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Contact CEH NORA team at  
[noraceh@ceh.ac.uk](mailto:noraceh@ceh.ac.uk)

1 **Annual variability in the radiocarbon age and source of dissolved CO<sub>2</sub> in a**  
2 **peatland stream**

3

4 Mark H Garnett, Kerry J Dinsmore and Michael F Billett

5

6 **ABSTRACT**

7 Radiocarbon dating has the capacity to significantly improve our understanding of the aquatic  
8 carbon cycle. In this study we used a new passive sampler to measure the radiocarbon (<sup>14</sup>C)  
9 and stable carbon (δ<sup>13</sup>C) isotopic composition of dissolved CO<sub>2</sub> for the first time in a peatland  
10 stream throughout a complete year (May 2010 – June 2011). The in-stream sampling system  
11 collected time-integrated samples of CO<sub>2</sub> continuously over approximately one month  
12 periods. The rate of CO<sub>2</sub> trapping was proportional to independently measured streamwater  
13 CO<sub>2</sub> concentrations, demonstrating that passive samplers can be used to estimate the time-  
14 averaged dissolved CO<sub>2</sub> concentration of streamwater. While there was little variation and no  
15 clear trend in δ<sup>13</sup>CO<sub>2</sub> values (suggesting a consistent CO<sub>2</sub> source), we found a clear temporal  
16 pattern in the <sup>14</sup>C concentration of dissolved CO<sub>2</sub>. The <sup>14</sup>C age of CO<sub>2</sub> varied from 707±35 to  
17 1210±39 years BP, with the youngest CO<sub>2</sub> in the autumn and oldest in spring/early summer.  
18 Mean stream discharge and <sup>14</sup>C content of dissolved CO<sub>2</sub> were positively correlated. We  
19 suggest that the observed pattern in the <sup>14</sup>C content of dissolved CO<sub>2</sub> reflects changes in its  
20 origin, with older carbon derived from deeper parts of the peat profile contributing  
21 proportionally more gaseous carbon during periods of low stream flow.  
22

23 **Keywords**

24 Carbon dioxide, Radiocarbon, Peatland, Streams, Carbon

25

26 **1. Introduction**

27 Peatland formation has produced a global terrestrial carbon store of approximately the same  
28 size as the current atmospheric carbon pool (Clymo and Bryant, 2008). Considerable research  
29 effort is now being focussed on the effect of man and climatic variability on this important  
30 terrestrial carbon store involving a combination of flux measurements and process-based  
31 studies (e.g. Billett et al., 2010). Drainage waters are increasingly being recognised as  
32 important conduits for carbon release from peatlands, and are now known to represent an  
33 important flux term in the annual carbon balance (Dinsmore et al., 2010; Koehler et al., 2011).

34

35 Organic-rich surface waters draining peatlands are typically acidic and supersaturated with  
36 respect to CO<sub>2</sub> and CH<sub>4</sub> (e.g. Dawson et al., 1995; Billett and Moore, 2008). In these systems  
37 carbon exists in three main forms: POC (particulate organic carbon), DOC (dissolved organic  
38 carbon) and DIC (dissolved inorganic carbon) (Eatherall et al., 1998). For DIC, carbon in  
39 streamwater can exist in the form of carbonate, bi-carbonate, or dissolved CO<sub>2</sub>, the proportion  
40 of which varies with pH and temperature according to the carbonate buffering system (Hope  
41 et al., 1995; Aufdenkampe et al., 2011).

42

43 In streams draining peatlands, where DIC is primarily present as CO<sub>2</sub> due to low pH, CO<sub>2</sub>  
44 supersaturation varies both spatially (Dawson et al., 1995; Dawson et al., 2001) and  
45 temporally (Dinsmore and Billett, 2008; Johnson et al., 2010). Degassing (evasion) of CO<sub>2</sub>  
46 from the water surfaces of peatlands and other saturated carbon-rich systems is known to  
47 represent an important emission pathway connecting the below-ground carbon store to the  
48 atmosphere (Kling et al., 1991; Dinsmore et al., 2011). Consequently, for a better assessment  
49 of the importance of peatland carbon fluxes, and their potential response to change (e.g.  
50 climate and/or management) a greater understanding is required of the size and source of CO<sub>2</sub>  
51 loss via peatland streams.

52

53 Radiocarbon (<sup>14</sup>C) analysis can provide important information on the age and rate that carbon  
54 is cycled through various components of ecosystems. <sup>14</sup>C dating of peat, or the constituents  
55 that form peat, has been widely used to reconstruct the development of peatlands and to  
56 quantify rates of carbon accumulation and loss (e.g. Clymo and Bryant, 2008). <sup>14</sup>C analysis of  
57 waters draining peatlands has largely focussed on the age of the DOC component (e.g. Benner  
58 et al., 2004; Evans et al., 2007). For waters draining intact peatlands, DOC has typically been  
59 found to have <sup>14</sup>C contents that exceed 100 %modern (Tipping et al., 2010), unambiguously  
60 indicating the presence of “bomb-<sup>14</sup>C” (Levin and Hesshaimer, 2000).

61

62 Analysis of the  $^{14}\text{C}$  age of the DIC component (or its gaseous constituent,  $\text{CO}_2$ ) transported by  
63 rivers has previously been undertaken using one of two methods: (1) an indirect method  
64 whereby water samples are collected in the field, returned to the laboratory and the entire DIC  
65 recovered as  $\text{CO}_2$  by “gas-stripping” (e.g. Mayorga et al., 2005), or (2) a direct method  
66 whereby  $\text{CO}_2$  evading from the water surface is captured using a floating chamber and  
67 adsorbed onto a molecular sieve, which can be subsequently processed in the laboratory to  
68 recover the  $\text{CO}_2$  for isotope analysis (Billett et al., 2006; Billett and Garnett, 2010).

69

70 Studies using the chamber method have revealed that in UK peatlands  $\text{CO}_2$  degassed from the  
71 water surface is often derived from a much older source (up to at least 1000 years BP) than  
72 the DOC component, and that its isotopic signature ( $^{14}\text{C}$  and  $\delta^{13}\text{C}$ ) can vary considerably both  
73 temporally and spatially between and within catchments (Billett et al., 2007). This within-  
74 catchment variability in source and age has also been demonstrated for  $\text{CO}_2$  released from  
75 peatland pipes (Billett et al., in press a), which are known to act as important point sources for  
76 greenhouse gas release from peatlands (Dinsmore et al., 2011). In contrast,  $\text{CO}_2$  evaded from  
77 a Finnish stream during the spring thaw was predominantly derived from carbon fixed within  
78 recent decades, as evidenced by the substantial component of bomb- $^{14}\text{C}$  (Billett et al., in press  
79 b). Using the gas-stripping method, Mayorga et al. (2005) showed that the majority of  $\text{CO}_2$   
80 evaded from Amazon rivers was derived from young (< 5 years old) carbon sources.

