

		Volume 72, Number 8 April 15, 2008			
Geochimica et Cosmochimica Acta					
JOURNAL OF THE GEOCHEMICAL SOCIETY AND THE METEORITICAL SOCIETY					
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Diffusion and mass flow of dissolved carbon dioxide, methane, and dissolved organic carbon in a 7-m deep raised peat bog

R.S. Clymo^{a,*}, C.L. Bryant^b

^a *School of Biological and Chemical Sciences, Queen Mary, University of London, London E1 4NS, UK*

^b *Natural Environment Research Council Radiocarbon Laboratory, Scottish Enterprise Technology Park, Rankine Avenue, East Kilbride G75 0QF, UK*

Received 24 April 2007; accepted in revised form 24 January 2008; available online 19 February 2008

Abstract

In 65 samples, we got values (unusually replicable and consistent for this type of work) of concentration, $^{14}\text{C}/^{13}\text{C}$ (AMS) age, and $\delta^{13}\text{C}$ for: peat, dissolved organic carbon (DOC), peat fractions, and dissolved CO_2 and CH_4 at 50-cm intervals down to 700 cm in Ellergower Moss, a rainwater-dependent raised (domed) bog in southwest Scotland. (1) We attribute the consistency of the results to Ellergower Moss being unusually homogeneous, with unusually low hydraulic conductivity, and containing only a few gas spaces; and to the sampling methods including 18-month equilibration of in situ samplers. (2) The dissolved gas concentration depth profiles are convex and very similar to each other, though CO_2 is 5–10 times more concentrated than CH_4 , while the profile of DOC is concave. (3) The age profile of peat is near linearly proportional to depth; that for DOC is about 500–1000 yr younger than the peat at the same depth; the dissolved gases are 500–4300 years younger than the peat. The age of the operational peat fractions humic acid and humin is similar to that of whole peat. (4) The $\delta^{13}\text{C}$ profile for deep peat is almost constant; $\delta^{13}\text{C}-\text{CO}_2$ is more enriched than the peat ($\delta^{13}\text{C}-\text{CO}_2$ 35‰ more); $\delta^{13}\text{C}-\text{CH}_4$ is the same amount more depleted. Nearer the surface both dissolved gases become steadily more depleted, $\delta^{13}\text{C}$ is about 20‰ less at the surface. (5) A simulation shows that mass flow can account for the concentration and age profiles of DOC, but for the gases diffusion and an additional source near the surface are needed as well, and diffusion accounts for over 99% of the dissolved gas movements. (6) The same processes must operate in other peatlands but the results for Ellergower should not be extrapolated uncritically to them.

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1. INTRODUCTION

Peatlands cover about 3% of the Earth's land surface and contain about as much carbon as does the atmosphere (Clymo et al., 1998). Decomposition processes result in the production of CO_2 and CH_4 . The net efflux of CO_2 and CH_4 from a peatland was first measured by Clymo and Reddaway (1971) who recorded differences among pools, hollows, and hummocks, and erratic effluxes from pools: results confirmed and extended in kind and magnitude hun-

dreds of times since. Wetlands in general are probably the main natural source of CH_4 in the atmosphere, and about a third of the total sources (IPCC, 2007). The main locus of CH_4 production in peatlands is a layer a few cm below the water table (Clymo and Pearce, 1995; Daulat and Clymo, 1998), but the concentration of CO_2 and CH_4 increases with depth in the peat, suggesting that there is continued gas production (decay) in deep peat too. How the dissolved gases move, if they do, is unclear. The advent of accelerator mass spectrometry (AMS) dating, which needs only a few mg of carbon, made it practicable to measure the age of dissolved gas samples from peat, and (among others) Aravena et al. (1993), Chanton et al. (1995), Charman et al. (1999), and Chasar et al. (2000a) have done that in peat 2 m or more deep. Dissolved gases were usually younger than peat

* Corresponding author.

E-mail addresses: r.clymo@QMUL.ac.uk (R.S. Clymo), c.bryant@NERCrl.gla.ac.uk (C.L. Bryant).

at the same depth, but in general the results have been few, unreplicated, and enigmatic, being interpreted mostly as gases produced from DOC that has moved down by mass flow. We planned the present work to have overt and covert replication of carefully taken samples, at numerous depths, in a relatively homogeneous deep peat. We report here the age and $\delta^{13}\text{C}$ of peat, peat fractions, and of DOC, dissolved CO_2 and dissolved CH_4 , at 50-cm intervals down to 720 cm in the Ellergower Moss peat bog in southwest Scotland.

2. METHODS

2.1. The site

Ellergower Moss near New Galloway in southwest Scotland (latitude $55^\circ 05'$ N, longitude $4^\circ 23'$ W; National Grid reference NX4879) is an elliptical rainwater-dependent raised (domed) bog about 500 m by 600 m and about 7 m deep in the middle, near which we sampled. It has a perched water table continually recharged by rainwater. It formed directly on a sandy plain about 9800 yr ago, and the unusually homogeneous peat is *Sphagnum*-dominated from 680 cm upwards. Humification on the 1–10 H-scale of von Post and Granlund (1926) is H4/5 at 1 m depth increasing to H7/8 at 1 m above the base. (This scale uses the results of squeezing peat in the hand: if un-coloured water runs out and all the solid remains in the hand the value is 1; if all the peat squeezes out leaving nothing behind the value is 10.) The bog, which is the first continuing the Silver Flowe series (Ratcliffe and Walker, 1958) southwards, is contiguous with Loch Dee which has a shallow basin with a sandy plain next to the bog but about 1.2 m lower than the bog base, and beyond that to the west a larger basin with deeps to 14 m.

Between Oct 1991 and Oct 1993 an automatic weather station recorded that precipitation was about 3000 mm yr^{-1} , mean annual air temperature was 8.1°C , the amplitude of the fitted annual sinusoidal cycle of temperature was 9.6°C , and mean wind speed was 4.5 m s^{-1} : the climate is equable, wet, and windy being without the regular droughts and extremes of temperature experienced by continental peatlands.

The surface vegetation of the central part of the bog, where we sampled, has a fairly complete cover of *Sphagnum* spp. with abundant liverworts including the Atlantic species *Pleurozia purpurea*. Hummocks 5–10 m across occupy about 67% of the area and are dominated by the ericaceous shrubs *Calluna vulgaris* and *Erica tetralix*, with abundant *Trichophorum cespitosum* and *Eriophorum vaginatum* sedges, and an understorey of *Sphagnum acutifolium*. In hollows, which occupy 10% of the area, the sedge *Rhynchospora alba* and other linear leaved species are abundant, with *Sphagnum papillosum* and *S. cuspidatum*. The remaining 23% is lawn. Around the margins of the bog the grass *Molinia caerulea* is abundant.

2.2. Peat samples

Samples for radiocarbon and $\delta^{13}\text{C}$ measurements were collected with a 'Russian' pattern corer, D-shaped in

cross-section (Belokopytov and Beresnevich, 1955), and cut into 4-cm thick slices.

Samples for dry bulk density measurement and for pore water extraction (see Section 2.5) were collected with a 1.5 m long, 100 cm^2 cross-section box corer (similar to that of Digerfeldt, 1966) and cut into 20 cm thick slices.

2.3. Gas sampling

Gases were collected by diffusion from the saturated peat through a gas-permeable membrane into an enclosed gas space. The sampler (Fig. 1) was a 300 mm long tube of aluminium alloy, of 35 mm outside and 28 mm inside diameter. In the lower half of the tube were eight rows of 10 holes, each 10 mm across. The total hole area of 63 cm^2 gave access to an internal volume of 175 cm^3 . This is sufficient to provide 5–20 mg of carbon as CO_2 and CH_4 . Over the holes a layer of 1 mm nylon mesh was stuck with thin but undeformable polyimide tape giving support to the gas-permeable silicone membrane (an incontinence condom), which was also fixed in place with polyimide tape. A second layer of nylon mesh was fixed by PVC tape around the outside of the membrane to protect it from damage.

Alloy plugs closed the ends of the metal cylinder, each fitted with an O-ring, and connected to each other by a central threaded rod. Screwing in these end plugs tightened the O-ring seals. The top plug had a lug to which a rope was knotted for recovering the sampler. The top plug also contained two 2.5 mm internal diameter stainless steel tubes. One finished flush with the inside of the plug. The other extended into the sample space and to it was attached a plastic tube that extended to the bottom of the sample space. To each of the outside tubes was attached a length, suitable for the depth at which the sampler was to be placed, of thick-walled PVC tube (outside diameter 6 mm, internal 2 mm). The tube gas volume of the deepest sampler was 2.5 cm^3 . This tube becomes quite rigid at field temperatures less than 5°C so it was extended by a wired-on 100 mm length of thick-walled butyl rubber tube which remained flexible at all field temperatures.



Fig. 1. A gas diffusion sampler. Holes through which gases diffuse are visible beneath the diffusion membrane and a layer of nylon mesh. See text for further details.

For inserting the samplers we took a 350 mm length of steel pipe, created a 10-mm slot along most of the side, and welded two steel wings to the pipe. The top end of this inserter was filled by a plug through which a 20 mm diameter threaded hole accommodated a two-start rod attached inside the tube to a piston, allowing the piston to be driven up and down within the tube. A sampler slid inside this pipe with tubes and recovery rope able to move in the slot. The threaded rod attached outside to a peat borer extension rod. In use, the piston started at the top of the pipe and the sampler lower end was flush with the bottom of the pipe. The whole was pushed down to just above the depth the sampler was to be placed at. Then the piston was screwed down, extruding the sampler into undisturbed peat, after which the inserter was withdrawn leaving the sampler in place. The inserter was then filled with peat from the same depth a few meters away and this was inserted by the same process immediately above the sampler.

Each sampler was flushed with at least 25 times its volume of He gas, then the ends of the two tubes were closed with a screw clip on the PVC and another on the butyl rubber, and with a glass rod in the end of the butyl tube. Pressure in the sampler was measured after attaching a mercury manometer to the top outlet tube. For the first few days after filling with He at atmospheric pressure the pressure *dropped* as He diffused out faster than gases in the peat diffused in. But after a week or so the pressure had risen again to atmospheric and thereafter increased to a steady value depending on how deep the sampler had been placed. On sampling, the glass rod at the end of the tube was removed under water: the emergence of bubbles would have indicated leakage past the clips, had any been seen (none ever was). To equilibrate the sampler with CH₄ from the peat would completely exhaust the dissolved gas from a cylinder about 10 cm diameter around the sampler (in practice of course there would be reductions in concentration further away). Equilibration with CO₂ would exhaust a cylinder just over 1 cm around the sampler.

Samplers were placed in the bog on 3 April 1996 at 50 cm depth intervals to 700 cm in a site 1 m square. The pattern of samplers was designed to maximise the distance between samplers: no two were closer than 150 cm apart. There were three replicate nests (of 14 samplers) about 3 m apart.

After 18 months pressure was measured and gas samples were taken for analysis (rejecting the first 50 ml or so to flush the tubes) driven partly by their own pressure and partly, if necessary in shallow samplers, by displacement with freshly boiled and cooled distilled water, into 300 cm³ glass flasks evacuated an hour before. The flasks had a high vacuum tap that was later attached directly in the laboratory to a vacuum line for gas separation. The whole process of gas transfer took less than 20 s.

The samplers were flushed again with He and re-sealed. After a further 10 months pressure was measured again.

