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1 **Annual variability in the radiocarbon age and source of dissolved CO$_2$ in a**

2 **peatland stream**

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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 (^{14}C)
9 and stable carbon (δ^{13}C) isotopic composition of dissolved CO$_2$ 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$_2$ continuously over approximately one month
12 periods. The rate of CO$_2$ trapping was proportional to independently measured streamwater
13 CO$_2$ concentrations, demonstrating that passive samplers can be used to estimate the time-
14 averaged dissolved CO$_2$ concentration of streamwater. While there was little variation and no
15 clear trend in δ^{13}CO$_2$ values (suggesting a consistent CO$_2$ source), we found a clear temporal
16 pattern in the ^{14}C concentration of dissolved CO$_2$. The ^{14}C age of CO$_2$ varied from 707$\pm$35 to
17 1210$\pm$39 years BP, with the youngest CO$_2$ in the autumn and oldest in spring/early summer.
18 Mean stream discharge and ^{14}C content of dissolved CO$_2$ were positively correlated. We
19 suggest that the observed pattern in the ^{14}C content of dissolved CO$_2$ 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_2 and CH_4 (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_2, 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_2 due to low pH, CO_2

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_2

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_2

51 loss via peatland streams.

52

53 Radiocarbon (^{14}C) analysis can provide important information on the age and rate that carbon

54 is cycled through various components of ecosystems. ^{14}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). ^{14}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 ^{14}C contents that exceed 100 % modern (Tipping et al., 2010), unambiguously

60 indicating the presence of "bomb-^{14}C" (Levin and Hesshaimer, 2000).

61

62   Analysis of the ^{14}C age of the DIC component (or its gaseous constituent, 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 CO_2 by "gas-stripping" (e.g. Mayorga et al., 2005), or (2) a direct method

66   whereby 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 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 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}C and $\delta^{13}C$) 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 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, 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]C (Billett et al., in press

79   b). Using the gas-stripping method, Mayorga et al. (2005) showed that the majority of 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}C concentration of aquatic

83   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}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 CO_2 for carbon isotope

89   analysis from a range of environments including soil-respired CO_2 (Garnett et al., 2009),

90   atmospheric CO_2 (Garnett and Hartley, 2010) and dissolved CO_2 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_2 from water-saturated soils, it has hitherto not

96   been employed to sample dissolved CO_2 in stream waters. Here, we report for the first time a

97   12 month series of carbon isotope (^{14}C and $\delta^{13}C$) analyses of dissolved CO_2 collected from a

98   peatland stream using the passive sampling technique. The volume of CO_2 recovered and rate

99   of CO_2 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_2 from peatland drainage waters for carbon isotope

102   analysis, and ii) that changes in the isotopic composition of streamwater dissolved CO_2

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 (55º47'34 N; 3º14'35W). The catchment has an area of 3.4 km^2, 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_2 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® 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® sensor.

125 Dissolved CO_2 concentrations were calculated from weekly headspace spot samples collected

126 approximately 10 m downstream from the location of the CO_2 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 epCO$_2$. 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_2 using passive samplers*

138 We deployed passive samplers similar in design to those previously used to sample CO_2 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_2 to enter the cartridge

156 and subsequently be adsorbed onto the molecular sieve. Prior to use, the samplers were

157 prepared by heating (500 ^{o}C) the molecular sieve under vacuum (see Hardie et al., 2005) and

158 filled with high-purity N_2. 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_2 .

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_2,

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_2 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_2 recovered and its carbon isotope ($\delta^{13}C$ and ^{14}C) content*

186 Sample CO_2 was recovered from the molecular sieve in the passive samplers by heating (500

187 ^{o}C) followed by cryogenic purification (see Hardie et al., 2005). The total volume of CO_2

188 recovered was measured in a calibrated volume using a pressure transducer, and the CO_2

189 divided into aliquots for ^{13}C and ^{14}C measurement. $\delta^{13}C$ (^{13}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_2 for ^{14}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). ^{14}C concentrations were determined relative to the oxalic acid

195 international radiocarbon standard and normalised to a $\delta^{13}C$ of -25 ‰ (using the $\delta^{13}C$ values

196 of the recovered CO_2) 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 $\delta^{13}C$ results; since the ^{14}C values are by definition normalised to $\delta^{13}C$ of -25

203 ‰ they are unaffected by this fractionation effect.