81

82 Whilst both the direct and indirect methods for determining the  $^{14}\text{C}$  concentration of aquatic  
83  $\text{CO}_2$  have provided valuable insights, they both rely on the collection of samples over short  
84 periods of time. Consequently we currently do not know whether these ‘spot samples’ are  
85 representative of longer timescales or the full hydrograph range. One solution would be to  
86 increase the temporal resolution of sample collection, however, this is time-consuming and  
87 the cost of  $^{14}\text{C}$  analysis is likely to make this approach prohibitive. Recently, a new passive  
88 sampling method has been developed and tested for the collection of  $\text{CO}_2$  for carbon isotope  
89 analysis from a range of environments including soil-respired  $\text{CO}_2$  (Garnett et al., 2009),

90 atmospheric CO<sub>2</sub> (Garnett and Hartley, 2010) and dissolved CO<sub>2</sub> in water-logged peat  
91 (Garnett and Hardie, 2009). The approach is similar to the established passive sampling  
92 methods used to collect time-integrated solute samples in surface waters over periods of  
93 weeks or months (e.g. Vrana et al., 2005; Rozemeijer et al., 2010). The technique is suited for  
94 the collection of samples over extended sampling times (up to several months) and whilst it  
95 has previously been deployed to sample CO<sub>2</sub> from water-saturated soils, it has hitherto not  
96 been employed to sample dissolved CO<sub>2</sub> in stream waters. Here, we report for the first time a  
97 12 month series of carbon isotope (<sup>14</sup>C and δ<sup>13</sup>C) analyses of dissolved CO<sub>2</sub> collected from a  
98 peatland stream using the passive sampling technique. The volume of CO<sub>2</sub> recovered and rate  
99 of CO<sub>2</sub> trapping are also reported. We relate these results to measurements of stream and  
100 climatic conditions and hypothesised that: i) the passive sampling method provides a reliable  
101 method for the collection of dissolved CO<sub>2</sub> from peatland drainage waters for carbon isotope  
102 analysis, and ii) that changes in the isotopic composition of streamwater dissolved CO<sub>2</sub>  
103 provides information on annual variability in source and age.

104

## 105 **2. Methods**

### 106 *2.1. Study site and measurement of site characteristics*

107 Sampling was performed in the Black Burn, a peatland stream draining Auchencorth Moss in  
108 central Scotland (55°47'34 N; 3°14'35W). The catchment has an area of 3.4 km<sup>2</sup>, spans an  
109 altitude range of ~250-300 m asl, and contains 85% peatland with peat depths reaching >5 m  
110 (Dinsmore et al., 2010). The vegetation in the catchment is predominantly a mixture of  
111 grasses and sedges covering a basal layer of mosses associated with a hummock/hollow  
112 microtopography. The dominant bryophytes are *Sphagnum* and *Polytrichum* species and the  
113 main vascular plants *Deschampsia flexuosa*, *Molinia caerulea*, *Festuca ovina*, *Eriophorum*  
114 *angustifolium*, *Eriophorum vaginatum*, *Juncus effusus*, *Juncus squarrosus* and *Calluna*  
115 *vulgaris* (Dinsmore et al., 2009a). The area is the focus of a long-term study of carbon cycling  
116 (Billett et al., 2010; Dinsmore et al., 2010) and is one of the UK Centre for Ecology and  
117 Hydrology's 'Carbon Catchments', with continuous measurement of particulate, dissolved

118 and gaseous forms of aquatic carbon since 2006. Carbon isotopic composition of both  
119 dissolved organic carbon and CO<sub>2</sub> evading from the stream surface (Billett et al., 2006, 2007)  
120 has been previously characterised.

121

122 Discharge in the Black Burn is monitored at 15 minute intervals using an In-Situ Inc Level  
123 Troll<sup>®</sup> pressure transducer and rating curve produced from manual dilution gauging  
124 measurements ( $r^2 = 0.88$ ); stream temperature was also provided by the Level Troll<sup>®</sup> sensor.  
125 Dissolved CO<sub>2</sub> concentrations were calculated from weekly headspace spot samples collected  
126 approximately 10 m downstream from the location of the CO<sub>2</sub> passive samplers throughout  
127 the study period. The headspace method involved equilibration of an ambient air volume (20  
128 ml) with a stream water sample (40 ml) by vigorously shaking in a syringe for one minute at  
129 stream temperature. The equilibrated headspace was then transferred to a separate gas-tight  
130 syringe and analysed, alongside an ambient air sample, using gas chromatography. Dissolved  
131 gas concentrations in the stream water at time of sampling were calculated using Henry's law  
132 (Hope et al., 1995) and expressed in units of ppmv and *ep*CO<sub>2</sub>. Environmental variables  
133 including soil temperature and depth of water table were provided from a  
134 micrometeorological station located ~400 m from the stream sampling point (M. Coyle,  
135 personal communication, 2011).

136

### 137 *2.2. Sampling of dissolved CO<sub>2</sub> using passive samplers*

138 We deployed passive samplers similar in design to those previously used to sample CO<sub>2</sub> from  
139 a range of environments (Garnett and Hardie, 2009; Garnett et al., 2009; Garnett and Hartley,  
140 2010). The samplers were constructed from glass tubing with a central compartment  
141 containing Type 13X zeolite molecular sieve (1/16" pellets, BDH, UK) held in place using  
142 quartz wool, and surrounded on either side by lengths of narrower glass tubing (Fig. 1). The  
143 central compartment was made from glass tubing with dimensions of 70 mm length and 11  
144 mm inner diameter. The ends of the cartridges were built from 100 mm lengths of glass  
145 tubing with inner diameters of 4 mm and 8 mm. Lengths (50 mm) of Tygon tubing (Fisher,

146 UK) were attached to either end of the cartridge, and a plastic clip (WeLoc, Scandinavia  
147 Direct, UK) placed over the Tygon tubing at the wider end to create a seal. At the upstream  
148 end of the sampler (the narrow end; 'inlet') we used a gas permeable hydrophobic filter to  
149 allow gas exchange with the inside of the cartridge but prevent the entry of water. The  
150 hydrophobic filter was constructed from a 5 cm length of Accurrel PP V8/2 HF tubing  
151 (Membrana GmbH, Germany; Gut et al., 1998) pushed onto a 5 cm length of nylon tubing,  
152 which was in turn inserted into the Tygon tubing of the inlet of the sampler. A glass stopper  
153 was used to seal the end of the Accurrel filter, and joins reinforced using a rubber sealant  
154 (Plasti-dip, USA). The resulting samplers were thus completely water-tight, but allowed rapid  
155 gas exchange to occur through the hydrophobic filter. This allowed CO<sub>2</sub> to enter the cartridge  
156 and subsequently be adsorbed onto the molecular sieve. Prior to use, the samplers were  
157 prepared by heating (500 °C) the molecular sieve under vacuum (see Hardie et al., 2005) and  
158 filled with high-purity N<sub>2</sub>. Before and after sampling a plastic clip was also placed across the  
159 Tygon tubing at the inlet of the sampler to prevent ingress of atmospheric CO<sub>2</sub> .

160

161 For deployment at the field site the sampler was protected inside a length of polystyrene pipe,  
162 and attached to a steel 'cradle' using cable ties. Posts were driven into the stream banks (to  
163 avoid disturbance to the stream bed) to which a length of PVC pipe (110 mm inner diameter x  
164 500 mm length) was secured, such that it was permanently submerged in the water, parallel to  
165 stream flow, and located just above the stream bed to allow free flow of water around the  
166 passive sampling system. The pipe was used to house the cartridge containing the passive  
167 sampler during sampling, ensuring that the sampler was consistently held at the same location  
168 and to provide protection from possible damage during high flow periods. Stream water was  
169 free to pass unhindered through the pipe which remained open at both ends (Fig. 1).

170

171 Prior to sampling, the cradle containing the passive sampler was submerged in the stream, the  
172 clip at the inlet removed, and the cradle inserted into the pipe with the inlet of the sampler  
173 pointing upstream. The samplers were left for between 27 and 83 days to accumulate CO<sub>2</sub>,

174 and then retrieved by first sealing the inlet with a clip before removal from the stream, and  
175 returning to the NERC Radiocarbon Facility for processing. A total of nine samples were  
176 collected over a complete year from 28 May 2010 to 2 June 2011, with a hiatus (14 Dec 2010  
177 to 18 January, 2011) when no sampling occurred. Although the reliability of the passive  
178 samplers had previously been demonstrated on several earlier occasions (Garnett et al., 2009;  
179 Garnett and Hardie, 2009; Garnett and Hartley, 2010), we performed a further test by  
180 deploying an additional second passive sampler simultaneously with the final two from the  
181 annual series; reliability of the samplers would be supported if the isotope concentration of  
182 the CO<sub>2</sub> from the additional sampler was equal to the average of that from the two shorter-  
183 term samplers.

