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Radiocarbon dating of methane and carbon dioxide evaded from a temperate peatland

2 **stream**

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14 **Abstract**

Streams draining peatlands export large quantities of carbon in different chemical forms and
are an important part of the carbon cycle. Radiocarbon (¹⁴C) analysis/dating provides unique
information on the source and rate that carbon is cycled through ecosystems, as has recently
been demonstrated at the air-water interface through analysis of carbon dioxide (CO₂) lost
from peatland streams by evasion (degassing). Peatland streams also have the potential to
release large amounts of methane (CH₄) and, though ¹⁴C analysis of CH₄ emitted by ebullition
(bubbling) has been previously reported, diffusive emissions have not. We describe methods
that enable the ¹⁴C analysis of CH₄ evaded from peatland streams. Using these methods, we
investigated the ¹⁴C age and stable carbon isotope composition of both CH₄ and CO₂ evaded
from a small peatland stream draining a temperate raised mire. Methane was aged between
1617-1987 years BP, and was much older than CO₂ which had an age range of 303-521 years
BP. Isotope mass balance modelling of the results indicated that the CO₂ and CH₄ evaded
from the stream were derived from different source areas, with most evaded CO₂ originating
from younger layers located nearer the peat surface compared to CH₄. The study demonstrates

the insight that can be gained into peatland carbon cycling from a methodological

30 development which enables dual isotope (^{14}C and ^{13}C) analysis of both CH_4 and CO_2 collected
at the same time and in the same way.

32

Introduction

34 The importance of surface waters including streams, rivers and lakes for the processing and
transport of carbon is increasingly being recognised, particularly when they are associated
36 with organic-rich terrestrial systems such as peatlands or wetlands (Dinsmore et al. 2010;
Koehler et al. 2011; Repo et al. 2007). Globally, it has been suggested that degassing of C
38 from all types of aquatic systems (excluding wetlands) returns at least 0.8 Pg C y^{-1} to the
atmosphere (Cole et al. 2007). Carbon exists in surface waters in several forms, including
40 dissolved organic carbon (DOC), particulate organic carbon (POC), dissolved inorganic
carbon (DIC; which includes free CO_2) and CH_4 . Radiocarbon (^{14}C) analysis/dating of each of
42 these forms of carbon has the potential to enhance our understanding of carbon cycling and
transport between the peatland, aquatic and atmospheric environments.

44

Radiocarbon analysis of aquatic C in freshwater systems has largely focused on the DOC and
46 POC components and has generally shown that in undisturbed systems, DOC is derived from
recently fixed carbon ($< \sim 5$ years old; e.g. Tipping et al. 2010, Billett et al. in press). While
48 DOC is often the dominant carbon component, peatland streams are also super-saturated in
both CO_2 and CH_4 with respect to the atmosphere (Dinsmore and Billett 2008; Johnson et al.
50 2010). Degassing of streamwater occurs resulting in the emission of these gases, referred to as
“evasion”. Rates of evasion can be determined by a number of methods, including monitoring
52 the build-up of CO_2 and CH_4 using floating chambers (e.g. Billett and Moore 2008; Repo et
al. 2007). The ^{14}C content of CO_2 lost by evasion can be established using a direct method
54 whereby the headspace of a floating chamber is sampled and the CO_2 component recovered
for analysis (e.g. using molecular sieve techniques; Billett et al. 2006, 2007). Alternatively,
56 the ^{14}C content of evaded CO_2 can be inferred from analysis of the total DIC component of a

sample of streamwater recovered by “gas-stripping” (e.g. Mayorga et al. 2005). Studies
58 applying these techniques have shown that evaded CO₂ can vary considerably in age, ranging
from a few years for CO₂ degassing from Amazonian rivers (Mayorga et al. 2005), to over
60 1000 years BP for some UK peatland streams (Billett et al. 2006, 2007).

62 Only a few studies have investigated the ¹⁴C age of CH₄ emitted from surface waters and
these appear to be limited to measurements of bubble emissions (ebullition) from lakes in
64 tundra or boreal regions (e.g. Nakagawa et al. 2002; Walter et al. 2006, 2008). These studies
have shown exceptionally wide ranges in the ¹⁴C age of CH₄ from modern to >40,000 years
66 BP (e.g. Walter et al. 2006). To our knowledge, there are no reported ¹⁴C results on the non-
ebullition diffusive CH₄ emissions from surface waters or of CH₄ emitted from peatland
68 streams, perhaps because emissions are typically less concentrated, leading to difficulties in
providing sufficient sample for ¹⁴C analysis (¹⁴C techniques have previously provided
70 evidence for diffusion of CH₄ within the peat profile; e.g. Chanton et al. 1995). However,
recent studies have highlighted the importance of peatland headwater streams for both CO₂
72 and CH₄ emissions, and indeed, Öquist et al. (2009) has shown that up to 90 % of soil-derived
CO₂ was lost within 200 m of entering a headwater stream in a boreal forest. This suggests
74 that inventories of catchment greenhouse gas emissions that do not consider headwater
streams may significantly underestimate total landscape scale emissions. Moreover, it
76 indicates that measurements of the ¹⁴C age of CH₄ emitted as ebullition from lakes cannot be
assumed to be representative of the catchment, and therefore there is a specific need for a
78 method to enable ¹⁴C analysis of diffusive emissions of CH₄ from peatland streams.

80 Here, we describe the application of new techniques to recover and process samples of CH₄
evaded from a temperate peatland stream for ¹⁴C (and δ¹³C) analysis. We also present ¹⁴C and
82 δ¹³C results for CO₂ that evaded from the stream surface at the same time as the CH₄, along
with the associated rates of CH₄ and CO₂ emission. We then consider the insights that ¹⁴C
84 analysis of paired samples of CH₄ and CO₂ may reveal about the production and transport of

these two important greenhouse gases and their role in the in the soil-water-atmosphere
86 system.

88 **Methods**

Sampling site and field collection

90

Samples were collected from a small first-order peatland stream draining Langlands Moss, a
92 temperate raised peat bog in central south-west Scotland (55° 44' 5.5" N, 4° 10' 25.8" W).

