and down with the water table with a lag of only a few hours. The speed and size of these changes indicate that this is the main zone of CH4 production. Diffusion and perhaps some mass flow carries the CH4 upward to the atmosphere through peat, plant litter, and intercellular gas spaces in plants.

Overall, peatlands remove CO2 from the atmosphere, sequester some of it as plant matter in peat [Clymo, 1984; Clymo et al., 1998], and return most of it to the atmosphere as a result of decay. They also generate and emit CH4, each molecule of which has (totalled over 100 years) ~20 times greater potential for climate change than the incoming CO2 molecule from which it originated [Houghton et al., 1996]. The net effect on climate of carbon sequestration and CH4 emission varies with conditions and with the age of the peatland [Ahl, 1997; Clymo, 1998; Rivers et al., 1998]. It is not yet clear whether the effect is generally positive or negative, but there is no doubt that the net efflux of CH4 must have a substantial influence, so any process that affects this efflux is important.

There have been numerous reports that the efflux of CH4 from hollows is greater than it is from hummocks, beginning with Clymo and Reddaway [1971] and summarized by Bartlett and Harris [1993] and Crill et al. [1993]. Almost as numerous have been the suggestions that this difference may result from CH4 oxidation in the acrotelm of hummocks, though most of these reports could not exclude the possibility that the differences are a result of different rates of production. However, Daulat and Clymo [1998] found that in experiments in which the water table was moved, the profile of efflux in relation to water table was almost the same for hummocks as it was for hollows. This is better support for the oxidation hypothesis, though it is indirect.

Several authors have made experiments in which slurries, small pieces or cores of peat, soil, or sediment, were put in a closed container (in some cases with inhibitors of CH4 oxidation such as CH3F) and the disappearance of CH4 from the gas phase or the appearance there of 13C or 12C or 3H tracer in CO2 was recorded [Iversen et al., 1987; Yavitt et al., 1988, 1990; Whalen et al., 1990; Whalen and Reeburgh, 1990; Reeburgh et al., 1991; Whalen et al., 1991; Crill, 1991; Whalen et al., 1992; Sundh et al., 1992, 1993; Crill et al., 1994; Sundh et al., 1994; Nedwell and Watson, 1995; Andersen et al., 1998; Saarnio et al., 1998;...
Reeburgh et al. [1993] suggested that 30% of the CH4 produced in the unsaturated layer of peatland was oxidized before it reached the atmosphere. It is clear from these works that the potential for CH4 oxidation is widespread, but most of the observations have attendant difficulties: they measure only potential or net potential, or they use inhibitors whose specificity may be uncertain [Ormeland and Capone, 1988], or the experiments were made in highly disturbed or far from natural conditions. One cannot extrapolate the results to different depths of acrotelm because they reveal little about the rates of those processes that contribute to the overall result: the rate of CH4 production, the rate of transport, and the rate of oxidation.

As far as we know nobody has yet tried to make direct measurements of the rate of CH4 oxidation in minimally disturbed peatland conditions and to establish the values of parameters with which to assess the importance of CH4 oxidation in peatlands in the wide range of conditions found in nature: a crucial element in the potential for climate change.

In this article we first describe measurements of the rate of CH4 oxidation in a peatland mesocosm, using 13CH4 as tracer. The experiment is expensive, so we then simulate it in a computer model and estimate the controlling parameter values so that the experimental results may be applied to other temperatures and other depths of acrotelm.

2. Materials and Methods

The principle of the experiment was simple. A 30 cm diameter core from the living surface of a peat bog, encompassing the acrotelm and the top of the catotelm, was put in a bucket on which a lid was sealed, enclosing some air above the surface of the core (the headspace). Water saturated with 13CH4 and with unmetabolized Kr as a physical tracer was injected at the water table. Samples of gas were then taken at intervals from the headspace, and the concentration of 13CH4 and of 13CO2 (and other gases) was measured with a mass spectrometer.

2.1. Experimental Cores

The peat core was taken from a hummock dominated by Sphagnum capillifolium with 5–10% cover of Calluna vulgaris shoots all less than 10 cm tall. It was one of a large series collected in northern Scotland [Daulat and Clymo, 1998]. An open-ended cylindrical stainless steel cutter, of 30 cm diameter and with sharpened sinuous teeth at the lower end, was pushed down with alternating rotation by ~30ø to a depth of 50 cm. A wedge of peat and CO2 during the long incubation.

In the second control experiment the bucket contained no vegetation or peat but was half filled with 14 dm³ of freshly distilled water and (in the gas phase) nitrogen and traces of CH4, excess 13CH4, and CO2. This experiment was to test the possibility that there might be exchange of 13C between CH4 and CO2 or that CH4 might oxidize in the absence of vegetation and peat. The surface of the water was at the same position in the bucket as the water table in the first two experiments.