The course of gas pressure change was checked at the laboratory with samplers (returned from the field) in an old fire extinguisher body filled with water saturated with

CO₂ and CH₄, and with the sampler tubes inside a larger water-filled tube fixed to the extinguisher body (and communicating with the water in the fire extinguisher) and extending 750 cm up the outside of the laboratory building. This simulated a sampler at 724 cm depth in peat: the intrinsic density of peat is about 1.6 g cm⁻³ and dry bulk density is about 0.06 g cm⁻³ (Clymo, 2004).

2.4. Gas sample preparation

The glass flasks containing the sample gases were attached to a glass and stainless steel vacuum line evacuated to about 1 mTorr. Methane and carbon dioxide were isolated from the field gas mixture by cryogenic separation using an external trap of liquid nitrogen (−196 °C). As methane will condense to some extent at this temperature, the methane was separated from the carbon dioxide in several stages by reducing the partial pressure above the cryogenic trap. The methane was oxidised to carbon dioxide in the presence of oxygen via a quartz tube packed with platinum-alumina pellets and heated to 950 °C. Combustion yields from bottled methane aliquots using this method were ≥97%. Carbon dioxide from the methane sample was dried with an alcohol/dry ice slush trap (−78 °C). The total volume of each gas aliquot was measured using a calibrated volume and corrected to standard temperature and pressure. Precision of ¹⁴C in field replicates ranged between 0.4% and 0.8% modern carbon (pMC) (mean SD = 0.7) for CO₂ and 0.4–1.4 pMC (mean SD = 0.8) for CH₄.

2.5. Peat and pore water sample preparation

(A) Sub-samples of moist peat were homogenised, oven dried at 40 °C, homogenised again, and combusted to CO₂ at 900 °C using copper oxide in quartz glass ampoules (Boutton et al., 1983). (B) Pore water containing DOC was separated by centrifuging field-moist peat, then filtering through 0.7 µm GF/F pre-combusted glass fibre filter paper. DOC was extracted by rotary evaporating, freeze-drying, and converting to CO₂ as for total peat. (C) Two operationally defined fractions of peat were isolated: humic acid (acid insoluble, alkali soluble) and humin (acid and alkali insoluble). Each was converted to CO₂, as in (A) above.

2.6. AMS ¹⁴C analysis

Sub-samples of CO₂ from 2.4, 2.5A, 2.5B, and 2.5C above were analysed for δ¹³C and converted to graphite for AMS ¹⁴C analysis. The program CALIB 5.0 (Stuiver and Reimer, 1993) was used with the intcal04.14c calibration set to get dendro-calibrated age probabilities. A single-value age was taken as the weighted mean of these (Telford et al., 2004). The (asymmetric) bars on graphs are the 0.16 and 0.84 quantiles which, were the distributions Gaussian (which they are not), would show ±1 SD. Stable carbon isotope values are reported relative to Vienna Pee Dee Belemnite in the standard δ notation.

3. RESULTS

3.1. Pressure in the samplers

Pressure inside the gas samplers (Fig. 2) was proportional to depth, as expected, and there was no consistent difference between measurements after 18 and a further 10 months. Laboratory measurements show that one month is sufficient to come close to a steady state. But the pressures in the field, though internally consistent, are only 44% of those measured with a silicon diaphragm sensor, which, in turn, agreed closely with the mass (of water and peat) per unit area above the measuring depth. Yet two of the *same* gas samplers when put, after recovery from the field, under a water column the equivalent of 724 cm deep in peat and measured with the *same* manometer developed 93% of the theoretical pressure after one month. We cannot account for this difference between field and laboratory measurements, but as it was proportional to the pressure in the peat we think it will not have affected our $\delta^{13}\text{C}$ or ^{14}C measurements. If there is any effect on dissolved gas concentration it will, again be proportional at all depths.

3.2. Concentration of dissolved gases and DOC in peat

The sum of partial pressures of CH_4 and CO_2 (not shown) increases curvilinearly with depth, paralleling the concentration profiles in Fig. 3, reaching about 85% at

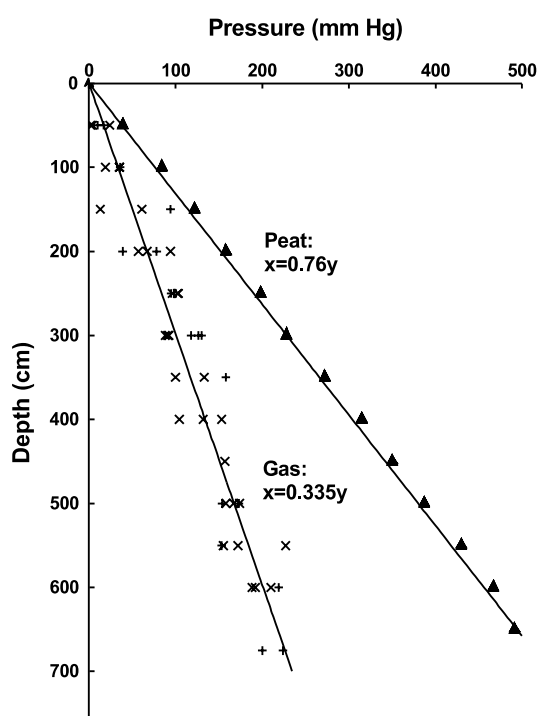


Fig. 2. Profile of pressure in samplers 18 months after flushing with He (upright crosses) and after re-flushing and a further 10 months (diagonal crosses), measured by mercury manometer. The line labelled 'Gas $x = 0.335y$ ' is fitted to these data. The line labeled 'Peat $x = 0.76y$ ' shows the theoretical relationship based on mass of water and peat above. The filled triangles are values of pressure in the peat measured by a silicon diaphragm sensor.

750 cm deep. The partial pressure of CH_4 in the gas space is about 3.3 times that of CO_2 at all depths.

To understand dissolved gas movement in peat, however, we need the molar concentration (C) in solution in the peat porewater. Directly from Henry's Law we get:

$$C = \frac{p}{100} \frac{P}{S} \frac{\alpha}{V_m} \quad (1)$$

where p is measured partial pressure of the chosen gas in the sampler (%); P is measured bulk pressure in the sampler; S is standard pressure (in the same units as P); α is the solubility coefficient of the gas in water ($\text{dm}^3 \text{dm}^{-3}$); and V_m is the volume occupied by 1.0 mol of gas at standard pressure and the prevailing temperature (23.1dm^3 at 8°C). Solubility coefficient α is really a partition coefficient. For CH_4 in water at 8°C its value is 0.0443 (Jähne et al., 1987)—the concentration of dissolved gas in the peat is about 4% of that in the sampler—and for CO_2 , α is much larger at 1.28. Thus, if the partial pressure of CH_4 in the sampler is about 3 times that of CO_2 (as it is in many samples), the calculated molar concentration of CO_2 in peat is then about 10 times that of CH_4 at the same depth. The assumption that the values of α are the same in peat as in water is probably wrong in detail, but as long as the bias is independent of pressure the inferences we make will not be seriously affected. The pH in the peat is 4.0 or less at all depths, so concentrations of bicarbonate and carbonate are negligible.

Dissolved gas concentrations at a site about 50 m away (Fig. 3), measured previously by a different diffusion method (Clymo and Pearce, 1995), are fairly similar to the present ones. Values for CO_2 are a little greater than in our present work but the other site is 200 cm shallower, and the concentration at its base is similar to that measured at the base in this work. Similar CH_4 concentration profiles are reported for a bog in the Lake Agassiz peatland in North America by Romanowicz et al. (1993) and by Romanowicz et al. (1995).

For peat and DOC we assume the concentration of carbon is 0.52g g^{-1} as measured on 50 samples at Ellergower (Clymo et al., 1998). The dissolved gas profiles are convex, but the DOC profile is concave, and near the base DOC concentration exceeds that of both dissolved gases. Most of the reported concentrations of DOC for raised bogs are for runoff, or for depths less than 50 cm. Chasar et al. (2000b) report values of about 6mmol dm^{-3} at depths to 3 m in a Minnesota peat bog, and Cole et al. (2002) report about 10mmol dm^{-3} at 50 cm depth in an English blanket bog. Both values are similar to those for DOC in the top two-thirds of Ellergower.

3.3. Age profiles

The dendro-calibrated ^{14}C age of dissolved CO_2 and CH_4 , of peat, of peat fractions, and of DOC are shown in Fig. 4 (details are in Appendix B). In all cases the reproducibility and consistency—high for this sort of work—is notable. The peat age profile is faintly convex. Constituent humic acid and humin fractions are similar to the whole peat. DOC is 500–1000 yr younger at a given depth than the peat. Both dissolved gases are only about half the age

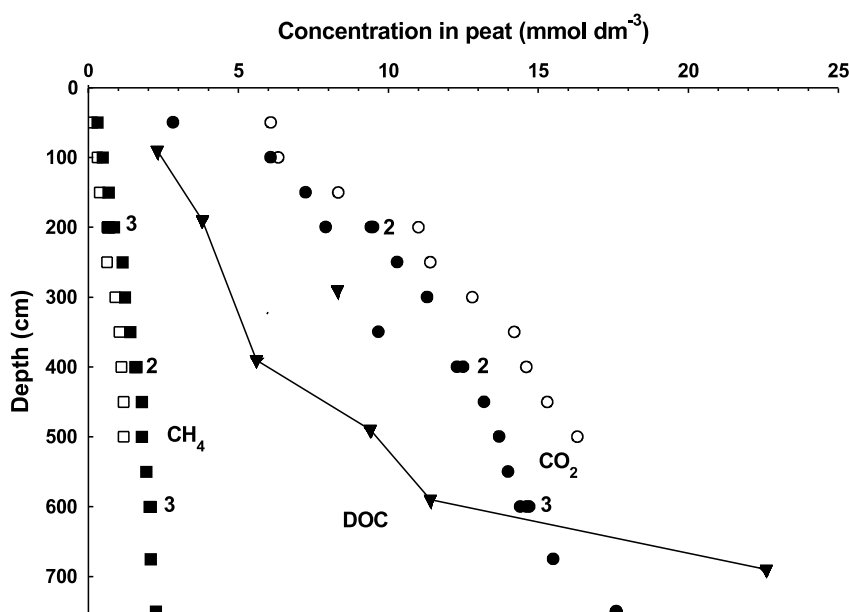


Fig. 3. Profile of concentration of dissolved CO_2 (circles) and CH_4 (squares), and of DOC (down-pointed triangles); measured in this work (filled symbols) and at a site 50 m away (unfilled symbols, Clymo and Pearce, 1995). Number of overlapping symbols, where this is not obvious, is shown by annotations '2' and '3' representing field replicates. Lines linking DOC measurements are to aid the eye. One apparently aberrant value is skipped.

