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Garnett, M., Hardie, S.M.L., and Murray, C. (2012) *Radiocarbon analysis of methane emitted from the surface of a raised peat bog*. *Soil Biology and Biochemistry*, 50 . pp. 158-163. ISSN 0038-0717

<http://eprints.gla.ac.uk/63592/>

Deposited on: 15th May 2012

Elsevier Editorial System(tm) for Soil Biology and Biochemistry
Manuscript Draft

Manuscript Number: SBB6036R2

Title: RADIOCARBON ANALYSIS OF METHANE EMITTED FROM THE SURFACE OF A RAISED PEAT BOG

Article Type: Research Paper (FLA)

Keywords: Methane; Radiocarbon; Peat; Carbon; Greenhouse gases

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Manuscript Region of Origin: UNITED KINGDOM

1 **RADIOCARBON ANALYSIS OF METHANE EMITTED FROM THE SURFACE OF A**
2 **RAISED PEAT BOG**

3

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10

11 **ABSTRACT**

12 We developed a method to determine the radiocarbon (¹⁴C) concentration of methane (CH₄)
13 emitted from the surface of peatlands. The method involves the collection of ~ 9 L of air from a
14 static gas sampling chamber which is returned to the laboratory in a foil gas bag. Carbon dioxide
15 is completely removed by passing the sample gas firstly through soda lime and then molecular
16 sieve. Sample methane is then combusted to CO₂, cryogenically purified and subsequently
17 processed using routine radiocarbon methods. We verified the reliability of the method using
18 laboratory isotope standards, and successfully trialled it at a temperate raised peat bog, where we
19 found that CH₄ emitted from the surface dated to 195-1399 years BP. The new method provides
20 both a reliable and portable way to ¹⁴C date methane even at the low concentrations typically
21 associated with peatland surface emissions.

22

23 **1. Introduction**

24 Peatlands are globally important carbon stores that emit CO₂ and CH₄ as a result of decay under
25 aerobic and anaerobic conditions (Laing et al., 2010). Of these greenhouse gases, CO₂ is the
26 most abundant in the atmosphere, though CH₄ has a much greater global warming potential

27 (IPCC, 2001). Peatland CH₄ emissions take place via several pathways including diffusion,
28 ebullition or plant mediated transport (Chanton, 2005) and can at times be considerable (e.g. at
29 the onset of freezing in tundra (Mastepanov et al., 2008) or during ebullition where emitted
30 bubbles can have a CH₄ concentration of up to 84 % (Strack et al., 2005)). The route from
31 peatland to atmosphere influences whether carbon is emitted as CH₄ or CO₂; a slow pathway
32 provides greater opportunity for CH₄ oxidation by methanotrophs.

33
34 Below the water table peat contains large quantities of CO₂ and CH₄, either dissolved in
35 porewater or within bubbles (Clymo and Bryant, 2008; Laing et al., 2010), but only at a very few
36 sites have they been analysed for stable- and radiocarbon (¹⁴C) content (e.g. Aravena et al., 1993;
37 Charman et al., 1999; Clymo and Bryant, 2008; Garnett et al., 2011). Results have provided
38 insights into the processes leading to production of these gases and the rate at which they are
39 cycled. For instance, CO₂ in deep peat is generally ¹⁴C-enriched relative to the surrounding peat
40 (e.g. Aravena et al., 1993; Clymo and Bryant, 2008), indicating that at least some CO₂ is derived
41 from sources younger than the encompassing peat. Clymo and Bryant (2008) found that
42 dissolved CO₂ and CH₄ in a Scottish peatland were broadly similar in ¹⁴C age throughout the
43 profile, suggesting derivation from a common source.

44
45 Fewer studies have investigated the ¹⁴C content of emissions from the peatland surface.
46 However, Hardie et al. (2009) found evidence that an important component of peatland surface
47 gas emissions was from relatively old CO₂ produced at depth that was emitted to the surface via
48 plants. In organic-rich tundra soils, Schuur et al. (2009) reported ¹⁴CO₂ values for ecosystem
49 respiration which indicated the release of old carbon as a consequence of permafrost melting.

50
51 Lassey et al. (2007a) presented a summary of studies on the ¹⁴C content of CH₄ emissions and
52 showed that only 3 studies have analysed the ¹⁴C content of peatland surface emissions (i.e.

53 Wahlen et al., 1989; Quay et al., 1991; Chanton et al., 1995). These studies were restricted to
54 north America (Minnesota and West Virginia) and gave values of between 113.5 and 120.3
55 %modern for samples collected between 1986 and 1991. These ^{14}C concentrations indicate that a
56 substantial component of the CH_4 was derived from carbon fixed within recent decades because
57 only since atmospheric testing of nuclear devices in the mid 1950s-60s has atmospheric ^{14}C
58 content exceeded 100 %modern (Levin and Hesshaimer, 2000).

59
60 ^{14}C analysis has been used to partition global sources of atmospheric CH_4 (e.g. Wahlen et al.,
61 1989; Lowe et al., 1988; Lassey et al., 2007a,b). However, given the insights into carbon cycling
62 that ^{14}C analysis of CH_4 emissions from peatlands can potentially provide, it is surprising that
63 further investigations have not been reported. This may in part be due to the challenge in
64 collecting samples, given the rate that CH_4 is emitted and the amount required for ^{14}C analysis,
65 which is typically considerably higher than that required for $\delta^{13}\text{C}$ measurement. This caveat thus
66 prohibits the use of standard techniques designed for stable carbon isotope analysis of methane.
67 Where the ^{14}C content of peatland CH_4 emissions have been reported the methods have required
68 the use of very large chambers (e.g. Wahlen et al., 1989; Quay et al., 1991; Chanton et al., 1995)
69 and compression of sample gas into pressurised cylinders in order to collect sufficient methane
70 for analysis (e.g. Wahlen et al., 1989; Quay et al., 1991; Chanton et al., 1995). Thus current
71 sampling methods are not ideal, particularly for application in frequently remote and inaccessible
72 peatland locations.