The peatland lies at an altitude of 217 m, has a mean annual temperature of 7.3 °C and annual
94 rainfall of 971 mm (Langdon and Barber, 2005). Maximum peat depth at Langlands Moss is
>8 m (Langdon and Barber, 2005) with the water table usually within the surface 20 cm.

96 Vegetation cover is typically a mixture of mosses (*Sphagnum* spp.), sedges (especially
Eriophorum vaginatum) and Ericaceous species (e.g. *Calluna vulgaris*). We sampled the main
98 peatland stream (width ~ 0.7 m, depth ~ 0.3 m) on the south-east fringe of the peatland, which
drains into the Rotten Calder, a tributary of the River Clyde that flows into the Irish Sea (west
100 coast Scotland).

102 Four sets of samples, comprising paired CH₄ and CO₂ components, were analysed in order to
perform a test of the method and examine the isotopic composition of evading gases at the
104 site. The samples were collected from two separate locations thus allowing assessment of
spatial and temporal variation (Site 1 was located approximately 10 m upstream of Site 2). In
106 addition, on one occasion two samples were collected consecutively from the same chamber,
providing us with replicate samples in order to test the reliability of the sampling procedures.

108

A large volume floating chamber was constructed using the lower portion of a 120 L plastic
110 barrel ('Open top keg', Ampulla Ltd, UK) which we inverted to place on the stream to trap
gas emitted from the stream surface (without disturbing the streambed). The chamber had a
112 cross-sectional area of 1520 cm², and a total volume of 42,580 ml. A ring of polystyrene

tubing (pipe insulation) was attached near the base of the chamber to aid floatation and
114 improve stability; when floating, the volume of the headspace was approximately 33,500 ml.
The chamber was entirely air-tight, except for two holes that were drilled into the top surface
116 and into which were inserted two auto-shutoff couplings (Colder Products Company, USA).
The couplings were used to allow sampling of the chamber headspace, but when not in use
118 were closed to provide an air-tight seal. When deployed in the stream, the chambers were
simply placed onto the stream surface, and secured in position using string connected between
120 the chamber and anchor points on the stream bank.

122 Carbon dioxide concentration was monitored in the chamber headspace by connecting (via the
couplings) a portable EGM-4 infrared gas analyser (IRGA; PPsystems, UK). Chamber CO₂
124 concentration was measured over a period of 5 minutes immediately after deployment of the
chamber, in order to calculate the CO₂ evasion rate. Methane concentration in the chamber
126 was determined using a Detecto Pack Infrared methane analyser (DP-IR; Gas Measurement
Ltd, UK) at various intervals over the sampling period. Stream and air temperature
128 measurements were also performed during the sampling period.

130 Sampling of chamber headspace for ¹⁴C analysis of both CH₄ and CO₂ was undertaken by
filling 10 L foil gas sample bags (SKC Ltd, UK) with chamber air. The bags were cleaned by
132 repeatedly flooding with high purity N₂ from a cylinder and evacuating several times prior to
use; an air pump (MiDan Co., California, USA) connected via an auto-shutoff coupling was
134 used to facilitate emptying the bag. Since a minimum of ~ 1 ml of both CH₄ and CO₂ was
required for ¹⁴C analysis of both gases we needed to collect samples with CH₄ and CO₂
136 concentrations in excess of 100 ppm. Chamber air was collected using the internal pump of
the DP-IR allowing us to measure the CH₄ concentration during sample collection. To avoid
138 creation of vacuum conditions inside the chamber during sampling, the chamber was vented
to atmosphere via one of the couplings. Samples were returned to the laboratory at the NERC
140 Radiocarbon Facility and processed within 8 days.

142 Laboratory processing of samples

144 IRGA measurement of chamber headspace indicated that the CO₂ concentration was much
greater than CH₄ (see Results), and therefore a much smaller volume of gas could be used to
146 provide sufficient CO₂ for ¹⁴C analysis. We therefore removed ~ 250 ml of chamber gas from
the 10 L bag samples using evacuated flasks for isotope analysis of the CO₂ component.
148 These samples were processed on a vacuum rig where they were first dried (using a trap
cooled to -78 °C containing dry ice/methylated spirits) and then sample CO₂ cryogenically
150 recovered by pumping through liquid nitrogen-cooled traps (-196 °C).

152 The remainder of the sample gas (~ 9 L) in the bags was used to analyse the CH₄ component.
Firstly, the large volume of CO₂ remaining in the bag was removed by pumping (~ 500 ml
154 min⁻¹) the sample gas from the foil bag through a glass cartridge (inner diameter 20 mm,
length 250 mm) filled with soda-lime (absorbs CO₂) and then into a second clean foil gas bag.
156 Complete removal of CO₂ was verified by passing the gas through the EGM-4 IRGA. The bag
containing the sample was then connected to a vacuum rig via another cartridge, this time
158 filled with ~ 3-4 g of type 13X zeolite molecular sieve (BDH Laboratory Supplies, UK),
which served as an additional adsorbent to ensure that all traces of CO₂ had been removed
160 from the sample. Sample gas then passed through a cartridge containing platinum-alumina
pellets (Johnson Matthey Chemicals, UK) heated to 950 °C, thus combusting the CH₄
162 component of the sample to produce CH₄-derived CO₂ (since the sample gas would have
contained a large volume of atmospheric O₂, at a much higher concentration than CH₄, it was
164 unnecessary to provide additional O₂). CH₄-derived CO₂ was cryogenically purified as above.
The reliability of the laboratory methods has been demonstrated previously using a range of
166 mixtures of CO₂ and CH₄ of differing isotopic composition (Garnett et al., 2012^b).

168 The CO₂ and CH₄-derived CO₂ samples were split into separate aliquots for ¹³C and ¹⁴C
analysis. δ¹³C (¹³C/¹²C ratio expressed relative to the international Vienna PDB standard) was
170 determined using isotope ratio mass spectrometry (Thermo Scientific Delta V Plus,
Germany). For ¹⁴C measurement, sample CO₂ was first converted to graphite using Fe-Zn
172 reduction (Slota et al. 1987) and then analysed by accelerator mass spectrometry (AMS) at the
Scottish Universities Environmental Research Centre AMS Facility. Following conventions,
174 ¹⁴C results were normalised to a δ¹³C of -25 ‰ to account for mass-dependent fractionation
effects and expressed as both ‰modern and conventional radiocarbon ages (years BP; before
176 present, where 0 BP = AD 1950; Stuiver and Polach 1977).