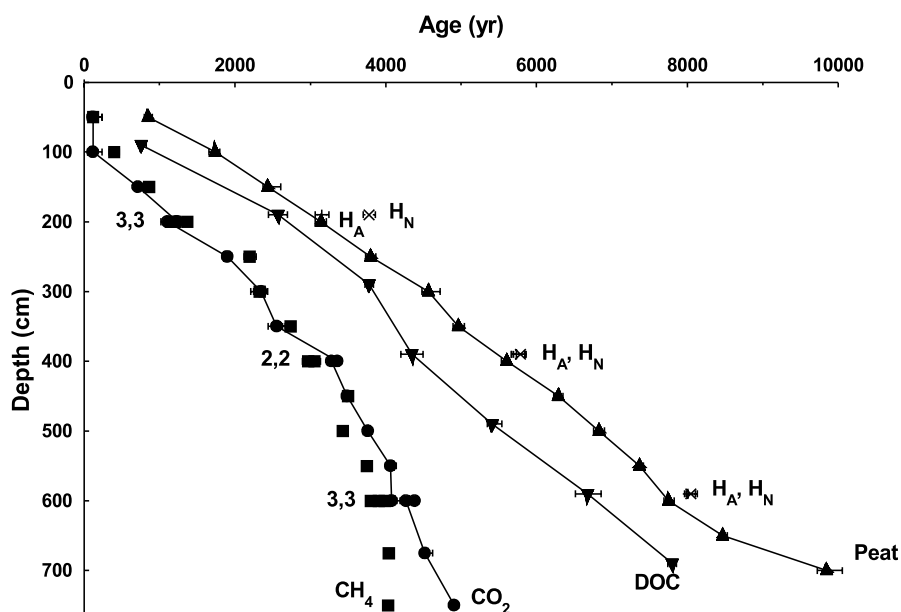


Fig. 4. Profile of dendro-calibrated weighted probability age of whole peat (up-pointed triangles), DOC (down-pointed triangles), of dissolved CO_2 (circles) and CH_4 (squares), of separate humic acid (H_A , upright crosses) and humin (H_N , diagonal crosses) fractions, and of near coincident fractions ($\text{H}_{A'}$, $\text{H}_{N'}$). Bars are the (asymmetric) 0.16 quantiles (± 1 SD if the age distributions were Gaussian) including analytical and calibration uncertainty; in many cases the bars end inside the symbol. The lines linking values for whole peat, DOC, and dissolved CO_2 are to aid the eye, and to reveal that the dissolved CH_4 profile crosses over that of CO_2 . Number of overlapping symbols, where not obvious, is shown by annotations '2' and '3' representing number of field replicates.

of the peat at the same depth. The dissolved gas profiles cross-over one another at about 400 cm (half way down): in the top half of the profile CH_4 is a few hundred years older than CO_2 , and a similar amount younger in the lower half of the profile.

3.4. $\delta^{13}\text{C}$ values

Values for $\delta^{13}\text{C}$ of peat and dissolved gases at the same depth are shown in Fig. 5. The results are, again, reproducible and consistent, and trends are unequivocal. Peat $\delta^{13}\text{C}$

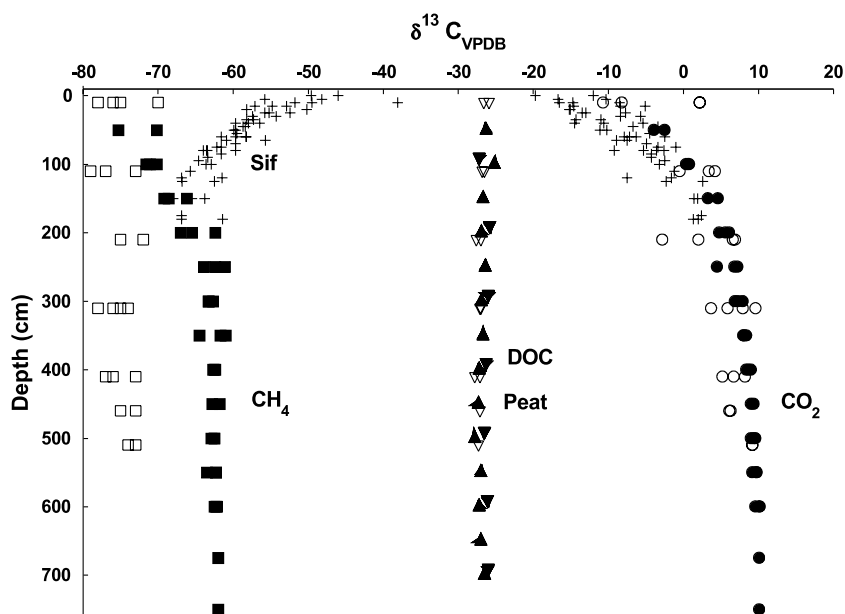


Fig. 5. Profile of $\delta^{13}\text{C}_{\text{VPDB}}$ (‰) for whole peat (up-pointed triangles), for DOC (down-pointed triangles), and for dissolved CO_2 (circles), and CH_4 (squares) in this work (filled symbols); at a site about 75 m away (unfilled symbols, Waldron et al., 1999); and in Sifton Bog, Ontario, Canada (upright crosses for both gases, Hornibrook et al., 1997).

has a mean value of -26.8‰ ($\text{SD} = 0.6$, $n = 14$) trending slightly linearly downward from -26.2 at the surface to -27.3‰ at 700 cm. Below 100 cm $\delta^{13}\text{C}$ -DOC is consistently less negative than that of peat by a mean value of 1.6‰ . In the lower half CH_4 is nearly exactly more ^{13}C -depleted than peat (at the same depth) as CO_2 is more ^{13}C -enriched. Mean differences from peat are -35.3 and $+36.5\text{‰}$ though the 95% confidence limits do not overlap zero difference between the offsets from the peat value. But the imbalance is only 1.2‰ —about 3% of the individual differences. Nearer the surface both dissolved gases become more ^{13}C -depleted and have near identical ‘hockey stick’ profiles.

Peat $\delta^{13}\text{C}$ measurements made in earlier work at Ellergower (Waldron et al., 1999) at a somewhat shallower site about 75 m away are fewer and rather more erratic. The $\delta^{13}\text{C}$ - CO_2 values are about the same, but CH_4 values are about 10‰ more depleted below 100 cm.

In the surface 200 cm of Sifton Bog in Canada (Hornibrook et al., 1997) $\delta^{13}\text{C}$ of CO_2 appears to be consistent with the Ellergower values; CH_4 values at 150 cm depth are similar at both sites, but nearer the surface, above about 150 cm the Sifton Bog ones become ^{13}C -enriched, whereas the Ellergower ones become more ^{13}C -depleted. (Sifton Bog has a floating *Sphagnum* mat and central open water, apparently similar to a European schwingmoor, and structurally different to Ellergower.) The offset between the surface values at the two sites is about 30‰ . A pattern similar to that at Sifton Bog was found by Kotsyurbenko et al. (2004).

In the hope that $\delta^2\text{H}$ values for CH_4 might help to identify microbial processes, Professor T. Fallick measured values of -288 and -256‰ (relative to VSMOW) at 150 and 350 cm deep.

4. DISCUSSION

We attribute the reproducibility and consistency of the results to four things: the homogeneity of the peat profile; the use of diffusion samplers that separate dissolved gas from peat in situ; willingness to leave the samplers for a long time to approach close to a steady state; and careful sample treatment in the laboratory. Diffusion samplers were chosen on merit, but in fact no other method for separating dissolved gas in the field was suitable. Other workers have preferred to sample pore water by ‘sippers’ that allow water to flow under natural pressure into a small, initially empty, sampler pushed into the peat (Hornibrook et al., 2000; Biester et al., 2005); or by suction (Dinel et al., 1988; followed by Aravena et al., 1993; Charman et al., 1994, 1999); or by direct peristaltic pumping at a rate slow enough to avoid dissolved gas bubbles (Chanton et al., 1995; Romanowicz et al., 1995; Reeve et al., 1996; Chasar et al., 2000a). All three methods are ‘immediate’ and imply a rather porous peat. A fourth method is the ‘peeper’ in which a $0.2\ \mu\text{m}$ filter allows solutes to diffuse from pore water into initially pure water, usually for several weeks (Avery et al., 1999; Chasar et al., 2000b). This method does not require a highly porous peat, though it does not preclude it. All four methods need a later separation of dissolved gases into a headspace.

The hydraulic conductivity of the peat at Ellergower is so low (Clymo, 2004) that only the last of these methods might have been used. In practice, laboratory centrifugation was necessary to obtain pore water from our peat, the yield of which was only a few % of the total water in the peat. Piezometer tubes inserted into the deep peat (Clymo, 2004) do fill up with water, but the rate is less than

50 cm in 10 days and that under a pressure difference of 0.7 bar.

4.1. Applicability of the results

In the main peat of the Ellergower bog, dissolved gas concentrations vary little with season (Clymo and Pearce, 1995). Peat humification increases rapidly down to 60 cm (Clymo, 2004) and then more slowly but steadily to 750 cm; dry bulk density is about 0.06 g cm^{-3} down to 550 cm increasing steadily below that to 0.1 g cm^{-3} (paralleled by mechanical stiffness); and the hydraulic conductivity is $5\text{e-}6$ to $1\text{e-}6 \text{ cm s}^{-1}$ (Clymo, 2004). A hydraulic gradient near the bog center of 0.01 m m^{-1} implies downward flow rates as small as $60 \text{ cm millennium}^{-1}$. This surprisingly small value results from the low hydraulic conductivity of the Ellergower peat: about two orders of magnitude smaller than that in inland bogs in North America and in Russia. There are few and only small gas bubbles in the Ellergower peat (only one sample in 123 showed any evidence of a gas phase, and that one only 15% by volume). The yearly temperature damping depth—the depth at which the amplitude of a sinusoidal fluctuation in temperature applied at the surface has fallen to $1/e$ (about 0.37) of that at the surface (Monteith, 1973)—is about 130 cm (Daulat and Clymo, 1998), and with the yearly amplitude of $9.6 \text{ }^\circ\text{C}$ implies a damped amplitude at 2.5 m deep of barely $1.5 \text{ }^\circ\text{C}$ (a value confirmed by direct measurements), and an even smaller range lower down. The pH is 4.0 or less throughout.

All this is in marked contrast with most of those bogs in North America in which similar work has been done. Pore water can be easily extracted from them (Chanton et al., 1995; Romanowicz et al., 1995; Reeve et al., 1996; Chasar et al., 2000a). They show large seasonal variations in CH_4 concentration and $\delta^{13}\text{C-CH}_4$ profiles (Kelley et al., 1992; Romanowicz et al., 1995; Avery et al., 1999; Glaser et al., 2004) and large and changing volumes of gases in bubbles (Romanowicz et al., 1995; Glaser et al., 2004; Strack et al., 2005). They are less humified, and have hydraulic conductivities (Chason and Siegel, 1986) 100–200 times greater than Ellergower. Most Siberian peatlands are probably similar.

Because of these differences what follows should not be uncritically extrapolated to other peatlands.

4.2. Peat fractions

The ^{14}C age of operationally defined humic acid and humin fractions sometimes differs by 500 to more than 1000 yr, though erratically positive and negative (Shore et al., 1995; Nilsson et al., 2001). In Fig. 4, however, five of the six humic acid and humin ages are similar to each other and to the whole peat, with a small tendency for the humin to be older than the peat. This implies that there is minimal transport of these operationally defined peat components or that any post-depositional transport of such components represents a small fraction of the total peat carbon, or both. A single humin sample was about 300 years older than the associated humic acid and peat. We suggest that in our

work the whole peat age may be used without serious misgivings.

