Radiocarbon analysis reveals that vegetation facilitates the release of old methane in a temperate raised bog

Mark H. Garnett · Susie M. L. Hardie · Callum Murray

Abstract Peatlands have accumulated vast quantities of organic carbon over thousands of years but it is unclear how these sensitive ecosystems will respond to future climate change. If emissions of methane from peatlands increase, then they may contribute increasingly towards climatic warming due to the higher greenhouse warming potential of this gas. We investigated the radiocarbon concentration of methane emissions from a temperate bog over 1.5 years, which we supported with measurements of the surface flux of methane and carbon dioxide. The radiocarbon content of methane emissions varied greatly, from modern (i.e. fixed from the atmosphere within recent decades) to ∼ 1400 years BP. Flux rates of methane were spatially and temporally highly variable. A vegetation clipping experiment showed that plants had a great influence on the carbon isotope composition and flux of methane emitted from the peat surface, consistent with earlier studies showing the key role of plants in peatland methane emissions. When plants were absent, emission rates were 70–94% lower and the radiocarbon age of methane emissions was much younger and less variable. Our radiocarbon measurements show that at this peatland, plant-associated methane emissions contain carbon originally fixed from the atmosphere up to hundreds of years earlier, consistent with a contribution from plant mediated transport of methane sourced from sub-surface layers.

Keywords Methane · Radiocarbon · Peatland · Climate change · Vegetation · Carbon dioxide

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Introduction

Northern peatlands have been estimated to contain 1016 to 1105 Gt of organic carbon (C) and to sequester around 60 Mt C year^{-1} from the atmosphere (Nichols and Peteet 2019). The rate of peat accumulation represents the balance between photosynthetic fixation of carbon dioxide (CO_2) and decomposition processes which result in the net flux of CO_2 and methane (CH_4). Whether the decay processes result in the production of CO_2 or CH_4 depends on factors such as the presence of aerobic or anaerobic conditions, and the extent of CH_4-oxidation (Clymo and Bryant 2008). This is important because although both CO_2 and CH_4 are

greenhouse gases, CH_4 has a greenhouse warming potential twenty-eight times that of CO_2 (over a 100 year time horizon; IPCC 2014) and has increased in the atmosphere by over 150% since pre-industrial times (Crill and Thornton 2017). Moreover, the climatic sensitivity of peatlands and their considerable contribution to global methane emissions (northern peatlands alone account for 12% of global emissions; Lai 2009) makes it essential that we understand the processes leading to peatland CH_4 production and emission if we are to more accurately forecast future atmospheric methane concentrations (Crill and Thornton 2017) and associated warming potential.

Factors controlling the production of methane include substrate availability and temperature in addition to the availability of oxygen (largely determined by the position of the water table e.g. Moore and Roulet 1993) and other electron acceptors. The onset of reduction in waterlogged systems takes place due to oxygen depletion which triggers a change in microbial populations and a concomitant change in the types of electron acceptors they can utilise. Facultative anaerobes use nitrate, manganese oxides and iron oxides whereas obligate anaerobes make use of sulphate and finally CO_2 (the last two electron acceptors in the sequential reduction reaction chain; Pulford and Flowers 2006). Methanogenic bacteria in peatlands (especially those containing low concentrations of nitrate and sulphate) convert accumulated organic matter to CH_4 and CO_2 under anaerobic conditions. Which methanogenic pathway (acetoclastic or hydrogenotrophic) is the dominant process in peatlands is thought to be dependent on the peatland type (e.g. hydrogenotrophic methanogenesis in ombrotrophic bogs; Hornibrook 2009) but can also be a matter of some dispute (e.g. discussion in Clymo and Bryant 2008).

The activity of plants has long been known to exact an important control on methane production in peatlands. For instance, Whiting and Chanton (1993) found a direct correlation between net ecosystem production and peatland methane efflux rate in sites spread across a range of latitudes. Multiple lines of evidence (including radiocarbon measurements) pointed to the importance of recent plant-derived carbon inputs driving methane emissions in several North American peatlands (Chanton et al. 1995, 2008). More recently, Bhullar et al. (2014)

demonstrated a direct, but small, role of root exudates in methanogenesis.

Once generated, methane within the peat can be liberated to the atmosphere by diffusion, ebullition or via the vascular systems of plants (Chanton 2005; Lai 2009). Plant mediated release of CH_4 occurs during the process of aerating tissues that are submerged in water, with diffusion gradients or pressure differences resulting in a flow to the atmosphere of gases that have accumulated in the root zone (Raskin and Kende 1983, 1985; Joabsson et al. 1999). In addition, loss of CH_4 can occur through oxidation by methanotrophic bacteria (Frenzel et al. 1992; Laanbroek 2010) and therefore emissions from wetlands are a result of the balance between the processes of methanogenesis and methanotrophy (Le Mer and Roger 2001). However, whilst the role of peatland plants in controlling methane release (Whiting and Chanton 1993; Shannon et al. 1996; Watson et al. 1997; Verville et al. 1998; Joabsson et al. 1999; Rinnan et al. 2003; Marinier et al. 2004; Ström et al. 2005) and production has been well established in the literature, in a recent synthesis, Carmichael et al. (2014) concluded that the role of vegetation in the global methane budget was the least understood of the identified natural sources.

It is currently thought that more accurate partitioning of sources will be key to closing the gap in the estimate of global methane budgets (Fisher et al. 2017). Partitioning of emissions can be achieved using the stable carbon isotopic composition ($\delta^{13}C$) of methane because plant mediated transport causes large isotopic fractionation effects (Chanton 2005; Conrad 2005) via diffusional fractionation. However, other processes, such as those associated with different methanogenic pathways, also cause large and differing isotopic fractionations (Whiticar et al. 1986) which complicates the overall picture and limits the understanding that can be gained from stable carbon isotope measurement alone. Further insight into the source of peatland methane emissions is possible by measurement of its radiocarbon (^{14}C) content (Chanton 2005; Clymo and Bryant 2008).

The ^{14}C content of carbon-containing decomposition products (e.g. CH_4) provides unique information on when the carbon was photosynthetically fixed from the atmosphere, the amount of time that the carbon has been sequestered, and within a peatland context, information on the location where it was generated (Clymo and Bryant 2008). Carbon fixed from the

atmosphere hundreds to thousands of years ago can be dated using conventional radiocarbon techniques and has been frequently used to determine the date of peatland initiation or rate of peat accumulation (e.g. Turunen et al. 2002; Nichols and Peteet 2019). Carbon fixed since the mid-AD1950s has elevated ^{14}C concentrations ($> 100\%$ modern) resulting from atmospheric testing of nuclear devices and unambiguously indicates an age of less than 60 years since sequestration. Previous studies of the ^{14}C age of peatland methane have largely been limited to samples collected from within the peat profile of temperate sites (e.g. Aravena et al. 1993; Bellisario et al. 1999; Charman et al. 1999; Chanton et al. 2008; Clymo and Bryant 2008; Garnett et al. 2011). Fewer studies have determined the ^{14}C content of methane emitted from the peat surface, probably because the lower concentrations make it more difficult to achieve the typical > 1 ml CH_4 required for radiocarbon analysis by accelerator mass spectrometry (AMS). Studies by Wahlen et al. (1989), Quay et al. (1991), Chanton et al. (1995) and Leith et al. (2014) all found the ^{14}C content of emitted methane to be similar to the contemporary atmospheric CO_2, indicating that a large proportion of methane is derived from recently fixed organic matter (Chanton et al. 1995; Leith et al. 2014). In contrast, Garnett et al. (2012) reported pre-bomb ^{14}C concentrations for emitted methane (up to 1400 years BP), suggesting a substantial contribution from much older sources. Prompted by this discrepancy, and the small number of ^{14}C analyses that have so far been performed, we undertook an assessment of the spatial and temporal variation in the age of peatland methane emissions with a particular aim to examine the influence of vegetation on the age and source of this greenhouse gas.