184

### 185 *2.3. Measurement of volume of CO<sub>2</sub> recovered and its carbon isotope ( $\delta^{13}\text{C}$ and $^{14}\text{C}$ ) content*

186 Sample CO<sub>2</sub> was recovered from the molecular sieve in the passive samplers by heating (500  
187 °C) followed by cryogenic purification (see Hardie et al., 2005). The total volume of CO<sub>2</sub>  
188 recovered was measured in a calibrated volume using a pressure transducer, and the CO<sub>2</sub>  
189 divided into aliquots for <sup>13</sup>C and <sup>14</sup>C measurement.  $\delta^{13}\text{C}$  (<sup>13</sup>C isotope enrichment relative to  
190 the Vienna PDB standard) was determined using isotope ratio mass spectrometry (VG  
191 Optima, Micromass, UK) at the NERC Radiocarbon Facility. The aliquot of CO<sub>2</sub> for <sup>14</sup>C  
192 analysis was graphitised using Fe/Zn reduction (Slota et al., 1987) and measured by  
193 accelerator mass spectrometry (AMS) at the Scottish Universities Environmental Research  
194 Centre (East Kilbride, UK). <sup>14</sup>C concentrations were determined relative to the oxalic acid  
195 international radiocarbon standard and normalised to a  $\delta^{13}\text{C}$  of -25 ‰ (using the  $\delta^{13}\text{C}$  values  
196 of the recovered CO<sub>2</sub>) to account for mass dependent fractionation effects (Stuiver and  
197 Polach, 1977). Radiocarbon results are expressed as %modern and conventional radiocarbon  
198 age (years BP, where 0 BP = AD 1950). By convention measurement uncertainties for isotope  
199 results are expressed as standard deviations (Stuiver and Polach, 1977). Previous tests have  
200 quantified a small isotopic fractionation that occurs during passive trapping (Garnett et al.,  
201 2009; Garnett and Hardie, 2009) and therefore a correction (+4 ‰) was applied when

202 interpreting the  $\delta^{13}\text{C}$  results; since the  $^{14}\text{C}$  values are by definition normalised to  $\delta^{13}\text{C}$  of -25  
203 ‰ they are unaffected by this fractionation effect.

204

205 Rate of  $\text{CO}_2$  trapping on passive samplers should be directly proportional to the  $\text{CO}_2$   
206 concentration of the environment being sampled as in the following equation based on Fick's  
207 Law (Bertoni et al., 2004):

208

$$209 \quad C_i = (Q_i \times L) / (S \times t \times D_i) \quad (1)$$

210

211 where  $C_i$  represents the  $\text{CO}_2$  concentration of the atmosphere being sampled,  $Q_i$  the volume  
212 of  $\text{CO}_2$  trapped during time  $t$ ,  $D_i$  is the diffusion coefficient of  $\text{CO}_2$  in air, and  $L$  and  $S$  are the  
213 length and cross-sectional area of the sampling probe (between mid points of inlet and  
214 molecular sieve). We used Equation 1 to determine the concentration of dissolved  $\text{CO}_2$  in the  
215 Black Burn during the periods of sample collection, based on the recovered volumes of  $\text{CO}_2$   
216 from passive samplers and their known exposure times.

217

### 218 **3. Results**

#### 219 *3.1 Variability in discharge, temperature and $\text{CO}_2$ concentrations*

220 Mean discharge from the Black Burn was  $54 \text{ L s}^{-1}$  and ranged from  $3 \text{ L s}^{-1}$  to  $1400 \text{ L s}^{-1}$  over  
221 the course of the sampling year (Fig. 2). Due to equipment failure there were two periods  
222 when discharge was not recorded. Mean air temperature was  $8.0^\circ\text{C}$  and ranged from  $-12.0$  to  
223  $24.1^\circ\text{C}$  (Fig. 2). Concentrations of dissolved  $\text{CO}_2$  in the stream (Fig. 3) determined from  
224 weekly spot sampling ranged from 1301 to 7745 ppmv with a mean of 3570 ppmv. These  
225 values represent a range in  $ep\text{CO}_2$  ( $ep$  is defined as excess partial pressure e.g.  $p\text{CO}_2$   
226 water/ $p\text{CO}_2$  atmosphere) from ~3 to 20.

227

#### 228 *3.2 Volume and rate of $\text{CO}_2$ trapped on passive samplers*

229 The volume of CO<sub>2</sub> recovered from the passive samplers (Table 1) ranged from 5.3 ml (27  
230 and 45 day sampling periods) up to 22.4 ml (83 day sampling period), and was highly  
231 positively correlated ( $r^2 = 0.788$ ;  $p < 0.001$ ) with exposure time. The CO<sub>2</sub> trap rate (volume of  
232 CO<sub>2</sub> recovered divided by number of sampling days) ranged from 0.118 to 0.299 ml day<sup>-1</sup>,  
233 with highest rates occurring during summer and lowest during mid-winter, coinciding with  
234 the highest and lowest CO<sub>2</sub> concentrations, respectively. Using Fick's law (Equation 1) the  
235 estimated average CO<sub>2</sub> concentration in the Black Burn, based on the trap rates of the passive  
236 sampler, was  $3336 \pm 229$  (SE) ppmv and therefore similar to the mean value derived from  
237 spot sampling ( $3570 \pm 225$  (SE) ppmv). Throughout the sampling year there was good  
238 agreement between the values of dissolved CO<sub>2</sub> concentration determined from weekly spot  
239 sampling and those calculated from the molecular sieve trap rate (Fig. 3) with an overall  
240 significant positive correlation ( $r^2 = 0.672$ ,  $p < 0.01$ ).

241

### 242 *3.3 Carbon isotope ( $\delta^{13}C$ and $^{14}C$ ) concentration of dissolved carbon dioxide*

243 All passive samplers provided sufficient CO<sub>2</sub> for both  $^{14}C$  and  $\delta^{13}C$  measurement.  
244 Radiocarbon concentration of the dissolved CO<sub>2</sub> ranged from 86.01 to 91.57 %modern  
245 (equivalent to 707 to 1210 years BP; Table 1). There was a trend of increasing  $^{14}C$   
246 concentration in CO<sub>2</sub> from the start of the sampling period (May 2010) to peak levels in  
247 samples collected between September and December 2010. Subsequently, the  $^{14}C$  content of  
248 dissolved CO<sub>2</sub> decreased to that at the start of the time series (Table 1).

249

250 Radiocarbon concentration of the dissolved CO<sub>2</sub> was compared to mean discharge rates  
251 (averaged over the sampling period for each sampler). Due to two gaps in the discharge data,  
252 only results for eight of the ten samplers could be reliably compared (Fig. 4). There was a  
253 positive correlation between discharge and  $^{14}C$  concentration of the dissolved CO<sub>2</sub> ( $r^2 = 0.766$ ,  
254  $p < 0.01$ ). However, one sample (collected 9 September 2010 to 6 October 2010) appeared to  
255 be an outlier, and when removed the correlation between discharge and  $^{14}C$  content of CO<sub>2</sub>  
256 considerably improved ( $r^2 = 0.965$ ,  $p < 0.001$ ). There was no significant correlation between

257 the  $^{14}\text{C}$  results and air temperature. In contrast to the  $^{14}\text{C}$  data,  $\delta^{13}\text{C}$  varied relatively little  
258 during the course of the sampling year (range -24.2 to -23.0 ‰) and was not significantly  
259 correlated with any other measured variables (Table 1).