4.3. Transport processes

That the age of dissolved CO_2 and CH_4 at a given depth (of 2 m or more) is less than that of peat at the same depth has hitherto been attributed (for example: Aravena et al., 1993; Chanton et al., 1995; Charman et al., 1999) to downward mass flow of pore water carrying dissolved gas in solution, or similar transport of DOC that is then attacked by bacteria with the release of gases younger than the peat at the same depth. If this were the only process one might expect the concentration profiles of DOC to be of similar shape to those of the dissolved gases, but Fig. 3 shows that the DOC profile is concave while the dissolved gas profiles are convex. One might also expect that DOC formed from newly created peat would be the most readily decomposed, yet the gap between the age profile for dissolved gases and that for peat (and for DOC) increases, rather than decreases, with depth. Finally, the rate of downward flow is so small that readily decomposable DOC would hardly have moved from where it formed before it decayed. So we consider a second process.

Diffusion has occasionally been mentioned (Aravena et al., 1993; Romanowicz et al., 1995) and its quantitative consequences over a year or so have been considered (Romanowicz et al., 1995), but its quantitative consequences over millennia have been ignored, perhaps because the diffusion coefficient of common gases dissolved in water is about $1.0\text{e-}5 \text{ cm}^2 \text{ s}^{-1}$, and this seems a very small value. In physiology and cell biochemistry diffusion may be effective in transport, but only for distances up to a few μm . In peat the distances are five orders of magnitude greater. But we have millennia—about nine orders of magnitude—longer in which the movement can occur: in more relevant units $1.0\text{e-}5 \text{ cm}^2 \text{ s}^{-1}$ is $315 \text{ cm}^2 \text{ yr}^{-1}$ or $3.2\text{e}5 \text{ cm}^2 \text{ millennium}^{-1}$.

Equations (Appendix A1 and A2) describing the combined effects of growth of peat and of movements by diffusion of dissolved gases in the peat cannot be solved analytically. So, to assess the relative importance of mass flow and diffusion, we programmed a computer simulation. We consider this simulation to be no more than an aid to discussion, as it is much less sure than the measured values released to us by Nature herself.

4.3.1. A simulation

We give here an informal description; formal details are in Appendix A.

Carbon is added by photosynthesis to the living plants growing on the surface of our peatland, the surface of which grows ever upwards. Because bog-mosses decay much more slowly than most other plants they soon come to dominate the peat. The new moss growth shades that below which then dies and begins to decay, mainly through the actions of fungi and bacteria. The moss carpet structure is mostly gas-filled (Hayward and Clymo, 1982), very porous to gases and water, and decay by fungi and bacteria is mostly aerobic. Eventually the increasing load of new growth above, and especially of the order of magnitude

greater associated water, causes the moss structure to collapse. This reduces the space between the dead leaves and stems, thus increasing by two or more orders of magnitude the resistance to water flow so the peat as it now is becomes waterlogged. Rain percolating down picking up DOC on the way is forced to flow sideways off the peatland at this interface. The diffusion rate of gases dissolved in water is barely 1/10,000 that in air and the microorganisms just below the watertable use up the molecular oxygen faster than it can be replaced from the air, so conditions become anoxic and a different suite of organisms (bacteria) takes over. A few cm below the current watertable the anaerobic rate of decay is high (Clymo and Pearce, 1995; Belyea, 1996; Daulat and Clymo, 1998) but below that, for unclear reasons, the rate of decay drops by about three orders of magnitude though decay does continue. Hydraulic conductivity at the surface is so high that the water table usually oscillates by only a few cm about its mean value, but in long dry periods during which evaporation and runoff exceed precipitation the water table sinks perhaps 30 cm into the usually anoxic peat. It recovers rapidly when the drought ends (Clymo and Pearce, 1995; Daulat and Clymo, 1998).

Ingram (1978) named the surface down to the depth to which the watertable sinks in a dry summer—about 50 cm or so at our measurement site—as the *acrotelm* (Greek ‘top peat’), and the permanently waterlogged anoxic peat below—about 650 cm thick at our site—the *catotelm* (‘bottom peat’). For our simulation we need to subdivide the top zone into the predominantly oxic acrotelm proper (10–20 cm thick) and the usually anoxic but periodically oxic *mesotelm* (30-cm thick) below it: the subzone in which anoxic decay is relatively fast.

The simulation then deals with the mesotelm and catotelm only. Processes in the unsaturated, predominantly oxic acrotelm proper are very different from the zones below it, and simulation would require speculative mechanisms with unknown parameters and their values. The rate of movement of gases is so much greater in the highly porous acrotelm proper than it is in the zones below that as far as gases go the zone is little different from the air above. We therefore simulate only the mainly anoxic mesotelm and the permanently anoxic catotelm. We can then ignore lateral runoff, the effects of transport through the aerenchyma of plant roots, and so on.

In our simulation the peat is grown a layer at a time with a time step typically 10–25 yr. New mass is added once only as a birthright of the new top layer at a rate that is the rate of addition of *peat*: it concerns that part of the material originally fixed by photosynthesis that has not been lost by predominantly aerobic decay while the acrotelm proper moved up past it as new mass was added at the surface. Then decay is allowed in all layers, producing DOC and dissolved CO₂ and CH₄ directly from the peat. (We assume here that DOC is *not* a substrate for gas producing microorganisms because the mass flow rate is so small at our site that any labile DOC would be metabolised before it could move an appreciable distance.) Decayed mass (as DOC, and as dissolved CO₂ and CH₄) is, and an equivalent number of molecules are, redistributed to other layers or the air above by mass flow (all three fractions) and by diffusion

(dissolved gases only, because the DOC molecules are, we suppose, much larger and have correspondingly smaller diffusion coefficients). The peat base is supposed impermeable, as the Ellergower base is (Clymo, 2004). Molecules are ‘time-stamped’ with the age of the peat layer from which they were formed, so the mean age of DOC and dissolved gases in a layer can be calculated. These operations are iterated until a chosen total age is reached.

So far we have simulated the catotelm. To simulate the mesotelm the upper layers of the simulation (representing the top 30 cm or so) were allowed a greater decay rate than the main catotelm peat mass below. This is unsatisfactory to the extent that the mesotelm becomes unsaturated and oxic for short periods, but the general idea is that there is a relatively thin mesotelm that produces gases, whether saturated or not, at a much greater rate than the main catotelm.

We are aware that there are other transport processes. Ebullition of bubbles is important in many peatlands (especially in pools), for example Rosenberry et al. (2003), Baird et al. (2004), Glaser et al. (2004), Tokida et al. (2007), but the main peat zone at Ellergower contains less than 1% gas space, so ebullition is probably unimportant. In any case the peat there is too resistant to allow bubbles to pass through it. Another process is gas efflux through the gas spaces in the roots of plants growing on the peat (for example Shannon et al., 1996; Stephen et al., 1998). This process is driven by diffusion or in some cases by pressure-flow (Armstrong et al. (1992) and is particularly important in peatlands dominated by sedges (Shannon et al., 1996), but at our site on Ellergower the only plant roots reaching the mesotelm in any abundance, and those not penetrating far, are those of cotton grass (*Eriophorum*). Another possibility is that CH₄ is oxidised to CO₂. This is known to happen in peat from Ellergower (Pearce and Clymo, 2001) but mainly in the acrotelm proper that we have not simulated. Other choices might be made, but as our purpose is to assess the role of diffusion, so we have tried to keep the simulation as simple as necessary for this purpose: our goal is understanding rather than exact replication of Nature’s complex machine.

Fig. 6 shows what happened when the mesotelm had the same decay properties as the catotelm, but otherwise the same values for other parameters as were eventually found for the ‘best fit’ (Table A2.1). The *shapes* of the profiles, concave or convex, are the same as the measured ones, and the profile of the age of DOC approximates the measured one, suggesting that mass flow is sufficient to account for the age profile of DOC; but the concentrations of DOC are much too high. The age profiles of the dissolved gases are 4000 yr too old at the top, falling to a realistic value at the base. It seems that some extra source of young dissolved gases is needed near the surface: a source that must be strong because dissolved gases from it can be lost to air more easily than those from lower down.

Next we supplied such a source (by increasing the rate of decay in the mesotelm using the eventual ‘best fit’ values of parameters in Table A2.1). Fig. 7 shows the results when diffusion was prevented. The profile of dissolved gas concentrations was concave (the measured profiles are convex)

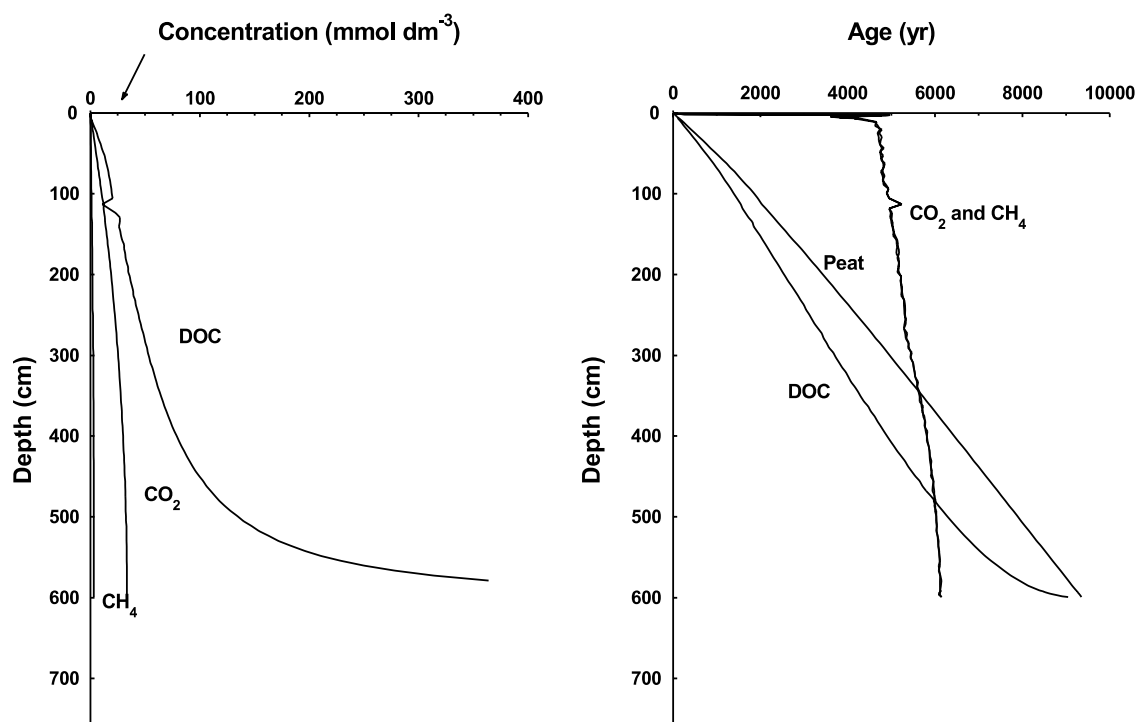


Fig. 6. Simulation (Appendix A2) of profiles of concentration of DOC and dissolved gases, and of age of peat, DOC, and dissolved gases, both in 9352 yr-old peat. Parameter values are those in Table A2.1, that gave the 'best' fit, except there is no mesotelm zone of enhanced decay rate. The concentration ranges to 400 mmol dm^{-3} , while in Fig. 8 it has only 1/16 this range, shown by the arrow.

and concentrations are three orders of magnitude greater than were measured. Age profiles of dissolved gas were similar to those of DOC and concave (the measured profiles are convex).

