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Garnett, M.H. and Hardie, S.M.L. (2009) *Isotope (^{14}C and ^{13}C) analysis of deep peat CO_2 using a passive sampling technique*. *Soil Biology and Biochemistry*, 41 (12). pp. 2477-2483. ISSN 0038-0717

<http://eprints.gla.ac.uk/26181/>

Deposited on: 27 May 2010

1 Isotope (^{14}C and ^{13}C) analysis of deep peat CO_2 using a 2 passive sampling technique

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4 M H Garnett¹ and S M L Hardie²

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6 ¹NERC Radiocarbon Facility (Environment), Rankine Avenue, East Kilbride, G75 0QF, UK.

7 ²Chemistry Department, Joseph Black Building, University of Glasgow, Glasgow, G12 8QQ,

8 UK.

9

10 **Abstract**

11

12 We developed and tested a new method to collect CO_2 from the surface to deep layers of a

13 peatland for radiocarbon analysis. The method comprises two components: i) a probe equipped

14 with a hydrophobic filter that allows entry of peat gases by diffusion, whilst simultaneously

15 excluding water, and, ii) a cartridge containing zeolite molecular sieve that traps CO_2 passively.

16 We field tested the method by sampling at depths of between 0.25 and 4 m at duplicate sites

17 within a temperate raised peat bog. CO_2 was trapped at a depth-dependent rate of between ~ 0.2-

18 0.8 ml d^{-1} , enabling sufficient CO_2 for routine ^{14}C analysis to be collected when left in place for

19 several weeks. The age of peatland CO_2 increased with depth from modern to ~ 170 BP for

20 samples collected from 0.25 m, to ~ 4000 BP at 4 m. The CO_2 was younger, but followed a

21 similar trend to the age profile of bulk peat previously reported for the site (Langdon and Barber,

22 2005). $\delta^{13}\text{C}$ values of recovered CO_2 increased with depth. CO_2 collected from the deepest

23 sampling probes was considerably ^{13}C -enriched (up to ~ +9 ‰) and agreed well with results

24 reported for other peatlands where this phenomenon has been attributed to fermentation

25 processes. CO_2 collected from plant-free static chambers at the surface of the mire was slightly

26 ¹⁴C-enriched compared to the contemporary atmosphere, suggesting that surface CO₂ emissions
27 were predominantly derived from carbon fixed during the post-bomb era. However, consistent
28 trends of enriched ¹³C and depleted ¹⁴C in chamber CO₂ between autumn and winter samples
29 were most likely explained by an increased contribution of deep peat CO₂ to the surface efflux in
30 winter. The passive sampling technique is readily portable, easy to install and operate, causes
31 minimal site disturbance, and can be reliably used to collect peatland CO₂ from a wide range of
32 depths.

33

34 *Keywords:* Peat, CO₂, Radiocarbon, Molecular sieve.

35

36 **1. Introduction**

37

38 Peatlands contain vast stores of carbon and have the potential to significantly enhance the current
39 rate of increase in atmospheric CO₂ if destabilization were to occur. As a result, the carbon
40 balance of peatlands has been the focus of much research in recent years. Radiocarbon analysis
41 of peatland organic materials (e.g. macrofossils) has been widely applied to determine peat
42 growth and carbon accumulation rates (e.g. Tolonen and Turunen, 1996; Oldfield et al., 1997).
43 Few studies have dated CO₂ within deep peat, perhaps due to technical challenges during
44 sampling, and we know of no study where both the profile of peat CO₂ and the surface efflux
45 from the same peatland have been dated. However, information on the age of surface and deep
46 peat gases such as CO₂ can provide valuable insights into their source and contribution to total
47 peatland CO₂ flux; ultimately these data will provide a more complete understanding of the
48 peatland carbon balance.

49

50 Several studies have previously reported the radiocarbon (¹⁴C) content of CO₂ dissolved in the
51 permanently water-logged layers of peatlands, but generally results have been few and

52 unreplicated (Clymo and Bryant, 2008). In these studies, dissolved CO₂ has consistently been
53 found to be younger than the surrounding peat. For example, in Canadian boreal peatlands
54 Aravena et al. (1993) and Charman et al. (1994) found peat CO₂ to be between 500 and 2000
55 years younger than the adjacent peat. Another study performed in an oceanic peatland in south-
56 west England (Charman et al., 1999) reported that peat CO₂ was younger than the surrounding
57 peat by between ~ 800 and 1500 years. Suggested mechanisms for this difference include the
58 downward migration of younger carbon by mass flow or diffusion, and as dissolved organic
59 carbon or CO₂ (Aravena et al., 1993; Charman et al., 1999; Clymo and Bryant, 2008). However,
60 the methods employed to recover deep peat CO₂ in several of these studies required drawing gas
61 into evacuated flasks which could have contributed to the downward transport of younger CO₂
62 (Aravena et al., 1993). Charman et al. (1999) also discuss the possibility of atmospheric CO₂
63 contaminating samples with the method that they employed. The gas sampling approach utilised
64 by Clymo and Bryant (2008) avoided similar issues since it was not reliant on a vacuum to
65 recover samples, however, Clymo's method required the manufacture of specialised sampling
66 equipment and a somewhat lengthy installation and sampling procedure. Therefore, our primary
67 aim was to develop a new method to collect CO₂ from the deep layers of a peatland for carbon
68 isotope analysis which minimizes site disturbance during installation and is simple and
69 inexpensive to construct, thus reducing some of the barriers to greater replication.

70
71 Like deep peat CO₂, few studies have analysed the ¹⁴C content of CO₂ emitted from the surface
72 of a peatland, yet the ¹⁴C content of the surface efflux could provide valuable information on the
73 age of the CO₂ emitted and the contribution of deep peat CO₂ to the surface efflux. The lack of
74 studies may be due to technical difficulties in collecting samples because the concentration of
75 CO₂ at the mire/atmosphere boundary is likely to be considerably less than that found within the
76 peat itself, due to dilution with air. However, Bol and Harkness (1995), Gaudinski et al. (2000)
77 and Hardie et al. (2005) all report molecular sieve based sampling methods which should be

78 suitable for the collection of CO₂ emitted from the surface of a peatland, although to our
79 knowledge, no published results are available for the ¹⁴C content of CO₂ emitted from the
80 surface of peatlands.