Here, we report measurements of the radiocarbon content (age) and supporting flux data on methane emitted from the surface of a temperate raised peat bog over a period of 1.5 years, encompassing two growing seasons. We also describe a plant-removal experiment where we use the natural abundance ^{14}C content of methane to investigate the role of vegetation in peatland surface methane emissions. Our objectives were:

1. To quantify the age and rate of methane emission and to assess temporal and spatial variation.

2. To evaluate the influence of plants on the age of peatland methane emissions.

We hypothesised that the presence of plants would exhibit a greater control on the age of methane emissions, compared to other factors including temperature and water table depth.

Methods

Site description

The study was conducted at Langlands Moss, an ombrotrophic raised peat bog (~ 25 hectares) in central south–west Scotland, United Kingdom (55° 44′ 5.5″ N, 4° 10′ 25.8″ W). The site has an altitude of 217 m and annual temperature and precipitation have been reported as 7.3 °C and 971 mm/year, respectively (Langdon and Barber 2005). The peat depth at our study area is approximately 6 m, although maximum peat depth further towards the centre of the bog has been reported to be at least 8 m (Langdon and Barber 2005). The predominant vegetation species at the site are *Eriophorum vaginatum*, *Calluna vulgaris*, *Erica tetralix*, and *Sphagnum* spp., with no trees being present. Langlands Moss has been the focus of numerous earlier radiocarbon studies investigating the age of peat with depth (Langdon and Barber 2005), surface emissions of methane (Garnett et al. 2012), sub-surface peat gases (CO_2 and CH_4; Garnett et al. 2011) and evasion of CO_2 and CH_4 in waters draining the peatland (Garnett et al. 2013; Dean et al. 2017).

We selected three microsites based on topography since this had been shown to strongly affect methane flux rates (Clymo and Pearce 1995; Lai 2009) and represented the dominant habitats at our site (Table 1). For each microsite, we established two permanent collars for the investigation of methane fluxes. The *Hummock* microsites (A1 and A2) were peat mounds that were relatively elevated to the surrounding terrain by ~ 30–50 cm, and were composed of sedges, *Calluna vulgaris* and bare peat. The *Intermediate* (B1 and B2) microsites occupied an elevation in between hummocks and the lowest parts of the bog and were predominantly vegetated by the sedge *Eriophorum vaginatum* and mosses. The *Hollow* microsites (C1 and C2) occupied relative depressions in the peatland surface and the vegetation consisted

Table 1 Characteristics of individual sampling plots. Vegetation composition was estimated from spatial coverage

Site	Microsite	Vegetation composition	Mean CH_4 flux (mg CH_4–C h^{-1} m^{-2})	Mean CO_2 flux (mg CO_2–C h^{-1} m^{-2})	Mean water table depth (cm ± SE)
A1	Hummock	Sedges (50%), Ericaceous (5%), Mosses (15%), Bare peat (30%)	0.56 ± 0.11[BC] (n = 15)	37.01 ± 4.51[A] (n = 13)	19.7 ± 1.1[A] (n = 40)
A2	Hummock	Sedges (55%), Ericaceous (20%), Mosses (25%), Bare peat (0%)	0.20 ± 0.03[C] (n = 15)	60.55 ± 8.72[A] (n = 15)	
B1	Intermediate	Sedges (45%), Ericaceous (10%), Mosses (45%), Bare peat (0%)	1.17 ± 0.18[A] (n = 15)	59.28 ± 10.11[A] (n = 15)	0.6 ± 0.6[B] (n = 40)
B2	Intermediate	Sedges (35%), Ericaceous (0%), Mosses (45%), Bare peat (20%)	0.42 ± 0.07[C] (n = 15)	41.19 ± 4.95[A] (n = 15)	
C1	Hollow	Sedges (30%), Ericaceous (0%), Mosses (70%), Bare peat (0%)	0.91 ± 0.15[AB] (n = 15)	57.30 ± 12.37[A] (n = 15)	2.2 ± 0.8[B] (n = 40)
C2	Hollow	Sedges (0%), Ericaceous (10%), Mosses (90%), Bare peat (0%)	0.17 ± 0.04[C] (n = 15)	42.79 ± 7.66[A] (n = 15)	

Mean gas fluxes and water table depth were determined using measurements collected over an entire year (from May 2011 to April 2012; i.e. before vegetation clipping). Means that do not share a superscripted letter differ significantly ($p < 0.05$)

predominantly of *Sphagnum* moss. Each pair of chambers were located $\sim$ 2 m apart, and all microsite plots were within 5–10 m of each other. Boardwalks were established next to the collars to prevent site disturbance.

The collars were circular (cross sectional area = 1257 cm^2, volume 60 L) and inserted vertically 20 cm into the peat surface on the 13th April 2011. The collars were constructed from high density plastic barrels (120 L Open Top Keg, Ampulla Ltd, UK) which were cut horizontally into two, with the top half being used for the collar. The lid to the barrel fitted securely to the collar, and when in place, created an enclosed, airtight chamber with an effective headspace of $\sim$ 25 L for flux measurement and gas sampling. To mimic surrounding vegetation, we painted the sides of the chambers green and to prevent heating effects covered the lids in reflective aluminium foil. We installed gas sampling ports by drilling two holes (5.5 mm o/d) at opposite sides of each lid into which we inserted $\sim$ 5 cm lengths of Tygon tubing (6 mm i/d and 8 mm o/d, Fisher, UK). Into the ends of the tubing we placed quick connect couplings with auto-shutoff valves (Colder Products Co (CPC), USA) which facilitated connection to our sampling equipment.

Field measurements

Methane concentration in the chambers was measured using a Detecto Pak-Infrared (DP-IR) CH_4 analyser (Heath Consultants Inc, USA). This instrument measures CH_4 concentration with a precision of 1 ppm and an accuracy of 10% and has previously been demonstrated to be reliable for determining methane fluxes from peatland chambers (Cooper et al. 2017). During measurement, the DP-IR was connected in-line to each chamber using Tygon tubing and CPC couplings in a closed loop, so that headspace air was returned to the chamber after measurement. The rate of methane emission was calculated from the increase in headspace CH_4 concentration assuming a linear rate over a period of 24-hours (with one exception when a 48-hour period was used in August 2012). Measurements during the May 2011 sampling showed that methane concentration increased linearly ($r^2 > 0.93$) over the first four days in all chambers. However, after four days several of the chambers visually showed a slight inhibition of emissions through 1 week, although the r^2 remained high (0.98) in five of the six chambers (Garnett et al. 2012; Supplementary Table S1 and Fig. S1). Carbon dioxide emissions were quantified over a 10-min period (immediately after sealing the chambers) using the same gas sampling

lines and an EGM-4 infrared CO_2 gas analyser (PPsystems, Hitchin, UK). Flux measurements were made from all chambers at approximately monthly intervals.