Lastly we used the full simulation with a differentiated mesotelm of greater decay rate, and allowing diffusion. We optimized the fit of the simulation model to the Ellergower data (Appendix A2 and Table A2.1). The 'best fit' results are shown in Fig. 8. The fit to the peat age profile is necessarily good (because it was separately and formally optimized). The shape of all six other profiles is the same as the measured ones, and four are close to the measured positions too. The two simulated dissolved gas age profiles are a bit too steep, and do not show the cross-over seen in the measured profiles at 400 cm deep. We used the same CH_4 : CO_2 ratio in both mesotelm and catotelm. Further experiments (not shown) with different CH_4 : CO_2 ratios in the mesotelm reproduced this cross-over. The fit of dissolved gas ages can be improved further by adding yet another parameter, but we recall that our purpose is to show the relative importance of diffusion and mass flow, not to achieve a very close fit to the measurements.

Yet more experiments showed that increasing the mass flow rate 10-fold had little effect except to increase the concavity of the DOC concentration profile, and to move it closer to the y -axis. Slowing or increasing diffusion 3-fold had little effect on the age profiles (and none on the DOC profiles which are not subject to diffusion), but it increased or decreased dissolved gas concentrations about 3-fold too.

4.3.2. Unmeasurable results from the simulation

This simulation reveals things that cannot be measured. (1) More than 99% of the dissolved gas movement, assessed by total vertical distances that the molecules moved, results from diffusion: less than 1% from mass flow. (2) For the fit in Fig. 8, 99.6% of the DOC produced in decay (in the main peat) is still in the peat, while only 0.3% of the dissolved gases are still in the peat: all but a tiny proportion of the dissolved gases has effluxed to the air. The simulated current efflux of CH_4 is about $0.3 \text{ mol m}^{-2} \text{ yr}^{-1}$ while the mean measured at Ellergower (Clymo and Pearce, 1995) was about $1.0 \text{ mol m}^{-2} \text{ yr}^{-1}$ —modest agreement considering the uncertainties in the measurements and simulation.

Three other features not amenable to measurement are shown in Fig. 9. (3) The proportion of dissolved gas molecules that formed from peat that was, at the time, in the mesotelm, where decay is more active, decreases with depth to about 15% at the base. (4) The efflux of gases gradually decreases, but (5) the age of effluxing gases increases the longer peat growth continues.

4.3.3. Simulation conclusions

The features of the simulation are consistent with the conclusions that for our site (1) mass flow can account for the concentration profile and the relatively small displacement of age profiles of DOC; (2) diffusion is a much more important cause of the movement of dissolved gases in this bog than is mass flow; (3) downward diffusion from the mesotelm is crucial in accounting for the observed large displacement of age profiles of dissolved gases.

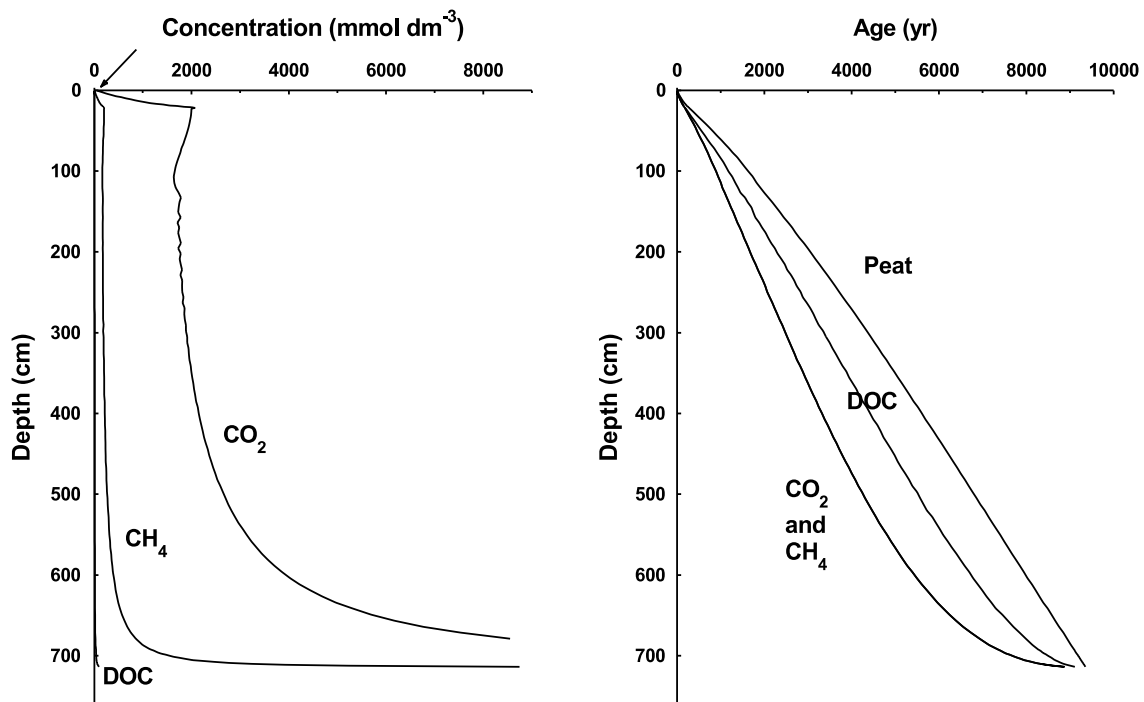


Fig. 7. Simulation (Appendix A2) of profiles of concentration of DOC and dissolved gases, and of age of peat, DOC, and dissolved gases, both in 9352 yr-old peat. Parameter values are those in Table A2.1, that gave the 'best' fit, except that diffusion is prevented. The concentration ranges to more than $8000 \text{ mmol dm}^{-3}$, while in Fig. 8 it has only 1/320 this range, shown by the arrow.

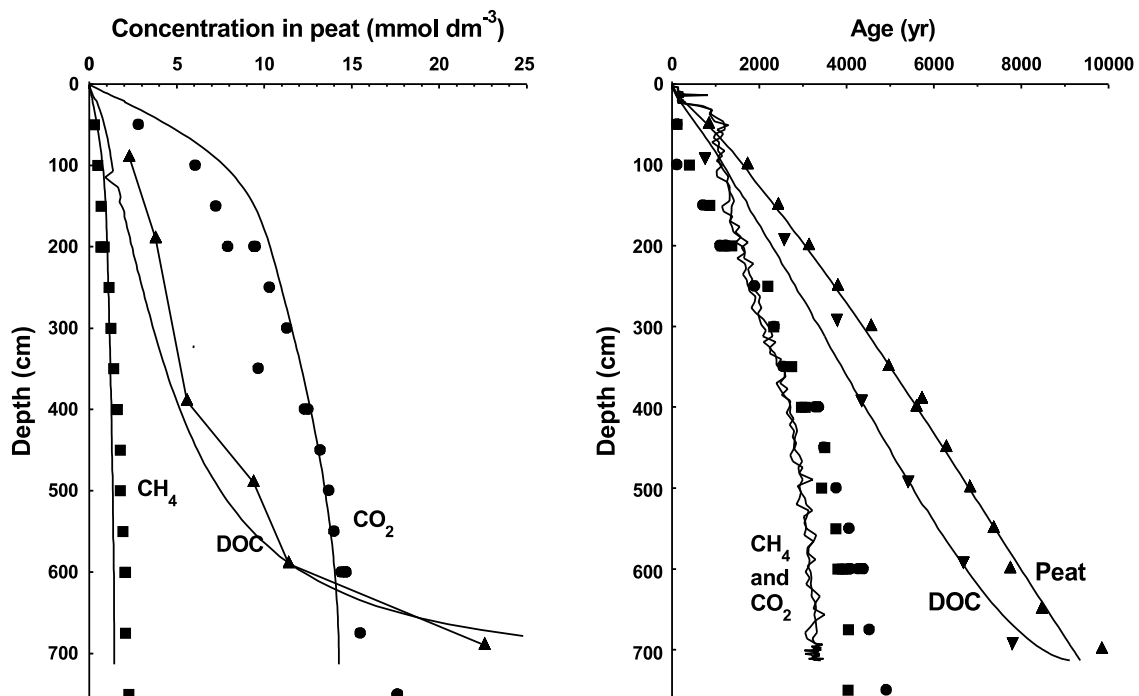


Fig. 8. 'Best fit' (see text) simulation (Appendix A2) of profile of concentration of DOC and dissolved gases, and of age of peat, DOC, and dissolved gases, both in 9352 yr-old peat. Lines are the simulation; filled symbols are measured values of peat (up-pointed triangles), DOC (down-pointed triangles), dissolved CO_2 (circles) and CH_4 (squares). Parameter values are those in Table A2.1. The concentration ranges to only 25 mmol dm^{-3} , while in Figs. 6 and 7 it is 16 and 320 times greater.

The simulation has 11 parameters. The diffusion and mass flow parameter values are physical measurements.

Four of the free parameters were optimized separately to get decay rates. The remaining five may seem to leave

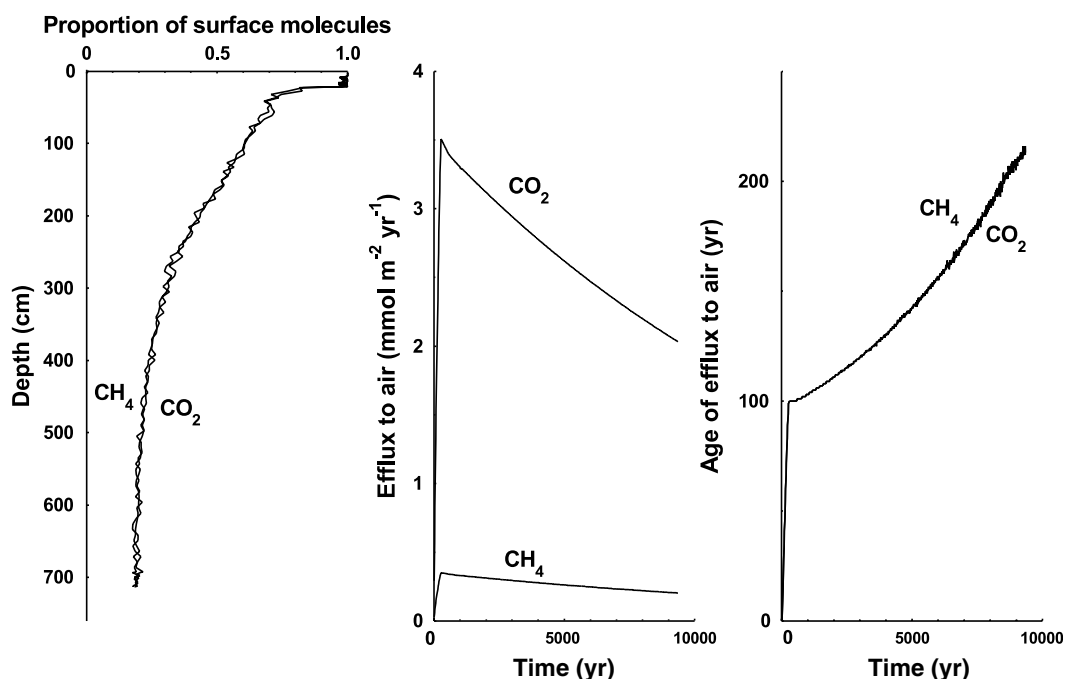


Fig. 9. Other features of the 'best fit' simulation (Fig. 8). Left: profile of the proportion after 9352 yr of molecules generated in what were then surface layers. Center: efflux of gases during the development of the peat. Right: age of gases effluxing to air during the development of the peat.

ample ability to fit six simple curves. The real system does have an intermittently oxic zone however with properties at least broadly similar to those assumed. Further, the *shapes* of profiles are correct, and it is possible to choose parameter values so that the *placement* of concentrations is correct.