81
82 Recently, a new method to recover CO₂ for ¹⁴C analysis by passive trapping with zeolite
83 molecular sieve to date soil respired CO₂ was reported (Garnett et al., 2009). Here, we describe
84 and test a development of this method that utilises a simple sampling probe which can be
85 inserted into any peat profile to a range of depths. At the peat surface the probes are attached to a
86 molecular sieve cartridge to enable passive sampling of deep peat CO₂. In addition, we used a
87 chamber-based passive sampling method (Garnett et al., 2009) to characterise the isotopic
88 composition of CO₂ emanating from the peatland surface. Our aims were i) to test the ability of
89 the new method to collect CO₂ from a range of depths in a deep peat profile for ¹⁴C analysis, and,
90 ii) to use measurements of the radiocarbon age and δ¹³C of deep peat CO₂ and surface CO₂ efflux
91 to provide information on the contribution of deep peat to the overall surface CO₂ emissions.

92

93 **2. Methods**

94

95 *2.1 Molecular sieve cartridge and sampling probe design*

96

97 The new method to collect deep peat CO₂ for radiocarbon analysis is composed of two parts; a
98 sampling probe and a molecular sieve cartridge (MSC). The sampling probes (Fig. 1) were
99 constructed from stainless steel tubing (6 mm OD) that were cut to lengths a few cm longer than
100 the depths of peat that were required to be sampled. To permit convenient transport of the
101 longest probe (4 m) to the field site the tubing was spilt into two sections that were easily
102 connected or disconnected by way of a stainless steel union (Swagelok, USA). The top 5 cm of
103 each probe was bent to an angle of 90 degrees allowing it to run parallel with the peatland

104 surface. This facilitated easy sampling by connection of a MSC via an auto-shutoff Quick
105 Coupling (Colder Products Company, USA). At the opposite end of the sampling probe (that
106 which would be placed into the peat) the steel tubing was sealed using a bolt (Fig. 1).
107 Approximately 10 cm above the base of the sampling probe, six holes (2 mm diameter) were
108 made through which peat gases could enter and make their way to the surface on the inside of the
109 steel tubing. The holes were covered by a length (5 cm) of gas permeable hydrophobic tubing
110 (Accurel PP V8/2 HF, Membrana GmbH, Germany; Gut et al., 1998) thus allowing peat gases
111 but not water, to enter the sampling probe. All joins were covered with heat shrink and a rubber
112 sealant (Plasti-dip, Minnesota, USA) to ensure that water could not gain entry, and leak-tested
113 prior to installation at the field site.

114
115 We used the same design of MSC that was previously used in pump-based (Hardie et al., 2005)
116 and passive (Garnett et al., 2009) CO₂ sampling methods, both developed for trapping soil-
117 respired CO₂ for ¹⁴C analysis. The design of the MSC has been described in detail by Hardie et
118 al. (2005), but briefly, consisted of a quartz glass cartridge containing ~ 3-4 g of Type 13X
119 zeolite molecular sieve (1/16" pellets, BDH, UK) held within a central chamber using quartz
120 wool. At both ends of the cartridge, auto-shutoff Quick Couplings were attached via short lengths
121 of PVC tubing (Tygon, Fisher, UK). Although the couplings seal automatically when not
122 connected we also used plastic clips (WeLoc[®], Scandinavia Direct, UK) placed across the PVC
123 tubing to form an additional seal when necessary. The MSCs were charged by heating (500 °C)
124 whilst under high vacuum (10⁻³ mb) for ~ 1.5 hours prior to use after which they were allowed to
125 cool and filled with high purity N₂ to just above ambient pressure.

126
127 *2.2 Experimental design*

128

129 Field testing aimed to determine whether the sampling probes provided sufficient CO₂ for ¹⁴C
130 analysis and in addition, whether the CO₂ collected was representative of deep peat CO₂ at the
131 depth being sampled. A simple measurement of the volume of recovered CO₂ would indicate
132 whether sufficient sample had been collected for ¹⁴C analysis. However, to assess whether the
133 recovered CO₂ was isotopically representative of the peat gas at the depth being sampled was
134 less easy, as we had no independent knowledge of the isotopic composition of the peat CO₂ for
135 this site. The criteria that we adopted to test the method firstly involved the collection of
136 duplicate samples with the assumption that deep peat CO₂ should have a similar carbon isotopic
137 composition when collected from adjacent locations. Secondly, we compared our results with
138 what we would expect based on the small number of measurements that have previously been
139 reported for deep peat CO₂. For example, previous studies have shown consistent increases in the
140 age and δ¹³C of deep peat CO₂ with increasing depth (Clymo and Bryant, 2008), and reported
141 that deep peat CO₂ was slightly younger compared to the age of the surrounding peat (e.g.
142 Aravena et al., 1993; Charman et al., 1994, 1999; Clymo and Bryant, 2008). Finally, a third
143 component of the testing involved a laboratory-based experiment: a standard CO₂/air mixture of
144 known CO₂ concentration and isotopic composition, contained within a large air-tight barrel, was
145 sampled using the probes to test that representative samples of CO₂ were recovered.

146
147 Field testing was performed at Langlands Moss, an ombrotrophic raised peat bog near Glasgow,
148 UK (55°44'05.9" N, 4°10'26.1" W). Sampling probes were inserted to four depths (0.25, 1, 2 and
149 4 m) at two sampling sites (Sites A and B) located approximately 20 m apart. Installation of the
150 probes was easily accomplished by simply pushing them vertically into the peat surface until the
151 required depth was reached, with only the sampling end of the probe being exposed (Fig. 1). For
152 at least 2 d prior to installation of the probes, atmospheric CO₂ was passively scrubbed from
153 inside the stainless steel tubes by covering the hydrophobic filter with a rubber seal and attaching
154 a cartridge filled with soda lime to the coupling. Only immediately prior to insertion of each

155 probe into the peat was the soda lime cartridge and rubber seal removed, thus minimizing
156 contamination from atmospheric CO₂. Following installation, sampling probes were left for 1
157 month before sampling commenced.

158
159 In addition to samples collected from the probes, we captured CO₂ emitted from the bog surface
160 using a chamber-based passive sampling method (Garnett et al., 2009). This method used the
161 same MSCs utilised for the sampling probes, which were attached to each closed chamber with
162 identical couplings. The chambers consisted of circular plastic soil pipe (10 cm ID x 15 cm
163 length) that was left open at one end (for contact with the peat surface) and sealed at the other.
164 Three Quick Couplings were installed into the side of each chamber, one of which contained a
165 hydrophobic filter (Accurel PP V8/2 HF, Membrana GmbH, Germany; Gut et al., 1998). Each of
166 the chambers were pushed into the surface of the peat to a depth of 5 cm at the same two sites
167 being used to test the deep peat sampling probes (all vegetation including moss was removed one
168 month before sampling commenced). Before collection of surface CO₂, each chamber headspace
169 was scrubbed to remove atmospheric CO₂ using a soda lime based scrubbing system (Hardie et
170 al., 2005). The chambers were then left in place for one month prior to sampling.