2.4. Measurements on Gas Samples

The 5 cm³ gas sample was allowed to expand into a partially evacuated glass bulb, and 10 subsamples were admitted, one after the other, to a Kratos MS50 RF magnetic sector mass spectrometer. The machine was set to allow automatic discrimination of mass/
2.5. Numerical Treatments

The mass spectrometer scans were first calibrated for m/e on the two most widely spaced unambiguously identifiable m/e peaks. Usually these were 68.995 (internal $^{12}$C$^{13}$F$_3$) and 14.003 ($^{14}$N$^{14}$N$^-$). Special care was taken to separate the following peaks with m/e close to one another: $^{12}$CH$_4$ and $^{16}$O$^{16}$O$^{++}$; $^{13}$CH$_4$ and $^{16}$O$^{18}$O$^+$; $^{15}$H$_2$O$^+$ and $^{40}$Ar$^+$. In some cases, however, a single real peak had been partially split by the machine into two or more, and these were recombined. Each peak was then expressed as a proportion of the total intensities in the scan. This allowed for small differences in subsample size. Finally, these proportions were converted using a separate standard to partial pressures. In the figures these partial pressures are given as ppm.

We abstracted from the records the following species at the m/e given: $^{12}$CH$_4$ at 16.032, $^{13}$CH$_4$ at 17.035, $^{40}$Ar$^+$ at 39.981, $^{14}$N$^{15}$N at 29.003, $^{16}$O$^+$ at 32.000, $^{12}$C$^{16}$O$_2$ at 43.990, $^{13}$CO$_2$ at 44.993, and $^{84}$Kr at 83.912. Natural CH$_4$ and CO$_2$ both contain a proportion 0.0111 of $^{3}$C. We were interested mainly in the fate of the extra $^{3}$C we had added. In the figures we have therefore subtracted from measured $^{12}$CH$_4$ and $^{12}$CO$_2$ the amount calculated as coming from the simultaneously measured $^{13}$CH$_4$ and $^{13}$CO$_2$. We call the remainder “excess.”

A measure of centrality and variation was then calculated for each m/e of interest for the (usually) 10 scans. The results contained ∼10% of wildly erratic values, most of them only 1/10 or less of the mean of the other nine in the sample which had a coefficient of variation of ∼0.05. We do not know the reason for these aberrant values, the mass spectrometer was 17 years old, but they are clearly distinct. Mean and standard deviation would have been strongly biased by these values, so we used the median and, as a measure of variability, the span of values containing 0.19 of the total observations below the median and the same value above the median. (This is like an interquartile range but with the bounds at 19% on either side of the median rather than at 25%.) If a sample distribution were Gaussian, then this span would be numerically the same as the standard deviation. We call this measure the G span and have plotted it on the figures. The calculation of proportions in general is described in appendix A.

In Figures 1–4, curves have been fitted using a self-adjusting simplex [Nelder and Mead, 1965]. In Figure 1b we use the negative exponential $y = y_m e^{-at}$, consistent with a decay process from initial maximum “$y_m$” at constant proportional rate “$a$,” and $y = y_m e^{-at} + c$ consistent with a similar process but falling to a baseline “c.” In all the others we use $y = y_m(1 - \exp(-at))$ consistent with constant rate of addition “b” (where the asymptote $y_m = b/a$ as well as constant proportional rate of decay “a.” We refer to these as “first-order flux equations,” but the curves in Figures 1–4 are simply to aid the eye to judge whether such simple processes may be consistent with the observed kinetics.

3. Results

G-span range bars are shown in Figures 1–4. In many cases they are smaller than the size of the symbol marking the median. It is clear that “measurement error” is small and mostly smaller than “sampling error” (judged from deviations from trends), which is itself much smaller than the effects in which we are primarily interested. We therefore make no further comment on measurement or sampling error.

3.1. First Control Experiment

The experiment without the addition of Kr or $^{13}$CH$_4$ gave results very similar to the main experiment for $^{12}$CH$_4$, $^{12}$CO$_2$,
Figure 2. Time course of partial pressure of $^{12}$CH$_4$ and of "labelled" excess $^{13}$CH$_4$ in the headspace over a hummock core. "Excess" is the total minus that naturally present in the measured $^{12}$CH$_4$. Values are medians; bars are ±1 G span (see appendix A). (a) Short-term course. The curves (see text) are fitted to $y = y_m(1 - e^{-at})$. (b) Long-term course. The curve (see text) through the $^{12}$CH$_4$ points is fitted to $y = y_m(1 - e^{-at})$. For excess $^{13}$CH$_4$ the points are simply linked by straight lines.

3.2. Second Control Experiment

In the experiment (results not shown), in which the bucket was half filled by water and half by a mixture of nitrogen, traces of CH$_4$, excess $^{13}$CH$_4$, and CO$_2$, the partial pressures fell for the first 7 days toward a steady value: $^{13}$CO$_2$ fell to 50% of its starting value, while $^{12}$CH$_4$ fell much less to 96% of its starting value. At 20°C the solubility of CO$_2$ is 0.880 cm$^3$ cm$^{-3}$, while for CH$_4$ the value is 0.033 cm$^3$ cm$^{-3}$, ~1/25 as large. (Gas solubility coefficients are similar to partition coefficients not upper limits as they are for solids.) These coefficients applied to the gas and water volumes used would lead to partial pressures of $^{12}$CO$_2$ and $^{12}$CH$_4$ of 53% and 97% of the initial values, consistent with those observed.