178 Chamber headspace would have contained a small amount of atmospheric CO₂ and CH₄ (e.g.
the chambers were vented to allow pressure equilibration during sample collection). However,
180 since we had determined the CO₂ and CH₄ concentration in the samples, we corrected for the
atmospheric component for both ¹⁴C and δ¹³C results using mass balance, assuming
182 atmospheric concentrations of 385 ± 5 ppm and 3 ± 1 ppm for CO₂ and CH₄ respectively, and
the following isotopic characteristics: for atmospheric CO₂ (δ¹³C = -9 ‰, Hemming et al.
184 2005; ¹⁴C content = 104.14 ‰modern, Levin et al. 2008) and CH₄ (δ¹³C = -47 ‰, ¹⁴C content
= 130 ‰modern; Lassey et al. 2007).

186

Results

188 The initial rate of CO₂ build-up in the floating chambers was linear (Fig. 1) and ranged from
59 ppm min⁻¹ (October Site 2) to 100 ppm min⁻¹ (September Site 2). These values correspond
190 to CO₂ evasion rates of 116-196 µg C-CO₂ m⁻² s⁻¹. In contrast, CH₄ build-up in the chambers
was considerably slower (~ 50-140 ppm d⁻¹; Fig. 2) and chambers had to be left for several
192 days to ensure sufficient CH₄ was collected for ¹⁴C analysis. At Site 2, the rate of CH₄ build-
up appeared to be approximately linear over at least 2 or 3 days, whereas at Site 1, CH₄
194 concentration appeared to rise rapidly within the first hour of installing the chamber, but
subsequently declined to a lower rate that was similar to Site 2. When the rate of CH₄ build-

196 up was linear, the emission rate was equivalent to $\sim 0.1 \mu\text{g C-CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ over several days,
whereas emission rate in September at Site 1 for the first hour of the sampling was equivalent
198 $1.2 \mu\text{g C-CH}_4 \text{ m}^{-2} \text{ s}^{-1}$.

200 Table 1 presents the results of the carbon isotope analyses before correction was made to
account for the presence of atmospheric CO_2 or CH_4 in the samples. Correction for air made
202 little difference to the ^{13}C and ^{14}C values for either CO_2 or CH_4 , because the air component
represented only a small fraction of the total sample. For CO_2 , chamber concentration at the
204 time of sampling had built up to between 12500-15000 ppm (after 2-3 days) and so the
atmospheric component only represented ~ 2.5 -3 % of the total recovered CO_2 . ^{14}C
206 concentration of the CO_2 therefore changed by less than the 1σ uncertainty of the age
measurements, following correction for air. $\delta^{13}\text{C}$ for evaded CO_2 decreased by 0.4 ‰
208 following air-correction. While CH_4 concentration in the chambers was only 110-214 ppm at
the time of sample collection, the atmospheric correction also did not make a great difference
210 because of the low CH_4 concentration of the free atmosphere (~ 2 ppm); $^{14}\text{CH}_4$ results became
older by between ~ 70 -140 years and $\delta^{13}\text{C}$ values declined by 0.2-0.4 ‰.

212

Figure 3 presents the ^{14}C results for evaded gases after removal of the atmospheric
214 contribution, and shows that CO_2 ranged in age between 303 and 521 years BP. The ^{14}C age
for CH_4 was considerably older, and ranged from 1617 to 1987 years BP. $\delta^{13}\text{C}$ for CO_2 ranged
216 from -24.0 to -25.0 ‰ whereas for CH_4 the range of $\delta^{13}\text{C}$ values was ~ -58.8 to -61.7 ‰ (Fig.
4). The ^{14}C and $\delta^{13}\text{C}$ values for the replicate samples (October Site 2a and October Site 2b)
218 were identical ($<1 \sigma$) when the CO_2 and CH_4 components were considered separately. The
age of CH_4 at Site 2 was within measurement uncertainty on the two sampling dates, however,
220 in September CH_4 evaded from Site 1 was significantly younger ($>2 \sigma$) than Site 2. In
contrast, the age of CO_2 was similar for the 2 different sites in September, but the CO_2 evaded

222 from Site 2 in October was younger than CO₂ emitted from this site on the earlier sampling
occasion.

224

Discussion

226 Rates of CO₂ and CH₄ evasion

228 Up to now previous methods used to collect CH₄ from surface waters for ¹⁴C analysis have
had to focus on locations where high rates of CH₄ ebullition were evident, such as the
230 Siberian thaw lakes (Walter et al. 2006). This was necessary to ensure there was sufficient
sample for analysis, and in some cases sediments have been deliberately disturbed (by
232 stirring) in order to facilitate ebullition (Nakagawa et al. 2002; Walter et al. 2008). Our
approach uses a large floating chamber similar to those used to determine gas evasion rates
234 from streams (e.g. Billett et al. 2006) and does not require disturbance to generate sufficient
CH₄. The samples we collected therefore should be more representative of natural evasion,
236 and allow quantification of evasion fluxes at the same time as the sample was collected for
isotope analysis.

238

We were not present at the sampling points throughout the sampling period, but when we
240 were, we did not observe bubble emissions at our sites. Time-concentration changes (Figs 1
and 2) confirm that the build-up of CO₂ and CH₄ concentrations within the chambers was
242 mostly linear and typical of diffusive emissions (Hornibrook 2009). In contrast, ebullition
events produce more temporally and spatially variable gas concentrations in collection
244 chambers (Hornibrook 2009; Walter et al. 2006, 2008) and periodically a much higher
emission rate (Walter et al. 2006 report emissions from ebullition “hot spots” of up to > 30
246 litres day⁻¹). Indeed, the evasion rates that we measured for both CO₂ and CH₄ were broadly
similar to rates previously reported from chamber measurements for peatland streams. Our
248 CO₂ evasion flux rate ranged from 116-196 μg C-CO₂ m⁻² s⁻¹ which compares with literature
values of between 17.6 - 114 μg C-CO₂ m⁻² s⁻¹ and 8.9-185.2 μg C-CO₂ m⁻² s⁻¹ for sites across

250 the UK reported by Billett et al. (2007) and Billett and Garnett (2010), respectively. Evasion
fluxes measured by soluble gas tracers were generally higher for UK peatland streams;
252 median and mean fluxes were 133 and 367 $\mu\text{g C-CO}_2 \text{ m}^{-2} \text{ s}^{-1}$, respectively (Billett and Harvey,
in press). Billett and Moore (2008) reported mean chamber-based evasion rates of 28.7 (range
254 2.4-137.8) $\mu\text{g C-CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ for CO_2 from Mer Bleue (Canada) and Aufdenkampe et al.
(2011) give average CO_2 outgassing rates for temperate streams (<60-100 m wide) of 83.4 μg
256 $\text{C-CO}_2 \text{ m}^{-2} \text{ s}^{-1}$.