204

205 Rate of CO_2 trapping on passive samplers should be directly proportional to the 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 $$Ci = (Qi \times L) / (S \times t \times Di) \qquad\qquad (1)$$

210

211 where Ci represents the CO_2 concentration of the atmosphere being sampled, Qi the volume

212 of CO_2 trapped during time t, Di is the diffusion coefficient of 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 CO_2 in the

215 Black Burn during the periods of sample collection, based on the recovered volumes of CO_2

216 from passive samplers and their known exposure times.

217

218 **3. Results**

219 *3.1 Variability in discharge, temperature and CO_2 concentrations*

220 Mean discharge from the Black Burn was 54 L s^{-1} and ranged from 3 L s^{-1} to 1400 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°C and ranged from -12.0 to

223 24.1°C (Fig. 2). Concentrations of dissolved 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$$CO_2$ (ep is defined as excess partial pressure e.g. $p$$CO_2$

226 water/$p$$CO_2$ atmosphere) from ~3 to 20.

227

228 *3.2 Volume and rate of CO_2 trapped on passive samplers*

- 8 -

229 The volume of CO_2 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_2 trap rate (volume of

232 CO_2 recovered divided by number of sampling days) ranged from 0.118 to 0.299 ml day^{-1},

233 with highest rates occurring during summer and lowest during mid-winter, coinciding with

234 the highest and lowest CO_2 concentrations, respectively. Using Fick's law (Equation 1) the

235 estimated average CO_2 concentration in the Black Burn, based on the trap rates of the passive

236 sampler, was 3336 ± 229 (SE) ppmv and therefore similar to the mean value derived from

237 spot sampling (3570 ± 225 (SE) ppmv). Throughout the sampling year there was good

238 agreement between the values of dissolved CO_2 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_2 for both ^{14}C and $\delta^{13}C$ measurement.

244 Radiocarbon concentration of the dissolved CO_2 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_2 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_2 decreased to that at the start of the time series (Table 1).

249

250 Radiocarbon concentration of the dissolved CO_2 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_2 ($r^2 = 0.766$,

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_2

256 considerably improved ($r^2 = 0.965$, $p < 0.001$). There was no significant correlation between

257 the ^{14}C results and air temperature. In contrast to the ^{14}C data, δ^{13}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}C and δ^{13}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 σ) 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 CO_2 for ^{14}C analysis.*

268 Passive samplers have been used reliably to trap CO_2 for monitoring purposes, for example to

269 provide time-weighted averages for atmospheric 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 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 CO_2 for carbon

282 isotope analysis.

283

284 Firstly, the dissolved CO_2 concentration determined from the rate of CO_2 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_2 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_2 concentration ~ 20 m downstream of the current study site (using in-situ CO_2

293 sensors with 30 min time resolution). This could explain why a slightly lower annual average

294 for CO_2 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^{-1}, compared to 53.98 L s^{-1} 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_2 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_2 concentration of

301 the spot samples becomes 3307 ppm, remarkably similar to the CO_2 concentration calculated

302 from the passive samplers (3336 ppm).

303

304 The strong correlation between the CO_2 concentrations derived from spot samples compared

305 to passive samplers shows that the rate of CO_2 trapping was related to the CO_2 concentration

306 of the environment being sampled. This is fundamentally important for the collection of

307 representative samples. The rate of CO_2 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_2). 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_2 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_2 less efficiently

318 due to it becoming saturated with either CO_2 or H_2O, since this sampler had the greater CO_2

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_2 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_2 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_2 trapped in the 83 day sample of ~ 1 ml. Clearly, if the passive samplers are to be used to

327 more accurately quantify CO_2 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 $\delta^{13}C$ and ^{14}C and not CO_2 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}C and ^{14}C values from the short period samplers

332 were within measurement uncertainty (2 σ) 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}C and $\delta^{13}C$) composition of dissolved CO_2.*

337 We found very little variation in the $\delta^{13}C$ of streamwater dissolved CO_2 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), $\delta^{13}C$ ranged from -20.2 to -

341   19.0 ‰. This range of values is similar to earlier measurements of evaded CO_2 from the Black

342   Burn collected using a floating chamber; Billett et al. (2006) reported values of ~ -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 $\delta^{13}C$ 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 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 CO_2 to the stream from a source area/areas with a