73
74 Here, we describe a method for the collection and processing of CH_4 emitted by peatlands (and
75 potentially other systems e.g. landfill) and subsequent analysis by accelerator mass spectrometry
76 (AMS) for ^{14}C content. We also present results of tests used to verify the method, and $^{14}\text{CH}_4$
77 results for initial measurements of emissions from a temperate peatland.

78

79 2. Methods

80 2.1. Field site

81 Field samples were collected from Langlands Moss, a typical temperate raised peat bog in
82 central south-west Scotland (55° 44' 5.5" N, 4° 10' 25.8" W). The site has an altitude of 217 m, a
83 mean annual temperature of 7.3 °C and annual rainfall of 971 mm (Langdon and Barber, 2005).
84 The depth of peat at the sampling site is ~6 m and the water table is usually within the surface 20
85 cm. Vegetation cover is typically a mixture of mosses (*Sphagnum* spp.), sedges (especially
86 *Eriophorum vaginatum*) and Ericaceous species (including *Calluna vulgaris*). Six chambers were
87 installed in pairs at three locations (A, B and C); paired chambers were separated by ~2 m, and
88 sites A, B and C were ~5 – 10 m apart. Chambers were installed on 13th April 2011 and flux
89 measurements commenced on 16th May, 2011. CH₄ concentrations were measured
90 approximately daily and sample collection was performed on 23rd May, 2011.

91

92 2.2. Sample collection and processing methods

93 Sample collection methods were designed to allow the recovery of at least 1 mL of CH₄ which is
94 typically the minimum requirement for routine ¹⁴C analysis by AMS. We used static chambers
95 (cross sectional area = 1257 cm², volume 60 L) to sample a large area that would be both
96 representative of the peatland and minimize sampling times. The chambers were constructed
97 from 120 L heavy duty plastic barrels with removable air-tight lids (Ampulla Ltd, UK). The
98 barrels were divided into two separate halves with the upper part only being used for the
99 sampling chamber. We installed two CPC quick connect auto-shutoff couplings (Colder Products
100 Company, USA) into the lid of each chamber to enable gas sampling; in addition, each lid was
101 covered with reflective aluminium foil to minimise heating effects. Chambers were inserted into
102 the peat surface to a depth of 20 cm after circumscribing with a knife (effective headspace
103 volume of ~25 L).

104

105 On collection of samples for $^{14}\text{CH}_4$ analysis lids were placed onto the chambers and the increase
106 in CH_4 concentration monitored using a Detecto Pak-Infrared (DP-IR) CH_4 analyser (Heath
107 Consultants Inc, USA). The DP-IR samples chamber air via an internal pump and analyses the
108 CH_4 concentration with a precision of 1 ppm, and an accuracy of 10 % (verified using standard
109 gases). The DP-IR was connected in-line to each chamber using CPC couplings and Tygon
110 tubing (Fisher, UK) in a closed loop (Fig. 1a).

111
112 Each sample was collected by attaching a 10 L foil gas sample bag (SKC, UK) to the exhaust of
113 the DP-IR (via CPC couplings). To prevent the creation of a vacuum, chamber pressure was
114 equilibrated to atmosphere during sample collection through a vent in the lid. Dilution by ingress
115 of atmospheric air caused chamber CH_4 concentration to fall during sampling; this was
116 monitored using the DP-IR.

117
118 All samples were immediately returned to the NERC Radiocarbon Facility and processed within
119 24 hours of collection. First, removal of the high concentration of CO_2 (4-5 %) that was
120 simultaneously collected along with chamber CH_4 was performed by pumping (500 mL/min) the
121 sample from the foil bag through a glass cartridge (dimensions diameter 20 mm, length 250 mm)
122 filled with soda-lime (that absorbed the CO_2) and into a second foil bag (Fig. 1b). Verification of
123 CO_2 removal was performed using an infrared gas analyser (IRGA; PPsystems, UK).

124
125 Finally, a further purification stage was performed by passing sample gas through a cartridge
126 filled with ~3-4 g of type 13X molecular sieve (BDH Laboratory Supplies, UK) for removal of
127 any remaining traces of CO_2 , after which combustion (platinum-alumina beads) of purified CH_4
128 to CO_2 took place at 950°C (Fig. 1c). CH_4 -derived CO_2 was cryogenically purified and aliquoted
129 into separate samples for ^{14}C and $\delta^{13}\text{C}$ analysis.

130

131 Sample $\delta^{13}\text{C}$ ($^{13}\text{C}/^{12}\text{C}$ ratio relative to the Vienna PDB standard) was determined on the CH_4 -
132 derived CO_2 using isotope ratio mass spectrometry. For ^{14}C measurement, an aliquot of CH_4 -
133 derived CO_2 was converted to graphite (Slota et al., 1987) and analysed at the Scottish
134 Universities Environmental Research Centre AMS Facility. Following conventions, ^{14}C results
135 were normalised to a $\delta^{13}\text{C}$ of -25 ‰ to account for mass-dependent fractionation and expressed
136 as %modern and conventional radiocarbon ages (years BP; before present, where 0 BP = AD
137 1950; Stuiver and Polach, 1977).

138

139 *2.3. Test of laboratory methods*

140 We tested the use of foil gas bags and laboratory procedures using a suite of gas standards
141 produced by adding ~3, 5 and 10 ml of ^{14}C -dead cylinder CH_4 to bags filled with ~10 L of
142 atmospheric air ('Mix' standards). The CH_4 was added using a 20 ml syringe which although
143 convenient, did not allow accurate determination of volume. We made no attempt to remove the
144 small amount of atmospheric CH_4 present in air, and the standards were processed using the
145 same methods as described above. We also performed ^{14}C analysis on three standards composed
146 of ~5 ml of (^{14}C -dead) cylinder CH_4 added to 1 L of pure O_2 , in order to quantify the amount, if
147 any, of ^{14}C added during the combustion procedure ('Blank' standards).