171
172 Sampling probes were left in place to trap deep peat CO₂ continuously for a total of ~ 2.5 months
173 (Site A: 3 October, 2008 to 9 December, 2008; Site B: 3 October, 2008 to 16 December, 2008).
174 Chambers were sampled continuously with MSCs for 1 week only and were then removed. A
175 total of three sets of chamber samples were collected at the start (3-10 October, 2008), middle
176 (26 November-3 December, 2008) and end (9-16 December, 2008) of the experiment. On at least
177 two occasions per month, including when chamber MSCs were exchanged, site variables
178 including water table depth, air and soil temperatures were recorded. In addition, over the course
179 of the experiment we made multiple measurements of CO₂ concentration inside the closed
180 chambers, and measured surface CO₂ emissions from the mire, using an identical closed chamber

181 that was only placed on the mire surface during flux measurement (~ 10 minutes). An EGM-4
182 infrared gas analyzer (PP Systems, UK) was used for all field CO₂ measurements. Immediately
183 after the final chamber MSC had been disconnected at the end of the experiment a further sample
184 of chamber CO₂ was collected from both sites using a pump-based molecular sieve sampling
185 system (Hardie et al., 2005).

186
187 In the laboratory experiment, sampling probes identical to those used in the field, were inserted
188 via a large rubber bung into a 30 L air-tight plastic barrel which contained air with an elevated
189 CO₂ concentration. The concentration (~ 24000 ppm) and δ¹³C (-24.6 ‰) of the CO₂ in the
190 air/CO₂ mix had previously been determined (the former using an IRGA, and the latter from sub-
191 samples collected from the barrel using an evacuated flask). For the laboratory test, MSCs were
192 used to passively trap CO₂ from the barrel using sampling probes of different lengths. This
193 experiment addressed two issues: first to test whether the sampling probe method collected
194 representative samples of CO₂ by comparison of the MSC-collected samples with the evacuated
195 flask samples. Second, to verify that the rate of CO₂ trapping obeyed Fick's law; this would
196 permit estimation of the CO₂ concentration in the atmosphere being sampled from the CO₂ trap
197 rate. Following Bertoni et al. (2004), we used an expression derived from Fick's law which
198 concerns the kinetics of molecular movement along a gradient (towards an absorbent) when the
199 movement is restricted to the inside of a tube:

200
201
$$C_i = (Q_i \times L) / (S \times t \times D_i)$$
 Equation 1

202
203 where C_i represents the CO₂ concentration of the environment being sampled, Q_i is the amount
204 of CO₂ trapped during time t , L and S are the length and cross-sectional area of the entire
205 sampling probe (from gas inlet to molecular sieve), and D_i is the diffusion coefficient of CO₂ in
206 air (Bertoni et al., 2004).

207
208 *2.3 CO₂ recovery and isotope analysis*
209
210 After each sampling occasion (field or laboratory), clips were placed on either end of each MSC
211 before being disconnected and returned to the NERC Radiocarbon Facility for CO₂ recovery.
212 Sample CO₂ was desorbed by heating (500 °C) the molecular sieve while attached to a vacuum
213 rig (see Hardie et al., 2005). The gas evolved was dried by passing through a slush trap (mixture
214 of dry ice and industrial methylated spirits; -78°C) and then purified by trapping in liquid N₂.
215 The quantity of CO₂ recovered was measured in a calibrated volume before being split into sub-
216 samples for analysis.

217
218 One sub-sample was analysed for $\delta^{13}\text{C}$ ($^{13}\text{C}/^{12}\text{C}$ ratio in ‰ units relative to the standard Vienna
219 Pee Dee Belemnite; VPDB) using a dual inlet isotope ratio mass spectrometer (VG Optima,
220 Micromass, UK) at the NERC Radiocarbon Facility. A second sub-sample was reduced to
221 graphite using Zn/Fe reduction (Slota et al., 1987) and analysed by accelerator mass
222 spectrometry (AMS) at the Scottish Universities Environmental Research Centre (SUERC), East
223 Kilbride, UK (Freeman et al., 2007). ^{14}C results were normalised to a $\delta^{13}\text{C}$ of -25 ‰ to account
224 for mass-dependant fractionation, and expressed as conventional radiocarbon ages (years BP)
225 and %modern (Stuiver and Polach, 1977). Following convention, measurement uncertainties
226 associated with isotope concentrations are expressed as standard deviations.

227
228 **3. Results**

229
230 A summary of site characteristics including temperature, water table depth and CO₂ flux rates
231 recorded during the sampling period is provided in Table 1. Both sampling locations were

232 similar in terms of air and soil temperature, mean water table depth and CO₂ flux rate, however,
233 CO₂ concentration in the closed chamber was consistently higher at Site B.

234
235 After ~ 2.5 months exposure, MSCs attached to sampling probes had trapped between 15 and 55
236 ml of CO₂, easily sufficient for ¹⁴C analysis. Trapping rates ranged from a minimum of ~ 0.2 ml
237 d⁻¹ at 0.25 m depth to a maximum of 0.8 ml d⁻¹ at 2 m depth (Fig. 2a). Since under the known
238 conditions of the laboratory experiment we found a very strong agreement between measured
239 and theoretical CO₂ trapping rate (based on Fick's law; Fig. 3), we used equation 1 to convert the
240 CO₂ trap rates measured using the sampling probes into estimates of CO₂ concentration within
241 the deep peat (assuming the diffusion coefficient of CO₂ in the probe gas to be the same as in
242 air). Results showed that CO₂ concentration in the peat gas increased linearly from ~ 1 % at 25
243 cm depth, to between 14 and 19 % at 4 m (Fig. 2b).

244
245 Carbon isotope ($\delta^{13}\text{C}$ and ^{14}C) results for both deep peat CO₂ and chamber CO₂ samples
246 (collected both passively and dynamically using the pump-based method) are presented in Table
247 2. Consistent with previous observations (Garnett et al., 2009), we found a ~ 4 ‰ offset for $\delta^{13}\text{C}$
248 measurements between the pumped and final set of samples collected passively with a MSC
249 (CHAMBER A-3 and CHAMBER B-3) which we attribute to fractionation during passive
250 trapping (Table 2). This difference in $\delta^{13}\text{C}$ was also observed between evacuated flask and
251 passive MSC samples collected during the laboratory test of the sampling probes (mean = 4.0 ±
252 0.2 ‰ SD; n = 4). The $\delta^{13}\text{C}$ results for deep peat CO₂ and chamber CO₂ illustrated in Figure 4a
253 have therefore been adjusted to account for this offset. The results show that chamber CO₂ had a
254 $\delta^{13}\text{C}$ of ~ -22 to -25 ‰, whilst within the peat profile, the $\delta^{13}\text{C}$ of CO₂ increased from ~ -13 ‰
255 (Site A) and -10 ‰ (Site B) at 0.25 m, to ~ +9 ‰ in the 4 m samples at both sites (Fig. 4a). ¹⁴C
256 age of deep peat CO₂ increased with depth from modern (Site A) and 169 ± 37 BP (Site B) at

257 0.25 m, to ~ 4000 BP at 4 m depth. All chamber ^{14}C concentrations fell within the range 106.51
258 to 108.08 % modern (Table 2; Fig. 4b).