The most important conclusion from this experiment is that in the absence of vegetation and peat, the rate of transfer of $^{13}$C from CH$_4$ to CO$_2$ is very small: autooxidation or exchange can be ignored in the main experiment.

3.3. Main Experiment

When the lid was removed the Calluna plants, which had been in the dark for 52 days, were (not surprisingly) distinctly yellow. They and the Sphagnum did resume growth when returned outdoors. During the experiment the plants must have been respiring and thus have been a source of CO$_2$. The aboveground parts had a dry mass only ~1% of that of the unsaturated layer of peat, the main source of CO$_2$, so we ignore this complication. The concentration of O$_2$ fell steadily from the initial 20%; by day 22 it had fallen to 18%, and by day 52 it had fallen to 15%.

3.3.1. Physical behavior of Kr. Figure 1 shows results for the added Kr, which we hoped would behave physically in a similar way to the added $^{13}$CH$_4$ but without the complications introduced by biological interactions. The short-term behavior of Kr is shown in Figure 1a. (Natural Kr has several moderately abundant isotopes. They all behaved in the same way so we show $^{84}$Kr only.) It took ~7 hours before extra Kr first appeared in the headspace. The partial pressure then jumped before settling to a steady, but slowly decreasing, rate of increase. The peak concentration was reached after ~7 days and then decreased for the next 40 days (Figure 1b). The dashed curve is fitted to a simple exponential decay, but the continuous one is fitted to exponential decay to a raised baseline.

There are several physical processes at work here. (1) In the short term, Kr diffuses upward from the water table through the unsaturated zone. Most of the movement must be in the gas phase, where the diffusion coefficient is much larger than it is in the interdigitating water. The process will, however, be modified by exchange between the gas and liquid phases. (2) Depletion in the water at the water table will slowly diminish the rate at which gas enters the unsaturated zone because it has first to diffuse from deeper down through water to the water table. (3) The headspace gas moves out slowly through the polyethylene container and possibly through small leaks around the edge of the lid. (4) Substantial amounts of CO$_2$ are produced in decomposition and raise the pressure in the headspace sufficiently to bubble out through the water seal, taking other gases with them. This would lead to an approximately negative exponential decline in concentration, as we observed. The kinetics of process 3 and 4 are not separable in the main experiment, but we note that in the subsidiary experiment there was no significant drop in gas concentrations after the initial solution changes. (5) Kr diffuses slowly down through the water in the peat below the layer to which it was added, and this decreases the concentration in the layer to which Kr was originally added, thus decreasing the rate at which it moves to the
Figure 3. Time course of partial pressure of $^{40}$Ar, $^{15}$N$^{14}$N (m/e = 29), and of $^{12}$CO$_2$ in the headspace over a hummock core. Values are medians; bars are ±1 G span (see appendix A). (a) Short-term course. The first day’s results for $^{15}$N$^{14}$N and the second day’s results for $^{40}$Ar are omitted to avoid confusion with the $^{12}$CO$_2$ results. The curve (see text) is fitted to $y = y_m(1 - e^{-at})$ for all the results, not just the short-term ones. (b) Long-term course. The curve (see text) for $^{12}$CO$_2$ is fitted to $y = y_m(1 - e^{-at})$ for all the results. To the results for $^{40}$Ar and $^{15}$N$^{14}$N, which were expected to be constant, straight lines were fitted. The slopes do not differ significantly from zero ($P < 0.01$).

It is possible that the initial jump follows the establishment of the gas:liquid partition, as in process 1. The slowly diminishing rate of appearance in the first 7 days is consistent with a diminishing concentration at the water table (process 2) or the onset of loss through the headspace walls (process 3) and water seal (process 4), or a combination of these. The long-term exponential decline seen in Figure 3 may be dominated by losses through the walls (process 3) or (more plausibly) the water seal (process 4) and by diffusion downward into the saturated zone (process 5). However, the main conclusion must be that there are several processes at work here with consequences that can only be postulated. Later we simulate them. For the time being, the kinetics of Kr provide a descriptive background for those of $^{13}$CH$_4$.

3.3.2. Efflux of CH$_4$ and CO$_2$. Figure 2 shows the short-term and long-term results for excess $^{13}$CH$_4$. Its behavior is very similar to that of $^{84}$Kr: an initial jump at 7 hours, a period to 7 days when the first-order flux equation is followed (Figure 1), and a much longer period during which there is a decline, in this case to ~1/5 of the peak value. The decline is proportionally greater than was that of Kr, and the difference may be a result of removal by oxidation to CO$_2$, though this evidence alone would be weak.

The behavior of $^{12}$CH$_4$ (also Figure 2) seems straightforward: it follows the first-order flux equation in both the short and long term, though the fitted efflux in the long term is only half that in the short term. We suppose the CH$_4$ is being produced by microbiological processes within the peat, and the efflux is the net efflux after any internal oxidation.

Figure 3 shows the short-term and long-term results for $^{12}$CO$_2$. The behavior is even simpler: the first-order flux equation is followed with the same parameter values throughout the experiment. Figure 3 also shows that as one would expect, the partial pressure of $^{15}$N$^{14}$N (m/e = 29) and of $^{40}$Ar changes little.