148

149 **3. Results**

150 *3.1. Test of laboratory methods*

151 The ^{14}C content of three 'Blank' standards ranged from 0.12-0.16 %modern (Table 1) and were
152 within the usual laboratory background, suggesting insignificant contamination associated with
153 the combustion procedure. The ^{14}C content of standards of different volumes of ^{14}C -dead CH_4
154 added to 10 L of atmospheric air ('Mix' standards) ranged from 0.58-1.48 %modern (Table 1),
155 significantly higher than the laboratory background for routine samples and 'Blank' standards.
156 However, 'Mix' standards would clearly contain atmospheric CH_4 . Mean atmospheric CH_4

157 concentrations are ~2 ppm, although can exceed 4 ppm in urban areas (Lowry et al., 2001).
158 Atmospheric CH₄ is ¹⁴C-enriched relative to atmospheric CO₂, partly because ¹⁴CH₄ is produced
159 by nuclear power generation (Wahlen et al., 1989). We used mass balance calculations to remove
160 the atmospheric CH₄ component from the results of the ‘Mix’ standards, made possible because
161 we knew the ¹⁴C content and volume of recovered CH₄-derived CO₂, and in addition, could
162 reasonably assume that the atmospheric CH₄ component in the bags of air would have been ~3 ±
163 1 ppm, with a ¹⁴C concentration of ~130 % modern (Lassey et al., 2007b). This correction
164 reduced the ¹⁴C content of ‘Mix’ samples so that all were lower or within measurement error of
165 the ‘Blank’ standards and laboratory background (Table 1). Due to the similarity in the δ¹³C of
166 atmospheric (~ -47 ‰; Lassey et al., 2007a) and cylinder CH₄, the correction did not
167 significantly change the δ¹³C values; all results were in the range of expected values.

168

169 3.2. Field samples

170 Chamber CH₄ concentration increased steadily during the sampling week (Fig. 2). There was a
171 large variation in emission rates between sites A, B and C, and even between pairs within the 3
172 sites. For example, the maximum CH₄ concentration (1690 ppm) was achieved at Site B1 after 7
173 days, whilst Site B2 had only reached 256 ppm after 7 days. The increase in CH₄ concentration
174 was linear in chambers for the first 3 days (all chambers), after which the rate of increase slowed
175 slightly in most chambers. One chamber (A2) showed a decline in CH₄ concentration between
176 the final two measurements, only achieving a concentration of 100 ppm on the day of sampling.
177 To ensure sufficient CH₄ for analysis of this sample we consecutively filled two 10 L bags; the
178 samples were combined in the laboratory after processing to CO₂.

179

180 ¹⁴C content of CH₄ collected from static chambers varied between different sites and paired
181 samples at 2 of the 3 sites (Table 2). For example, samples A1 (97.86 % modern) and C2 (97.53
182 % modern) had the most ¹⁴C-enriched CH₄, whereas the other samples paired with these sites

183 were both relatively ^{14}C -depleted (91.80 and 91.26 % modern for A2 and C1, respectively). The
184 most ^{14}C -depleted CH_4 was emitted from Site B where samples B1 and B2 gave very similar
185 values of 85.53 and 84.69 % modern, respectively. $\delta^{13}\text{C}$ values also varied considerably both
186 between sites and within pairs, ranging from -64.0 to -74.5 ‰. As no attempt had been made to
187 remove atmospheric CH_4 from the chambers before sampling, mass balance calculations were
188 again used to subtract the atmospheric CH_4 component from the field samples. The same
189 assumed values for the concentration and ^{14}C content of atmospheric CH_4 as used for the ‘Mix’
190 standards were used, as well as the mean concentration of CH_4 recorded from the DP-IR
191 measurements during sample collection. However, correction for atmospheric CH_4 made little
192 difference, and shifted the age by less than the 2σ measurement uncertainty. Sample A2 was an
193 exception, and increased in age by 160 years when correcting for the air. The final results for
194 field samples corrected for atmospheric CH_4 gave ^{14}C ages of between 195-1399 years BP (Fig.
195 3). Similarly, correcting the $\delta^{13}\text{C}$ values for atmospheric CH_4 only significantly altered the result
196 for sample A2 (decreasing it by 0.9 ‰).

197

198 **4. Discussion**

199 *4.1. Test of laboratory methods*

200 Our new method to determine the ^{14}C content of methane emitted from the surface of a peat bog
201 was based on an earlier method validated by Garnett et al. (2011) for smaller gas volumes (~200
202 ml) containing CH_4 at higher concentrations (1-20 %). The methods of Garnett et al. (2011), and
203 similar ones used by others (Charman et al., 1999; Clymo and Bryant, 2008), are unsuitable for
204 analysis of CH_4 emitted from the peat surface because the much lower methane concentration in
205 chamber samples (relative to deep peat) would not provide sufficient material for measurement.
206 However, the larger gas volume (~9 L) we used in the present study could have caused a number
207 of problems, e.g. due to the amount of CO_2 . The results for the ‘Mix’ standards showed this was
208 effectively removed. Even if we had not corrected for atmospheric CH_4 present in the foil bags,

209 the total sample that could have been CO₂ contamination was less than 1.5 %; such a level of
210 contamination would only affect field samples if they contained CO₂ and CH₄ components of
211 vastly different ¹⁴C contents. Once atmospheric CH₄ was factored out of the results, the ¹⁴C
212 content of the ¹⁴C-dead CH₄ component of the ‘Mix’ standards was within measurement
213 uncertainty of the laboratory background.