259

260 **4. Discussion**

261

262 *4.1 Sampling probe technique*

263

264 Our main aim was to test a new method to collect deep peat CO_2 for carbon isotope
265 measurement, with tests first focusing on whether sufficient CO_2 could be recovered for analysis,
266 and whether this was representative of CO_2 produced at the peat depths being sampled. Previous
267 tests on the use of Type 13X molecular sieve have verified its reliability for collecting samples
268 of CO_2 for both ^{13}C and ^{14}C analysis (Bauer et al., 1992). In addition, the MSCs that we utilised
269 have been shown not to suffer from contamination, sample carry-over (hysteresis), or isotopic
270 fractionation when used with a pump-based sampling system (Hardie et al., 2005). Subsequent
271 tests by Garnett et al. (2009) showed that the same MSC could be used reliably to passively trap
272 soil-respired CO_2 for ^{14}C analysis. Consequently, we consider it reasonable to assume that the
273 MSC cartridge performed equally well when attached to the steel sampling probes, and therefore
274 our tests were essentially investigating the application of the probes.

275

276 According to Fick's law (equation 1), the rate of CO_2 trapping in an absorbent is dependent on a
277 number of factors including exposure time, the CO_2 concentration of the environment being
278 sampled and the distance between the source and absorbent (Bertoni et al., 2004). Our field test
279 results showed that after ~2.5 months the MSCs had trapped between 15 and 55 ml CO_2 ,
280 suggesting that even at the lowest trap rates, sufficient CO_2 (~ 5 ml) for both ^{13}C and ^{14}C analysis
281 could have been recovered after just one month of sampling. Alternatively, since Garnett et al.
282 (2009) have shown that the MSCs can passively trap at least 120 ml CO_2 , the MSCs could well

283 have continued sampling for at least ~ 6 months (i.e. before saturation occurs). Clearly the
284 method is easily capable of providing sufficient CO₂ for carbon isotope analysis, and the CO₂
285 capacity of the MSCs allows for uncertainty in estimating the required exposure time in
286 applications where prior knowledge of the CO₂ concentration of the environment being sampled
287 is not available. That we found very good agreement between measured (laboratory experiment)
288 and theoretical (estimated from Fick's law) rates of CO₂ trapping is particularly valuable for
289 estimating the required sampling time (e.g. for different lengths of sampling probes). However,
290 our values for %CO₂ in the peat gas (Fig. 2b) could be underestimates if the rate of CO₂ removal
291 by the molecular sieves was greater than the rate that CO₂ was replenished around the sampling
292 probe (i.e. from CO₂ production and diffusion within the peat). Indeed, Clymo and Bryant
293 (2008) reported higher CO₂ concentrations in similar depths at another Scottish ombrotrophic
294 mire, and underestimates of the CO₂ concentration by probe samples may explain the anomalous
295 observation that the static chambers on the surface of the mire were more concentrated in CO₂
296 than the peat at 0.25 m depth (Table 1 and Fig. 2b).

297
298 Atmospheric CO₂ was a possible source of contamination in the probes prior to their insertion
299 into the peat and therefore we attempted to remove it by scrubbing with soda lime. However, we
300 calculate from the volume of the sampling probes and ambient CO₂ concentration, that the
301 maximum volume of atmospheric CO₂ that could have caused contamination at the beginning of
302 the experiment, would only have been ~ 0.02 ml. This represented less than 0.2 % of the CO₂
303 recovered from any of the MSCs over the course of the experimental period. Thus, even if we
304 had not removed this contaminant at the start of the experiment our results would have been
305 affected by an amount considerably less than the precision of the ¹⁴C measurements.

306

307 In their study of a raised bog Clymo and Bryant (2008) found very close agreement between
308 replicates of peat CO₂ from the same depth, and therefore we considered that a test of the

309 reliability of the sampling probes was through comparison of results for duplicate samples. We
310 similarly found very good agreement between our duplicate samples from different depths.
311 Closest agreement occurred in the deeper samples, with for example, ^{14}C concentrations for
312 duplicate samples from the 2 m and 4 m depths agreeing to within 1σ . That there was a greater
313 difference in the results for samples closer to the mire surface may be due to variations in
314 contributions of recent carbon inputs that have occurred during a period when atmospheric ^{14}C
315 has been relatively variable (i.e. due to bomb- ^{14}C), or alternatively, it may be a result of
316 exchange between the shallower peat layers and the atmosphere. Waldron et al. (1999) measured
317 the ^{13}C isotope of deep peat CO_2 and similarly found that variation between sites decreased with
318 increasing depth.

319
320 Our results collected using the passive sampling approach are similar to previous studies. Firstly,
321 as also reported by Clymo and Bryant (2008), we found that the ^{14}C content of deep peat CO_2
322 showed a consistent decrease with depth. We also found that the age of deep peat CO_2 followed
323 a similar trend, but was consistently younger, compared to bulk peat that had been sampled from
324 the same raised mire (Fig. 4b); an observation that has also been reported for other peatlands by
325 Clymo and Bryant (2008), Aravena et al. (1993) and Charman et al. (1994, 1999). Although
326 there was a difference between the ^{14}C contents at the same depths between our results and those
327 of Clymo and Bryant (2008), this may well be due to site differences such as peat accumulation
328 rates, for example, total peat depth at our study site was in excess of 8 m, while the peatland of
329 Clymo and Bryant (2008) only extended to a depth of ~ 7 m. For $\delta^{13}\text{C}$, there was even closer
330 agreement between the relationship with depth for our results and previous studies. For example,
331 at 4 m depth, we found that deep peat CO_2 had a $\delta^{13}\text{C}$ of between +8.6 to +9.2 ‰, while for the
332 same depth at their peatland Clymo and Bryant (2008) report values of between +8.7 and +9 ‰.
333 Although both sets of results are from different sites, it is reasonable to suppose that the same
334 processes responsible for producing the trend of increasing $\delta^{13}\text{C}$ with depth are occurring, and

335 therefore we might expect similar $\delta^{13}\text{C}$ profiles if both sampling approaches collected deep peat
336 CO_2 that was representative of the depths sampled.