258 While our chambers exhibited linear build-up of CO_2 over the first 5 minutes after
deployment (Fig. 1), after several days CO_2 concentrations stabilised when presumably an
260 equilibrium was reached with the $p\text{CO}_2$ of the stream. In contrast, CH_4 concentration in the
chambers was still increasing at approximately linear rates after 2-3 days (Fig. 2). The CH_4
262 build-up at Site 1 in September suggested a decreasing rate of CH_4 emission over time, and
hence, CH_4 evasion rates determined for the first hour following chamber deployment were
264 substantially greater than the average over several days. In this case, the CH_4 emission flux
would better be determined using an exponential model, rather than a linear one (e.g. Forbrich
266 et al. 2010), and the observation may indicate shortcomings in the technique we employed to
quantify the CH_4 evasion flux; since the DP-IR only measures to ppm precision, relatively
268 large time intervals between measurement points are required resulting in low temporal
resolution that could hide changes in rates of CH_4 emission. Alternatively, despite taking great
270 care, it is possible that the initial high CH_4 emission rate at Site 1 was a result of a small
amount of disturbance when deploying the chamber, causing some ebullition. The increase in
272 CH_4 concentration in both the September and October Site 2 chambers was clearly linear,
which would support both the method and calculated evasion rates.

274

The solubility of CH_4 in water is much lower than that of CO_2 (Steinmann et al. 2008) and
276 therefore it is perhaps not surprising that CH_4 evasion rates were lower. Although relatively
few measurements of CH_4 evasion have been reported our range of ~ 0.1 to $1.2 \mu\text{g C-CH}_4 \text{ m}^{-2}$

278 s^{-1} compares well with literature values of 0.09-0.47 $\mu\text{g C-CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ for a west Siberian
pond and lake (Repo et al. 2007), and a range of 0.02–0.27 $\mu\text{g C-CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ for surface
280 waters at Mer Bleue peatland, Ontario, Canada (Billett and Moore 2008). Median and mean
CH₄ evasion rates of 0.22 and 1.45 $\mu\text{g C-CH}_4 \text{ m}^{-2} \text{ s}^{-1}$ were recently measured by Billett and
282 Harvey (in press) for UK peatland headwater streams.

284 Reliability of carbon isotope measurements

286 To provide a test of the reliability of our field sampling and laboratory methods we collected
duplicate gas samples from the same chamber for the October sampling at Site 2. The results
288 for the duplicates of both ¹⁴C content and $\delta^{13}\text{C}$ were within measurement uncertainty of each
other, supporting the reliability of the sampling method and laboratory techniques. Although
290 all chambers create artefacts (Davidson et al. 2002; Vachon et al. 2010) they are often the
only suitable methods available. In the current study it was necessary to use large chambers in
292 order to collect sufficient sample for analysis, which could have increased the likelihood of
artefacts, particularly in a relatively narrow stream. Though we did not observe changes in
294 stream flow conditions (e.g. turbulence) caused by the floating chambers, they will to some
extent have altered conditions (e.g. Billett and Garnett 2010). However, tests of similar
296 (though smaller) floating chambers for use in collecting evasion CO₂ samples for isotope
analysis have demonstrated reliability (e.g. Billett et al. 2006; Billett and Garnett 2010).
298 Similarly, the laboratory techniques we used to separate and date the individual CO₂ and CH₄
components have been verified through analysis of standards containing a range of mixtures
300 of CO₂ and CH₄ with contrasting ¹⁴C and $\delta^{13}\text{C}$ concentrations (Garnett et al. 2012^b).

302 While we did not prevent contamination of the chamber headspace with atmospheric gas, we
were able to reliably correct the results using isotope mass balance calculations. The revised
304 results were in most cases very similar to the originals because the atmospheric contaminant
represented only a small fraction of the total sample (<3 % for both CO₂ and CH₄). It would

306 have been relatively simple to prevent/reduce the atmospheric CO₂ component in the samples,
for example, by scrubbing the chamber headspace by circulating through soda lime to remove
308 the CO₂ in the floating chambers before CO₂ build-up (e.g. Billett et al. 2006), and similarly
ensuring that only CO₂-free air entered the chamber during sample collection. However, it
310 would have been less simple to prevent contamination of the chamber headspace with
atmospheric methane as we are unaware of a suitable adsorbent for removal of CH₄ from air.
312 A system could have been devised to remove the atmospheric CH₄ in the chamber headspace
using combustion, and thence to remove the resulting CH₄-derived CO₂ using soda lime, and
314 indeed if the CH₄ build-up in the chambers had been much lower such an approach may have
been necessary. However, given the low proportion of atmospheric CH₄ in the samples, and
316 the fact that the concentration and ¹⁴C content of atmospheric CH₄ is reasonably well defined
(Lassey et al. 2007), we consider that the results after correction for atmospheric CH₄ are
318 reliable and that such a procedure was unnecessary.