We monitored water table depth at each microsite using dip-wells located in between each pair of chambers. The dip-wells were made from drain pipe (50 cm long, 5 cm o/d, with holes drilled along the sides), and were installed at the same time as the chambers. Water table depth was determined relative to the peat surface with a tape measure, and when not being measured, the dip-wells were covered with an upturned plastic cup. Air temperature at the peat surface, and peat temperature at 10 cm depth were measured every 15 min using a Tiny Tag 2 temperature logger fitted with a temperature probe (Gemini Data Loggers Ltd, Chichester, UK).

Radio- and stable carbon isotope analysis of methane

To enable radiocarbon measurement of emitted methane we collected samples of chamber headspace gas on five occasions between May 2011 and August 2012. In both 2011 and 2012, samples were collected at the beginning of the growing season ("Early") and in late summer ("Late"). Samples were also collected during the middle of the growing season in 2011 only ("Mid"; see Table 2 for sampling dates). Headspace gases were collected by connecting the inlet of the DP-IR to a gas sampling port on a chamber, and a 10 L foil gas bag (SKC Ltd, UK) to the exhaust port of the DP-IR, thus using the internal pump (~ 1 L min^{-1}) of the instrument to fill the gas bag at the same time as chamber CH_4 concentration was being measured. To prevent a vacuum being created in the chamber, the other gas port of the chamber was vented, allowing the

Table 2 Dates when chambers were sealed for collection of $^{14}CH_4$ samples

Reference	Dates
Early-11	16–23 May, 2011
Mid-11	11–15 July, 2011
Late-11	12–14 September, 2011
Early-12	21–24 May, 2012
Late-12	20–23 August, 2012

headspace to be backfilled with atmospheric air. We did not prevent the inclusion of atmospheric methane in samples, either from this backfilling of the chamber, or when the chambers were sealed. Instead, we measured the chamber CH_4 concentration during bag filling with the DP-IR and mathematically corrected all chamber carbon isotope measurements based on the average methane concentration and assuming an atmospheric methane content of 3 ± 1 ppm, with a ^{14}C concentration of $\sim 130\%$ modern and a $\delta^{13}C$ of $-47\permil$ (Lassey et al. 2007; Garnett et al. 2012). To ensure the minimum of 1 ml CH_4 required for ^{14}C analysis, chambers were left for between 2 and 7 days before gas collection (Table 2). Closure of the chambers for this length of time appeared visually to have no deleterious effects on the vegetation.

Gas sample bags were returned to the NERC radiocarbon facility and processed within a few days of collection. Garnett et al. (2012) describe the laboratory procedures in detail, but briefly, processing involved removal of CO_2 using soda lime and 13X zeolite molecular sieve, combustion of sample methane to CO_2 (using a platinum catalyst heated to 950 °C), followed by cryogenic purification. The volume of the recovered CO_2 was measured, and the sample split. One aliquot of sample CO_2 was used to determine $\delta^{13}C$ (relative to the Vienna PDB standard) using isotope ratio mass spectrometry (IRMS). A second aliquot was converted to graphite using Fe:Zn reduction (Slota et al. 1987) and measured for ^{14}C content using AMS at the Scottish Universities Environmental Research Centre (East Kilbride, UK). Following convention, ^{14}C results were corrected for isotopic fractionation using the IRMS $\delta^{13}C$ values and reported as both %modern and conventional radiocarbon ages (in years BP, where 0 BP = AD 1950; Stuiver and Polach 1977).

Partitioning of methane sources

One month before the fourth set of methane samples were collected (Early-12), we began a partitioning experiment to investigate the contribution of plants to the age and rate of methane emissions. For each of the microsites, we removed the vegetation by clipping one of the two plots. Where possible, all vegetation was removed to the bare peat surface. In plots where *Sphagnum* was abundant (especially Hollow collars), we clipped all vegetation, including the surface layer

of green moss, so that the underlying pale-yellow moss (not photosynthetically active) defined the peatland surface. To discourage regrowth, a layer of black permeable (to water and air) weed control fabric was placed on the surface of clipped plots. Plots were inspected during each site visit and new growth of plant material removed from clipped collars. Flux measurements continued to be undertaken at approximately monthly intervals and all plots (vegetated and clipped) were sampled for isotope analysis of methane using the methods described above.

The effect of vegetation on the flux of methane was determined using mass balance (Eq. 1) and the ^{14}C and ^{13}C content of the methane emitted due to the presence of plants was determined using isotope mass balance (Eq. 2):

$$F_p(\%) = (F_v - F_c)/F_v \times 100 \tag{1}$$

$$\Delta_p = (\Delta_v \times F_v - \Delta_c \times F_c)/F_p \tag{2}$$

where F represents the rate of methane emission (during collection of the isotope samples; mg CH_4–C h^{-1} m^{-2}) and Δ the ^{14}C (%modern) or δ^{13}C (‰) of vegetated ($_v$) and clipped ($_c$) plots. F_p is the proportion of the methane flux due to the presence of plants, and Δ_p is the ^{14}C or δ^{13}C of the methane that is solely due to vegetation.

We used the measurements from the two late season sampling occasions, with the results from Late-11 (i.e. before clipping) representing sites with intact vegetation, and results from Late-12 (4 months after clipping) representing the plant-free treatment. This allowed us to make comparisons at the same time of year, and therefore avoided complications caused by seasonal patterns. To control for inter-annual variation, we performed the same tests on the unclipped plots from the same two sampling dates (Late-11 and Late-12).

Statistical analyses

We used mixed-effects models to examine flux rates of CH_4 and CO_2 from microsites prior to clipping, with chamber as a random factor. Analysis of variance with Tukey post-hoc tests was used to identify differences between sites. Pearson correlation coefficients were calculated to examine relationships between measured variables, and paired t-tests were undertaken to test for significant differences in chambers before and after clipping. All statistical tests were performed using the statistical software package Minitab (versions 18 and 19).

Results

Field and carbon isotope measurements

Air temperature at the peat surface of Langlands Moss ranged from − 5 to 30 °C over the ∼ 1.5 years of the study (Fig. 1) and had an annual mean of 8.0 °C (May 2011–May 2012). Peat temperature at 10 cm depth displayed far less variation than air temperature and exhibited a progressive increase from a winter minimum (e.g. ∼ 2 °C in January 2012) to peak temperatures in September (2011 = ∼ 16 °C; 2012 = ∼ 15 °C). Annual average peat temperature at 10 cm depth was 9.1 °C (May 2011–May 2012).

Water table depth at Intermediate and Hollow microsites was significantly (p < 0.0001) closer to the peat surface compared to the Hummock microsite (Fig. 1). The water table during the 2011 growing season was relatively low at all three microsites, compared to the same time in the following year (Fig. 1).