214

215 We could have prepared ‘Mix’ standards with CH₄-free air, but did not because field samples
216 would have also contained the same atmospheric CH₄ component anyway. In fact, applying the
217 same correction used for the ‘Mix’ standards to the field samples gives additional confidence in
218 the correction for atmospheric CH₄ in field samples. This was confirmed by sampling a 9 L bag
219 of atmospheric air at Langlands Moss at the same time as the field samples; from this we
220 recovered 0.02 ml of CH₄-derived CO₂, which although insufficient for us to analyze
221 isotopically, provides independent evidence of an atmospheric CH₄ concentration of ~2.2 ppm.
222 For field samples with CH₄ concentrations >300 ppm the correction for atmospheric CH₄ was
223 insignificant, shifting the ¹⁴C result by less than the 1 σ analytical precision. Given current
224 levels, accounting for atmospheric CH₄ using this approach is unlikely to introduce significant
225 uncertainty in peatland ¹⁴CH₄ measurements.

226

227 *4.3. Field samples – test of method*

228 To obtain sufficient CH₄ in all chambers we sealed them for 1 week prior to sample collection.
229 While all chambers produce artefacts, problems may be amplified with long periods of closure.
230 The closed chamber is the most widely used technique to measure CH₄ fluxes from peatlands
231 (Forbrich et al., 2010), but has the disadvantage of potentially altering diffusion gradients
232 between the peat and chamber headspace. This gradient affects the rate that CH₄ is emitted; as
233 the CH₄ concentration in the chamber headspace increases, in theory it will approach the
234 concentration in the underlying peat, causing flux rates to be lower than if the chamber was not

235 present. Potentially this alteration of the diffusion gradient could also affect the isotopic
236 composition of the CH₄ emitted. However, Forbrich et al. (2010) found that in the majority of
237 cases, CH₄ build-up in closed chambers followed a linear rather than exponential trend, implying
238 that alteration of diffusion gradients using closed chambers was insufficient to affect efflux rates.
239 The conclusions of Forbrich et al. (2010) were based on sealing chambers for 24 minutes, much
240 shorter than our chambers were deployed. However, the CH₄ concentration measurements over
241 the sampling period show that in all but one chamber, CH₄ continued to increase throughout the
242 7 days, and usually at a linear rate ($r^2 > 0.98$ for 5 of the 6 chambers). This suggests that even
243 where our chambers were left for 1 week that the diffusion gradient was not greatly affected.
244 This was particularly the case in the first 3 days ($r^2 > 0.96$ for all chambers), however, flux rates
245 did subsequently decline in most chambers, but this could also reflect changing rates of CH₄
246 production or oxidation. Clymo and Bryant (2008) showed that CH₄ concentrations in some peat
247 layers can reach as high as ~5 %; these concentrations are much greater than the values we
248 observed in chambers (Site B1, 0.17 %), so clearly at all times a substantial CH₄ concentration
249 gradient existed.

250
251 While it is unlikely that the carbon isotope results were affected by perturbation of the diffusion
252 gradient it would clearly be preferable if chambers were closed for a shorter time. This could be
253 achieved by modifying the chambers to cover a larger area, or sampling at a lower CH₄
254 concentration using larger bags. There would be disadvantages with the latter approach because
255 the atmospheric CH₄ component would represent a larger proportion of the sample. However, we
256 could have collected suitable samples much earlier for some of the sites, potentially within one
257 day (e.g. Site B1).

258

259 *4.3. Field samples – comparison to other studies*

260 Previous studies that have reported the ^{14}C measurement of methane emitted from the surface of
261 peatlands required the collection of such large volumes of gas (with low CH_4 concentration) that
262 it had to be compressed into pressurised containers for transport back to the laboratory (e.g.
263 Wahlen et al., 1989; Quay et al., 1991; Chanton et al., 1995). Very large chambers were also
264 required, with, in the case of Wahlen et al. (1989), the use of flux box enclosures of up to 20 m^3 .
265 Thus the equipment employed to undertake sampling in these earlier studies was clearly
266 considerable, and must have posed logistical challenges particularly for deployment within
267 peatland sites, which may at least partly explain the limited number of $^{14}\text{CH}_4$ measurements that
268 have been reported up to now. The methods that we have developed have the advantage of
269 requiring minimal sampling equipment (i.e. chamber, gas sample bag and DP-IR) that is much
270 easier to transport. In addition, because our laboratory methods are reliable, even with as little as
271 a few ml of methane (as shown by the tests with standard gases), we are able to collect sufficient
272 material for ^{14}C analysis in conveniently sized 10 L gas bags. The relatively recent availability of
273 the DP-IR provides a considerable benefit, firstly, for informing when the CH_4 concentration in
274 the chamber headspace is sufficient for collection of a suitable sample, and secondly, for transfer
275 of sample gas from chamber to foil bag.

276
277 Our ^{14}C results for CH_4 in chambers at Langlands Moss differ considerably to earlier studies
278 from north American peatlands (Wahlen et al., 1989; Quay et al., 1991; Chanton et al., 1995). In
279 these studies $^{14}\text{CH}_4$ emissions were all modern (113-120 %modern) and therefore unequivocally
280 contained carbon fixed since the 1950s-mid 1960s. Our results show no evidence of post-bomb
281 ^{14}C in the CH_4 , since all values were <100 %modern. This does not mean that the CH_4 emissions
282 from Langlands Moss do not contain carbon fixed post-bomb, but does imply that a substantial
283 proportion was produced from peat laid down in earlier centuries or millennia.