320 Age and source of evaded CO₂ and CH₄

322 We found that CH₄ evaded from the peatland stream was considerably older than CO₂ emitted
at the same time, by between 1096 to 1684 years. The age of the CO₂ component of evasion
324 ranged between 303-521 years BP, and is well within the range of ages found for evasion CO₂
in other UK peatland streams. For example, Billett et al. (2007) reported values of between
326 1450 years BP to modern for sites from across the UK, and ages of between ~ 850 to 1450
years BP for an earlier study at a Scottish peatland site (Billett et al. 2006). Methane emitted
328 from our peatland stream was aged between 1617 and 1987 years BP. We are not aware of
other ¹⁴C measurements for CH₄ evaded from streams, but our ages for CH₄ are older than
330 evaded CO₂ from UK peatland streams (Billett et al. 2006, 2007). CH₄ emitted by ebullition
from tundra and boreal lakes (Walter et al. 2008) and Siberian thaw lakes (Walter et al. 2006)
332 has been reported to have considerably wider ranges in ¹⁴C age, from > 40 000 years BP to
modern (e.g. Walter et al. 2008). Given our sampling location at Langlands Moss was subject

334 to Pleistocene glaciation it is considered unlikely that pre-Holocene organic matter occurs at
the site, excluding the possibility of generating much older CH₄.

336

Our observation that CH₄ evasion from the peatland stream draining Langlands Moss was
338 considerably older than the CO₂ emitted at the same time suggests that either the gases are
derived from different sources, or that they are composed from a mixture of sources. It seems
340 reasonable that the gases evaded from our stream were acquired in the adjacent peatland
(Langlands Moss) given that this is the source for the streamwater and since it is known that
342 large concentrations of both CO₂ and CH₄ exist in the waterlogged layers of peatlands (e.g.
Clymo and Bryant 2008). Studies of the ¹⁴C age of gases in the waterlogged layers of
344 peatlands have shown that CO₂ and CH₄ have generally similar ages (e.g. Chanton et al. 2008;
Clymo and Bryant 2008) since both gases are produced due to methanogenic decomposition
346 of the same substrates (e.g. peat). However, Steinmann et al. (2008) commented that CO₂
from the more aerated surface layers (acrotelm) diffuses down the peat profile, and hence it
348 would be expected that at least in the near surface layers that CO₂ would be younger in age
than CH₄; Garnett et al. (2011) showed evidence to support this at Langlands Moss with ages
350 for CO₂ and CH₄ from a depth of 1 m of 1150-1454 and 1580-2068 years BP, respectively.
While the ¹⁴C age for the CH₄ component at 1 m depth is similar to our measured values for
352 the age of CH₄ in evasion, implying that the evasion CH₄ is derived from about this depth in
the peatland, the dissolved CO₂ at this same depth is still much older than what we observed
354 in the evaded CO₂. This therefore suggests that an additional, much younger source is
contributing to evasion CO₂. Evidence for an additional source for evasion CO₂ is also
356 supported by the δ¹³C values; in the peatland adjacent to our stream dissolved CO₂ had a δ¹³C
value of -2.6 and -0.6 ‰ at 1 m depth (Garnett et al. 2011), whereas CO₂ evasion was much
358 more ¹³C-depleted (-25 to -24 ‰). Therefore an additional source contributes to evaded CO₂
that is relatively young and with a δ¹³C value of less than ~ -25 to -24 ‰. Several studies (e.g.
360 Chasar et al 2000; Clymo and Bryant 2008) have shown that δ¹³C of dissolved CO₂ increases
with depth in peatlands from less than -20 ‰ near the surface to ~ +10 ‰ in deep layers.

362 Thus the suggestion from our ^{14}C results that the additional source in the evaded CO_2 is
derived from near the peatland surface is corroborated by the $\delta^{13}\text{C}$ values.

364

We can use a mass balance mixing model to explore the contribution of separate sources to
366 explain the isotopic differences between the CO_2 and CH_4 . First, we assume that CH_4 has a
single source, the methanogenic decomposition of substrates in the waterlogged peat. The
368 evaded CH_4 is unlikely to originate from a single peat depth, but if we assume that the CH_4 in
our peatland stream has a ^{14}C age that reflects the average depth in the peat where the CH_4
370 was acquired, this corresponds to a depth of ~ 1 m (Garnett et al. 2011). Given that the
concentration of CO_2 in the peat at this depth is likely to have been approximately the same
372 (Garnett et al. 2011) or even greater (Clymo and Bryant 2008) than CH_4 , then it is reasonable
also to assume that a proportion of the evaded CO_2 in our peatland stream may also have been
374 sourced from around this depth. For reasons mentioned above (Steinmann et al. 2008), CO_2
was slightly younger than CH_4 at this depth (Garnett et al. 2011), but still considerably older
376 than the evaded CO_2 ; this fraction therefore represents the ‘old’ component (aged 1150-1454
years BP i.e. on average ~ 85 %modern) and based on measurements at our site we also know
378 that it should have a $\delta^{13}\text{C}$ value of ~ -1.6 ‰ (Garnett et al. 2011). We can therefore calculate
the isotopic composition of the ‘young’ component using our measured values for evaded
380 CO_2 (averaged $^{14}\text{C} = 95$ %modern and $\delta^{13}\text{C} = -24$ ‰) and isotope mass balance:

382
$$\Delta_{\text{measured}} \times F_{\text{measured}} = \Delta_{\text{young}} \times F_{\text{young}} + \Delta_{\text{old}} \times F_{\text{old}} \quad (1)$$

384 Where, Δ represents the isotopic composition (either ^{14}C or $\delta^{13}\text{C}$), and F represents the
fractional contribution of the measured evaded CO_2 , and its ‘young’ and ‘old’ components.

386 Possible values of the ‘young’ component in the evaded CO_2 were modelled assuming
different fractional contributions (Fig. 5). Considering that ‘young’ CO_2 with a $\delta^{13}\text{C}$ less than
388 -30 ‰ is unlikely to occur in peatlands, the mass balance modelled results show that the ‘old’

component of the evasion CO₂ must, at most, represent a minor component of the evaded
390 CO₂, and that in fact, ~ 80-100 % of the evasion was derived from a young source with an
average ¹⁴C content of between ~ 95-97.5 %modern. These calculations indicate that whereas
392 CH₄ evaded from the peatland stream is derived predominantly from relatively deeper layers
in the peatland, most evaded CO₂ is sourced from much younger layers located nearer the peat
394 surface. This conforms with the idea that most peatland CO₂ is produced from the relatively
rapid aerobic (and therefore near-surface) mineralisation of organic matter, whereas CH₄
396 production is restricted to water-logged, and therefore deeper/older, layers.