350   consistent $\delta^{13}C$ 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 $\delta^{13}C$ 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}C values of dissolved 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}C age of the dissolved CO_2 ranged from 1210

362   to 707 years BP, and again was similar to the age of evaded CO_2 collected from the Black

363   Burn in previous studies. For example, Billett et al. (2006) reported ^{14}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}C ages of 312 to 1127

- 13 -

368 years BP. These results broadly imply that the age of CO_2 evaded at this site differs little from

369 the streamwater dissolved CO_2; this concurs with the results of Billett and Garnett (2010) who

370 for the same site found similar ^{14}C values for evaded CO_2 and dissolved CO_2 (derived from

371 ^{14}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 ^{14}C measurements of dissolved CO_2 shows a general pattern of increasing [14]C

376 concentrations from May, to greatest ^{14}C-enrichment in the September samples, followed by a

377 progressive decline and return to the lowest ^{14}C levels the following May (Fig. 4). The [14]C

378 values imply that the dissolved CO_2 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_2 with a contemporary ^{14}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_2 mineralised from recently deposited plant litter or

384 surface peat can explain the pattern of [14]CO_2 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 ^{14}C results suggest greatest

387 contributions from younger carbon much later (September-December). There could be a time

388 delay between CO_2 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_2

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_2 cycling in aquatic systems (Hope et al.

392 2004; Dinsmore et al. 2009b). However, to explain the pattern of our [14]CO_2 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 [14]CO_2

395 because there was no significant correlation between mean air temperature and %modern of

- 14 -

396   dissolved CO_2 (which would be expected to correlate even with a time delay).

397

398   Instead, a strong correlation was observed between the ^{14}C content of the dissolved CO_2 and

399   stream discharge, such that there was a greater proportion of younger carbon in the dissolved

400   CO_2 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 (^{14}C-

404   dead) dissolved CO_2, an explanation for the correlation between the ^{14}C content of

405   streamwater dissolved CO_2 and discharge in our results, could be a change in the proportion

406   of groundwater-derived CO_2. 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_2 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 ^{14}C content of the dissolved CO_2. This is similar to what we have

413   observed. However, given the known extremes in the $\delta^{13}C$ values between a geological CO_2

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 $\delta^{13}C$ and discharge. The

416   fact that we do not see this relationship, and if anything, $\delta^{13}C$ becomes more enriched at

417   higher flows (converse to what would be expected), suggests that the pattern in ^{14}C of

418   dissolved CO_2 is not a result of differences in the proportion of groundwater-derived CO_2. 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 ^{14}C

421   content of dissolved CO_2.

422

- 15 -

423 It is well known that intact peatlands generally exhibit decreasing ^{14}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 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 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 CO_2 with a ^{14}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 CO_2 derived from the peat surface will be relatively ^{14}C-enriched (and

446 younger), we would expect a positive relationship between discharge and the ^{14}C content of

447 streamwater dissolved CO_2, which we found.

448

449 Although the above interpretation explains the observed positive correlation between [14]C

450 concentration in the dissolved CO_2 and stream discharge, we found $\delta^{13}CO_2$ 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 $\delta^{13}C$ of dissolved CO_2 in peat profiles varies

453   considerably, with a trend of increasing ^{13}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 $\delta^{13}CO_2$ 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 $\delta^{13}C$ of streamwater-dissolved 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 CO_2 in peats increases with depth. Therefore, if

462   deeper layers are responsible for contributing proportionally more CO_2 to stream flow during

463   periods of low discharge, we would also expect that the 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 CO_2 concentration in streamwater (Fig.

466   5); Dinsmore and Billett (2008) have previously reported a similar negative CO_2

467   concentration-discharge relationship for the study stream, Black Burn.

468

469   If linear regression is applied to the stream discharge and $^{14}CO_2$ results we obtain the equation

470     $y = 0.0607x + 85.607$ ($r^2 = 0.766$, $p < 0.01$), where $y = {}^{14}C$ %modern and x = discharge (Fig.