There was a clear seasonal pattern in methane fluxes with highest values generally occurring in September/October and lowest fluxes during winter (Fig. 2). When considering measurements prior to clipping, a mixed-effects model showed that methane flux varied significantly with microsite (p < 0.001), with Intermediate chambers emitting on average more methane than the other sites (averages: Hummock 0.38 mg CH_4–C h^{-1} m^{-2}, Intermediate 0.80 mg CH_4-C h^{-1} m^{-2}, Hollow 0.54 mg CH_4–C h^{-1}; Table 1). Significant differences were not found for carbon dioxide emissions when grouped by microsite (p = 0.992), although a clear seasonal pattern of highest fluxes during summer (> 100 mg CO_2–C h^{-1} m^{-2}), and lowest fluxes in winter (< 10 mg CO_2–C h^{-1} m^{-2}) was observed (Fig. 2).

Across all microsites there was no significant correlation between air temperature and methane emission rate (p > 0.155), though peat temperature (at 10 cm depth) did correlate positively (p < 0.001) with CH_4 flux. A significant negative correlation was observed between water table depth and CH_4 flux rate across all sites (p < 0.001); when examined by
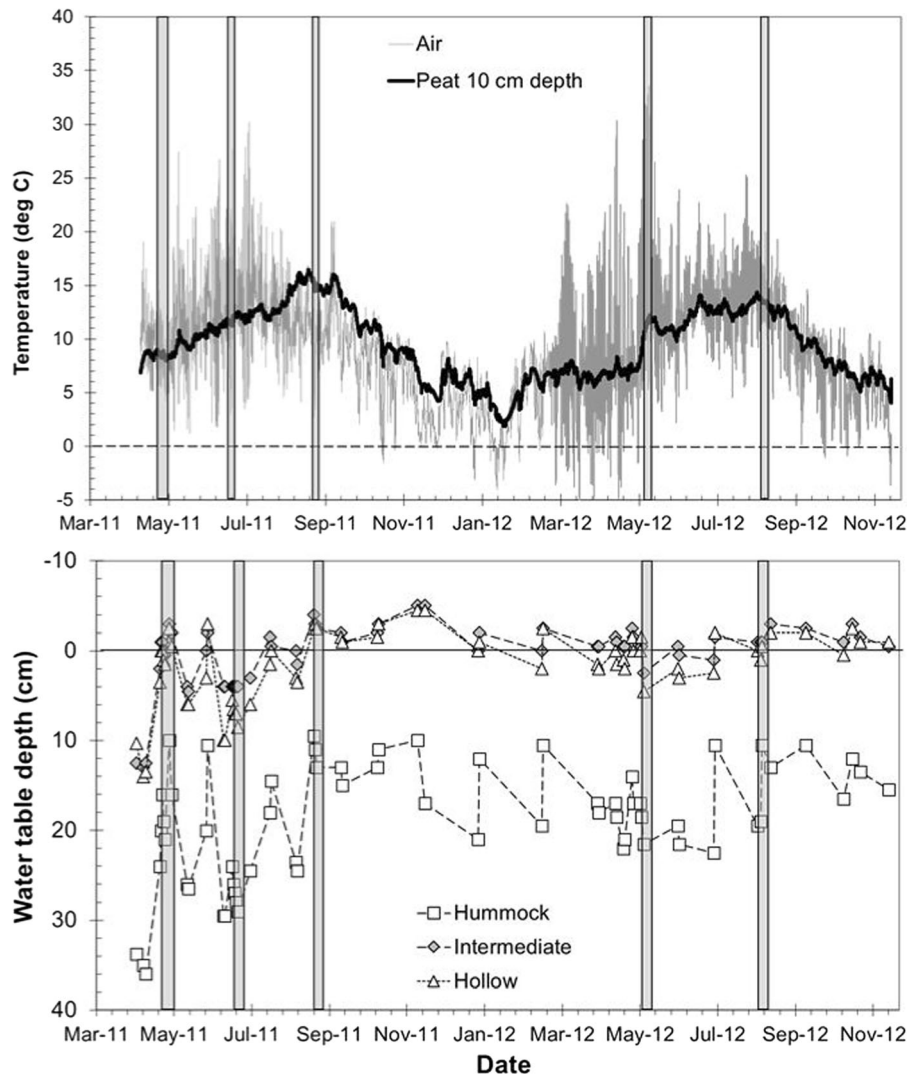
Fig. 1 Temperature (°C) of air (at the peat surface) and peat (at 10 cm depth) measured $\sim$ 10 m from the sampling sites at a temperate raised bog from May 2011 to November 2012 (top). Water table depth (bottom) at the three microsites (Hummock, Intermediate and Hollow) from April 2011 to November 2012. Shaded rectangles represent the five sampling events when gas collection for isotope analysis took place. During sampling events water table was measured daily, but less frequently at other times. Lines connecting data points are to aid interpretation and not to imply the depth of water table between measurements

microsite this relationship was strongest for the Hummock microsite ($p < 0.01$), but was marginally ($p < 0.09$) and not ($p = 0.297$) significant at the Intermediate and Hollow sites, respectively. The situation was again somewhat different for carbon dioxide compared to methane, with a significant correlation ($p < 0.001$) between CO_2 flux and air temperature. However, as also found for CH_4 emissions, the CO_2 fluxes correlated with peat temperature ($p < 0.001$). There was no significant correlation between CO_2 emissions and water table depth ($p = 0.542$).