398 Our $\delta^{13}\text{C}$ values for evaded CH₄ (-58.8 to -61.7 ‰) are similar to results from other Northern
hemisphere wetlands (Walter et al. 2008). However, the values from Langlands Moss are
400 significantly more depleted than evasion-derived CH₄ measured at the outlet of a peatland
catchment in N England (Billett et al. 2012) where $\delta^{13}\text{C}$ of CH₄ ranged from -42.0 to -53.1
402 ‰. Methane produced from the outlets of natural peatland pipes (subsurface structural
drainage features that occur widely in peatlands; Billett et al. 2012) in the same catchment
404 varied from -47.9 to -67.7 ‰, with the deepest pipe associated with the most ¹³C-depleted
values. This may provide further evidence to suggest that evaded CH₄ at Langlands Moss was
406 derived from a relatively deep peat source, although not unequivocally since Hornibrook
(2009) found that $\delta^{13}\text{C}$ of pore water CH₄ in bog soils can increase or decrease with depth.

408
We also tested for spatial and temporal differences in the isotopic composition of evaded CO₂
410 and CH₄ by analysing samples from 2 locations and on 2 sampling dates. For CH₄, samples
collected on the two different sampling occasions did not differ significantly in age, although
412 the associated CO₂ components did differ with the sample collected in September being
slightly older (99-171 years) than the two samples collected from the same location in
414 October. These results imply that the age of CO₂ in evasion may be more temporally variable
than CH₄, and indeed, given that CH₄ is derived from deeper peat layers than CO₂ it is less
416 likely to be influenced by seasonal or weather-related changes than CO₂ which is derived from

shallow parts of the peat. Billett et al. (2007) and Garnett et al. (2012^a) have previously
418 reported temporal variations in the age of evaded CO₂ from peatland streams. It is unlikely
that incorporation of CO₂ from oxidation of chamber CH₄ could explain the older September
420 age results for CO₂, given the considerably lower CH₄ concentrations compared to CO₂.

422 In contrast, the age of the CH₄ component of evaded gases showed a difference between
upstream and downstream sampling sites when collected at the same time (September); with
424 CH₄ from the downstream site being slightly older (by 315 years). This may indicate that even
within the short distance (10 m) between these two sampling points that there was an
426 additional source of older CH₄ entering the peatland stream. Alternatively, as noted above,
CH₄ build-up in the first hour after chamber deployment at Site 1 was more rapid than later
428 on, and may indicate a contribution of CH₄ released by ebullition due to disturbance.

Although we did not observe bubble emissions at our sites, we do not know whether the
430 evaded CH₄ we analysed was entirely composed of diffusive emissions, or if there were
contributions from ebullition; differences in the contribution of ebullition and diffusive
432 emissions may explain the slight difference in the ¹⁴C age of CH₄ at these sites as they are
likely to be associated with different aged CH₄ (e.g. Walter et al. 2008). Clearly further
434 investigation is required into the temporal and spatial variations in the age of evaded CO₂ and
CH₄, but methodological improvements reported here in both field collection and laboratory
436 procedures advance our ability to make these measurements and improve our understanding
of the processes associated with CO₂ and CH₄ dynamics in peatland systems.

438

Conclusions

440 In this study we determined the carbon isotopic (¹⁴C and δ¹³C) composition of CO₂ and CH₄
evaded from a stream draining a temperate raised peat bog. The CO₂ component was aged
442 between ~ 300-500 years BP and was similar to results reported for other UK peatland
streams. In contrast, the evaded CH₄ was considerably older (~1600-2000 years BP), implying
444 that it was derived from deeper layers in the peatland. Mass balance calculations indicate that

most of the CO₂ evaded from this peatland stream is derived from much shallower layers than
446 the CH₄, which fits with CH₄ production being restricted to relatively deeper water-logged
layers, whereas CO₂ production occurs at a more rapid rate in near-surface aerobic layers.
448 Contrasting carbon isotope results for evaded CO₂ and DOC have previously implied
differences in their source (Billett et al. 2007) helping to reveal the processes responsible for
450 their production. Here, our results also indicate differences in sources between evaded CO₂
and CH₄. This study demonstrates that the dual carbon isotope (¹⁴C and δ¹³C) analysis of CO₂
452 and CH₄ evaded from streams draining peatlands (and potentially other wetland ecosystems
including areas of permafrost thaw) can provide new insights into the cycling of carbon in
454 these important terrestrial carbon stores.

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460

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578 **Tables**

580 **Table 1** Results of carbon isotope analyses of evaded CH₄ and CO₂ collected in 2011 from a
 peatland stream draining Langlands Moss, near East Kilbride, Scotland, UK. The isotope
 582 results have not been corrected for an atmospheric component. For Oct 2011, Site 2 (a) and
 Site 2 (b) represent replicate samples collected consecutively from the same chamber.

584

Month / Site	Material	Volume recovered (ml)	Publication code (SUERC-)	¹⁴ C content (%modern ±1σ)	δ ¹³ C _{V_{PDB}} ± 0.1 ‰
Sept Site 1	CH ₄	1.9	37019	82.52 ± 0.38	-58.6
Sept Site 1	CO ₂	2.2	37007	94.03 ± 0.43	-23.6
Sept Site 2	CH ₄	1.0	37022	80.03 ± 0.37	-59.5
Sept Site 2	CO ₂	2.1	37008	94.58 ± 0.41	-23.6
Oct Site 2 (a)	CH ₄	2.1	37024	78.81 ± 0.35	-61.4
Oct Site 2 (a)	CO ₂	2.3	37026	96.51 ± 0.42	-24.5
Oct Site 2 (b)	CH ₄	1.8	37025	79.25 ± 0.35	-61.4
Oct Site 2 (b)	CO ₂	1.9	37027	95.67 ± 0.44	-24.6

586

588 **Figure captions**

590 **Fig. 1** Build-up of CO₂ inside floating chambers on a peatland stream draining Langlands
Moss, near East Kilbride, UK at two different locations and sampling dates in 2011.

592 Regression lines and associated equations used to calculate CO₂ evasion rate are also shown.

594 **Fig. 2** Build-up of CH₄ inside floating chambers on a peatland stream draining Langlands
Moss, near East Kilbride, UK at two different locations and sampling dates in 2011. Error

596 bars represent the 10 % manufacturer-quoted accuracy of the DP-IR methane analyser.