471   6). Therefore, the intercept shows that when discharge is zero, the ^{14}C content of the dissolved

472   CO_2 is 85.6 %modern (equivalent to ~ 1250 years BP). This may imply that there is a baseline

473   source of CO_2 to the stream, representing the age of the CO_2 that enters the stream when

474   contributions from younger surface layers are insignificant. At two other Scottish sites, 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

- 17 -

479 sampling year, a depth where presumably CO_2 dissolved in the peat water would be much

480 younger; this therefore suggests that even under baseflow conditions streamwater dissolved

481 CO_2 is likely to be derived from a range of depths (but with an average age of ~ 1250 years

482 BP). The ^{14}C content of the dissolved CO_2 under baseflow conditions implied from the

483 intercept also indicates that geological sources cannot represent a major component of the

484 streamwater dissolved CO_2 (otherwise we would have expected the ^{14}C content of dissolved

485 CO_2 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_2 to the

487 Black Burn.

488

489 It was notable that the correlation between stream discharge and ^{14}C content of dissolved CO_2

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 ^{14}C content of the dissolved CO_2 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 ^{14}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_2 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_2 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_2 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_2 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_2 as it is transported from headwater source to sea (e.g.

511 Dawson et al., 2009).

512

513 The δ^{13}C value of streamwater dissolved CO_2 collected using the passive samplers varied only

514 slightly over the study year, indicating relatively little change in the source of the CO_2. ^{14}C

515 analysis of the CO_2 confirmed the results of earlier studies at the site and demonstrated the

516 release of old CO_2 from this peatland stream. Unlike the δ^{13}C results, the ^{14}C values for

517 dissolved CO_2 showed a clear seasonal pattern, with the oldest CO_2 being transported by the

518 stream in spring/early summer. Based on the above observations, and a positive correlation

519 between the ^{14}C age of dissolved CO_2 and discharge, we conclude that although total CO_2 in

520 this peatland stream is likely derived from a range of peat depths, shallower/younger peat

521 layers contribute greater amounts of CO_2 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_2 sources and

524 transport processes in a range of different soil-stream systems.

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646

647 **Figure Captions**

648

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

650 Burn.

651

652 **Fig. 2** Discharge from the Black Burn and air temperature (measured ~ 400 m from the

653 stream sampling point) over the course of the sampling year from May 2010 to June 2011.

654

655 **Fig. 3** Concentration of dissolved CO_2 in the Black Burn from May 2010 to June 2011

656 determined by i) continuous trapping using passive samplers and ii) spot sampling of stream

657 water. CO_2 concentration determined for the passive samplers based on the CO_2 trap rate and

658 Fick's law (see text). Mean, min and max values for spot samples reflect the sampling periods

659 of the associated passively collected sample.

660

661 **Fig. 4** Mean discharge ($\pm$ SE) of the Black Burn and ^{14}C content of dissolved CO_2 ($\pm$ 1 σ)

662 over the sampling year from May 2010 to June 2011, showing increased ^{14}C content of CO_2 at

663 times of greater discharge. Using all data points resulted in a positive correlation ($r^2 = 0.766$; p

664 < 0.01; n = 8) which improved considerably when the September 2010 sample was omitted (r^2

665 $= 0.965$; $p < 0.001$; n = 7).

666

667 **Fig. 5** Mean discharge of the Black Burn and CO_2 concentration determined from spot

668 samples ($\pm$ SE). Mean values for both discharge and CO_2 concentration reflect the sampling

669 periods of the associated passively collected sample. There was a strong negative correlation

670 between discharge and CO_2 concentration ($r^2 = 0.855$; $p < 0.001$; n=8; note 2nd y-axis is

671 reversed).

672

673 **Fig. 6** Radiocarbon concentration of dissolved CO_2 (± 1 σ) versus mean discharge ($\pm$ SE) of

674 the Blackburn for samples collected over the sampling year from May 2010 to June 2011.

675 Mean values for discharge reflect the sampling periods of the associated passively collected

676 $^{14}CO_2$ sample.

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Table 1 Details of dissolved carbon dioxide samples collected using passive samplers from the Black Burn, including dates of collection, volume of CO_2 recovered, and carbon isotope concentrations. *NB used for normalisation of ^{14}C result and representative of recovered CO_2 and not corrected for fractionation during trapping. [#]Due to possible disturbance resulting from the installation of a control structure upstream, samplers were removed for 7 days during the sampling period as a precaution.