284

285 Differences in the $^{14}\text{CH}_4$ values between our results and earlier studies may be due to variations
286 in peatland characteristics such as vegetation or peat depth; e.g. differences in ^{14}C signatures of
287 peat components (including CH_4) have been observed between sedge- and *Sphagnum*-dominated
288 peatlands (Chanton et al., 2008). Deep peats such as Langlands Moss are repositories for large
289 volumes of old CH_4 ; Clymo and Bryant (2008) report values for CH_4 ranging from modern to
290 3960 years BP across depths from 0.5-7.5 m. At Langlands Moss, Garnett et al. (2011) dated
291 CH_4 up to 4030 years BP at 4 m depth, while even at 25 cm depth CH_4 was aged up to 260 years
292 BP. Wahlen et al. (1989) and Quay et al. (1991) provide no details about the depth of peat at
293 their sites, and therefore it is unclear whether they contained much old peat; if not, then clearly it
294 would be less likely that aged CH_4 contributed to emissions. However, this appears not to be an
295 explanation, since Chanton et al. (1995) found surface CH_4 emissions similar in ^{14}C content to
296 those of Wahlen et al. (1989) and Quay et al. (1991), yet also found high concentrations of aged
297 (up to 3500 years BP) CH_4 contained in the peat porewater at depths of up to 3 m.

298
299 The continued decline in the ^{14}C content of atmospheric CO_2 since the sampling of the north
300 American peatlands may explain their more ^{14}C -enriched CH_4 values. Contemporary (2011) ^{14}C
301 levels in atmospheric CO_2 are ~104 % modern (Levin et al., 2008), but when the samples of e.g.
302 Wahlen et al. (1989) were collected (1986) the atmosphere had a $^{14}\text{CO}_2$ content of ~118
303 % modern (Levin et al., 2008). The $^{14}\text{CH}_4$ values of ~116 % modern reported by Wahlen et al.
304 (1989) therefore suggest a component of carbon fixed in pre-bomb times, in order to explain the
305 lower $^{14}\text{CH}_4$ values relative to the contemporary atmospheric $^{14}\text{CO}_2$. We could therefore
306 postulate that CH_4 emitted from the peatland studied by Wahlen et al. (1989) was composed of 2
307 components: i.e. young and old sources. E.g. assume that ~40 % of the CH_4 emissions at this site
308 were derived from an old/deep source (with ^{14}C of ~80 % modern; ~1800 years BP) and the
309 remaining 60 % from a younger source. To explain the measured ^{14}C concentration of the CH_4
310 emissions (~116 % modern), using mass balance, a younger source would have a ^{14}C

311 concentration of ~140 % modern (which would represent carbon fixed on average ~1974 i.e. 12
312 years before sampling). Using the same proportions for the 2 components, and the relative ages
313 for the carbon sources, but applying this for sampling in 2011, we calculate that $^{14}\text{CH}_4$ emitted
314 now would be ~98 % modern; i.e. within measurement uncertainty of the ^{14}C values for CH_4
315 emitted from 2 of our Langlands Moss samples (i.e. assuming 40 % old CH_4 with 80 % modern,
316 and 60 % young carbon fixed 12 years earlier i.e. 1999 when atmospheric $^{14}\text{CO}_2$ was ~109.6
317 % modern). While the above may be speculation, particularly since we are dealing with possibly
318 very dissimilar peatlands, it does show that part of the difference between studies could be
319 explained by changes in atmospheric $^{14}\text{CO}_2$. Interestingly, it has been suggested that greatest
320 CH_4 production in a peat bog is just below the water table (Clymo and Pearce, 1995); thus the
321 suggestion that peatland CH_4 emissions are derived predominantly from a young post-bomb
322 source, and a smaller contribution from older/deeper CH_4 is not unreasonable.

323
324 Other factors may contribute to differences between our results and earlier studies (e.g. our
325 samples were corrected for air and would be unlikely to be affected by plant-derived volatile
326 organic compounds; it is unclear if this applies equally to earlier studies). But whatever they are,
327 the present study at least raises a question over the representativeness of the ^{14}C values used for
328 peatland emissions in partitioning studies of global CH_4 sources and assessments of the fossil
329 carbon component (e.g. Lowe et al., 1988; Wahlen et al., 1989; Lassey et al., 2007a,b).

330
331 It has been noted that certain plant species which possess aerenchymateous tissues act as
332 conduits to facilitate gas release from peat to the atmosphere (Chanton, 2005). This “plant
333 mediated transport” has been implicated in emissions of CH_4 and CO_2 from peatlands. Indeed,
334 from ^{14}C measurements Hardie et al. (2009) postulated that 10-23 % of peatland CO_2 emissions
335 may come from plant mediated transport of CO_2 aged between ~900 and 2000 years BP. It is
336 reasonable, given the broadly similar ^{14}C ages for CO_2 and CH_4 reported from 2 different peat

337 profiles (Clymo and Bryant, 2008; Garnett et al., 2011) that aged CH₄ is also released. Moreover,
338 the aged CH₄ that we have measured at our site (~200-1400 years BP) clearly fits within the
339 range of values suggested by Hardie et al. (2009) for CO₂, and therefore provides independent
340 evidence to support their assertion of old carbon release via plant mediated transport. Indeed, the
341 sedge *Eriophorum vaginatum*, linked to plant mediated transport in peatlands (Greenup et al.,
342 2000; Marinier et al., 2004), is common to both our site and that of Hardie et al. (2009).

343

344 The above discussion illustrates the potential that ¹⁴C analysis of peatland CH₄ emissions
345 provides, even with the limited data currently available. Further studies are required, first to
346 better assess variation in the ¹⁴C content of emissions, and secondly to identify the controls and
347 processes leading to the differences in age of emitted CH₄. Such studies can be more easily
348 undertaken using the methods reported here, and will lead to a better understanding of the
349 processes governing storage and release of this greenhouse gas.