598 **Fig. 3** Radiocarbon age (years BP) of CH₄ and CO₂ evaded from a peatland stream draining
Langlands Moss, near East Kilbride, UK at two different locations and sampling dates in

600 2011. Results have been corrected for an atmospheric contribution (see Methods) and error
bars represent the combined uncertainty (1 σ) of the age measurement and correction for

602 atmosphere.

604 **Fig. 4** $\delta^{13}\text{C}$ (‰) of CH₄ and CO₂ evaded from a peatland stream draining Langlands Moss,
near East Kilbride, UK at two different locations and sampling dates in 2011. Results have

606 been corrected for an atmospheric contribution (see Methods) and error bars represent the
combined uncertainty (1 σ) of the isotope measurement and correction for atmosphere.

608

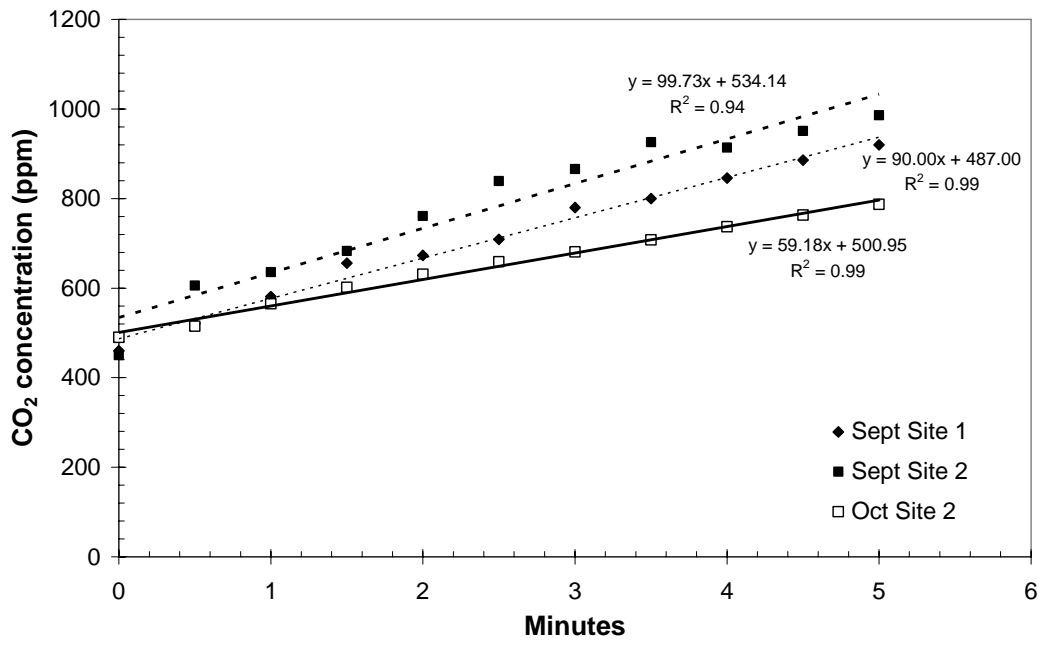
Fig. 5 Mass balance model used to partition evaded CO₂ into ‘young’ and ‘old’ components.

610 Data points represent the calculated ¹⁴C and ¹³C content of the ‘young’ component of evaded
CO₂ assuming different fractional contributions (indicated by value above each data point).

612 Shaded box represents the only realistic values given that the young component cannot
represent a fraction greater than 1 and that values for $\delta^{13}\text{C}$ of ‘young’ CO₂ are unlikely to be

614 less than -30 ‰.