Start date	End date	Sampling days	CO_2 recovered (ml)	Publication code (SUERC-)	Conventional radiocarbon age (years BP)	^{14}C content (%modern ± 1σ)	*$\delta^{13}C_{VPDB}$ ± 0.1 ‰
28 May 2010	29 Jun 2010	32	8.3	33624	1139 ± 35	86.78 ± 0.38	-23.6
29 Jun 2010	29 Jul 2010	30	9.0	34183	996 ± 37	88.34 ± 0.41	-23.1
03 Aug 2010	09 Sep 2010	37	10.3	34184	1124 ± 37	86.94 ± 0.40	-23.1
09 Sep 2010	06 Oct 2010	27	5.3	34185	707 ± 35	91.57 ± 0.40	-23.0
06 Oct 2010	16 Nov 2010	41	7.2	34186	760 ± 37	90.98 ± 0.42	-23.2
16 Nov 2010	14 Dec 2010	28	5.5	34187	842 ± 37	90.05 ± 0.41	-23.2
18 Jan 2011	04 Mar 2011	45	5.3	34705	1013 ± 37	88.15 ± 0.40	-23.8
04 Mar 2011	21 Apr 2011	48	10.8	34707	1044 ± 39	87.81 ± 0.42	-23.0
21 Apr 2011	02 Jun 2011	35[#]	8.9	34708	1210 ± 39	86.01 ± 0.42	-24.2

| 04 Mar 2011 | 02 Jun 2011 | 83[#] | 22.4 | 34706 | 1106 ± 37 | 87.14 ± 0.40 | -24.0 |

Fig. 1

Accurel PP v8/2 HF tubing

Polystyrene pipe and steel cradle for field deployment

Glass tubing

Section of drainpipe secured to stream bed

Handle larger than width of drainpipe to hold in place

Molecular sieve held in place by quartz wool

Tygon tubing with removable clip to seal

Water flow direction

Fig. 2

Fig. 3

x-axis: Mid-point of sampling period

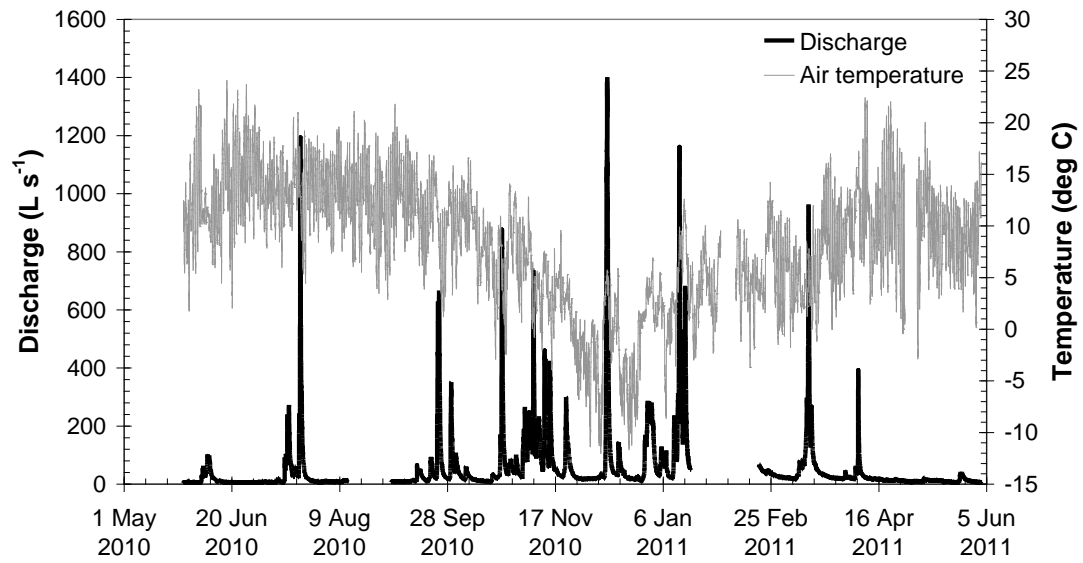*y-axis: CO_2 concentration (ppmv)*

Legend:
- ■ Passive samplers
- □ Spot samples (mean)
- – – Spot samples (min/max)

Fig.4

Fig. 5

Fig. 6

The figure shows a scatter plot with error bars. The y-axis is labeled $^{14}CO_2$ (%modern) ranging from 85 to 93, and the x-axis is labeled Mean discharge (L s^{-1}) ranging from 0 to 120.

$$y = 0.0607x + 85.607$$
$$r^2 = 0.7661$$
$$p < 0.01$$