3.3.3. Oxidation of CH$_4$. The relation between all 52 measurements of the partial pressure of $^{12}$CO$_2$ (m/e = 44) and $^{13}$CO$_2$ (m/e = 45) is shown in Figure 4 for comparison with the line to be expected from the natural abundances of $^{12}$C and $^{13}$C. There is little doubt that there is an excess of $^{13}$CO$_2$. The excess $^{13}$C is barely 10% of the total, but because the measurement error and sampling error (judged from the scatter about the trends) were both small, the main result shown in Figure 4b is clear: the excess $^{13}$CO$_2$ is ~90 ppm at a time, 7 days, when excess $^{13}$CH$_4$ is at a peak of 120 ppm. In terms of carbon, these concentrations are 22 and 78 ppm, so ~22% of the $^{13}$CH$_4$ has been oxidized to $^{13}$CO$_2$ during passage up through the unsaturated layer.

We have assumed that there is no microbiological discrimination between $^{12}$C and $^{13}$C in the production and oxidation of CH$_4$. This is untrue in detail, but the effect is relatively small.

4. Simulating the Experiment

4.1. Main Simulation and Parameter Optimization

The purpose of the simulation was to get best fit values of parameters, which could then be used to extend the applicability of the experiment. Details of the simulation are given in appendix B. It consists of a series of layers, 0.5 cm thick in the peat, different in the headspace and container walls. The initial concentration of the five measured substances (Kr, $^{12}$CH$_4$, $^{12}$CO$_2$, "excess" $^{13}$CH$_4$, and "excess" $^{13}$CO$_2$) is set in each layer, as are initial rates of the processes in each layer assumed to be governing transfer between adjacent layers. These assumptions required seven parameters: $D_g$, $D_w$, and $D_c$, the transfer coefficients of gases in the gas phase, in water, and in the walls of the container or through the water seal (cm$^2$ s$^{-1}$); $P_M$ and $P_C$, the proportional rate of production on a dry
Figure 4. (a) Relation of partial pressure of $^{13}$CO$_2$ to that of $^{12}$CO$_2$ for the 52 samples of the headspace over a hummock core. Values are medians; bars are ±1 G span (see appendix A). The straight line is not fitted but is that expected for the natural abundance of $^{13}$CO$_2$ in the measured $^{12}$CO$_2$. At the highest partial pressures, equivalent to longest times, the excess of $^{13}$CO$_2$ is only ~10% of the natural abundance. (b) Time course of partial pressure of excess $^{13}$CO$_2$. The error bars include contributions from both $^{13}$CO$_2$ and $^{12}$CO$_2$ as both are involved in the calculation of excess $^{13}$CO$_2$. The curve (see text) is fitted to $y = y_m(1 - e^{-at})$.

4.2. Extension of the Simulation

Finally, we modified the model to simulate different temperatures and thicknesses of the unsaturated layer but kept the best fit parameter values. The relation between diffusion rate of gases in water and temperature in the range 0ø-25øC is exponential [Briggs et al., 1961] with an increase of 0.02øC - equivalent to a $Q_{10}$ of 1.2.

The relation between rate of CH$_4$ and CO$_2$ production and temperature is also exponential [e.g., Dunfield et al., 1993; Daulat and Clymo, 1998; Neddwell and Watson, 1995] with $Q_{10}$ values from 4 to 6 with isolated values as high as 16. For the simulation we used $Q_{10}$ of 5.0, equivalent to an exponent of 0.16øC$^{-1}$.

The relation between CH$_4$ oxidation rate and temperature is less clear. King and Adamsen [1992] working on 6 cm diameter cores of soil from a mixed deciduous and conifer forest found [King and Adamsen, 1992, Figure 2] no consistent effect of temperature in the range 0ø-30øC (but summarize these results by rate constant = aT$^{-2}$, which seems implausible). Crill [1991], working on similar samples with similar techniques, also found little effect of temperature in the range 5ø-27øC. However, other authors report larger effects. Whalen et al. [1990, Figure 5b] used 7 cm diameter cores from soil covering landfill, and Dunfield et al. [1993, Figure 4] used peat slurries. Both showed rates of CH$_4$ oxidation near zero at temperatures below 5øC and ~1-5 μmol cm$^{-3}$ d$^{-1}$ (converted to a volume basis) at 25øC. Both report a $Q_{10}$: 1.9 and 1.4-2.1.
respectively. Finally, *Nedwell and Watson* [1995], using peat slurries, report a good fit to an Arrhenius plot and a $Q_{10}$ of 2.2 but show no data. We note that this range of absolute temperature ($273^\circ - 298^\circ K$) is so small that many functional relationships would appear to be a good fit on an Arrhenius plot. One may doubt the validity and use of "activation energy" derived from such plots of complex systems, but even the concept of a $Q_{10}$ implies an exponential relationship, with a nonzero intercept at $0^\circ C$. *Whalen et al.* [1990, Figure 5b] and *Dunfield et al.* [1993, Figure 4] are better fitted by a linear relation with very small or zero intercept at $0^\circ C$ than they are by an exponential one. For the simulation therefore we have assumed a linear relationship between oxidation rate and Celsius temperature, with zero intercept at $0^\circ C$.