337

338 The third test of the sampling method was performed by way of a laboratory experiment using a
339 standard air/ CO_2 mixture. Although we did not measure the ^{14}C content, we found that the $\delta^{13}\text{C}$
340 of all passively collected MSC samples was identical (when considering the analytical precision
341 of the measurement) at all probe lengths tested. Furthermore, there was very good agreement
342 between the measured trapping rate and the theoretical rate based on Fick's law, when taking
343 into account the dimensions (inner diameter and length) of the sampling probes. Comparison of
344 the $\delta^{13}\text{C}$ values of evacuated flask and passive MSC samples confirmed previous observations
345 that a ~ 4 ‰ fractionation occurs during passive trapping; isotopic fractionation has been
346 reported for molecular sieves (Garnett et al., 2009) and when trapping CO_2 in a hydroxide
347 absorbent (Davidson, 1995), and is likely a result of fractionation during diffusion through air.
348 The adjustment of the $\delta^{13}\text{C}$ results for this fractionation effect may slightly increase the
349 uncertainty in $\delta^{13}\text{C}$ values, but the results of the laboratory test suggest that the adjustment factor
350 does not vary with probe length. Furthermore, the corrected $\delta^{13}\text{C}$ results from the field samples
351 agree remarkably well with values reported by others e.g. Clymo and Bryant (2008). It should
352 also be remembered that following convention, ^{14}C results were corrected for mass-dependent
353 fractionation by normalising to a $\delta^{13}\text{C}$ of -25 ‰, which will have accounted for fractionation of
354 the ^{14}C isotope during passive sampling.

355

356 *4.2 Implications for peatland carbon emissions*

357

358 As reported above, we found trends in the ^{14}C and $\delta^{13}\text{C}$ of peat CO_2 that were very similar to
359 results from the few other peatlands where the isotopic composition of deep peat CO_2 has been
360 studied. That peat CO_2 was also consistently younger at our site compared to the bulk peat

361 supports previous suggestions that it is derived not only from the surrounding peat, but that it
362 also contains a component that has migrated from higher in the peat profile. It seems likely (as
363 reported by others), that fermentation processes such as acetoclastic methanogenesis (Aravena et
364 al., 1993; Charman et al., 1999) or hydrogenotrophic methanogenesis (Whiticar et al., 1986) are
365 taking place at depth, since these processes would result in the highly ^{13}C -enriched CO_2 observed
366 at depth within the peatland at Langlands Moss.

367
368 That we found chamber CO_2 to be slightly ^{14}C -enriched relative to the contemporary atmosphere
369 may suggest that the surface efflux was predominantly derived from carbon fixed within the last
370 few years, and that CO_2 derived at depth contributed little to the surface efflux. This explanation
371 seems to fit with current peatland carbon balance models. However, some CO_2 derived from
372 deep in the peat profile may well escape from the surface, and slight differences in the rate of
373 CO_2 exchange between the upper layers of the peatland and the atmosphere may be one
374 explanation for the divergence in results between our two sampling sites. Similarly, since
375 Wahlen et al. (1989) reported that ^{14}C results of methane emanating from the peatland surface
376 showed that aged carbon in methane contributed to surface gas emissions, it can probably be
377 expected that surface emissions will also contain a component of old CO_2 . Indeed, if CO_2
378 derived from deep peat contributed only a few percent to the surface emission, it is unlikely that
379 we would be able to detect this simply from a few ^{14}C measurements of surface CO_2 emissions
380 unless the contribution of pre-bomb carbon was so great that it caused the ^{14}C content of surface
381 emissions to fall below the ^{14}C content of the contemporary atmosphere, as recently
382 demonstrated within an arctic ecosystem (Schuur et al., 2009).

383
384 The surface chamber $\delta^{13}\text{C}$ results show that CO_2 became increasingly ^{13}C -enriched over the
385 course of the experiment, while a less significant but consistent difference is suggested by
386 chamber ^{14}C results. At both Sites A and B, chamber CO_2 at the end of the experiment was

387 slightly depleted in ^{14}C relative to the beginning, while $\delta^{13}\text{C}$ increased significantly by between
388 1.6 to 3.1 ‰ between October and December. This observation is consistent with an increased
389 contribution to the chamber of CO_2 that was both depleted in ^{14}C and enriched in ^{13}C . Since the
390 sampling period began in autumn and ended in early winter, and because the sampling plots were
391 plant-free, one explanation may be that the relative proportion of a ^{14}C -depleted and ^{13}C -
392 enriched component to chamber CO_2 increased as a result of a smaller contribution from the
393 decay of organic matter at the surface of the peatland (due to lower temperatures). Two potential
394 sources of relatively ^{14}C -depleted and ^{13}C -enriched CO_2 that could plausibly explain the
395 observed change in isotopic composition of chamber headspace (and would presumably not be
396 greatly affected by seasonal changes), are either atmospheric CO_2 or deep peat CO_2 . In terms of
397 the former, there is likely to have been at least some atmospheric CO_2 in the chamber because its
398 base (inserted to 5 cm depth below the peat surface) did not always extend below the water table
399 (Table 1). Alternatively, the surface efflux could contain a greater relative contribution from
400 deep peat CO_2 during colder months because, unlike CO_2 production in the surface layers, deep
401 peat CO_2 is likely to be less affected by seasonal changes (for example, Clymo and Pearce, 1995,
402 state that gas concentration profiles in the catotelm change little with season, presumably due to
403 a much smaller variation in annual temperature at depth).

404
405 Isotope mass balance calculations suggest that the observed isotopic changes in chamber CO_2
406 cannot be explained by a greater component of atmospheric CO_2 in the chambers because this
407 would require an increased atmospheric contribution of at least 8-15 % (based on $\delta^{13}\text{C}$
408 calculations; even greater contributions are required to satisfy the ^{14}C results). However, the
409 maximum contribution of air CO_2 in the chamber cannot have been more than about 1.6 %
410 (assuming an ambient atmospheric CO_2 concentration of 380 ppm and a total chamber CO_2
411 concentration of ~ 24700 ppm; Table 1). Moreover, the observed isotopic shifts in chamber CO_2
412 concentration can be explained by contributions of deep peat-derived CO_2 , requiring for

413 example, a fractional increase in chamber CO₂ (in December relative to October) of 2-8 % being
414 derived from deep peat CO₂ with an average isotopic composition of that measured at 2 m.
415 Interestingly, Hirsch et al. (2002) similarly found evidence of a shift to a greater release of older
416 (pre-bomb) carbon in soil respiration when moving from summer to autumn during a study of
417 deep soil respiration in a boreal forest. They at least partly attributed this shift to a relative
418 increase in the contribution of deep soil CO₂ due to the surface litter layer becoming colder than
419 the deep soil (and thus a decrease in CO₂ produced from younger, more shallow soil).