260

261 The means of the  $^{14}\text{C}$  and  $\delta^{13}\text{C}$  values for the two samples collected consecutively between 4  
262 March 2011 to 21 April 2011 and 21 April 2011 to 2 June 2011 were within measurement  
263 uncertainty ( $2\sigma$ ) of the results for the replicate sampler that was exposed during the same  
264 sampling period (4 March 2011 to 2 June 2011).

265

#### 266 **4. Discussion**

##### 267 *4.1 Reliability of the passive sampler for collecting dissolved $\text{CO}_2$ for $^{14}\text{C}$ analysis.*

268 Passive samplers have been used reliably to trap  $\text{CO}_2$  for monitoring purposes, for example to  
269 provide time-weighted averages for atmospheric  $\text{CO}_2$  concentrations (e.g. Bertoni et al.,  
270 2004). The sampler used in the present study has previously been shown to perform reliably  
271 for sampling and subsequent carbon isotope analysis of  $\text{CO}_2$  recovered from a range of  
272 environments (Garnett et al., 2009; Garnett and Hardie, 2009; Garnett and Hartley, 2010); the  
273 many tests performed in these studies included comparison of replicate field samples and  
274 verification using isotopic standards under controlled laboratory conditions. Indeed, given that  
275 the layers of peatlands beneath the water table have moisture contents of typically  $> 90\%$ , the  
276 tests performed by Garnett and Hardie (2009) have already shown the reliability of the  
277 samplers under similar conditions to this study. We therefore mainly rely on the detailed  
278 method testing carried out by Garnett and Hardie (2009) and others (Garnett et al., 2009;  
279 Garnett and Hartley, 2010), that have demonstrated the reliability of the samplers. However,  
280 the results from the present study also provide additional evidence for the reliability of the  
281 passive sampling method for recovering samples of streamwater dissolved  $\text{CO}_2$  for carbon  
282 isotope analysis.

283

284 Firstly, the dissolved CO<sub>2</sub> concentration determined from the rate of CO<sub>2</sub> trapping in passive  
285 samplers was remarkably similar to the mean of independently determined values from spot  
286 samples (Fig. 3). This is despite the fact that the spot samples were collected at an average  
287 frequency of one per week, whereas the passive samplers were sampling continuously. It is  
288 possible that the frequency of the spot sampling collection meant that periods of high  
289 discharge (Fig. 2) were under-represented, and therefore average CO<sub>2</sub> concentration of the  
290 spot samples would be slightly biased towards periods of lower flow. Dinsmore and Billett  
291 (2008) previously found a strong negative curvilinear relationship between discharge and  
292 dissolved CO<sub>2</sub> concentration ~ 20 m downstream of the current study site (using in-situ CO<sub>2</sub>  
293 sensors with 30 min time resolution). This could explain why a slightly lower annual average  
294 for CO<sub>2</sub> concentration was calculated using the passive samplers compared to the spot  
295 sampling approach. Indeed, discharge during the sampling year on the days when spot  
296 samples were collected was on average 50.28 L s<sup>-1</sup>, compared to 53.98 L s<sup>-1</sup> from the  
297 continuous logger; thus over the sampling year the mean discharge was 7.37 % greater than  
298 when spot samples were collected. If we decrease the mean CO<sub>2</sub> concentration for the spot  
299 samples by the same percentage difference to account for the spot sampling bias to low flows  
300 (i.e. assuming a negative linear relationship over this small range), the CO<sub>2</sub> concentration of  
301 the spot samples becomes 3307 ppm, remarkably similar to the CO<sub>2</sub> concentration calculated  
302 from the passive samplers (3336 ppm).

303

304 The strong correlation between the CO<sub>2</sub> concentrations derived from spot samples compared  
305 to passive samplers shows that the rate of CO<sub>2</sub> trapping was related to the CO<sub>2</sub> concentration  
306 of the environment being sampled. This is fundamentally important for the collection of  
307 representative samples. The rate of CO<sub>2</sub> trapping in the samplers appears to have been  
308 unaffected by the length of exposure time, since the latter varied considerably (from 27 to 83  
309 days) throughout the sampling year. This indicates that the sampling capacity of the passive  
310 samplers was not exceeded (Garnett et al. (2009) found that the capacity of the sieves was at  
311 least 100 ml CO<sub>2</sub>). It should however be noted that in the replicated samples at the end of the

312 annual series, that the summed volume (19.7 ml) recovered from the two short-period samples  
313 (4 March to 21 April 2011, and 21 April to 2 June 2011) was slightly less than the volume  
314 (22.4 ml) recovered from the single sampler that was exposed for the entire period (4 March  
315 to 2 June 2011). Previous tests of the passive sampler have generally shown closer agreement  
316 in the volumes of CO<sub>2</sub> recovered from replicate samplers (e.g. Garnett et al., 2009). Clearly,  
317 we can discount the possibility that the longer-term sampler was trapping CO<sub>2</sub> less efficiently  
318 due to it becoming saturated with either CO<sub>2</sub> or H<sub>2</sub>O, since this sampler had the greater CO<sub>2</sub>  
319 volume. While we aimed to place replicate samplers as close to each other as possible in the  
320 stream, there may have been slight differences in the concentration of CO<sub>2</sub> at the locations  
321 where these samplers were deployed (using Equation 1 we calculate that a difference of ~ 460  
322 ppm (i.e. < 14 %) in streamwater CO<sub>2</sub> concentration would explain the different volumes  
323 recovered). Alternatively, part of the discrepancy could be due to small differences in the  
324 dimensions of passive samplers, for example, a difference in the distance between the gas  
325 inlet and molecular sieve of just 1 cm would have resulted in a difference in the volume of  
326 CO<sub>2</sub> trapped in the 83 day sample of ~ 1 ml. Clearly, if the passive samplers are to be used to  
327 more accurately quantify CO<sub>2</sub> concentrations in streamwater further investigation of this  
328 discrepancy is required. However, it should be reiterated that the main purpose of this study  
329 was to measure  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  and not CO<sub>2</sub> concentration, and that these were unaffected by the  
330 above mentioned issues. It is also important to note that when carbon isotope values for these  
331 replicate samples were combined, both the  $^{13}\text{C}$  and  $^{14}\text{C}$  values from the short period samplers  
332 were within measurement uncertainty (2  $\sigma$ ) of the results for the long period sample,  
333 supporting the earlier studies that demonstrated the reliability of the samplers for isotopic  
334 determinations.

335

#### 336 *4.2 Carbon isotope ( $^{14}\text{C}$ and $\delta^{13}\text{C}$ ) composition of dissolved CO<sub>2</sub>.*

337 We found very little variation in the  $\delta^{13}\text{C}$  of streamwater dissolved CO<sub>2</sub> collected in the  
338 passive samplers over the course of the sampling year, and no clear temporal pattern or  
339 significant correlations with variables such as flow or temperature. After correction of the

340 results for fractionation during passive trapping (see Methods),  $\delta^{13}\text{C}$  ranged from -20.2 to -  
341 19.0 ‰. This range of values is similar to earlier measurements of evaded  $\text{CO}_2$  from the Black  
342 Burn collected using a floating chamber; Billett et al. (2006) reported values of  $\sim$  -21.6 to -  
343 21.0 ‰ and Billett et al. (2007) values of -26.5 to -18.3 ‰. The lack of a clear pattern in the  
344 annual series or correlations with other variables means that alone, the series of  $\delta^{13}\text{C}$  values is  
345 of limited use in unravelling the carbon dynamics at this site, other than to say that the values  
346 themselves could result from a mixture of sources, including dissolved  $\text{CO}_2$  from shallow or  
347 deep peat, and with potentially a small contribution from a weathering source. The lack of  
348 variation in the values over the 12 month period may suggest that hydrological flow paths  
349 within the catchment are delivering  $\text{CO}_2$  to the stream from a source area/areas with a  
350 consistent  $\delta^{13}\text{C}$  value. Alternatively, the results may partly reflect the time-integrated  
351 sampling method, which in some situations could be a disadvantage of the technique.  
352 Although our results clearly indicate that no seasonal pattern in  $\delta^{13}\text{C}$  existed, we cannot rule  
353 out the possibility that significant variability such as that observed by Billett et al. (2007)  
354 exists across shorter time scales i.e. at a diurnal level or in response to short term storm  
355 events. But as long as prior consideration is given to the scale of variability being targeted,  
356 and the length of time over which integration occurs is adjusted to suit, the smoothing which  
357 occurs due to time integration is not necessarily a disadvantage.