350

351 **Acknowledgments**

352 We thank staff at the NERC Radiocarbon and SUERC AMS Facilities, and NERC for funding
353 the isotope analyses. We are grateful to South Lanarkshire Council and John Hawell for site
354 access, and to two anonymous reviewers.

355

356 **References**

- 357 Aravena, R., Warner, B.G., Charman, D.J., Belyea, L.R., Mathur, S.P., Dinel, H., 1993. Carbon
358 isotopic composition of deep carbon gases in an ombrogenous peatland, northwestern
359 Ontario, Canada. *Radiocarbon* 35, 271-276.
- 360 Chanton, J.P., Bauer, J.E., Glaser, P.A., Siegel, D.I., Kelley, C.A., Tyler, S.C., Romanowicz,
361 E.H., Lazrus, A., 1995. Radiocarbon evidence for the substrates supporting methane

362 formation within northern Minnesota peatlands. *Geochimica et Cosmochimica Acta* 59,
363 3663-3668.

364 Chanton, J., 2005. The effect of gas transport on the isotope signature of methane in wetlands.
365 *Organic Geochemistry* 36, 753-768.

366 Chanton, J., Glaser, P.H., Chasar, L., Burdige, D., Hines, M., Siegel, D.I., Tremblay, L., Cooper,
367 W., 2008. Radiocarbon evidence for the importance of surface vegetation on
368 fermentation and methanogenesis in contrasting types of boreal peatlands. *Global*
369 *Biogeochemical Cycles* 22, GB4022.

370 Charman, D.J., Aravena, R., Bryant, C.L., Harkness, D.D., 1999. Carbon isotopes in peat, DOC,
371 CO₂, and CH₄ in a Holocene peatland on Dartmoor, southwest England. *Geology* 27,
372 539-542.

373 Clymo, R.S., Bryant, C.L., 2008. Diffusion and mass flow of dissolved carbon dioxide, methane,
374 and dissolved organic carbon in a 7-m deep raised peat bog. *Geochimica et*
375 *Cosmochimica Acta* 72, 2048-2066.

376 Clymo, R.S., Pearce, D.M.E., 1995. Methane and carbon-dioxide production in, transport
377 through, and efflux from a peatland. *Philosophical Transactions of the Royal Society of*
378 *London Series A - Mathematical Physical and Engineering Sciences* 351, 249-259.

379 Forbrich, I., Kutzbach, L., Hormann, A., Wilmking, M., 2010. A comparison of linear and
380 exponential regression for estimating diffusive CH₄ fluxes by closed-chambers in
381 peatlands. *Soil Biology & Biochemistry* 42, 507-515.

382 Garnett, M.H., Hardie, S.M.L., Murray, C., 2011. Radiocarbon and stable carbon analysis of
383 dissolved methane and carbon dioxide from the profile of a raised peat bog. *Radiocarbon*
384 53, 71-83.

385 Greenup, A., Bradford, M.A., McNamara, N., Ineson, P., Lee, J.A., 2000. The role of
386 *Eriophorum vaginatum* in CH₄ flux from an ombrotrophic peatland. *Plant & Soil* 227,
387 265-272.

388 Hardie, S.M.L., Garnett, M.H., Fallick, A.E., Ostle, N.J., Rowland, A.P., 2009. Bomb-¹⁴C
389 analysis of ecosystem respiration reveals that peatland vegetation facilitates release of old
390 carbon. *Geoderma* 153, 393-401.

391 IPCC, 2001. *Climate Change 2001: the Scientific Basis*, pp. 881. Edited by J. T. Houghton & D.
392 Yihui. Cambridge: Cambridge University Press.

393 Laing, C., Shreeve, T., Pearce, D.M.E., 2010. The fine scale variability of dissolved methane in
394 surface peat cores. *Soil Biology & Biochemistry* 42, 1320-1328.

395 Langdon, P.G., Barber, K.E., 2005. The climate of Scotland over the last 5000 years inferred
396 from multiproxy peatland records: inter-site correlations and regional variability. *Journal*
397 *of Quaternary Science* 20, 549-566.

398 Lassey, K., Etheridge, D., Lowe, D.C., Smith, A., Ferretti, D., 2007a. Centennial evolution of the
399 atmospheric methane budget: what do the carbon isotopes tell us? *Atmospheric*
400 *Chemistry and Physics* 7, 2119-2139.

401 Lassey, K., Lowe, D.J., Smith, A., 2007b. The atmospheric cycling of radiomethane and the
402 "fossil fraction" of the methane source. *Atmospheric Chemistry and Physics* 7, 2141-
403 2149.

404 Levin, I., Hammer, S., Kromer, B., Meinhardt, F., 2008. Radiocarbon observations in
405 atmospheric CO₂: Determining fossil fuel CO₂ over Europe using Jungfrauoch
406 observations as background. *Science of the Total Environment* 391, 211-216.

407 Levin, I., Hesshaimer, V., 2000. Radiocarbon - A unique tracer of global carbon cycle dynamics.
408 *Radiocarbon* 42, 69-80.

409 Lowe, D.C., Brenninkmeijer, C.A.M., Manning, M.R., Sparks, R., Wallace, G., 1988.
410 Radiocarbon determination of atmospheric methane at Baring Head, New Zealand.
411 *Nature* 332, 522-525.

412 Lowry, D., Holmes, C., Rata, N., 2001. London methane emissions: use of diurnal changes in
413 concentration and $\delta^{13}\text{C}$ to identify urban sources and verify inventories. *Journal of*
414 *Geophysical Research* 106, 7427-7448.

415 Marinier, M., Glatzel, S., Moore, T.R., 2004. The role of cotton-grass (*Eriophorum vaginatum*)
416 in the exchange of CO_2 and CH_4 at two restored peatlands, eastern Canada. *Ecoscience*
417 11, 141-149.