4.4. $\delta^{13}\text{C}$

4.4.1. Comparison with other work

The $\delta^{13}\text{C}$ - CO_2 values of Waldron et al., 1999, taken about 75 m away from ours, agree reasonably well with ours (Fig. 5), but their $\delta^{13}\text{C}$ - CH_4 values are lower and more erratic than ours. They interpret them as showing two zones meeting at 250 cm depth. Our $\delta^{13}\text{C}$ measurements (Fig. 5) seem to us to form smooth 'hockey stick' profiles. The simulation shows (Fig. 8) that the shape of the profile of proportion of dissolved gas molecules produced in the surface layer above the main peat is the mirror image of the $\delta^{13}\text{C}$ - CO_2 and $\delta^{13}\text{C}$ - CH_4 profiles. This is consistent with dissolved gases produced in the surface by one set of processes diffusing down to mix with dissolved gases produced in the main peat by a different set of processes having a different signature, as Hornibrook et al. (1997) suggest. We then agree with Waldron et al. (1999) that there may be two zones, but our division would be at about 50 cm depth: much shallower than their 250 cm one.

Our most negative $\delta^{13}\text{C}$ - CH_4 value was -71‰ , but -90‰ has been recorded in efflux from a Welsh blanket bog by Boves and Hornibrook (2006) who give a detailed discussion of possible explanations.

4.4.2. $\delta^{13}\text{C}$ and microbial processes

In the periodically oxic mesotelm, sulphate reduction is rapid (Clymo, 1966). This fermentation competes strongly with methanogenesis and may be as (or more) important than methanogenesis in converting carbon to gaseous form (Watson and Nedwell, 1998; Vile et al., 2003). In the main catotelm peat, however, sulphide (in H_2S) is abundant (Clymo, 1991) and sulphate rare (Claricoates, 1990), while readily available nitrogen is as NH_4^+ rather than NO_3^- . In the deep main peat decay rates are very low, and the simulation assumes that all the carbon mass loss can be accounted for in CH_4 , CO_2 , and DOC.

Anaerobic decay of natural materials has long been known to produce CH_4 depleted, and CO_2 enriched, in ^{13}C relative to the source material (Games and Hayes, 1976). Part of the explanation of the almost equal and opposite preferences for ^{13}C - CH_4 and ^{13}C - CO_2 might be acetate fermentation with preference for $^{12}\text{CH}_3^{13}\text{COO}^-$ over $^{13}\text{CH}_3^{12}\text{COO}^-$. But if that were the only process one might expect the concentration of the two dissolved gases to be similar, which it is not (Fig. 2). Whiticar et al. (1986) define $\alpha_{\text{C}} = (\delta^{13}\text{C}-\text{CO}_2 + 1000) / (\delta^{13}\text{C}-\text{CH}_4 + 1000)$ with a value less than 1.05 as characteristic of acetate fermentation, and above that of CO_2 reduction. Our value is about 1.075 at all depths at Ellergower (the $\delta^{13}\text{C}$ - CH_4 and $\delta^{13}\text{C}$ - CO_2 profiles are almost parallel). Similar values were measured in peat bogs by Lansdown et al. (1992), Aravena et al. (1993), Waldron et al. (1999), and Hornibrook et al. (2000), though Lansdown et al. (1992) got values mostly around 1.05–1.06. These values thus point to CO_2 reduction (Whiticar et al., 1986). A further complication is that Kotsyurbenko et al. (2004) found the proportions of CH_4 pro-

duced at 40 cm depth by acetate fermentation and CO₂ reduction was 65: 35 with α_C increasing from 1.03 at the surface, indicative of acetate fermentation, to 1.07 at 120 cm depth, while Avery et al. (1999) found the same ratio changed from -10: 110 in January to 85: 15 in June, though Lansdown et al. (1992) report that in August and September peat from 40 cm depth to which ¹⁴C-labelled acetate or bicarbonate had been added showed that almost all the CH₄ was produced by CO₂ reduction. The situation is confused.

Near the surface our $\delta^{13}\text{C}-\text{CH}_4$ values continue the trend to depleted ¹³C values, while the Sifton Bog values diverge in the opposite direction. A similar difference, between bog and fen, was found by Chasar et al. (2000a). It seems that the microbial processes in the surface of rainwater-dependent raised bogs may be different from those of other types of peatland.

We conclude that peat bogs are microbiologically complex, differ in space, and may vary in time. Gas production is the result of consortia of microbes of differing composition and great variety (Sisova et al., 2003; Galand, 2004; Kotsyurbenko et al., 2004). We need more microbiological observations and experiments, particularly in *deep* peat (which most microbiologists lack the equipment to reach) before being able to make sense of our results at Ellergower.

4.4.3. $\delta^{13}\text{C}$ and mass conservation

At the base of the peat, in the simulation, 62% of the mass had decayed. We had expected that any isotopic discrimination, in favor of or against ¹³C, in the dissolved gases produced by decay (Ågren et al., 1996) would be shown by enrichment in the remaining peat of the less favored isotope. But there is no sign of any such enrichment in Fig. 5. This indicates that at least until the production of the final small substrate from which dissolved gases are to be produced there is no discrimination between ¹³C and ¹²C.

Mass conservation requires that the total mass of ¹³C and of ¹²C in the end products of decay be the same as that in the peat. Consider the hypothetical case of the macromolecules in peat being reduced in stages, by processes that do not discriminate between the isotopes, to a final substrate which is broken up into a final (gaseous) product containing all the carbon by a process that does discriminate against ¹³C by a proportion s (perhaps 0.05 for illustration) such that the quotient $Q_{\text{GAS}} = {}^{13}\text{C}/{}^{12}\text{C} = (1 - s)/(1 + s) = 0.905$ while in the peat and substrate, $Q_{\text{SUBS}} = 1.0$. How can this be consistent with mass conservation? The older peat has been in an environment with little variation for centuries or millennia so we suppose it to be in a steady state in which there is a constant sized pool of substrate to which is added material with the $Q_{\text{PEAT}} = 1$ of peat at a rate exactly balanced by loss of the gaseous end product. How was the steady state reached? Production of the first batch of ¹³C-depleted dissolved gas leaves the substrate pool slightly enriched in ¹³C. The first addition to the pool from peat partly, but not entirely, counters this. The same effects follow the second batch of removals and additions, so the pool is now even more enriched, though by a smaller

increment than after the first batch. This process continues with Q_{SUBS} approaching the asymptote $1/Q_{\text{GAS}} = (1 + s)/(1 - s) = 1.105$, while Q_{GAS} approaches 1.0. In short, the dissolved gas comes to have the same Q as the peat, and discrimination is possible in the production of dissolved gas because the substrate pool has become and remains enriched. If the substrate pool is included in DOC but is only a small fraction of it then Q_{DOC} will be little altered. But the dissolved gas itself has the same $\delta^{13}\text{C}$ as the peat. That is contrary to the facts.

Another way to achieve mass conservation is for there to be two (or more) final products with the Q values of one less than Q_{PEAT} and of the other greater than it. The values for CO₂ and CH₄ in the lower peat (Fig. 5) fit this rather exactly. But the concentration of CO₂ at our site is much greater than that of CH₄ (Fig. 3) so mass conservation is not achieved. Q_{DOC} from 200 cm downwards is consistently slightly greater (by $\delta^{13}\text{C} = 1.3\%$) than it is in peat, but not by enough to give mass conservation. In the top 200 cm the imbalance is greater as both the CH₄ and CO₂ $\delta^{13}\text{C}$ curves bend to the left. At Sifton Bog the $\delta^{13}\text{C}-\text{CH}_4$ curve for the top 150 cm does bend towards the CO₂ one and in that case there may be mass conservation.

There are isotope fractionation effects between CO₂ in gas and in water which will, we suppose, be reflected in the $\delta^{13}\text{C}-\text{CO}_2$ values (Vogel et al., 1970), but at the Ellergower peat temperature these effects will have been less than 1 ‰, so we ignore them (and any similar effects for $\delta^{13}\text{C}-\text{CH}_4$) here. A further possible complication is that the diffusion coefficient of dissolved ¹³C gases may be smaller than that of the ¹²C gas. Graham's Law would suggest about 3% difference for CH₄ and 1% for CO₂. These small differences operating over millennia may have large effects and might result in the observed enrichment in ¹³C of both dissolved gases. But the diffusion coefficients for the different sized CH₄ and CO₂ in water are nearly the same (Jähne et al., 1987) and both are in any case anomalous. Differences between diffusion coefficients for ¹³C and ¹²C variants may also be anomalous. Finally, the simulation shows that after nine millennia most of the dissolved gas has effluxed to air, and we have no idea of the history of its $\delta^{13}\text{C}$ values.

Until we know more about peat microbiology and about differences in the diffusion coefficients of ¹³C and ¹²C variants of the dissolved gases, simulation is too speculative to be productive. We remain unable to account for our $\delta^{13}\text{C}$ results.

In conclusion: Ellergower bog has sequestered carbon as peat, and decay in the peat has produced DOC, CH₄ and CO₂. The simulation model with relatively high decay rate in surface layers produces concentrations and ages of components that are consistent with the measured ones, and shows that after nine millennia more than 99% of the CO₂ and CH₄ produced in decay has effluxed to the atmosphere, with consequent effects on the climate, and more than 99% of the vertical component of dissolved gas molecule movement has been by diffusion rather than mass flow.

It is only because the Ellergower raised bog is almost diagrammatically simple, of small hydraulic conductivity, and with few and small contained gas spaces that it has been possible to show the dominance of diffusion and the

relative unimportance of mass flow. The same processes must operate in all peatlands, but the results at Ellergower should not be extrapolated *mutatis mutandis* to other peatlands, where it seems likely that mass flow and ebullition are of greater significance than they are at Ellergower.

ACKNOWLEDGMENTS

We thank K. Lee, B. Morgan, and P. Ratnesar for making the samplers; L. Belyea, and B. Giles for help with the fieldwork; C. Murray for preparing the samples for AMS dating; J. Southon for AMS dates and advice; A. Fallick for the two δD measurements and comments on the draft article; M.M.R. Williams for the solution in Appendix A1 to the diffusion equation; A. Sirin for comments on the draft article; E.R.C. Hornibrook and an anonymous reviewer for numerous constructive comments; Forest Enterprise for access to the site; and the NERC for radiocarbon allocations and for Small Grant GR9 1231.

C.B. is responsible for laboratory sample preparation leading to measurements of concentration, ^{14}C and $\delta^{13}C$; R.S.C. conceived the work in 1988 and is responsible for the field sampling, the rest of the laboratory work, the simulation, and for drafting this article.

APPENDIX A. DETAILS OF THE COMPUTER SIMULATION

A.1. Diffusion

Solids form less than 5% of the water-saturated peat volume, and they are mostly well dispersed. We therefore consider the problem of diffusion of dissolved gas molecules through stationary water (as it might be through an agar gel), allowing for the effects of solids by suitable choice of diffusion coefficient (Jähne et al., 1987).