358

359 In contrast, the  $^{14}\text{C}$  values of dissolved  $\text{CO}_2$  collected from this peatland stream using the  
360 passive samplers showed a clear pattern over the course of the year and were strongly  
361 correlated with stream discharge (Fig. 4). The  $^{14}\text{C}$  age of the dissolved  $\text{CO}_2$  ranged from 1210  
362 to 707 years BP, and again was similar to the age of evaded  $\text{CO}_2$  collected from the Black  
363 Burn in previous studies. For example, Billett et al. (2006) reported  $^{14}\text{C}$  ages of 1454 to 852  
364 years BP for samples collected at two locations along the Black Burn on the same day, and  
365 Billett et al. (2007) gave an age range from 1127 years BP to modern (104.58 %modern) for  
366 samples collected at two sites along the Black Burn on four seasonal sampling occasions; of  
367 these two sites, the one nearest our sampling point had a range of  $^{14}\text{C}$  ages of 312 to 1127

368 years BP. These results broadly imply that the age of CO<sub>2</sub> evaded at this site differs little from  
369 the streamwater dissolved CO<sub>2</sub>; this concurs with the results of Billett and Garnett (2010) who  
370 for the same site found similar <sup>14</sup>C values for evaded CO<sub>2</sub> and dissolved CO<sub>2</sub> (derived from  
371 <sup>14</sup>C analysis of total streamwater DIC) when samples were collected concurrently (e.g. for site  
372 A10 on two separate occasions, evasion/DIC were respectively, 759/714 years BP, and  
373 940/890 years BP).

374

375 The series of <sup>14</sup>C measurements of dissolved CO<sub>2</sub> shows a general pattern of increasing <sup>14</sup>C  
376 concentrations from May, to greatest <sup>14</sup>C-enrichment in the September samples, followed by a  
377 progressive decline and return to the lowest <sup>14</sup>C levels the following May (Fig. 4). The <sup>14</sup>C  
378 values imply that the dissolved CO<sub>2</sub> in streamwater contains a greater proportion of younger  
379 carbon in autumn and early winter, compared to the rest of the year. An obvious source for  
380 younger carbon in peatlands is vegetation; CO<sub>2</sub> with a contemporary <sup>14</sup>C signal (~104.5  
381 %modern at the time of this study; Levin et al., 2008) is fixed through photosynthesis and  
382 released into the soil via plant respiration, root exudates or litter decomposition. However, it  
383 seems unlikely that plant activity or CO<sub>2</sub> mineralised from recently deposited plant litter or  
384 surface peat can explain the pattern of <sup>14</sup>CO<sub>2</sub> in the streamwater in the annual series, since we  
385 would expect greatest plant activity and/or greatest decay of fresh litter/surface peat during  
386 the summer season when temperatures were highest; in fact the <sup>14</sup>C results suggest greatest  
387 contributions from younger carbon much later (September-December). There could be a time  
388 delay between CO<sub>2</sub> production and transfer to the stream as has been reported for DOC in  
389 peatland sites (Clark et al., 2005; Dawson et al. 2011). Regression analysis of CO<sub>2</sub>  
390 concentrations in soils and associated surface waters have found that introducing lag times of  
391 <1 day to 14 days improved the modelling of CO<sub>2</sub> cycling in aquatic systems (Hope et al.  
392 2004; Dinsmore et al. 2009b). However, to explain the pattern of our <sup>14</sup>CO<sub>2</sub> results the time  
393 delay would need to be much greater than this (and greater than the 4-6 weeks reported for  
394 DOC). It further seems unlikely that a simple time delay can explain the pattern of <sup>14</sup>CO<sub>2</sub>  
395 because there was no significant correlation between mean air temperature and %modern of

396 dissolved CO<sub>2</sub> (which would be expected to correlate even with a time delay).  
397  
398 Instead, a strong correlation was observed between the <sup>14</sup>C content of the dissolved CO<sub>2</sub> and  
399 stream discharge, such that there was a greater proportion of younger carbon in the dissolved  
400 CO<sub>2</sub> during sampling periods when discharge was greatest (Fig. 4). Previous studies have  
401 shown using supporting geochemical measurements (e.g. Ca concentrations; Tipping et al.,  
402 2010) that streams draining peats can contain a significant groundwater signature. Given that  
403 groundwater that has passed through carbonate geology is likely to contain some ancient (<sup>14</sup>C-  
404 dead) dissolved CO<sub>2</sub>, an explanation for the correlation between the <sup>14</sup>C content of  
405 streamwater dissolved CO<sub>2</sub> and discharge in our results, could be a change in the proportion  
406 of groundwater-derived CO<sub>2</sub>. Thin limestone bands, within a dominantly sandstone-shale  
407 sequence are known to occur beneath the peat and fluvioglacial drift in the Auchencorth Moss  
408 catchment (Dinsmore et al., 2010) and are a potential source of groundwater-derived CO<sub>2</sub> to  
409 the stream system. If for example, streamwater had a constant groundwater component, but  
410 changes in discharge resulted from the incorporation of different levels of surface runoff or  
411 water from the surface layers of peat, then we would expect to find a positive correlation  
412 between discharge and the <sup>14</sup>C content of the dissolved CO<sub>2</sub>. This is similar to what we have  
413 observed. However, given the known extremes in the δ<sup>13</sup>C values between a geological CO<sub>2</sub>  
414 source (~0 ‰) and an organic-derived (C3 plants) source (~ -30 to -25 ‰), we would expect  
415 based on mass balance to also find a correlation between streamwater δ<sup>13</sup>C and discharge. The  
416 fact that we do not see this relationship, and if anything, δ<sup>13</sup>C becomes more enriched at  
417 higher flows (converse to what would be expected), suggests that the pattern in <sup>14</sup>C of  
418 dissolved CO<sub>2</sub> is not a result of differences in the proportion of groundwater-derived CO<sub>2</sub>. We  
419 do not preclude a groundwater contribution to the streamwater at our site, but suggest that  
420 other processes are more likely to be responsible for the observed annual pattern in the <sup>14</sup>C  
421 content of dissolved CO<sub>2</sub>.  
422