420
421 We have shown from respiration chamber results that it is likely that the proportion of total CO₂
422 efflux derived from deep peat CO₂ increased between October and December, however, we
423 cannot estimate a total flux from deep peat CO₂ using these results. But, using our measurements
424 of average CO₂ efflux at the study site (Table 1) we can suggest that the emission of deep peat
425 CO₂ was at least ~ 0.2 to 1.2 mg C m⁻² hr⁻¹. Although further investigation is required to support
426 these findings, it seems likely that deep peat CO₂ does contribute significantly to the surface
427 efflux from this peatland, and that the contribution it makes to the total flux varies seasonally.

428

429 **5. Conclusions**

430

- 431 1. The technique of passive sampling using probes coupled to zeolite molecular sieve
432 cartridges is inexpensive, easy to install and operate, and provides a reliable method to
433 recover deep peat CO₂ for radiocarbon analysis and δ¹³C measurement.
- 434 2. Probes of a wide range of lengths can be used, although it should be noted that the rate of
435 trapping will decline with increasing probe length thereby increasing the exposure time
436 required to provide sufficient CO₂ for analysis; this can be easily estimated using Fick's
437 law.

- 438 3. Profiles of decreasing ^{14}C content and increasing $\delta^{13}\text{C}$ of peat CO_2 with depth compared
439 well with results reported for other peatlands. Peat CO_2 was younger than bulk peat at the
440 same depth, suggesting that although being predominantly derived from the surrounding
441 peat, there was a contribution to the CO_2 pool by carbon produced from younger sources
442 closer to the peatland surface.
- 443 4. The carbon isotope composition of surface chamber CO_2 samples suggested that the
444 majority of the surface efflux was derived from recently fixed carbon. However,
445 differences in the isotopic composition between the start and end of the sampling period
446 are most likely explained by differing contributions from deep peat-derived CO_2 to
447 surface emissions.
- 448 5. The sampling probes were designed for recovering dissolved CO_2 from deep peats.
449 However, since peat is composed typically of 90 % water, the probes could also be used
450 to collect CO_2 for carbon isotope analysis from other environments including aquatic
451 systems (lakes/rivers).

452

453 **Acknowledgments**

454

455 We thank staff at the NERC Radiocarbon Facility (Environment) and SUERC AMS Facility.
456 NERC is acknowledged for funding the isotope analyses and we are grateful to John Hawell and
457 South Lanarkshire Council for site access. We are grateful to two anonymous referees for
458 comments which improved the manuscript.

459

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461

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527

528

529

530 Table 1 Temperature (air and soil at 10 cm), water table depth (relative to peat surface), surface
 531 CO₂ efflux and static chamber CO₂ concentration from plant-free plots. Measurements were
 532 performed between ~10 am and 11:30 am at both sampling sites during field visits throughout
 533 the course of the experiment (October to December 2008).

	Site A			Site B		
	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Air temperature (°C)	7.8	-2.3	14.6	7.8	-2.3	14.6
Soil temperature at 10 cm (°C)	6.3	1.3	11.9	6.7	1.8	12.2
Water table depth (cm)	5.2	1.0	7.0	6.6	2.0	9.5
CO ₂ efflux (mg CO ₂ -C m ⁻² hr ⁻¹)	14.7	7.1	30.8	12.1	5.7	22.6
Chamber CO ₂ concentration (%)	3.46	2.47	3.80	4.73	4.37	5.30