418 Mastepanov, M., Sigsgaard, C., Dlugokencky, E., Houweling, S., Strom, L., Tamstor, F.M.,
419 Christensen, T.R., 2008. Large tundra methane burst during onset of freezing. *Nature*
420 456, 628-630.

421 Quay, P.D., King, S.L., Stutsman, J., Wilbur, D., Steele, L., Fung, I., Gammon, R., Brown, T.A.,
422 Farwell, G., Grootes, P., Schmidt, F., 1991. Carbon isotopic composition of atmospheric
423 CH_4 : fossil and biomass burning source strengths. *Global Biogeochemical Cycles* 5, 25-
424 47.

425 Schuur, E.A.G., Vogel, J.S., Crummer, K.G., Lee, H., Sickman, J., Osterkamp, T., 2009. The
426 effect of permafrost thaw on old carbon release and net carbon exchange from tundra.
427 *Nature* 459, 556-559.

428 Slota, P., Jull, A.J.T., Linick, T., Toolin, L.J., 1987. Preparation of small samples for ^{14}C
429 accelerator targets by catalytic reduction of CO. *Radiocarbon* 29, 303-306.

430 Strack, M., Kellner, E., Waddington, J.M., 2005. Dynamics of biogenic gas bubbles in peat and
431 their effects on peatland biogeochemistry. *Global Biogeochemical Cycles* 19, GB1003.

432 Stuiver, M., Polach, H.A., 1977. Reporting of ^{14}C data. *Radiocarbon* 19, 355-363.

433 Wahlen, M., Tanaka, N., Henry, R., Deck, B., Zeglen, J., Vogel, J.S., Southon, J., Shemesh, A.,
434 Fairbanks, R., Broecker, W., 1989. Carbon-14 in methane sources and in atmospheric
435 methane: the contribution from fossil carbon. *Science* 245, 286-290.

436

437 **Figure captions**

438

439 **Fig. 1.** Schematic of the three stages of the method: a. sample collection in the field (note after
440 passing through the DP-IR air was either directed (using clips) back to the chamber or into a gas
441 bag; if the latter the chamber was also vented to atmosphere); b. removal of CO₂ by passing
442 sample through soda lime and into an empty gas bag; c. combustion of CH₄, cryogenic
443 purification and collection of the sample CH₄-derived CO₂.

444

445 **Fig. 2.** CH₄ concentration in the 6 surface chambers at Langlands Moss raised peat bog prior to
446 sampling for carbon isotope analysis. Error bars indicate accuracy ($\pm 10\%$) of individual
447 measurements made by the DP-IR analyser.

448

449 **Fig. 3.** Radiocarbon concentration of CH₄ emitted from the surface of Langlands Moss raised
450 peat bog. The effect of a small amount of atmospheric CH₄ on the ¹⁴C results has been removed
451 using mass balance calculation, assuming a concentration of 3 ± 1 ppm and a ¹⁴C content of 130
452 %modern (see text). Error bars represent the combined uncertainty (1σ) of the ¹⁴C measurement
453 and estimated air-derived CH₄ component.

454

Sample reference	Publication code (SUERC-)	CO ₂ recovered (ml ± 0.1)	$\delta^{13}\text{C}_{\text{VPDB}} \text{CH}_4$ (± 0.1 ‰)	$^{14}\text{CH}_4$ (%modern ± 1σ)	$^{14}\text{CH}_4$ corrected* for air-CH ₄ (%modern ± 1σ)
Blank 1 (5 ml)	33626	5.16	-39.2	0.13 ± 0.01	-
Blank 2 (5 ml)	33627	4.90	-38.9	0.16 ± 0.01	-
Blank 3 (5 ml)	34695	4.77	-39.4	0.12 ± 0.01	-
Mix 1 (10ml)	33221	9.86	-39.6	0.58 ± 0.01	0.19 ± 0.13
Mix 1 (5 ml)	33224	4.97	-38.5	0.68 ± 0.01	-0.11 ± 0.26
Mix 1 (3 ml)	33225	3.32	-39.6 [#]	1.21 ± 0.01	0.04 ± 0.40
Mix 2 (10 ml)	33628	9.87	-39.4	0.66 ± 0.01	0.27 ± 0.13
Mix 2 (5 ml)	33237	5.06	-39.6	0.76 ± 0.01	-0.01 ± 0.26
Mix 2 (3 ml)	33629	3.49	-39.1	1.48 ± 0.02	0.37 ± 0.38

467

468 **Table 1** Test of laboratory methods for processing samples for $^{14}\text{CH}_4$ analysis. In Sample reference, “Blank” represents CH₄ standard added to 1 L of
469 pure O₂, “Mix” denotes CH₄ standard added to 10 L of air, number outside bracket is the sample batch (3 corresponds to the field samples in Table 2)
470 and number within brackets gives estimated volume of CH₄ standard used. Also shown are the radiocarbon publication codes, volume of CO₂
471 recovered following combustion, and carbon isotope results. All ^{14}C results in this Table have not been corrected for laboratory background. *Air

472 used in “Mix” samples would have contained a small amount of atmospheric CH₄, which we have accounted for by assuming a concentration of 3 ± 1
473 ppm and a ¹⁴C content of 130 %modern (see text); the uncertainty on these results was determined by propagating the errors on the estimate of the air-
474 derived CH₄ and analytical ¹⁴C measurement. # estimated value.