Figure 7 shows the results of 66 such simulations. For a hummock of height 30 cm and temperature $10^\circ C$, the simulation suggests that 40% of the CH$_4$ would be oxidized before reaching the atmosphere. A 50% error in the temperature exponent for diffusion produces a slightly greater proportion oxidized at $5^\circ C$ but a very slightly decreased proportion at $25^\circ C$. The proportion oxidized is in direct proportion to an error in the oxidation rate, and (not shown) errors in the rate of CH$_4$ and CO$_2$ (decay) have almost no effect on the proportion oxidized, though they do of course affect the efflux of these gases.

![Figure 5. Time course of measured (filled symbols with ±1 G span bars) and modeled (open symbols) concentrations of five gases in the headspace, using the best fit of seven parameters (see text and appendix B). Both axes are scaled logarithmically spanning 3 orders of magnitude, to accommodate the long times and big differences in concentration. This causes deviations at low concentrations to be unduly prominent.](image)

Table 1. Parameter Values and Relative Sensitivities for the “Best Fit” (Minimum) Criterion Value

<table>
<thead>
<tr>
<th>Parameter Symbol</th>
<th>Name</th>
<th>Units</th>
<th>Value</th>
<th>Relative Sensitivity$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_g$</td>
<td>Transfer coefficient of gas in the gas phase</td>
<td>cm$^2$ s$^{-1}$</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$D_w$</td>
<td>Transfer coefficient of gas in water</td>
<td>cm$^2$ s$^{-1}$</td>
<td>6.5e-6</td>
<td>1.3</td>
</tr>
<tr>
<td>$D_k$</td>
<td>Transfer coefficient of gas in the container wall$^a$</td>
<td>cm$^2$ s$^{-1}$</td>
<td>0.032</td>
<td>3.0</td>
</tr>
<tr>
<td>$P_M$</td>
<td>Proportional rate of CH$_4$ generation</td>
<td>yr$^{-1}$</td>
<td>0.50</td>
<td>-0.7</td>
</tr>
<tr>
<td>$P_C$</td>
<td>Proportional rate of CO$_2$ generation</td>
<td>yr$^{-1}$</td>
<td>0.25</td>
<td>4.0</td>
</tr>
<tr>
<td>$H_V$</td>
<td>Maximum rate of oxidation of CH$_4$ to CO$_2$</td>
<td>mmol s$^{-1}$</td>
<td>0.01</td>
<td>0.5</td>
</tr>
<tr>
<td>$H_K$</td>
<td>Concentration for half-maximum rate of oxidation</td>
<td>mmol dm$^{-3}$</td>
<td>2.1</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

$^a$Includes transfer through the polyethylene and the more significant escape through the water trap.

$^b$Read 6.5e-6 as 6.5 × 10$^{-6}$.

$^c$Proportional change in the optimization criterion when the parameter value is changed by 5%, expressed as log$_{10}$. Larger is more sensitive.
After 7 days, when the concentration of $^{13}$CH$_4$ in the headspace was at its maximum (Figure 2), 2.0% of the added $^{13}$C was in CH$_4$ in the headspace, 23.6% was in CH$_4$ in the water in the unsaturated layers, 1.2% was in the gas phase of the unsaturated layers, and 64.8% was still in the saturated layers where it had been added. Already oxidized to CO$_2$ was 0.9% in the headspace and 2.0% in the unsaturated layers. About 5.3% had escaped from the system.
5. Discussion

5.1. Main Experiment

The main result of this experiment is that at ~20°C, 22% of the added $^{13}$CH$_4$ was oxidized to $^{13}$CO$_2$ on its way up through the 10 cm of unsaturated Sphagnum to the headspace. The experiment was made with an intact system that was actively growing for a year before the experiment and resumed growth after it. The system preserved the microbial and fungal communities and the natural physical juxtapositions of organisms and materials. However, it is widely believed that part at least of the CH$_4$ in peatlands is produced from simple carbohydrates secreted from active roots [e.g., Chanton et al., 1995] and the plants were in the dark during the experiment. It is also true that the temperature of the experiment was ~10°C higher than would be common in the field and that the water table was static. Yet the measured net efflux of CH$_4$ fitted to the results in Figure 2b was 280 μmol m$^{-2}$ hr$^{-1}$, while in the field the efflux from a 10 cm hummock with temperature at 10 cm depth of 14°C was 115 μmol m$^{-2}$ hr$^{-1}$ [Clymo and Pearce, 1995]. This difference is exactly almost that calculable from the exponential effect of temperature on net efflux of CH$_4$ [Daulat and Clymo, 1998] from cores similar to those used in this experiment, which in any case contained only 5–10% by area of vascular plants, the rest being Sphagnum—covered. We also note that the water table in raised peatlands is within 2.5 cm of the mean height for nearly 70% of the time. These results are consistent with the view that the experimental core behaved much as one in natural conditions would do.