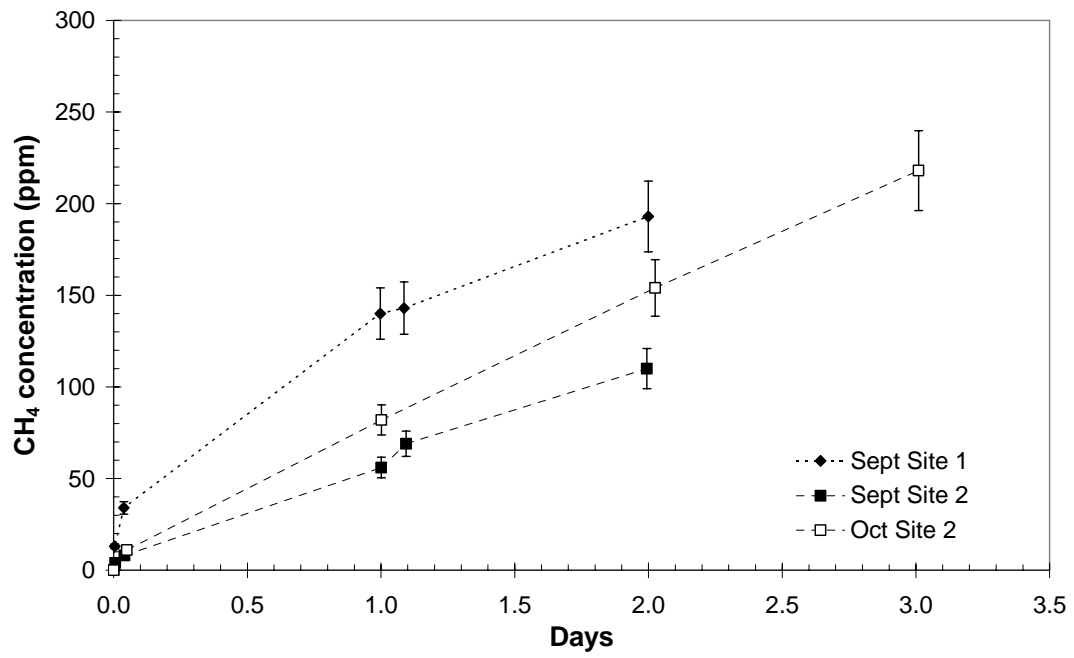
Fig. 1



616

Fig. 2

618



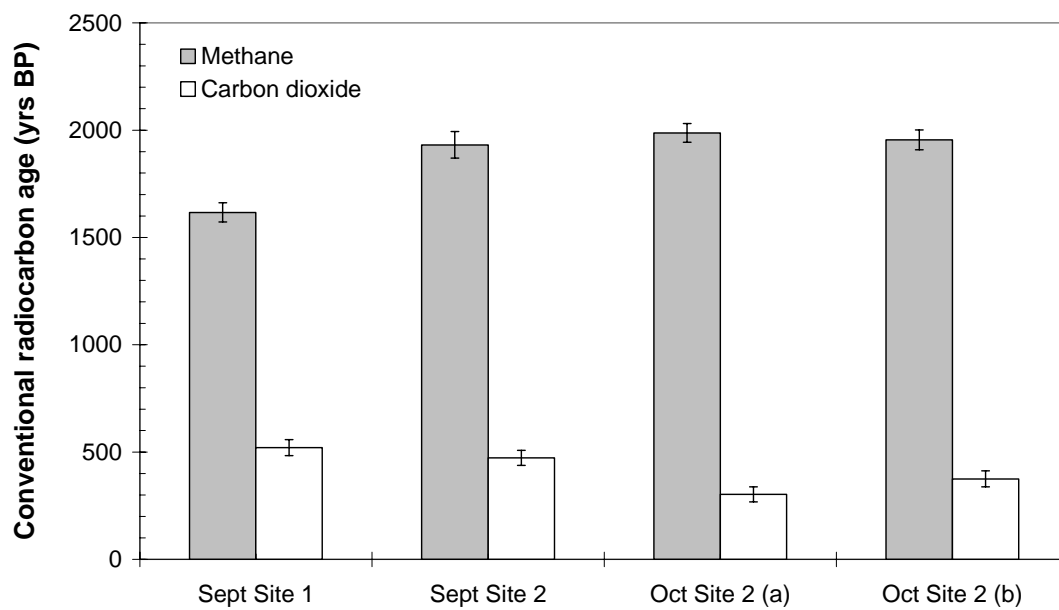
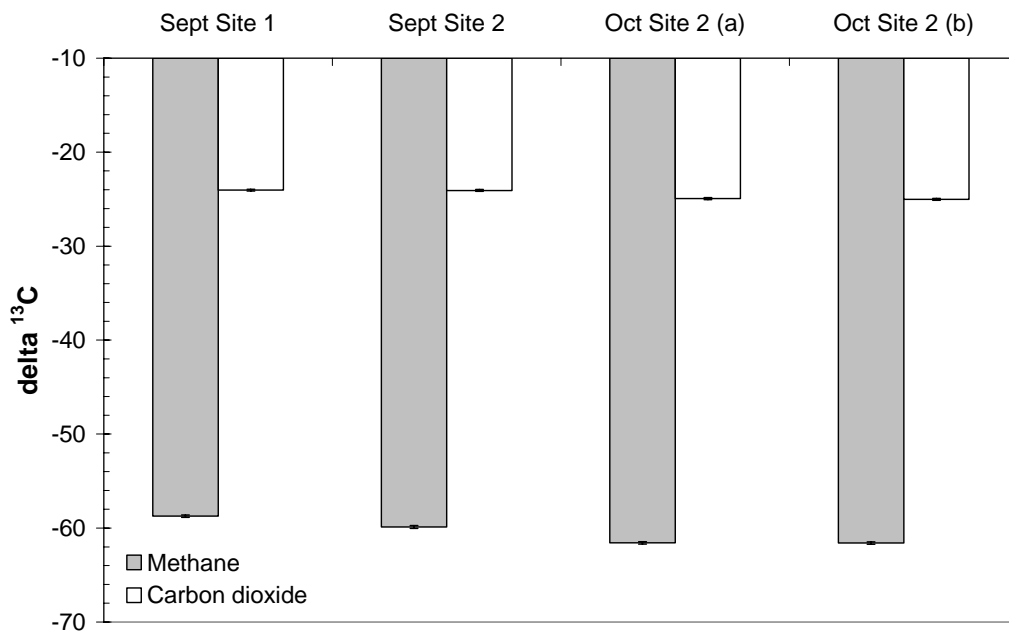
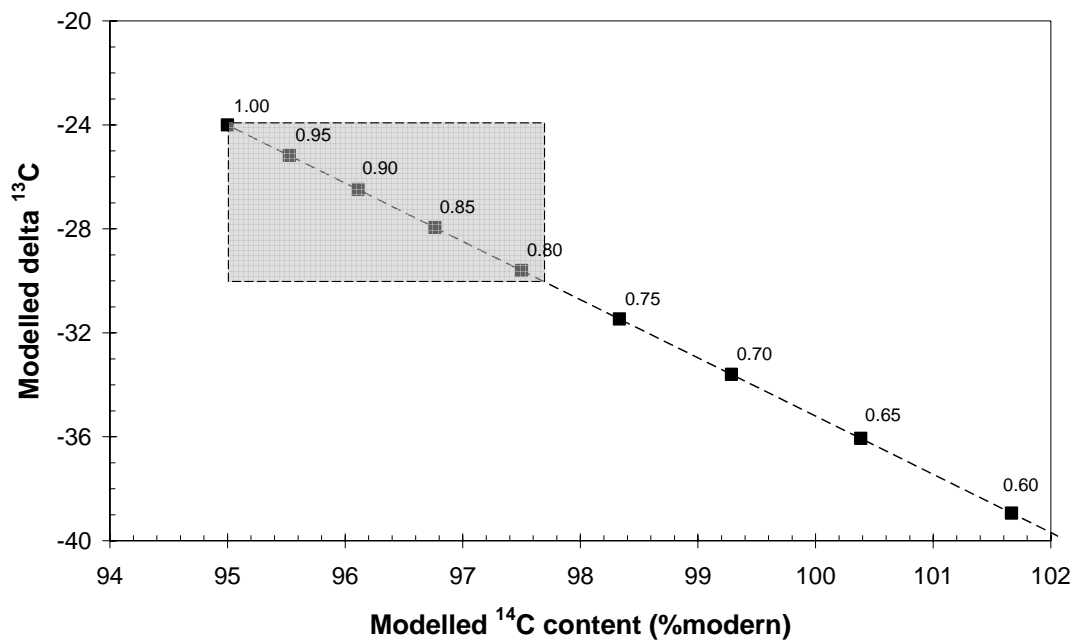


Fig. 4

624



626 Fig. 5



628