In general, dissolved gas molecules move by diffusion to layers below and above. Movement by diffusion in water from a particular layer may be treated independently of the other layers because diffusion is a random molecular process and one of ‘our’ dissolved gas molecules is impeded by at least 4000 times as many water molecules as by ‘other’ dissolved gas molecules. At Ellergower there is a sharp drop in physical pressure below the base of the peat (Clymo, 2004) so we treat the base as impermeable. At the top, molecules escape to the air and the concentration at the surface is therefore held at zero. Boundary and initial conditions are shown diagrammatically in Fig. A1.1.

Let x be depth, X the depth of the base of the peat, a and b the depth of the upper and lower limits of a layer in which the concentration of dissolved gas is C_0 before diffusion, and D the diffusion coefficient. Formally, where $C(x, t)$ is concentration of dissolved gas at x and time t , the defining diffusion equation is

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2} \tag{A1.1}$$

with boundary conditions $C(0, t) = 0$, and $D \left. \frac{\partial C(x, t)}{\partial x} \right|_{x=X} = 0$ and initial conditions

$$C(x, 0) = C_0, \quad a < x < b;$$

$$C(x, 0) = 0, \quad 0 < x < a, \quad b < x < X.$$

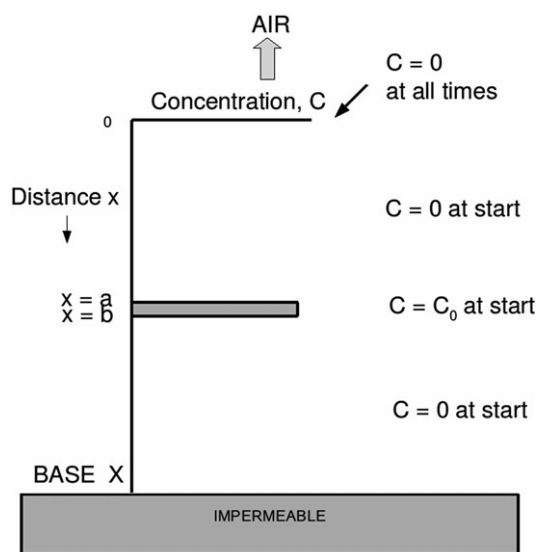


Fig. A1.1. Conditions for Eq. (A1.1).

The solution (derived by M.M.R. Williams) is:

$$C = C_0 \frac{8}{\pi} \sum_{n=0}^{\infty} \left\{ \frac{\exp(-DH_n^2 t)}{2n+1} \sin \frac{H_n(a+b)}{2} \times \sin \frac{H_n(b-a)}{2} \sin H_n x \right\} \tag{A1.2}$$

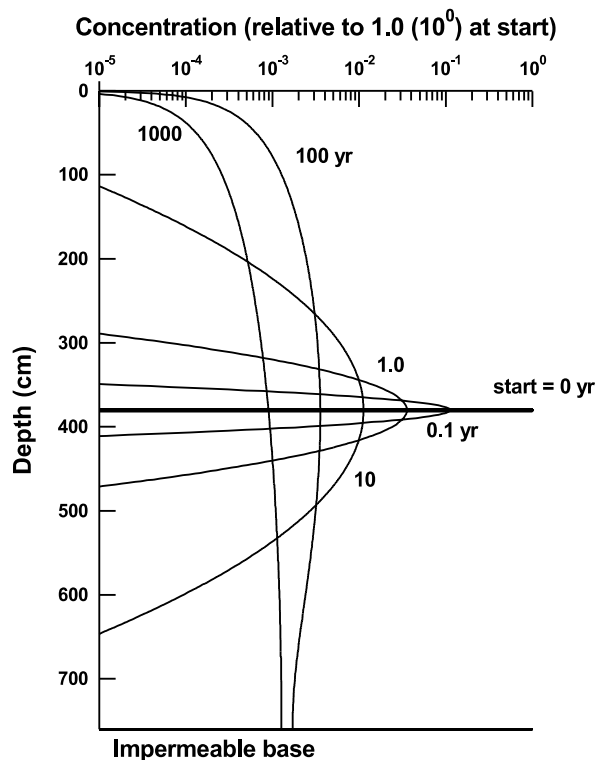


Fig. A1.2. Profile of concentration (relative to 1.0 at the start in the source layer at 350 cm) at different times, according to Eq. (A1.2). The diffusion coefficient was $1.0 \times 10^{-5} \text{ cm}^2 \text{ yr}^{-1}$. Note the log scale and the difference between base and top after 100 and 1000 yr.

where

$$H_n = \frac{(n + 0.5)\pi}{X}.$$

Examples of the concentration profile after various times following Eq. (A2.1) are shown in Fig. A1.2. The amount of movement by diffusion for 100 yr—barely 1% of the time the Ellergower peat has been growing—is notable, and by 100 yr the asymmetry between base and top is obvious as a significant part of the dissolved gas has escaped to air 350 cm from where it was generated a century before.

A.2. Simulation of peat growth and of movement of DOC, and dissolved CO₂ and CH₄

The basic simulation is concerned with that part of the peat mass that is permanently waterlogged and anoxic. It is built layer by layer, just as the peat bog itself grows upwards. Each layer occupies unit area and spans a time Δt (typically fixed in the range 5–25 yr). Each new layer receives dry mass (peat) according to $p \cdot e^{-\beta T} \cdot \Delta t$ where p is the original rate of addition to the peat (akin to plant productivity but reduced by aerobic decay losses); $e^{-\beta T}$ is a factor depending on the time, T , since peat growth began and on the parameter β , expected to be of the order $1e-5 \text{ yr}^{-1}$ so the overall rate of addition decreases slowly as the peat grows.

After the new layer is added at T since peat growth began a mass Δm is released from the peat by decay in each layer j according to $\Delta m_{j,T} = \alpha m_{j,T} \cdot (m_{j,T}/m_{j,0})^v$ where α (usually of the order $1.0e-5 \text{ yr}^{-1}$) is the proportional decay rate when the peat formed. It is modified (expected to reduce the decay rate as the more readily decomposed matter is removed and what remains is therefore more refractory) by the factor $(m_{j,T}/m_{j,0})^v$ where $m_{j,0}$ is the peat mass in the layer when it formed and the power v is a parameter, expected to be in the range 1–5 (Clymo, 1992; Clymo et al., 1998).

The effect for the peat as a whole, with mass M_T in n layers at time T is

$$\frac{\Delta M_T}{\Delta t} = p \cdot e^{-\beta T} \Delta t - \sum_{j=1}^n \left[\left(\frac{m_{j,T}}{m_{j,0}} \right)^v \cdot \alpha m_{j,T} \right] \quad (\text{A2.1})$$

The released mass in each layer is then apportioned among DOC, and dissolved CO₂ and CH₄; the proportion of DOC (P_{DOC}) and the quotient CO₂/CH₄ (G_Q) are free parameters.

Each layer is then given a number of molecules of these three components in proportion to their mass. Each molecule is ‘time-stamped’ (a 2-byte unsigned integer being the layer number in the computer simulation) with the time when the peat from which it comes was formed.

Movement of dissolved gases and DOC is then allowed for each layer from the bottom upwards. Diffusion of CO₂ and CH₄ follows Eq. (A1.2), using Gaussian integration (two-point as the concentration profile over a single slab is almost linear). The diffusion coefficients, D , for the two

dissolved gases are measured physical parameters. They do not follow Graham’s Law (Jähne et al., 1987) and are almost identical. The value used for both allows for temperature and the peat solids. DOC was not allowed to diffuse: the molecules are probably much larger and diffusion coefficient(s) much smaller therefore, and we judged that it would also be useful to have a component for comparison that was unaffected by diffusion.

For mass flow, the proportion of the top layer to move down is specified as the measured physical parameter (Clymo, 2004) bulk average downward velocity, R , diminishing with depth, z , as a proportion of the full depth as $R_z = R(1 - z^{-\omega})$ to zero one layer below the base. This simulates the way in which the vertical component of flow diminishes with depth near, but not exactly at, the center of a groundwater mound (Siegel et al., 1995; Reeve et al., 2000). The lateral component of flow increases with depth; we suppose that lateral inflow and outflow have negligible effects on concentration and age. Experiment showed that values of ω (which controls the proportion of the full flow rate R operating at different depths) in the range 1–4 have only small effects on the outcome.

Potential mass flow and diffusive movements of the two dissolved gases and of DOC are calculated. For mass flow all three component masses are then moved down one layer, and so are an equivalent number of molecules taken systematically from those *longest resident* and therefore lowest in the layer under consideration. For diffusion to *all* layers below that being processed the dissolved gas masses are moved, followed by an equivalent number of molecules chosen *at random* from all those in the layer. For diffusive movements of dissolved gas upwards the mass and molecules are held in a temporary store for the destined layer. (This avoids premature transfers that would affect the result of later calculations.) Any dissolved gas mass or randomly chosen molecules in the $\Delta m_{j,T}$ of the layer not accounted for by calculated retention in the layer from equation A1.1 or by diffusion into other peat layers are removed to air above the top (emptied before each iteration). After the layer under consideration has been dealt with its accumulated temporarily held molecules are transferred to its main store.

Experiment showed that reversing the order of implementation of mass flow and of diffusion had negligible effects.

The simulation also includes a ‘temperature asymmetry’ factor that decreases with depth. Peat decay rates increase exponentially as temperature increases from 0 to 20 °C (Daulat and Clymo, 1998) so a time spent at 5 °C above the mean will more than compensate the same time at 5 °C below the mean (Clymo, 1984). The daily damping depth in peat at Ellergower is less than 10 cm, so daily asymmetry effects are negligible in most of the peat. But the yearly damping depth is about 130 cm and with the annual surface amplitude of 9.6 °C (Daulat and Clymo, 1998) one gets an asymmetry factor of 1.02 at the top becoming <1.002 below 150 cm.

The top intermittently oxic mesotelm was simulated by specifying the number N_M of layers in it, the proportion

P_{DM} of DOC in the decay products, and a multiplier F_M of the calculated decay rate. An enhanced value of p_M , the rate of addition to a new layer, was calculated and used such that the mass of peat remaining in a layer after the period of more rapid decay while the next N_M layers were added would be exactly what would have been there had the rate for new layers been simply $p e^{-\beta T}$. The depth of this zone was then calculated from the measured bulk density profile. This elaborate procedure was necessary because each layer is defined as spanning Δt and its physical thickness is a result, not something that can be specified.

This simulated the zone in which decay is known to be most rapid (Clymo and Pearce, 1995; Belyea, 1996; Daulat and Clymo, 1998). It would be trivial to have allowed CO_2/CH_4 ($G_{Q,M}$) to be different from that in the catotelm ($G_{Q,C}$), but our purpose was to investigate the relative rôles of mass flow and diffusion, not to produce as accurate a simulation as possible. So we chose to limit the number of free parameters.

The simulation thus has 11 parameters (Table A2.1). Two of these— D and R —have measured physical values. The other nine were optimized in two groups.

First, as the age profile is nearly linear it might be thought that a simple line with two parameters would be sufficient. But what we need for the present work is the best possible estimate of what becomes available as DOC, CO_2 , and CH_4 in decay. So we used the four-parameter model. The addition (p , β) and decay parameters (α , ν) were optimized by minimizing deviations of the measured profiles of (dendro-calibrated ^{14}C) age and of concentrations of Ca, Sr, and P (which have a different shaped profile, not shown here, from the age one) from the simulated ones, using the formal simplex procedure of Nelder and Mead (1965).