5.2. Simulation

The best fit parameter values for the simulation (Table 1) were determined with widely differing sensitivity. The transfer coefficients of gases in the gas phase and in water ($D_g$, 0.8; $D_w$, 6.4 × 10$^{-6}$ cm$^{-2}$ s$^{-1}$) are not dissimilar to the accepted values of the molecular diffusion coefficients obtained by direct measurement (0.2 and 1.2 × 10$^{-5}$ cm$^{-2}$ s$^{-1}$) and to the 0.6 cm$^{-2}$ s$^{-1}$ inferred for $C_3H_8$ in the unsaturated top 7 cm of a peatland by Fechner and Hemond [1992]. The transfer coefficient of the container wall ($D_w$, 0.032 cm$^{-2}$ s$^{-1}$) is several orders of magnitude greater than the production rates of gases through polythene, but the model also shows that 18% of the Kr and 19% of the $^{13}$C have disappeared from the system after 13 days. These features are consistent with the suggestion that pressure driven escape of gases through the water seal is causing the headspace to behave like a dilution vessel. The gas production (peat decay) coefficients ($P_M$, 0.50 yr$^{-1}$ and $P_C$, 0.25 yr$^{-1}$) seem plausible at the mean temperature of 20°C: they seem to indicate that anaerobic CH$_4$ production is, within its thin zone, an even more effective decay process than aerobic CO$_2$ production, a conclusion consistent with the findings of Belyea [1996]. However, we note that $P_M$ is imprecisely determined.

The CH$_4$ oxidation parameter values were $H_r = 0.6$ nmol s$^{-1}$ and $H_m = 2.1$ nmol dm$^{-3}$, but both were imprecisely determined, the latter being the most insensitive of all the parameters. The hyperbolic definition of the oxidation process was formally identical to that of an enzyme reaction. However, Michaelis-Menten kinetics assume a well-stirred solution and relatively simple chemistry, while our experiment and natural conditions in peat are unsterred and complex. We think that the dynamics of oxidation are probably much more affected by the rate of diffusion of substrates and products than by the properties of the enzymes involved, and the insensitivity of determination of these oxidation parameters reflects this: a wide range of values produces almost as good a fit because the factory is limited by transport to and from it not by its machinery and internal organization. Conrad [1996] reviewed the ways in which soil microorganisms may control atmospheric trace gases but did not consider the role of diffusion. Yet this is not a new idea: much of the early work on uptake of solutes by plants was shown [Olsen, 1953a, 1953b; Bircumshaw and Riddiford, 1952; Briggs et al., 1961] to be studying diffusion rather than the biochemical processes the authors intended.

The experiment was made in a closed container with minimal mass flow of air. In the field, one would expect wind-induced mixing in the unsaturated zone to be greater than in the experiment. We therefore tried the effect of increasing the value of $D_g$ by a factor of 10. The results were little affected. This is not a good representation of turbulent flow, but we recall that the spaces between structural elements in the unsaturated zone are no bigger than a few millimeters, and turbulent mixing is probably small anyway.

5.3. Wider Application

The values in Figure 7 have been extrapolated from a single measurement at 20°C with the water table at 10 cm depth: caution is necessary. In the field the net efflux from 40 cm high hummocks at a mean summer temperature of 14°C was 40% of that from hollows [Clymo and Pearce, 1995] implying, if one accepts that the production rate beneath both is the same [Daulat and Clymo, 1998], that 60% had been oxidized. Figure 7 suggests 50% is oxidized. In the circumstances this seems to be a reasonable approximation. Reubergh et al. [1993] suggested that 30% of the CH$_4$ produced in high-latitude wetlands was oxidized before emerging into the atmosphere: close to the value in Figure 7 for 20 cm hummocks at a summer temperature of 10°C.

Can these effects be applied on a larger scale? Suppose that the mean temperature 10°C and that the acrotelm (unsaturated layer) depth is 30 cm. Suppose also that the CH$_4$ production in a given time is 100 units, oxidation (Figure 7) is 0.42 × 100 = 42 units, giving net efflux of 58 units. Now increase the temperature by 1°C to 11°C. Production ($Q_{lo} = 4$) would increase by 50% to 150 units, oxidation becomes 0.45 × 150 = 68 units, and net efflux is 82: an increase of 24 units but less than half the 50 units it would have been without oxidation. Because production has an exponential response to temperature but the oxidation response seems to be near linear (or at least, if exponential, has a much smaller exponent than production does), any increase in temperature will produce some increase in efflux. If, however, in the example above, the change of temperature was accompanied by a drop in water table of 10 cm, then the increases in oxidation caused by higher temperature and deeper unsaturated zone would result in no overall change in efflux.

These calculations are quite sensitive to the depth of the unsaturated zone and to the mean temperature. We do not know the distribution of depth of the unsaturated zone for even a single small peatland, nor do we have better than a vague idea of how that distribution might change over 10–50 years in response to a step change in precipitation. For these reasons it is unhelpful, if not misleading, to try to apply the results of this experiment to the global scale at present. This sort of calculation also ignores possibilities such as Northern Hemisphere peatlands at the southern end of their range disappearing altogether, while new ones form in the north.