475

476

Chamber	Publication code (SUERC-)	$\delta^{13}\text{C}_{\text{VPDB}} \text{ CH}_4$ ($\pm 0.1 \text{ ‰}$)	$^{14}\text{C}_{\text{CH}_4}$ (%modern \pm 1 σ)
A1	34697	-74.5	97.86 \pm 0.43
A2	34703	-66.3	91.80 \pm 0.42
B1	34698	-67.5	85.53 \pm 0.39
B2	34701	-64.0	84.69 \pm 0.39
C1	34702	-70.1	91.26 \pm 0.42
C2	34704	-64.3	97.53 \pm 0.45

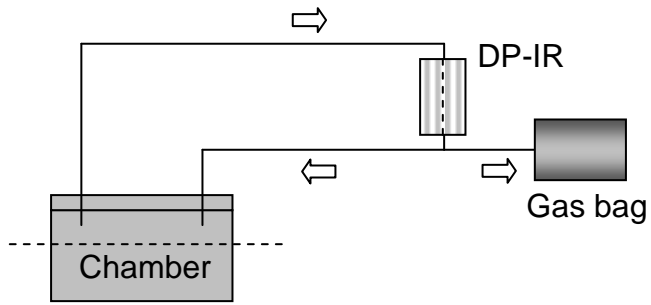
477

478 **Table 2** Carbon isotope values for CH₄ emitted from the surface of Langlands Moss raised peat bog. Following standard procedures, the ¹⁴C results
479 have been corrected for laboratory background (based on the results for “Blank” standards in Table 1), however, they have not been corrected to
480 account for the small amount of atmospheric CH₄ contamination.

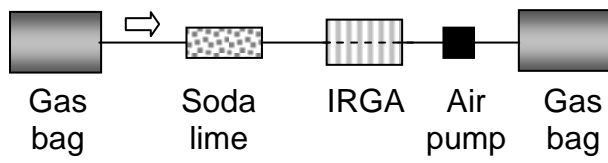
481

Figure 1

a. Field sampling



b. CO₂ removal



c. CH₄ combustion and sample collection

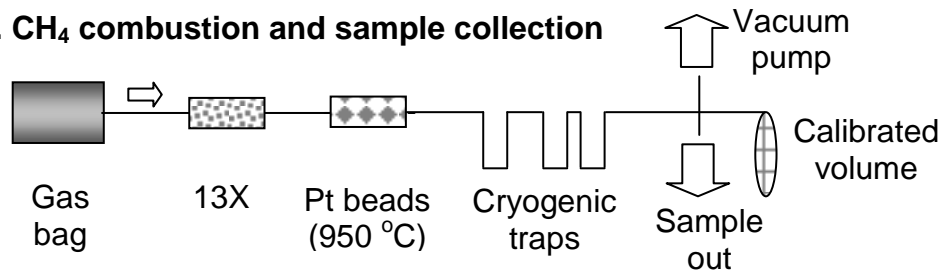


Figure2

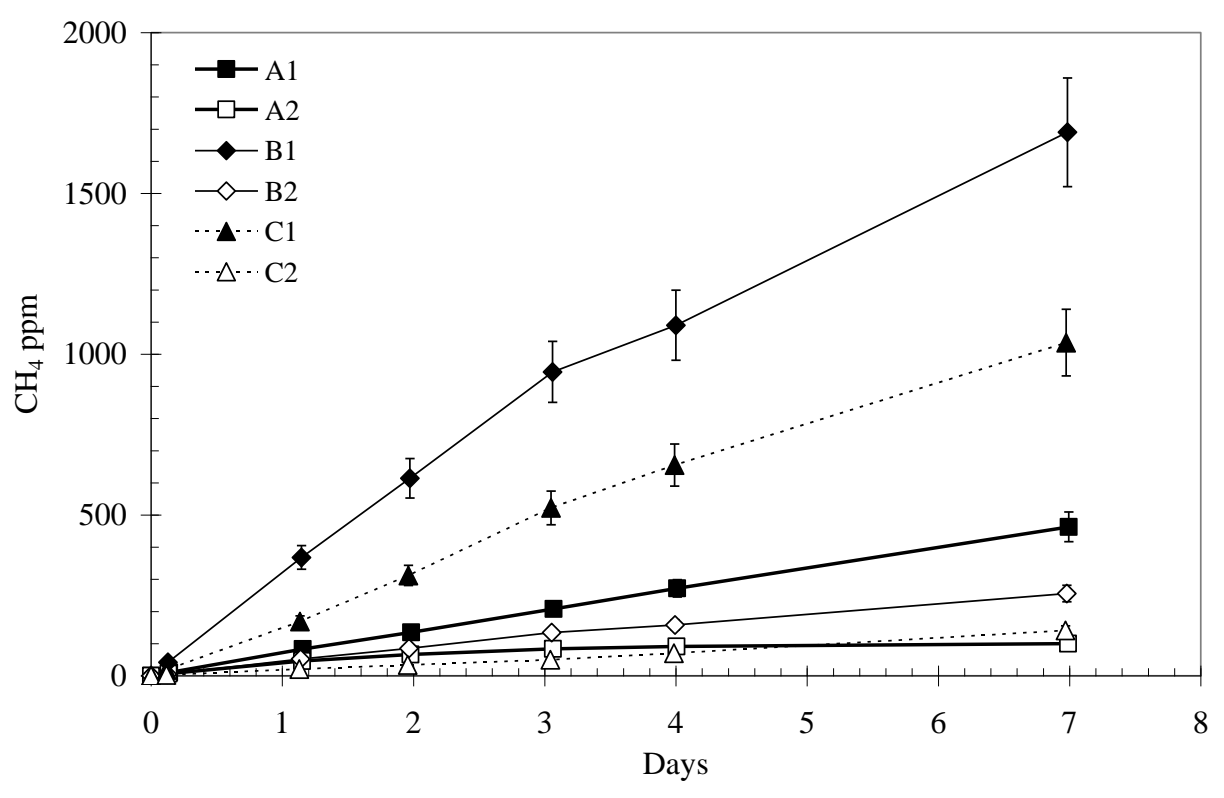


Figure3