In 2011 (before clipping), the radiocarbon concentration of methane emissions ranged from 84.0 to 108.2%modern, equivalent to a ^{14}C age range of 1400 years BP to modern (Fig. 3). Four of the chambers had ^{14}C contents less than 100%modern on each sampling occasion in 2011, while two chambers had CH_4 emissions that were modern during the Mid-11 and Late-11 samplings. When grouped by
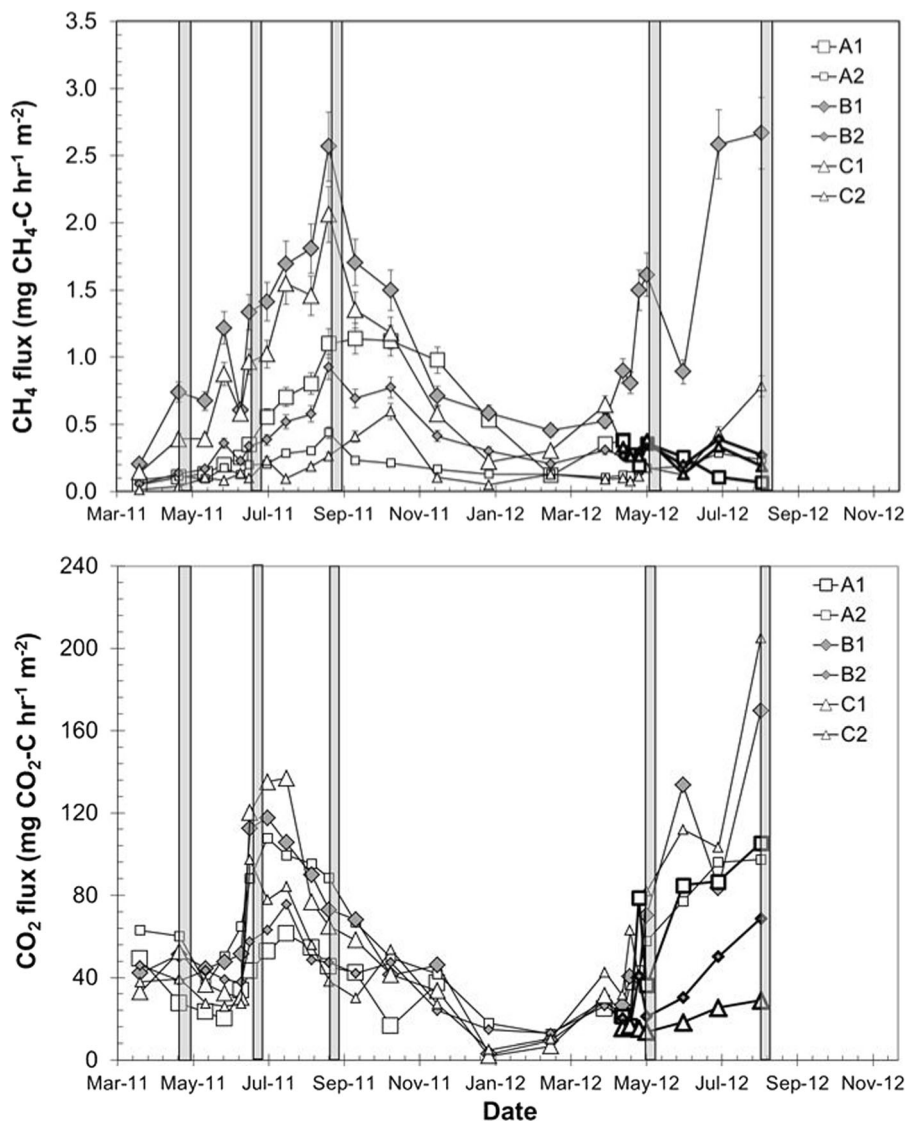
Fig. 2 Rate of methane (top) and carbon dioxide (bottom) emission (mg C h^{-1} m^{-2}) from the surface of a temperate raised bog during 2011 and 2012. Measurements were taken from three microsites: Hummock (A), Intermediate (B) and Hollow (C). Shaded rectangles represent the five sampling events when gas collection for isotope analysis took place. Bold symbols represent the three plots (A1, B2 and C1) after vegetation had been removed by clipping (April 2012); all other data points are for plots with intact vegetation. Lines connecting data points are to aid interpretation and not to imply emission rate between measurements. Error bars based on the precision of the gas analysers used (for CO_2 they are smaller than the symbols). See supplementary Tables S2 and S3 for data

microsite, the Intermediate chambers emitted methane that was ^{14}C-depleted relative to the Hollow sites ($p = 0.04$). No differences were found in the stable carbon isotope composition of CH_4 in 2011, when grouped by microsite ($p > 0.05$). Methane ^{14}C content did not correlate significantly ($p > 0.05$) with temperature (air and soil), water table depth, or methane δ^{13}C. However, there was a pattern of increasing methane ^{14}C content with time during 2011, which resulted in a significant ($p = 0.014$) correlation between methane %modern and day of year (Fig. 4; a similar pattern of increasing methane %modern with day of year was also observed in 2012).
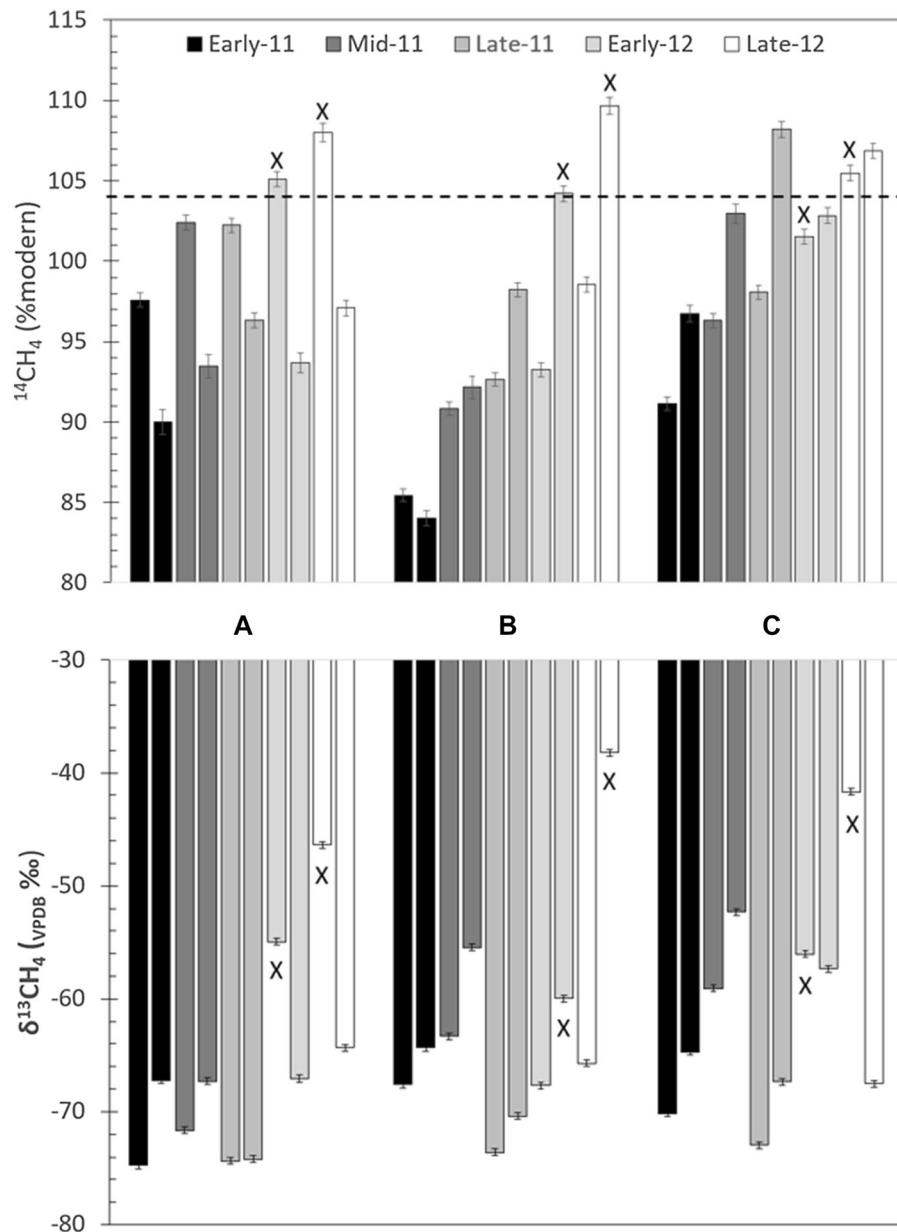
Fig. 3 Radiocarbon (top; %modern ± 1σ) and stable carbon (bottom; $\delta^{13}C_{VPDB}$; ‰ ± 1σ) isotope concentration of methane emitted from the surface of a temperate raised bog on five occasions during 2011 and 2012. Samples were collected from three microsites: Hummock (A), Intermediate (B) and Hollow (C). All results are for plots with intact vegetation, except those columns with an "X" above or below where the vegetation had been clipped. Results have been corrected for a small component of atmospheric CH_4 (see "Methods" section). Dashed line indicates the ^{14}C concentration of atmospheric CO_2 at the time of sampling. Results for the Early-11 samples were previously reported in Garnett et al. (2012). See supplementary Table S4 for data

Partitioning of methane sources

We found that the ^{14}C content of methane emitted from clipped plots was significantly higher than when the same plots had contained vegetation one year earlier (p = 0.004). However, the ^{14}C content of the unclipped control plots was also significantly (p = 0.039) higher in Early-12 compared to

Early-11, whereas for the late growing season the same comparison showed no significant differences in ^{14}C, δ^{13}C or flux (p = 0.493, 0.196 and 0.568 for the ^{14}C, δ^{13}C and CH_4 flux measurements, respectively). We therefore restricted our analysis of the partitioning experiment to the late growing season samples to control for inter-annual variation.