534

535

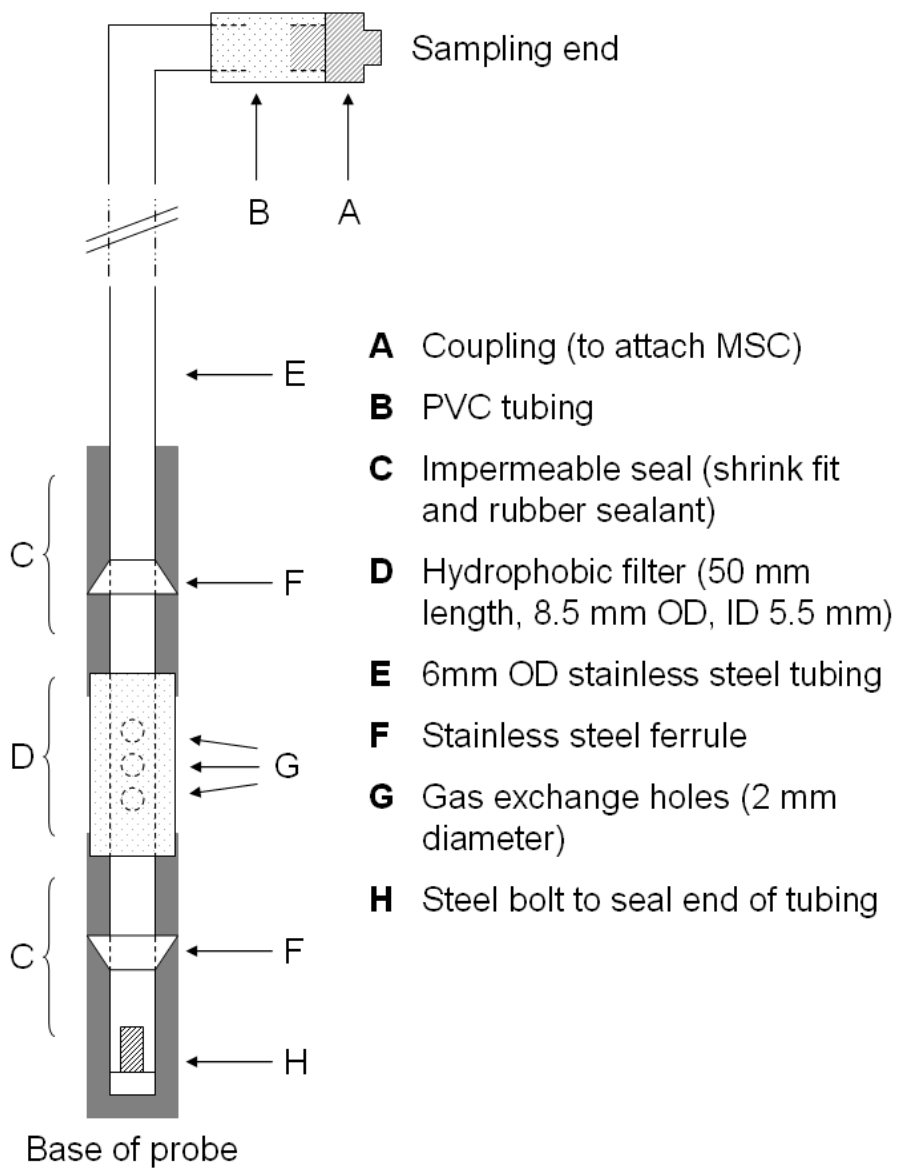
536

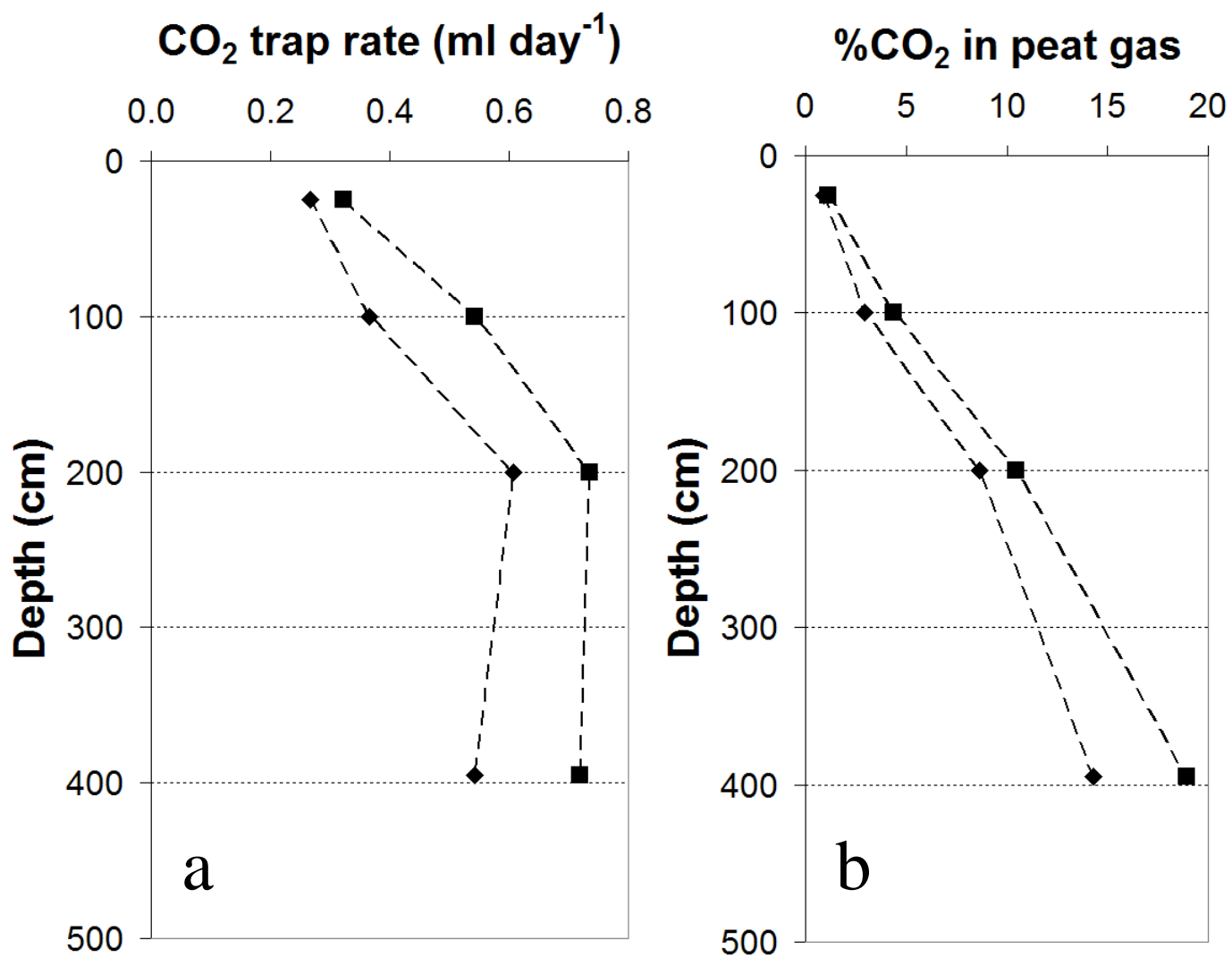
537 Table 2 Carbon isotope results and radiocarbon publication codes for CO₂ collected from the
538 deep peat sampling probes and surface chambers at Langlands Moss, East Kilbride, UK.
539 Radiocarbon results expressed as both %modern and conventional radiocarbon ages (CRA).
540 Sample identifiers differentiate CO₂ from i. different depths in the peat profile (PEAT CO₂), ii.
541 soil surface chambers (collected by passive trapping with molecular sieve; CHAMBER) and, iii.
542 soil surface chamber CO₂ (collected by dynamic trapping with molecular sieve; PUMPED). *NB
543 δ¹³C values represent the actual CO₂ samples recovered and have not been corrected for
544 fractionation during passive trapping.

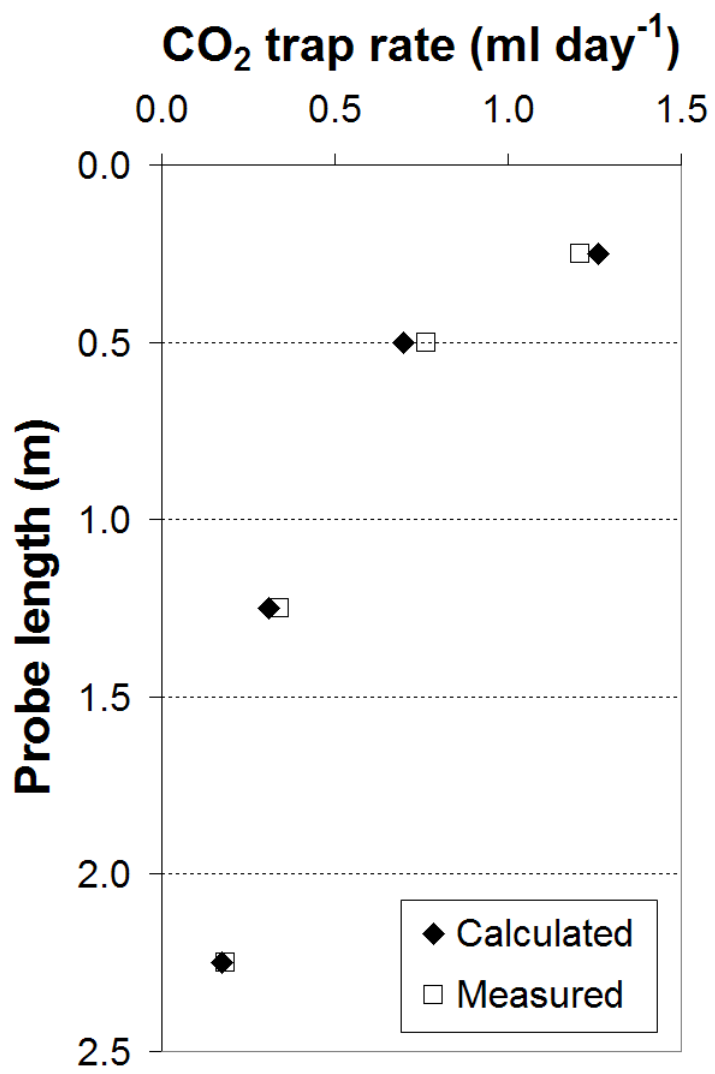
Site	Sample identifier	δ ¹³ C _{VPDB} *	Publication	%modern	CRA (BP)
		± 0.1 ‰	code (SUERC-)	± 1 σ	± 1 σ
A	PEAT CO ₂ 25 cm	-17.5	22362	105.47 ± 0.46	Modern
A	PEAT CO ₂ 100 cm	-6.4	22366	88.56 ± 0.39	976 ± 35
A	PEAT CO ₂ 200 cm	+2.3	22367	72.61 ± 0.43	2571 ± 48
A	PEAT CO ₂ 400 cm	+5.2	22365	60.73 ± 0.48	4006 ± 63
A	CHAMBER A-1	-29.1	22360	108.08 ± 0.50	Modern
A	CHAMBER A-2	-28.1	-	-	-
A	CHAMBER A-3	-27.5	22372	107.36 ± 0.50	Modern
A	PUMPED	-23.8	-	-	-
B	PEAT CO ₂ 25 cm	-14.3	22368	97.91 ± 0.45	169 ± 37
B	PEAT CO ₂ 100 cm	-2.8	22369	81.63 ± 0.39	1631 ± 38
B	PEAT CO ₂ 200 cm	+3.7	22370	71.85 ± 0.43	2656 ± 48
B	PEAT CO ₂ 400 cm	+4.6	22371	61.56 ± 0.48	3897 ± 62
B	CHAMBER B-1	-28.8	22361	107.58 ± 0.50	Modern
B	CHAMBER B-2	-26.8	-	-	-
B	CHAMBER B-3	-25.7	22375	106.51 ± 0.49	Modern
B	PUMPED	-21.9	-	-	-