Before we began this work, it was widely assumed that CH$_4$ was oxidized during passage up through peatland hummocks, but most of the evidence was indirect and qualitative only. We now have direct evidence of the process and can calculate, tentatively, the proportion of CH$_4$ oxidized to CO$_2$ at realistic temperatures and depths of acrotelm.

Appendix A: G Span Variability Measure

For reasons given earlier, we needed to calculate proportionality (quantiles), i.e., that value of the measured variable, which includes...
a specified proportion of the sample or population. Statistics textbooks deal with this, usually for the 25 and 75% cases needed for the interquartile range, but they use a surprising number of nonequivalent recipes to do this. We devised the following.

Let \( n \) be the number in the sample or population. Let \( p \) be the proportionile required, where \([1/(2n)] < [p] < [1 - 1/(2n)]\). (For the median, \( p = 0.5 \); for the interquartile range, \( p = 0.25 \) and 0.75.) Let \( a \) be trunc\((np)\), and \( g \) be the value of the \( a \)th member of the sample or population when it has been arranged in ascending order from \( a = 1 \). We use linear interpolation between the value of the \( a \)th and \((a + 1)\)th members. We want the value (in the units of the variable) for the given \( p \). Let this be \( E_\text{p} \).

\[
p = a + [np - (a - 0.5)][(a + 1) - a].
\]

We define the G span as that distance which, were the sample or population distributed in a Gaussian ("normal") fashion, would give the same numerical value as the standard deviation. Specifically, \( G \) span = \( 0.69 - 0.31 - \).

**Appendix B: Details of the Simulation**

**B1. Physical Conditions**

The model comprised 66 layers representing a horizontal slice through the container and its contents plus a computational sentinel layer at top and bottom. The saturated and unsaturated zone layers were 0.5 cm thick; the headspace had a 9 cm layer sandwiched between two 0.5 cm layers; the lid of the container was 0.3 cm thick (and the area of the headspace sidewalls was added to it). The headspace was entirely gas phase. The saturated and unsaturated zones were assumed to contain organic matter at a dry bulk density of 0.05 g cm\(^{-3}\) and of intrinsic density 1.5 g cm\(^{-3}\), so a proportion 0.05/1.5 = 0.033 (just over 3%) of the space in these layers was occupied by solid matter. Most of this solid matter is in almost unhumified macroscopic pieces, so it was assumed to be physically, but not biologically, inert and without direct influence on transfer processes. In the unsaturated zone the associated water probably does influence transport, so it must be included in the simulation. Most of the solid matter is Sphagnum cell walls, which present little resistance to diffusion: in effect the tortuosity is small. This contrasts with mineral soils in which most of the solid matter is in small impermeable pieces causing large tortuosity and kinetics dominated by bottlenecks.

The saturated zone contained organic matter and water only: measurements of wet mass and dry mass on slices of accurately known volume from cores similar to the experimental one [Clymo, 1983, 1984, 1992, unpublished manuscript, 1995] show no sign of an extensive gas phase below the water table. Nor did vertical probes attached directly to a mass spectrometer: gas bubbles manifest themselves by a large increase in partial pressure (W. Daulat, unpublished manuscript, 1995). We do not deny that gas bubbles may be found in the peat below pools (for example), but we think they were unimportant in this experiment so we made no attempt to simulate them or their movement.

In the unsaturated zone the proportion of the void volume occupied by water, \( p_w \) was given by \( p_w = 10^{-x/z; -} \), where \( z \) is the distance down into the unsaturated zone and \( L \) is its total thickness. This function is a negative exponential from 10% of the void volume occupied by water at the top of the top layer to 100% at the bottom of the lowermost unsaturated layer. This approximates experimental measurements [Clymo, 1983, 1984, 1992, unpublished, 1995].

**B2. Processes**

Mass transfers were made first and were simply sums of rates in and out multiplied by the time step. After mass transfers, the total gas in the unsaturated layers was redistributed between gas and...
water phases using the solubility coefficients for 20°C: Kr, 0.067; CH₄, 0.033; and CO₂, 0.880 cm² cm⁻³.

Nine rates were calculated. Five were fluxes described formally by \( \Delta M/\Delta t = D \cdot \Delta C/\Delta x \), where \( M \) is mass, \( t \) is time, \( C \) is concentration, \( x \) is distance, and \( D \) is a transfer coefficient. These five fluxes were of Kr, \( ^{12}\text{CH}_4 \), \( ^{13}\text{CO}_2 \), \( ^{13}\text{CH}_4 \), and \( ^{12}\text{CO}_2 \) between adjacent layers. We used one value of \( D \) for all gases in the gas phase and a second value for all gases in water.

There were complications in the unsaturated layers: the overall (effective) transfer coefficient depends on how the gas and water are arranged. If a half-thickness layer of one follows a half-thickness layer of the other in either order (series arrangement), then the conductance is low: only double what it would be if the whole layer were of low-conductance material. If, however, the two materials are in parallel, then the overall conductance is high: only half that if the whole layer was of high-conductance material.