We found highly significant (p = 0.002) differences in methane δ^{13}C, with CH_4 emissions when the chambers contained vegetation (-74.3 to -70.4‰) being much more ^{13}C-depleted compared to plant-free chambers (-46.3 to -38.2‰; Table 3). Although CH_4 fluxes were not quite significantly different when clipped or vegetated (p = 0.08), the same chambers had CH_4 emission rates that were 3–14 times greater when vegetation was present. Isotope mass balance indicated that methane emitted due to the presence of vegetation had a ^{14}C content of 93.42–101.85%modern, showing that it contained a substantial component of pre-bomb carbon and was older than the total methane flux (Table 3). Methane that was associated with the presence of plants in the Intermediate and Hollow sites was the oldest and had ^{14}C contents that were equivalent to radiocarbon ages of $\sim$ 550 and 220 years BP, respectively. Isotope mass balance also showed that methane emitted by peatland plants was highly ^{13}C-depleted, with δ^{13}C values of -76.1 to -83.9‰ (Table 3).
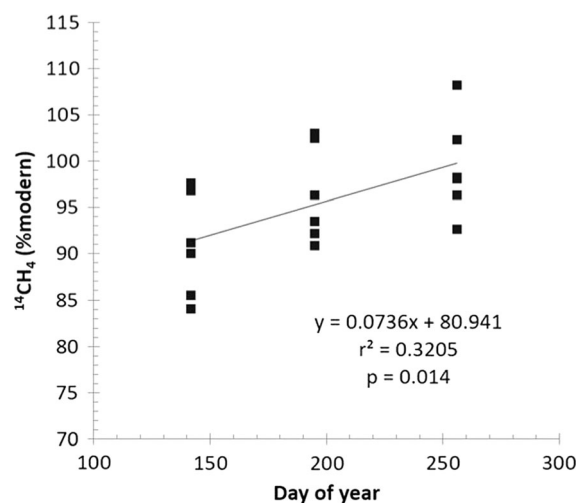

Fig. 4 Plot of radiocarbon concentration of methane emitted from the surface of a raised peat bog versus day of year, for six sites sampled on three occasions (prior to vegetation removal) during 2011

Discussion

Potential chamber effects

The chambers that we used were primarily designed to enable the collection of enough methane for radiocarbon analysis and were broadly similar to other chambers used for the determination of methane fluxes from soils (Pihlatie et al. 2013). It was particularly important that our chambers contained a relatively large headspace since this would allow the collection of enough methane for ^{14}C analysis at relatively low concentrations (recognising that excessive methane concentrations in the headspace could introduce artefacts through disturbance of the natural methane concentration gradient). A caveat was that it was necessary to close the chambers for several days to enable enough methane to be collected for analysis (although we reduced this to between 2 and 4 days after the first sampling). While all chambers produce artefacts (Davidson et al. 2002; Lai et al. 2012) it is possible that the prolonged chamber closure time might have introduced additional artefacts. We did observe that methane emission rates in vegetated plots remained linear for up to 4 days and sometimes longer (see Supplementary Table S1 and Fig. S1), which supports the reliability of our calculated flux rates (mostly determined over 1 day), and visual examination did not indicate that the vegetation had been negatively impacted. In addition, we note that Leith et al. (2014) collected their $^{14}CH_4$ samples in chambers that were sealed for even longer (5 to 9 days). Moreover, it is very likely that plant-free chambers would be less affected by prolonged chamber closure, and indeed, Hartley et al. (2013) demonstrated the collection of $^{14}CO_2$ samples from plant-free chambers sealed for several months. Nevertheless, we recognise that artefacts might have been induced by the extended chamber closure times and that shorter closure times may have been preferable. Perhaps noteworthy however is that since these field experiments were carried out, recent analytical developments in the radiocarbon analysis of methane have meant that it is now possible, through reductions in the volume required for radiocarbon analysis (e.g. Garnett et al. 2019), to facilitate shorter chamber deployment times.

Table 3 Partitioning of methane emissions using isotope mass balance (see text for details)

Microsite (chamber)	Vegetated plot			Plant-free plot			Partitioned			
	%modern ± 1σ	δ^{13}C ± 0.3‰	CH$_4$ flux mg CH$_4$–C h^{-1} m^{-2}	%modern ± 1σ	δ^{13}C ± 0.3‰	CH$_4$ flux mg CH$_4$–C h^{-1} m^{-2}	%Plant flux	%Non-plant CH$_4$ flux	Plant %modern ± 1σ	Plant δ^{13}C ± 0.4‰
Hummock (A1)	102.23 ± 0.45	− 74.3	1.01	108.02 ± 0.57	− 46.3	0.07	94	6	101.85 ± 0.73	− 76.1
Intermediate (B2)	98.23 ± 0.45	− 70.4	0.93	109.67 ± 0.53	− 38.2	0.27	70	30	93.42 ± 0.70	− 83.9
Hollow (C1)	98.07 ± 0.45	− 73.0	2.06	105.49 ± 0.49	− 41.7	0.19	91	9	97.31 ± 0.67	− 76.2

Calculations performed for individual chambers sampled during the late growing season before (Vegetated; 2011) and after (Plant-free; 2012) vegetation removal by clipping. Atmospheric $^{14}CO_2$ was 104.36 % modern and 103.76 % modern in 2011 and 2012, respectively (Levin and Kromer 2004; Hammer and Levin 2017)

Spatial and temporal variation in the flux rate and carbon isotope (^{14}C and ^{13}C) composition of methane surface emissions

Our study was primarily concerned with radiocarbon analysis of CH$_4$ which is an expensive and labour-intensive analysis and therefore the number of chambers that we used was small (n = 6) compared to studies quantifying peatland methane emission rates. However, like previous studies (Lai 2009; Turetsky et al. 2014) we found high spatial and temporal variability in peatland methane emissions. When vegetation was present, the chamber with the highest average flux emitted CH$_4$ at a rate more than six times greater than the plot with the lowest average flux, despite all plots being within 10 m of each other (Table 1). The range of methane emission rates that we recorded was also similar to values that have been reported previously for temperate peatlands. For example, in a review of peatland dynamics, Lai (2009) reported average CH$_4$ flux rates for northern peatlands ranging from 5 to 80 mg m^{-2} day^{-1} (0.2 to 3.3 mg m^{-2} h^{-1}) which compares to mean fluxes from our Langlands Moss microsites of 0.17 to 1.17 mg m^{-2} h^{-1} (Table 1). Green and Baird (2017) observed methane emission rates of 0.18 to 2.5 mg CH$_4$ m^{-2} h^{-1} from multi-year sampling of 22 chambers on a blanket bog in north Wales, UK. We also observed substantial temporal variation in emission rates of methane, with lowest fluxes in winter, and highest fluxes in late summer, which resembles observations made elsewhere (Turetsky et al. 2014). Carbon dioxide emissions from the surface of Langlands Moss were on average around 60–300 times greater than the methane flux (Table 1) which supports observations in previous studies (e.g. McNamara et al. 2008; Leroy et al. 2017).