423 It is well known that intact peatlands generally exhibit decreasing  $^{14}\text{C}$ -enrichment in the peat  
424 profile with depth which reflects the increasing age of deeper peat (e.g. Clymo and Bryant,  
425 2008). Studies have shown that in these peat profiles, large volumes of  $\text{CO}_2$  exist in horizons  
426 particularly below the water table, which usually refers to depths greater than 10-30 cm.  
427 Clymo and Bryant (2008) and others (Charman et al., 1999; Garnett and Hardie, 2009; Billett  
428 et al. in press b) have shown that the dissolved  $\text{CO}_2$  in peat profiles also increases in age with  
429 depth (although is typically younger than the surrounding peat). Studies of peatland  
430 hydrology have also shown that in periods of high precipitation and/or low evapo-  
431 transpiration, water tables are usually within a few centimetres of the peat surface, but that  
432 during relative droughts can fall considerably. At the meteorological station on Auchencorth  
433 Moss ~ 400 m from our passive sampling site, average water table depth during the sampling  
434 year was 5 cm, and fell to a maximum depth of 37 cm in July 2010. Clymo and Bryant (2008)  
435 note that the hydraulic conductivity of peats is generally higher at the surface and declines  
436 with depth. Thus, during periods when discharge in streams draining peats is highest, it is  
437 likely that the water table across the catchment will be close to the peat surface, and since  
438 hydraulic conductivity is greatest in the surface peat, it is reasonable to expect that a  
439 proportionally greater amount of the stream discharge is represented by water that has passed  
440 through the surface layers. In contrast, during periods of relative drought, stream discharge is  
441 lower and water tables are set relatively deeper in the peat profile. Assuming that peatland  
442 water acquires  $\text{CO}_2$  with a  $^{14}\text{C}$  signature that reflects the depths in which it has moved  
443 through, then we would expect that during periods of high stream flow that the streamwater  
444 would contain a proportionally greater amount of water from nearer the peat surface or from  
445 overland flow. Since  $\text{CO}_2$  derived from the peat surface will be relatively  $^{14}\text{C}$ -enriched (and  
446 younger), we would expect a positive relationship between discharge and the  $^{14}\text{C}$  content of  
447 streamwater dissolved  $\text{CO}_2$ , which we found.

448

449 Although the above interpretation explains the observed positive correlation between  $^{14}\text{C}$   
450 concentration in the dissolved  $\text{CO}_2$  and stream discharge, we found  $\delta^{13}\text{CO}_2$  was unrelated to

451 annual changes in stream discharge. Clymo and Bryant (2008), Steinmann et al. (2008) and  
452 Garnett and Hardie (2009) have all shown that  $\delta^{13}\text{C}$  of dissolved  $\text{CO}_2$  in peat profiles varies  
453 considerably, with a trend of increasing  $^{13}\text{C}$ -enrichment with depth as a consequence of  
454 anaerobic decomposition. However, since the zone of water table fluctuation at this site and  
455 others (e.g. Tipping et al., 2010) is typically restricted to only a few 10's of centimetres in the  
456 surface layers of the peat profile, the depth-related changes in  $\delta^{13}\text{CO}_2$  in the peat water are  
457 unlikely to be more than a few per mil. Therefore, we would not expect to observe a  
458 correlation between  $\delta^{13}\text{C}$  of streamwater-dissolved  $\text{CO}_2$  and discharge.

459

460 Studies (e.g. Clymo and Bryant, 2008; Steinmann et al., 2008; Garnett and Hardie, 2009) have  
461 also shown that the concentration of dissolved  $\text{CO}_2$  in peats increases with depth. Therefore, if  
462 deeper layers are responsible for contributing proportionally more  $\text{CO}_2$  to stream flow during  
463 periods of low discharge, we would also expect that the  $\text{CO}_2$  concentration in the streamwater  
464 would be higher in periods of low flow. We indeed found this to be the case, with a strong  
465 negative correlation observed between discharge and  $\text{CO}_2$  concentration in streamwater (Fig.  
466 5); Dinsmore and Billett (2008) have previously reported a similar negative  $\text{CO}_2$   
467 concentration-discharge relationship for the study stream, Black Burn.

468

469 If linear regression is applied to the stream discharge and  $^{14}\text{CO}_2$  results we obtain the equation  
470  $y = 0.0607x + 85.607$  ( $r^2 = 0.766$ ,  $p < 0.01$ ), where  $y = ^{14}\text{C} \text{ \%modern}$  and  $x = \text{discharge}$  (Fig.  
471 6). Therefore, the intercept shows that when discharge is zero, the  $^{14}\text{C}$  content of the dissolved  
472  $\text{CO}_2$  is 85.6 %modern (equivalent to  $\sim 1250$  years BP). This may imply that there is a baseline  
473 source of  $\text{CO}_2$  to the stream, representing the age of the  $\text{CO}_2$  that enters the stream when  
474 contributions from younger surface layers are insignificant. At two other Scottish sites,  $\text{CO}_2$   
475 of approximately this age was found to occupy depths in the peat profile of 1 m (Garnett and  
476 Hardie, 2009) and 2 m (Clymo and Bryant, 2008), which may imply that much of the baseline  
477 flow of the Black Burn is derived from similar depths. However, water table depth at  
478 Auchencorth Moss only fell to a maximum depth of 37 cm below the surface during the

479 sampling year, a depth where presumably CO<sub>2</sub> dissolved in the peat water would be much  
480 younger; this therefore suggests that even under baseflow conditions streamwater dissolved  
481 CO<sub>2</sub> is likely to be derived from a range of depths (but with an average age of ~ 1250 years  
482 BP). The <sup>14</sup>C content of the dissolved CO<sub>2</sub> under baseflow conditions implied from the  
483 intercept also indicates that geological sources cannot represent a major component of the  
484 streamwater dissolved CO<sub>2</sub> (otherwise we would have expected the <sup>14</sup>C content of dissolved  
485 CO<sub>2</sub> to be closer to 0 %modern). This is in contrast to the suggestion by Billett et al. (2007)  
486 that weathering of carbonate may provide a significant contribution to dissolved CO<sub>2</sub> to the  
487 Black Burn.

488

489 It was notable that the correlation between stream discharge and <sup>14</sup>C content of dissolved CO<sub>2</sub>  
490 improved considerably after the removal of an outlier. While it would be wrong to draw  
491 substantial interpretations from a single data-point, it is perhaps worth commenting that for  
492 the sample collected between September to October the <sup>14</sup>C content of the dissolved CO<sub>2</sub> was  
493 considerably higher than expected based on the discharge values. Net ecosystem exchange  
494 measurements made using an eddy covariance system within the catchment show a strong  
495 seasonal cycle in vegetation productivity (Billett et al., 2004). The <sup>14</sup>C outlier identified could  
496 therefore represent a flush of young carbon being released into the drainage water at the end  
497 of the growth period and perhaps merits further investigation.

498

## 499 **5. Conclusions**

500 The present study has demonstrated the value of a new passive sampling method for the  
501 collection of dissolved CO<sub>2</sub> from streamwater. Our results support earlier tests used to  
502 validate and apply the method in the field environment (Garnett et al., 2009; Garnett and  
503 Hardie, 2009; Garnett and Hartley, 2010). A clear benefit of the method is that the recovered  
504 sample is composed of CO<sub>2</sub> collected continuously throughout the sampling period, and  
505 therefore is not vulnerable to under-sampling short-term events such as floods, when most  
506 dissolved CO<sub>2</sub> is transported at these sites (Dinsmore and Billett, 2008). While we chose to

507 deploy the method to investigate the time-series of dissolved CO<sub>2</sub> in our study, the simplicity  
508 of the technique and minimal infrastructure requirements (e.g. it requires no external power)  
509 means that it could also be conveniently used, for example, to investigate changes in the  
510 isotopic composition of dissolved CO<sub>2</sub> as it is transported from headwater source to sea (e.g.  
511 Dawson et al., 2009).

512

513 The δ<sup>13</sup>C value of streamwater dissolved CO<sub>2</sub> collected using the passive samplers varied only  
514 slightly over the study year, indicating relatively little change in the source of the CO<sub>2</sub>. <sup>14</sup>C  
515 analysis of the CO<sub>2</sub> confirmed the results of earlier studies at the site and demonstrated the  
516 release of old CO<sub>2</sub> from this peatland stream. Unlike the δ<sup>13</sup>C results, the <sup>14</sup>C values for  
517 dissolved CO<sub>2</sub> showed a clear seasonal pattern, with the oldest CO<sub>2</sub> being transported by the  
518 stream in spring/early summer. Based on the above observations, and a positive correlation  
519 between the <sup>14</sup>C age of dissolved CO<sub>2</sub> and discharge, we conclude that although total CO<sub>2</sub> in  
520 this peatland stream is likely derived from a range of peat depths, shallower/younger peat  
521 layers contribute greater amounts of CO<sub>2</sub> during periods of high discharge, as a result of a  
522 greater proportion of streamwater having passed through shallower peat. The method clearly  
523 has the potential to make a significant contribution to our understanding of CO<sub>2</sub> sources and  
524 transport processes in a range of different soil-stream systems.