Let \( D_1 \) and \( D_2 \) be the conductivity of the two substances that are in proportions \( P_1 \) and \( P_2 \), with \( P_T = P_1 + P_2 \), then \( D_S \) and \( D_P \), the effective series and parallel conductivity, are

\[
D_S = P_T / (P_1/D_1 + P_2/D_2) \\
D_P = (P_1/D_1 + P_2/D_2)/P_T.
\]

Figure 8 shows the effective conductivity of differing proportions of the two materials: in series at the bottom (and the topmost sloping straight line) in parallel. Figure 8 also shows the effects of taking a simple arithmetic or geometric average of the two values of \( D \).

The parallel arrangement is not wholly realistic, even though many of the structural elements in the unsaturated layer, and their associated water, do run vertically. The effective conductivity is too great (except at the ends of the proportion scale). The series and simple average are wildly unsatisfactory giving as they do little increase in effective conductivity until the proportion of the low conductivity material has become very small, when there is a very large increase. We therefore used a weighted effective mean defined by

\[
D_w = (P_1/D_S + P_2/D_P)/P_T,
\]

where \( D_1 < D_2 \). As Figure 8 shows, when the layer is mostly unsaturated (the proportion of \( D_1 \) is small), the layer behaves close to parallel, but by the time the proportion of \( D_1 \) is 90% and the layer is mostly saturated, it behaves close to the series arrangement.

These rate calculations required three parameters: the transfer coefficients in the gas phase, in water, and in the container lid and headspace walls, \( D_{gw} \), \( D_{sw} \), and \( D \).

Two of the other four rates concerned the generation of natural CH₄ and CO₂ by decay. We assumed, for simplicity, that all the CO₂ was generated in the unsaturated layers at a rate proportional to the mass in the layer. The CH₄ was assumed to be generated in a layer 3 cm thick 10 cm below the top of the topmost saturated layer, consistent with measurements [Daulat and Clymo, 1998, unpublished manuscript, 1996]. The decay processes required one parameter each for CH₄ and CO₂: \( k_M \) and \( k_C \).

The remaining two rates were of the oxidation of CH₄ to CO₂ for \( ^{12}\text{C} \) and excess \( ^{13}\text{C} \), which we supposed to follow the same hyperbolic relation between rate and concentration of CH₄ in water. This required two more parameters: \( H_V \) representing the maximum rate when concentration is not limiting and \( H_X \) the concentration for half-maximal rate. The oxidation process was restricted to the unsaturated layers: Nedwell and Watson [1995] reported that CH₄ oxidation at Ellergower Moss was entirely aerobic, though anaerobic oxidation is known to be possible [e.g., Alperin and Reeburgh, 1985].

B3. Running the Simulation

The method used is outlined in the main text. At the start of a run, all concentrations were set to zero, and there was no Kr or excess \( ^{13}\text{C} \) anywhere. The model was then run for 10⁶ min, with increments of 0.2 min, or until no layer showed more than 0.05% change from the previous iteration in concentration of any gas. This established the initial gas concentration profiles. The water in the top 1.5 cm of the saturated layers was then notionally removed and replaced by water saturated with Kr and \( ^{13}\text{CH}_4 \), and the run resumed.

In early runs we set the time increment to 5 min, but the behavior was unstable with alternate layers building up increasing and reversing oscillations in concentration. We cured this by two actions. First we calculated full mass changes, but then implemented only half the full change plus half change left over from the previous iteration. This is similar to the partial explicit, partial implicit technique used in finite difference hydrological modeling. Second we made the time increment very short (0.2 min) and increased it cautiously only if no concentration was more than 1% different from its value on the previous iteration. If this limit was exceeded for any difference in any layer, the time increment was substantially reduced. These approaches required far more computing time (a single run took more than an hour on a 100 MHz machine), but the results were stable.

The criterion to be minimized was similar to a chi-square quantity: \( 2[(y_{\text{obs,j}} - y_{\text{calc,j}})/y_{\text{GS,j}}]² \), where the sum is over all sample times and \( j = 1 \ldots 5 \) gases, \( y_{\text{obs,j}} \) is the measured value of the \( j \)th gas in the headspace at time \( t \), \( y_{\text{calc,j}} \) is the corresponding value calculated in the model, and \( y_{\text{GS,j}} \) an inverse weight, is the measurement error of \( y_{\text{obs,j}} \) assessed by the G span. We applied a further weight to each quantity in the sum because observations were far more frequent in the early part of the experiment. This weight was the logarithm of the time into the experiment, standardized so that the mean weight was 1.0. We also applied a third weight that was the inverse of the mean proportional error for each gas, standardized to a mean weight of 1.0. The values for the five gases ranged from 0.4 to 2.1. This weighting was to make the importance proportional to the precision of measurement for the different gases.

We optimized the parameter values (minimized the criterion) by the method of Nelder and Mead [1965]. This is a simple and robust method, though not the fastest. The model and optimization were programmed in PASCAL.

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References


Belyea, L. R., Separating the effects of litter quality and micro environment on decomposition rates in a patterned peatland, Oikos, 77, 529–539, 1996.

Clymo, R. S., and E. J. F. Reddaway, Productivity of Sphagnum (bog-moss) and peat accumulation, Hydrobiologia, 12, 181–192, 1971.