The radiocarbon content of the methane surface emissions at Langlands Moss varied greatly, from 84.01 ± 0.45%modern (1399 ± 43 years BP; Chamber B2, Early-11) to 108.20 ± 0.53%modern ("modern"; Chamber C2, Late-11) when vegetation was present. There was high spatial and temporal variation in methane ^{14}C content. For example, on the first sampling occasion (Early-11) chamber A1 produced the most ^{14}C-enriched methane at 97.60 ± 0.44%-modern (195 ± 36 years BP), and chamber B2 the most ^{14}C-depleted methane at 84.01 ± 0.45%modern (1399 ± 43 years BP); but the latter chamber emitted

much more ^{14}C-enriched methane just four months later (98.23 ± 0.45%modern). These ^{14}C results suggest that the source and pathways of methane being emitted at the peat surface are complex.

The oldest methane ages that we observed at Langlands Moss (up to 1399 ± 43 years BP) are older than previous measurements of peatland methane emissions (Wahlen et al. 1989; Quay et al. 1991; Chanton et al. 1995; Leith et al. 2014). They imply a source located deep below the peat surface at depths of up to $\sim$ 1 m based on the age of peat (Langdon and Barber 2005) and pore water methane previously measured at this site. For example, Garnett et al. (2011) reported pore water methane ^{14}C ages of 220 ± 36 and 264 ± 35 years BP at 0.25 m depth, and 1580 ± 37 and 2033 ± 35 years BP at 1 m. This depth is below that thought to be responsible for the highest methane production (0 − 50 cm; Clymo and Pearce 1995) and implicated as the source of emissions in other peatlands where methane had a similar ^{14}C content to atmospheric CO_2 (Wahlen et al. 1989; Quay et al. 1991; Chanton et al. 1995; Leith et al. 2014). It may be of significance, however, that the ^{14}C content of methane in peat pore waters has shown great variation between peatlands with some sites showing modern ^{14}C contents down to at least 50 cm (e.g. Bellisario et al. 1999; Campeau et al. 2017), while others provided much older values at similar depths (650 ± 70 years at 65–85 cm, Aravena et al. 1993; Garnett et al. 2011), perhaps resulting from differences in peat hydraulic conductivity and mass flow of dissolved organic carbon (DOC; Clymo and Bryant 2008). While we have no measurements of hydraulic conductivity for Langlands Moss, we have found it very difficult to extract porewater samples from the peat using suction devices, suggesting low hydraulic conductivity, which may help explain why the pore water methane at Langlands Moss is relatively old in near surface layers.

Our measurements are not the only ones to show pre-bomb ^{14}C concentrations in peatland surface emissions of methane. Cooper et al. (2017) also reported aged methane emissions, though they were younger than the oldest ages observed at Langlands Moss, despite being from Canadian thermo-karst wetlands containing large stores of recently-thawed organic matter and older methane within the peat profile. It therefore remains to be seen whether our observations at Langlands Moss are atypical of peatlands or reflect crucial differences in peatland carbon cycling and pathways of methane emissions.

The modern ^{14}C values (i.e. > 100%modern) that we measured at Langlands Moss in methane emissions agree more with other studies (Wahlen et al. 1989; Quay et al. 1991; Chanton et al. 1995; Leith et al. 2014) and provide irrefutable evidence for much younger carbon contributing to the methane emissions. These results also suggest a source much nearer to the peatland surface (i.e. within the surface 0.25 m; Garnett et al. 2011). Products of peatland decay (including CH_4, CO_2 and DOC) are likely derived from various sources of different age since carbon fixation, and therefore it is not always possible to provide a definitive age for them. However, we can be certain that our site emitted methane that was on some occasions over one thousand years old, while at other times was likely to have been derived from carbon photosynthetically fixed from the atmosphere within the last few decades or years (and potentially was derived from recent plant fixation; e.g. Öquist and Svensson 2002).

When considering only plots with intact vegetation the stable carbon isotope ($\delta^{13}C$) composition of surface methane emissions at Langlands Moss covered a range typical of emissions for northern peatlands, although it was notable that some of the most ^{13}C-enriched values appeared more typical of minerotrophic, rather than ombrotrophic peatlands (Hornibrook 2009).

Factors affecting the flux and age of methane emissions and the importance of vegetation

Based on previous studies (e.g. Clymo and Pearce 1995; Turetsky et al. 2014), we expected that the Hummock microsites would have the lowest methane fluxes compared to the others because of lower water tables which for example, creates a greater depth of aerobic peat in surface layers and therefore a greater opportunity for methane oxidation (Lai 2009). We did indeed observe both lower methane fluxes and a significantly deeper water table at the Hummock microsites, consistent with earlier reports. However, despite significantly higher water tables at the Hollow microsites compared to the Hummocks, the rate of methane emission between the two microsites was not significantly different, and overall, only the Hummocks microsite had a methane flux that was

significantly correlated with water table depth, suggesting that other factors had a stronger control over methane flux at the other sites. Nevertheless, across all sites methane flux did negatively correlate ($p < 0.001$) with water table depth which agrees with earlier studies (e.g. Moore and Roulet 1993), although we note that others have also reported the absence of a relationship (Lai 2009).

We anticipated the ^{14}C age of methane emissions would correlate with water table depth, since it has been suggested that a zone of maximum methane production occurs in peatlands at around the depth of the water table (Laing et al. 2010) which fluctuates within the mesotelm (between the permanently saturated catotelm and the acrotelm). The zone around the water table provides both a relatively labile substrate and the anaerobic conditions necessary for methanogenesis, and therefore, clearly would occur in deeper and older layers when the water table is lower. However, we found no correlation between water table depth and the age of emitted methane, again suggesting that other factors exert a greater control.

Plant respiration, and soil respiration from the surface aerobic layers of peat, are responsible for most of the CO_2 emissions which is reflected in predominantly modern radiocarbon concentrations for peatland CO_2 emissions (e.g. Hardie et al. 2009; Walker et al. 2016; this study, supplementary Table S5); hence we found CO_2 emissions were strongly linked to air temperature. Methane emissions from peatlands have been found to be strongly controlled by temperature, as shown by many studies using a variety of techniques (e.g. Hargreaves and Fowler 1998; Turetsky et al. 2014; Gill et al. 2017). While the Langlands Moss methane emission rates were not significantly related to air temperature, they did positively correlate with peat temperature at 10 cm depth. Given that the anaerobic conditions necessary for methanogenesis are present only below the water table, it therefore seems reasonable that, assuming methane flux is linked to production, methane efflux and peat temperature would be related. However, we found no significant effect of peat temperature on the ^{14}C content of methane emissions.