525

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530

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645

646 **Figure Captions**

647

648 **Fig. 1** Schematic diagram illustrating how the passive samplers were deployed in the Black  
649 Burn.

650

651 **Fig. 2** Discharge from the Black Burn and air temperature (measured ~ 400 m from the  
652 stream sampling point) over the course of the sampling year from May 2010 to June 2011.

653

654 **Fig. 3** Concentration of dissolved CO<sub>2</sub> in the Black Burn from May 2010 to June 2011  
655 determined by i) continuous trapping using passive samplers and ii) spot sampling of stream  
656 water. CO<sub>2</sub> concentration determined for the passive samplers based on the CO<sub>2</sub> trap rate and  
657 Fick's law (see text). Mean, min and max values for spot samples reflect the sampling periods  
658 of the associated passively collected sample.

659

660 **Fig. 4** Mean discharge ( $\pm$  SE) of the Black Burn and <sup>14</sup>C content of dissolved CO<sub>2</sub> ( $\pm$  1  $\sigma$ )  
661 over the sampling year from May 2010 to June 2011, showing increased <sup>14</sup>C content of CO<sub>2</sub> at  
662 times of greater discharge. Using all data points resulted in a positive correlation ( $r^2 = 0.766$ ;  $p$   
663  $< 0.01$ ;  $n = 8$ ) which improved considerably when the September 2010 sample was omitted ( $r^2$   
664  $= 0.965$ ;  $p < 0.001$ ;  $n = 7$ ).

665

666 **Fig. 5** Mean discharge of the Black Burn and CO<sub>2</sub> concentration determined from spot  
667 samples ( $\pm$  SE). Mean values for both discharge and CO<sub>2</sub> concentration reflect the sampling  
668 periods of the associated passively collected sample. There was a strong negative correlation  
669 between discharge and CO<sub>2</sub> concentration ( $r^2 = 0.855$ ;  $p < 0.001$ ;  $n=8$ ; note 2<sup>nd</sup> y-axis is  
670 reversed).

671

672 **Fig. 6** Radiocarbon concentration of dissolved CO<sub>2</sub> ( $\pm 1 \sigma$ ) versus mean discharge ( $\pm$  SE) of  
673 the Blackburn for samples collected over the sampling year from May 2010 to June 2011.  
674 Mean values for discharge reflect the sampling periods of the associated passively collected  
675 <sup>14</sup>CO<sub>2</sub> sample.

676 Fig. 1

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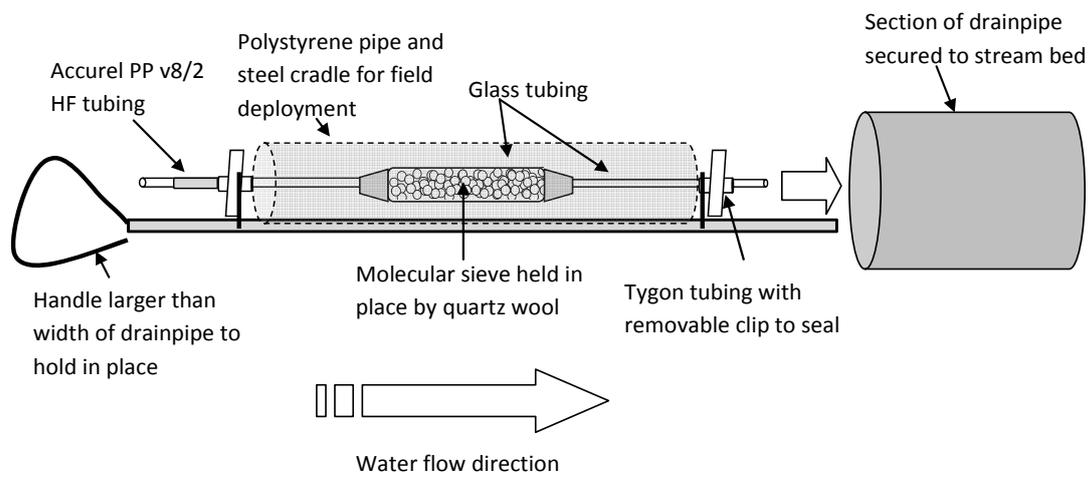
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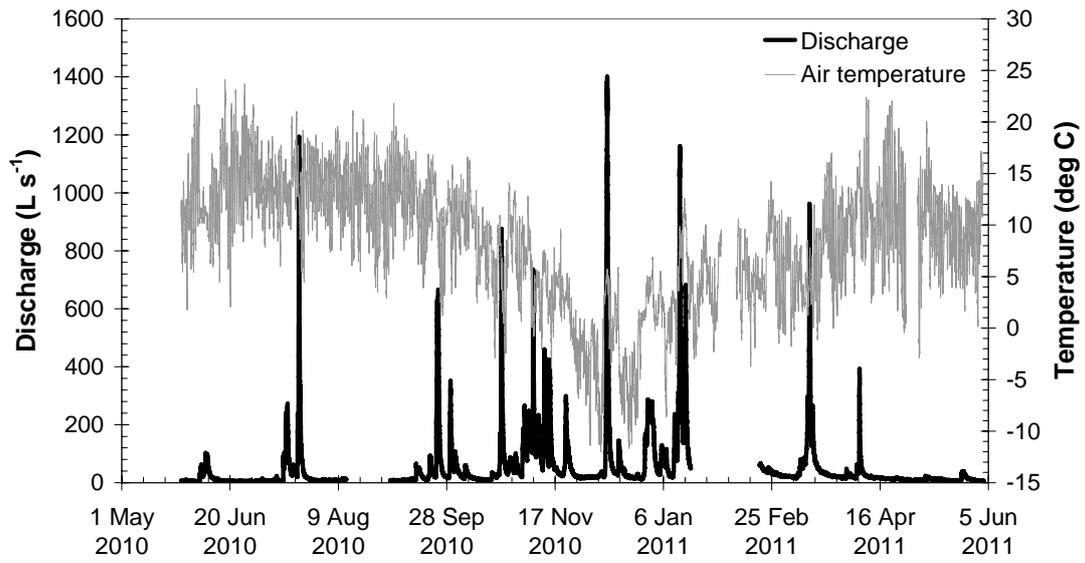
684 Fig. 2