545 **Figure captions**

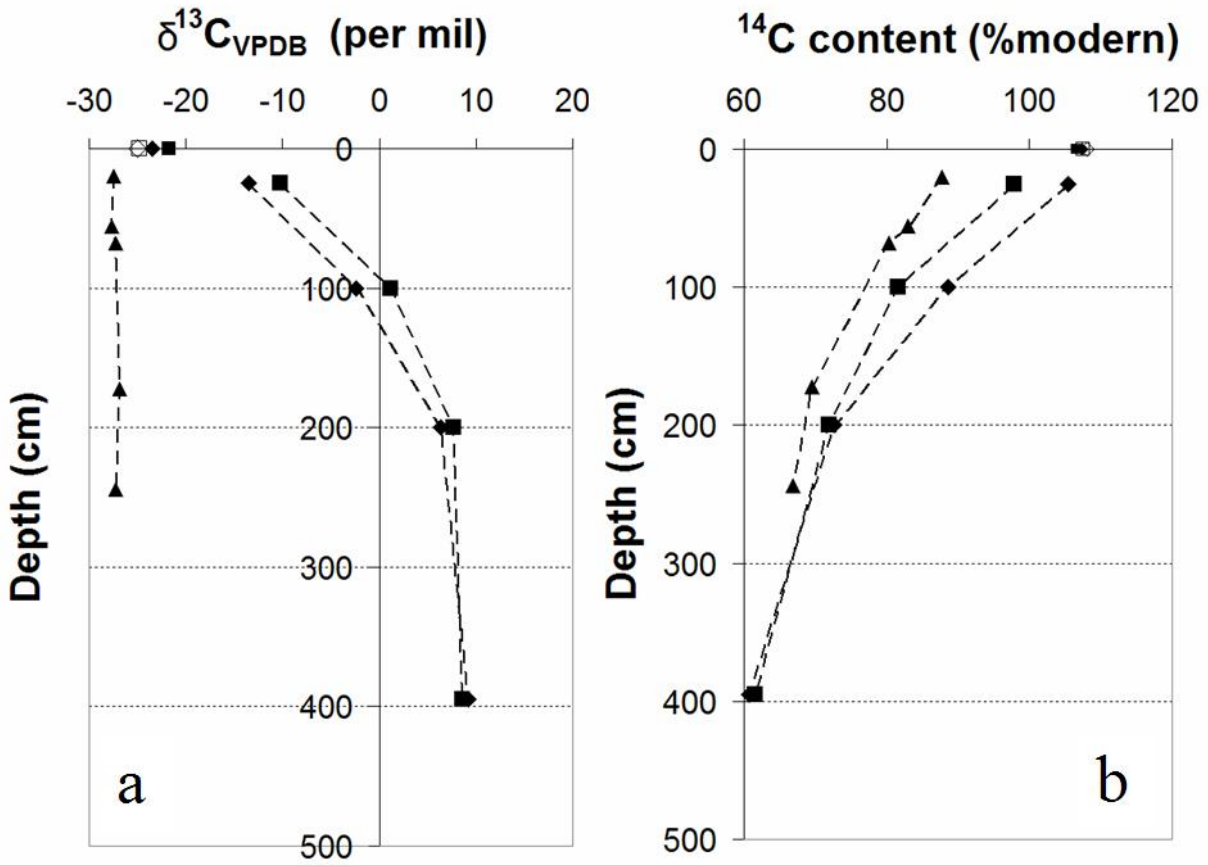
- 546 1. Schematic diagram of a deep peat sampling probe (not to scale). See text for further
547 details.
548
- 549 2. CO₂ trap rate (a) and calculated % CO₂ of peat gas (b) collected by passive sampling with
550 zeolite molecular sieve from the peat profiles at Langlands Moss, East Kilbride, UK. Site
551 A (diamonds) and Site B (squares).
552
- 553 3. CO₂ trap rate for passive sampling probes of different lengths exposed to a fixed
554 atmosphere (~ 24000 ppmv). Comparison of calculated (Fick's Law) and actual measured
555 results.
556
- 557 4. $\delta^{13}\text{C}$ (a) and ^{14}C content (b) of CO₂ collected passively using both sampling probes and
558 surface chambers, at Langlands Moss, East Kilbride, UK. Results of carbon isotope
559 analyses for bulk peat (made during an earlier study at Langlands Moss) are provided for
560 reference (derived from Langdon and Barber, 2003). Note that $\delta^{13}\text{C}$ values have been
561 corrected for fractionation during passive trapping by applying a +4 ‰ correction factor
562 (see text).
563
564
565







Figure



Peat profile

- ◇- Site A } CO_2
- Site B }
- ▲- Peat

CO_2 efflux

- ◇ Chamber A-1
- ◆ Chamber A-3
- Chamber B-1
- Chamber B-3