Second, we did the best we could with an informal optimization of the remaining five parameters: $P_{D,M}$ and $G_{Q,C}$ for the catotelm peat, N_C , $P_{D,C}$, and F_C for the more active mesotelm (Table A2.1). Informality was necessary because each run of the simulation took an hour or more, and a formal optimization would take weeks or months. In practice we made 212 runs taking the parameters in turn and adjusting the parameter value upward and then downward by a suitable small proportion, accepting the direction that produced what was judged informally to be an improvement in pairs of graphs such as the ‘best fit’ shown in Fig. 8. The final ‘best fit’ parameter values are in Table A2.1

We also simulated CH_4 oxidation (Pearce and Clymo, 2001) and the reservoir effect (Kilian et al., 1995) caused by plants at the surface incorporating some ‘old’ CO_2 that has effluxed from deeper in the peat (Rydin and Clymo, 1989; Raghoebarsing et al., 2005), though the parameter values are little better than guesses. The consequences of these processes were relatively tiny, so we removed them from the simulation reported here to keep it as simple as possible.

The 5000-line simulation is written in C99. In the results shown here it was set to run for 9352 yr with a layer time step Δt of 15 yr giving 623 layers. This time step gave differences between the integral and sum that were allowed for by extrapolation to zero from several longer times, and finally confirmed by using a Δt of 4 yr. This is less than ideal, but a typical run with a 15 yr time step took 65 min during which $7e9$ molecule movements were simulated, and needed about 150 MB of store. Run time is roughly inversely proportional to the cube of the time step, and store inversely to the time step, so shorter time steps for all the optimization runs were not practicable.

Table A2.1
Parameters in the simulation

Description	Symbol	Dimensions	‘Best’ value ^a	Units	Estimate
<i>Main (catotelm) peat</i>					
Rate of addition (‘productivity’)	p	$\text{ML}^{-2} \text{T}^{-1}$	2.8e-3	$\text{kmol m}^{-2} \text{yr}^{-1}$	SPM ^b
Proportional rate of change of p	β	T^{-1}	6.1e-5	yr^{-1}	SPM
Basic proportional rate of decay	α	T^{-1}	6.5e-5	yr^{-1}	SPM
(Mass now/initial) ^p multiplies α	ν	—	3.15	—	SPM
CO_2 and CH_4 diffusion coefficient	D	$\text{L}^2 \text{T}^{-1}$	9.2e-6 (8 °C)	$\text{cm}^2 \text{s}^{-1}$	MV ^c
Rate of downward mass flow at top	R	LT^{-1}	60	cm (1000 yr)^{-1}	MV
Proportion of DOC in decayed mass	$P_{D,C}$	—	0.17	—	IMM ^d
CO_2/CH_4 quotient in decayed mass	$G_{Q,C}$	—	10.0	—	IMM
<i>Top (mesotelm) peat</i>					
Proportion of DOC in decayed mass	$P_{D,M}$	—	0.002	—	IMM
Multiplier of decay parameter α	F_M	—	52	—	IMM
Number of layers in zone	N_M	—	18 (38 cm) ^e	—	IMM

Those for the main (catotelm) peat are in the basic simulation; the rest are added for the extended simulation.

^a Values giving the fit in Fig. 8.

^b SPM = separate 4-parameter programmed minimisation.

^c MV = measured value.

^d IMM = informal 5-parameter manual minimisation.

^e Depth from the number of layers specified.

APPENDIX B.

Conventional ^{14}C ages and $\delta^{13}\text{C}$ at Ellergower Moss

Sample identifier	Publication code	^{14}C Enrichment (% Modern $\pm 1\sigma$)	Conventional radiocarbon age (Years BP $\pm 1\sigma$)	$\delta^{13}\text{C}_{\text{VPDB}} \pm 0.2\text{‰}$
<i>Peat</i>				
Total peat EMF 50a	AA-29942	88.94 \pm 0.49	940 \pm 45	-26.3
Total peat EMF 100a	AA-29943	79.86 \pm 0.41	1805 \pm 40	-25.2
Total peat EMF 150a	AA-29944	74.24 \pm 0.40	2395 \pm 45	-26.7
Total peat EMF 200a	AA-29945	69.15 \pm 0.38	2965 \pm 45	-26.9
Total peat EMF 250a	AA-29946	64.44 \pm 0.36	3530 \pm 45	-26.4
Total peat EMF 300a	AA-29947	60.27 \pm 0.34	4070 \pm 45	-26.9
Total peat EMF 350a	AA-29948	57.88 \pm 0.41	4395 \pm 60	-26.7
Total peat EMF 400a	AA-29949	54.56 \pm 0.32	4865 \pm 45	-27.2
Total peat EMF 450a	AA-29950	50.48 \pm 0.33	5490 \pm 50	-27.3
Total peat EMF 500a	AA-29951	47.43 \pm 0.32	5990 \pm 55	-27.8
Total peat EMF 550a	AA-29952	44.75 \pm 0.30	6460 \pm 55	-27.0
Total peat EMF 600a	AA-29953	42.29 \pm 0.33	6915 \pm 65	-27.2
Total peat EMF 650a	AA-29954	38.45 \pm 0.28	7675 \pm 60	-27.0
Total peat EMF 700a	AA-29955	33.42 \pm 0.26	8805 \pm 60	-26.5
<i>Dissolved organic carbon</i>				
E1 DOC 80–100 cm	CAMS-60830	89.92 \pm 0.38	860 \pm 40	-27.2
E1 DOC 180–200 cm	CAMS-57203	73.18 \pm 0.67	2610 \pm 80	-25.8
E1 DOC 280–300 cm	CAMS-60831	64.59 \pm 0.30	3510 \pm 40	-26.0
E1 DOC 380–400 cm	CAMS-57204	61.41 \pm 0.74	3920 \pm 100	-26.3
E1 DOC 480–500 cm	CAMS-60832	55.70 \pm 0.24	4700 \pm 40	-26.5
E1 DOC 580–600 cm	CAMS-57205	48.20 \pm 0.84	5860 \pm 140	-26.1
E1 DOC 680–700 cm	CAMS-60833	41.97 \pm 0.21	6970 \pm 40	-26.0
<i>Humic acid (alkali soluble)</i>				
E1 HUMIC 180–200 cm	AA-35075	69.06 \pm 0.44	2975 \pm 50	-27.2
E1 HUMIC 380–400 cm	AA-35076	53.68 \pm 0.37	5000 \pm 55	-27.6
E1 HUMIC 580–600 cm	AA-35077	40.84 \pm 0.32	7195 \pm 60	-27.2
<i>Humic acid (alkali insoluble)</i>				
E1 HUMIN 180–200 cm	AA-35078	64.66 \pm 0.56	3505 \pm 65	-27.0
E1 HUMIN 380–400 cm	AA-35079	53.46 \pm 0.37	5030 \pm 55	-27.5
E1 HUMIN 580–600 cm	AA-35080	40.67 \pm 0.31	7225 \pm 60	-26.6
<i>Methane (Nests A, B, C)</i>				
A150-CH ₄	CAMS-48644	88.67 \pm 0.39	970 \pm 40	-66.2
A200-CH ₄	CAMS-48646	83.20 \pm 0.44	1480 \pm 50	-65.5
A450-CH ₄	CAMS-48648	66.53 \pm 0.36	3270 \pm 50	-61.8
A600-CH ₄	CAMS-48650	63.90 \pm 0.35	3600 \pm 50	-62.3
B50-CH ₄	CAMS-48652	102.20 \pm 0.50	Modern	-70.2
B100-CH ₄	CAMS-48654	95.75 \pm 0.50	350 \pm 50	-71.1
B200-CH ₄	CAMS-48656	85.40 \pm 0.45	1270 \pm 50	-67.0
B250-CH ₄	CAMS-48658	76.37 \pm 0.31	2170 \pm 40	-62.4
B300-CH ₄	CAMS-48660	75.05 \pm 0.40	2310 \pm 50	-63.3
B350-CH ₄	CAMS-48662	72.33 \pm 0.30	2600 \pm 40	-61.0
B400-CH ₄	CAMS-48664	69.59 \pm 0.31	2910 \pm 40	-62.5
B500-CH ₄	CAMS-48666	67.02 \pm 0.36	3210 \pm 50	-62.5
B550-CH ₄	CAMS-48668	64.95 \pm 0.25	3470 \pm 40	-62.3
B600-CH ₄	CAMS-48670	63.43 \pm 0.34	3660 \pm 50	-62.2
B675-CH ₄	CAMS-48672	63.10 \pm 0.29	3700 \pm 40	-61.7
B750-CH ₄	CAMS-48674	61.08 \pm 0.29	3960 \pm 40	-61.6
C200-CH ₄	CAMS-48676	85.88 \pm 0.45	1220 \pm 50	-62.4
C400-CH ₄	CAMS-48678	70.16 \pm 0.38	2850 \pm 50	-62.4
C600-CH ₄	CAMS-48680	64.41 \pm 0.29	3530 \pm 40	-62.5
<i>Carbon dioxide (Nests A, B, C)</i>				
A150-CO ₂	CAMS-48645	90.78 \pm 0.61	780 \pm 60	4.6
A200-CO ₂	CAMS-48647	84.97 \pm 0.40	1310 \pm 40	6.1
A450-CO ₂	CAMS-48649	66.61 \pm 0.41	3260 \pm 50	9.4

(continued on next page)

Appendix B (continued)

Sample identifier	Publication code	^{14}C Enrichment (% Modern $\pm 1\sigma$)	Conventional radiocarbon age (Years BP $\pm 1\sigma$)	$\delta^{13}\text{C}_{\text{VPDB}}$ $\pm 0.2\text{‰}$
A600-CO ₂	CAMS-48651	62.87 \pm 0.36	3730 \pm 50	9.6
B50-CO ₂	CAMS-48653	102.40 \pm 0.57	Modern	-2.5
B100-CO ₂	CAMS-48655	99.63 \pm 0.62	Modern	0.6
B200-CO ₂	CAMS-48657	85.22 \pm 0.36	1280 \pm 40	5.6
B250-CO ₂	CAMS-48659	78.46 \pm 0.45	1950 \pm 50	7.2
B300-CO ₂	CAMS-48661	74.78 \pm 0.43	2330 \pm 50	7.9
B350-CO ₂	CAMS-48663	73.55 \pm 0.34	2470 \pm 40	8.0
B400-CO ₂	CAMS-48665	67.75 \pm 0.31	3130 \pm 40	9.0
B500-CO ₂	CAMS-48667	64.78 \pm 0.30	3490 \pm 40	9.4
B550-CO ₂	CAMS-48669	62.92 \pm 0.36	3720 \pm 50	9.8
B600-CO ₂	CAMS-48671	61.20 \pm 0.24	3940 \pm 40	10.1
B675-CO ₂	CAMS-48673	60.47 \pm 0.30	4040 \pm 50	10.3
B750-CO ₂	CAMS-48675	58.34 \pm 0.29	4330 \pm 50	10.2
C200-CO ₂	CAMS-48677	86.33 \pm 0.58	1180 \pm 60	4.8
C400-CO ₂	CAMS-48679	68.34 \pm 0.33	3060 \pm 40	8.7
C600-CO ₂	CAMS-48681	61.89 \pm 0.24	3850 \pm 40	10.2

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Associate editor: Jacques Schott