In contrast to microsite type, water table depth and temperature, clipping of the above-ground vegetation had a dramatic influence on the flux, stable and radiocarbon concentration of methane emissions. Methane flux when vegetation was no longer present

was only 6–30% of the flux when the same plots were vegetated, representing an additional methane flux rate of 0.66–1.87 mg CH_4–C h^{-1} m^{-2} that was attributed to the presence of plants (Table 3), and is consistent with numerous earlier studies showing the controlling factor of plants on peatland methane emissions (Shannon et al. 1996; Popp et al. 1999; Chanton 2005). Although paired t-tests indicated that the flux difference between vegetated and unvegetated plots was only marginally significant ($p = 0.08$), this may be due to the high spatial variability and the small number of paired chambers used ($n = 3$), and therefore it is possible that more highly significant differences would have been identified from a more extensive dataset.

Indeed, numerous earlier studies have recognised that most methane emitted from the surface of peatlands does so via transport through plants (Whiting and Chanton 1993; Shannon et al. 1996; Watson et al. 1997; Verville et al. 1998; Joabsson et al. 1999; Rinnan et al. 2003; Marinier et al. 2004; Ström et al. 2005). The same gas transport processes are also known to cause isotopic fractionation (by discriminating against the heavier ^{13}C isotope relative to ^{12}C; Chanton 2005; Conrad 2005; Hornibrook 2009) with a theoretical depletion in ^{13}C of peatland methane emissions relative to source of up to ∼ 19‰ being possible due to the mass difference of [13]CH_4 and [12]CH_4 (Chanton 2005). This is reflected in the large difference in the δ^{13}C of methane from our vegetated and plant-free plots, since discrimination of the ^{13}C isotope due to plant mediated transport would affect vegetated plots, but not plant-free plots. We note, however, that this factor alone cannot account for the ∼ 30‰ difference between our vegetated and plant-free plots, which we postulate may additionally be due to (i) ^{13}C-enrichment resulting from methane oxidation (Popp et al. 1999; which may have had a proportionally greater influence in plant-free plots due to the lower rate of methane efflux) and/or (ii) a greater contribution of relatively ^{13}C-enriched methane being generated in the surface layers of the plant-free plots by acetate fermentation (Whiticar et al. 1986; Hornibrook 2009; Garnett et al. 2011; this is supported by the [14]CH_4 values which indicate a younger, and therefore shallower, carbon source for plant-free plots; see below).

Our results show that plants have a significant influence on the age of peatland methane emissions.

When plants were present, we found the methane efflux to be significantly depleted in ^{14}C compared to when plants were absent, with all three vegetated plots emitting methane that was ^{14}C-depleted relative to the contemporary atmospheric [14]CO_2, and all non-vegetated plots releasing relatively ^{14}C-enriched methane. While the methane is likely derived from multiple sources of different age, by far the most likely interpretation of these results is that the peatland emitted older methane when plants were present.

Source of peatland methane emissions

Isotope mass balance of our [14]CH_4 results suggests that plants were responsible for over 70% of the methane emitted from the peat surface, and that this methane was up to at least 500 years old (Table 3). Although two of our sites clearly showed that plants caused the release of methane in the order of hundreds of years old to be emitted, the third site indicated that the plant associated methane was not as old (and most likely a mixture of carbon fixed during both pre- and post-bomb times). The small number of chambers that we examined in our partitioning study provides limited evidence to explain why plants caused the emission of old methane in some chambers (B2 and C1), but much younger methane in another (A1). However, given the well-known ability of some peatland plants to act as conduits for the release of methane (Chanton 2005; Conrad 2005; Hornibrook 2009), it seems likely that plant mediated transport is at least part of the explanation through providing a pathway for deep peat gases to escape and reducing methane oxidation due to more rapid gas transit. Indeed, this explanation is supported by the vast difference in $\delta^{13}C$ of methane emissions when the plots did, and did not, contain plants (Chanton 2005; Conrad 2005; Hornibrook 2009). Furthermore, present in all three of the chambers examined in our partitioning study was the sedge *Eriophorum vaginatum*, which has been previously linked to plant mediated transport (e.g. Greenup et al. 2000; Marinier et al. 2004) and is known to possess a root system that can penetrate deep into the peat profile (Wang et al. 2016). We also note that Hardie et al. (2009) invoked plant mediated transport to explain the emission of aged CO_2 from an ombrotrophic bog using a similar vegetation clipping experiment.

When devoid of plants the peatland surface emitted methane with a narrow range of post-bomb radiocarbon signatures in the Late-12 sampling, unequivocally indicating that much of this methane was derived from carbon photosynthetically fixed from the atmosphere within the last ∼ 60 years. We cannot exclude that some pre-bomb carbon contributed to the methane emissions when plants were absent. Though if we assume that it did not, and that the methane was derived from carbon fixed after the AD1963 bomb-^{14}C peak (e.g. Hartley et al. 2012), then matching the ^{14}C concentrations of the plant-free emissions to the atmospheric [14]CO_2 record (Levin and Kromer 2004) suggests that this methane carbon was fixed on average 2–10 years before the sampling date. This indicates that in the absence of plants, methane surface emissions may be derived from a relatively narrow layer near the surface of the peatland.

Numerous previous studies have shown that plants provide a dominant control on peatland methane emissions (Whiting and Chanton 1993; Watson et al. 1997; Shannon et al. 1996; Verville et al. 1998; Rinnan et al. 2003; Marinier et al. 2004; Ström et al. 2005). Several studies have indicated that these emissions are derived from recently fixed organic matter. For example, Öquist and Svensson (2002) found lower methane emissions concomitant with reduced photosynthetic activity induced by shading, and Chanton et al. (1995) observed emissions with a ^{14}C signature equivalent to atmospheric CO_2 at the time of sampling. However, others have suggested that the influence of plants on peatland emissions is largely through the transport of methane from the soil to the atmosphere rather than promoting methanogenesis (e.g. Verville et al. 1998; Bhullar et al. 2014). Our ^{14}C results show that at times, a substantial proportion of methane emitted by peatland plants is at least hundreds of years old. This indicates that at our site, peatland emissions are not all derived from recently fixed organic matter and therefore supports the role of plants in transporting old methane from sub-surface layers to the atmosphere.

Conclusions

During the 1.5 years of monitoring at a temperate ombrotrophic raised bog, we observed high temporal and spatial variation in the radiocarbon content and

efflux of methane emissions from the peatland surface. Our methane flux results are in agreement with many earlier studies that have shown that plants have a large control on methane flux since emissions fell by $\sim$ 70 to 90% when their influence was removed by clipping. However, in contrast to the few earlier studies where ^{14}C analysis showed that peatland methane emissions were predominantly derived from recently fixed organic matter, our results suggest that at this site, plant mediated transport of older peat gases from sub-surface layers of peat is also important. These results highlight the complexity of peatlands, which must be better modelled to improve predictions of their response to climatic warming. Our results demonstrate that radiocarbon measurements of methane surface emissions can contribute to achieving this goal.

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