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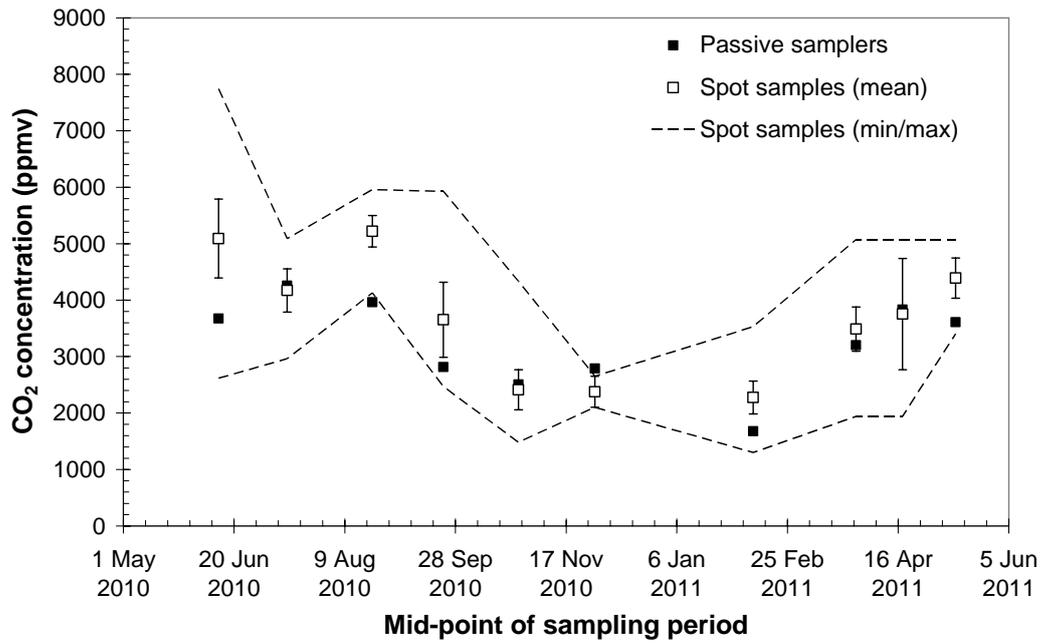
690 Fig. 3

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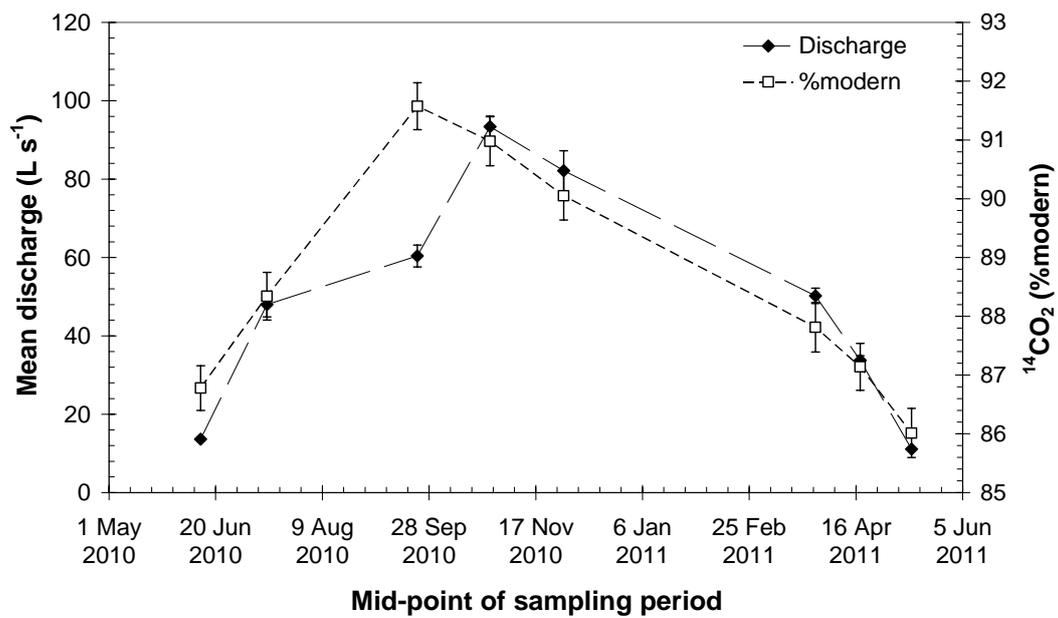
696 Fig.4

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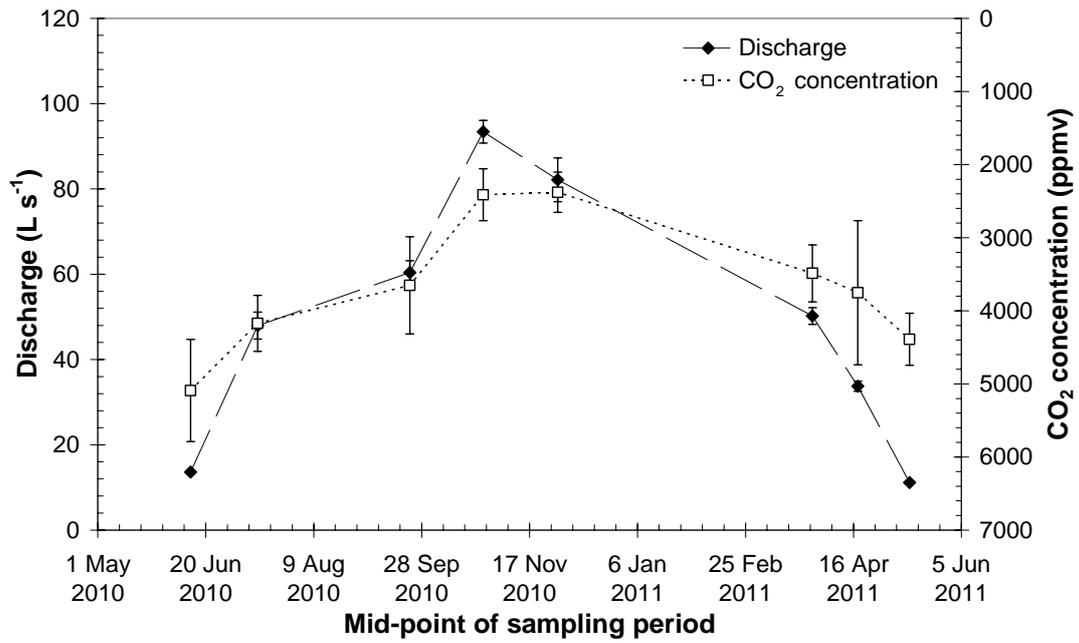
702 Fig. 5

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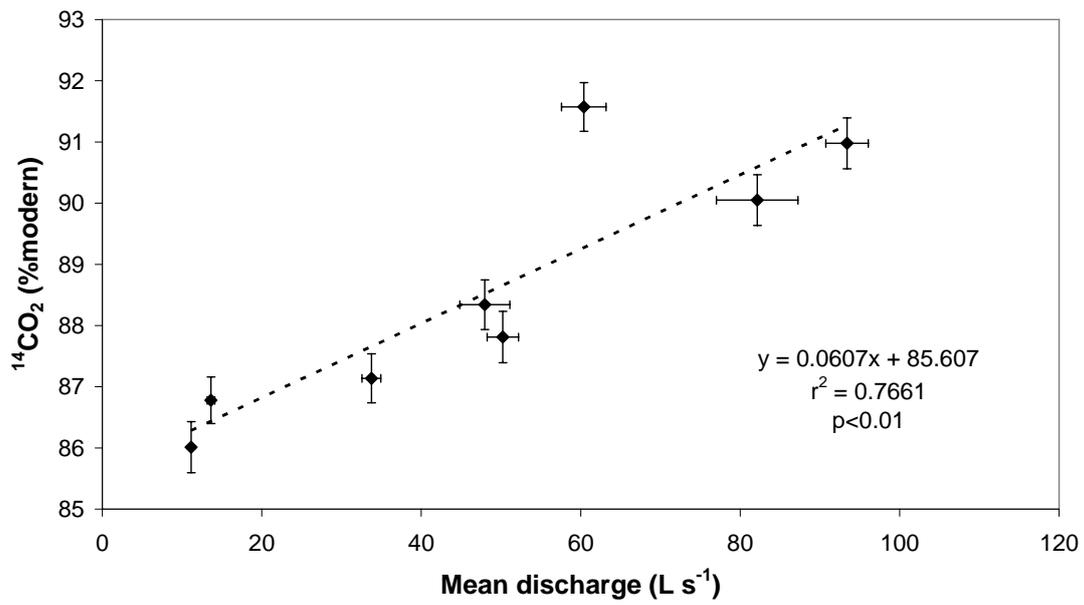
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708 Fig. 6

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